BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

SEPTEMBER, 1939.

Laboratory experiments in organic chemistry. N. D. CHERONIS (J. Chem. Educ., 1939, **16**, 165—170; cf. A., 1938, II, 122). L. S. T.

Colour and constitution of organic compounds from the viewpoint of modern physical theory. T. FÖRSTER (Z. Elektrochem., 1939, **45**, 548—573).—A review. J. W. S.

Thermal decomposition of petroleum hydrocarbons into free radicals. B. L. EVERING (J. Amer. Chem. Soc., 1939, **61**, 1400—1405).—The thermal decomp. of petroleum hydrocarbons in an apparatus essentially that of Rice *et al.* (A., 1932, 1108) gives free radicals, which are allowed to react with Pb mirrors, freshly formed by condensation of Pb vapour. The concn. of free radicals formed was determined by determination of Pb in the Pb alkyl. In the pressure range 0·25—6·0 mm. the concn. of free radicals decreases with pressure but is not affected by the mol. wt. of the hydrocarbon which is decomposed, by dilution of the hydrocarbon stream with N_2, or by increasing the surface to vol. ratio. W. R. A.

Halogenation in reactive solvents. II. Addition of halogen and acetoxyl to ethylene. F. C. WEBER, G. F. HENNION, and R. R. VOGT (J. Amer. Chem. Soc., 1939, **61**, 1457—1458; cf. A., 1938, II, 388).—Chlorination of C_2H_4 in AcOH or MeOAc, using low concns. of Cl_2, gives $C_2H_4Cl_2$ and 29·6—44·7% of $CH_2Cl{\cdot}CH_2{\cdot}OAc$ (I). In Ac_2O the yield of (I) is 16·9% at 10—15° and 87·1% at 40—43°. By-products are $(CH_2{\cdot}OAc)_2$ (in AcOH), AcCl (in Ac_2O), or $CCl_3{\cdot}CH_2{\cdot}OAc$ + MeCl (in MeOAc). R. S. C.

Reaction of propylene with *iso*olefines in the presence of sulphuric acid. V. N. IPATIEV, H. PINES, and B. S. FRIEDMAN (J. Amer. Chem. Soc., 1939, **61**, 1825—1826).—C_3H_6 in 96% H_2SO_4 at 0° or 25°, with or without $CuSO_4$ or $HgSO_4$, gives $Pr^{\beta}HSO_4$ and only traces of hydrocarbons. However, passage of mixed C_3H_6 and $CH_2{:}CMe_2$ into H_2SO_4 gives 8—35% of hydrocarbons utilising C_3H_6, the exact amount depending on the concn. of the acid, temp., and mode of addition of the gas; the products are shown by hydrogenation, followed by fractionation and identification by b.p., n, d, and Raman spectra, to be $CH_2{:}CH{\cdot}CH_2Bu^{\gamma}$ and $CH_2{:}CMeBu^{\gamma}$ (from $2Pr^{\beta}HSO_4$), and a βγ-dimethylpentene (formed by isomerisation of the other products); the H_2SO_4 contains $Pr^{\beta}HSO_4$, but no $Bu^{\gamma}HSO_4$. C_3H_6 and *iso*pentenes give, when mixed, similarly 16% of C_8H_{16} and 17% of $C_{13}H_{26}$, but admixture with *n*-butenes is ineffective. Passage of the olefine mixture into $Pr^{\beta}HSO_4$ is more effective than into H_2SO_4. R. S. C.

Stereoisomerism of unsaturated compounds. IV. Identification of *cis–trans* isomerides by rate studies. W. G. YOUNG, D. PRESSMAN, and C. D. CORYELL. **V. Mechanism for the formation of butenes from βγ-dibromobutanes by the action of iodide ion.** S. WINSTEIN, D. PRESSMAN, and W. G. YOUNG (J. Amer. Chem. Soc., 1939, **61**, 1640—1644, 1645—1647; cf. A., 1937, II, 132).—IV. The kinetics of the reaction $CHRBr{\cdot}CHR'Br + 3I^- \rightarrow CHR{:}CHR' + I_3^- + 2Br^-$ at ~59° and ~75° are reported and discussed in detail for the dibromides from *cis*- and *trans*-$(CHMe)_2$, -CHMe:CHEt, -$(CHEt)_2$, and -$(CHPr^{\alpha})_2$, maleic and fumaric acids. In all cases in which R = or is similar to R′, the *trans*-derivative reacts faster than the *cis* and has a smaller heat of activation.

V. Elimination of Br from $(CHMeBr)_2$ (I) by I in aq. PrOH at ~95° or $O(CH_2{\cdot}CH_2{\cdot}OH)_2$ at ~200° is largely *trans*. Thus, *meso*-(I) gives 96%-pure *trans*-C_4H_8, and *dl*-(I) gives 91%-pure *cis*-C_4H_8; the nature of the C_4H_8 is proved by conversion into the dibromide and measurement of its rate of reaction with I. Details of the reaction mechanism are discussed. R. S. C.

Addition of hydrogen halides to *cis*- and *trans*-Δ^{β}-pentene. M. S. KHARASCH, C. WALLING, and F. R. MAYO (J. Amer. Chem. Soc., 1939, **61**, 1559—1564).—*trans*- (prepared from $CHMePr^{\alpha}Br$ or $CHEt_2Br$), n_D^{20} 1·3797, and *cis*-Δ^{β}-pentene (prepared from CMe:CEt by H_2–Pd–$BaSO_4$ in MeOH at 0°), n_D^{20} 1·3823, add HBr alone, in AcOH, or in presence of $NHPh_2$, PhSH, $C_6H_4Me{\cdot}SH$, $FeBr_3$, ascaridole, or Bz_2O_2 to give a 1 : 1 mixture of $CHMePr^{\alpha}Br$ and $CHEt_2Br$. A similar mixture of chlorides is obtained by HCl in AcOH or in presence of $FeCl_3$. This mode of addition is due to the nearly equal activation energies of the two reactions, caused by the similarity of the Me and Et substituents on the C:C. The halide mixtures are analysed by n and formation of the anilides (mixed m.p. curves given). CH:CEt, b.p. 10—20°, is obtained in 64% yield from C_2H_2, Na, and Et_2SO_4 in liquid NH_3, and is converted into CMe:CEt by treatment in Et_2O first with MgEtBr and then with Me_2SO_4. R. S. C.

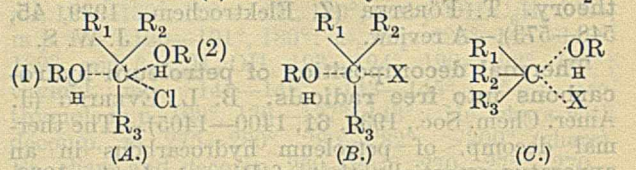
Conjugated hexadienes. C. PRÉVOST (Compt. rend., 1939, **208**, 1589—1591).—Propylvinyl- (I) and ethylpropenyl-carbinol when heated with Al_2O_3 at 360° or $NaHSO_4$ at 170° give mixtures of hexa-$\Delta^{\alpha\delta}$-diene (II), hexa-$\Delta^{\alpha\gamma}$-diene (III), and hexa-$\Delta^{\beta\delta}$-diene (IV). In each case a trace to 2% of (II) is formed. When (I) is heated with $NaHSO_4$, mainly (III) (85%) is formed, although the total yield is low (45%). In the other reactions 83—94% of (IV) is formed. When (IV) is heated with Al_2O_3 at 360°,

some (III) is formed; at 450—480°, (III) (15%), (II) (20%), and penta-$\Delta^{\alpha\gamma}$-diene (8%) are formed. J. L. D.

Substituted acetylenes and their derivatives. XXXII. Halogenation in reactive solvents. III. Chlorination of vinylacetylene in methanol. A. A. Baum, R. R. Vogt, and G. F. Hennion. **XXXIII and IV. Chlorination of Δ^{α}-hexinene in reactive solvents.** R. O. Norris, R. R. Vogt, and G. F. Hennion (J. Amer. Chem. Soc., 1939, **61**, 1458—1460, 1460—1461; cf. A., 1939, II, 197).—XXXII. Passage of CH_2:CH·C:CH (I) into MeOH at 30° and of Cl_2 over the surface so that only a slight excess of Cl_2 is present causes the following reactions: (I) → *α-chloro-β-methoxy-*$\Delta^{\alpha\gamma}$*-butadiene* (II) (10%), b.p. 57·4—57·6°/48 mm. → CH_2:CH·C(OMe)$_2$·$CHCl_2$ → (+HCl) *ααδ-trichloro-ββ-dimethoxybutane* (III) (20%), b.p. 103°/3 mm.; (II) → CH_2:CH·CCl(OMe)·$CHCl_2$ → MeCl + CH_2:CH·CO·$CHCl_2$ → *ααδ-trichlorobutan-2-one* (IV) (8%), b.p. 81·5—82·5°/18 mm. Only (II), (III), (IV), and MeCl were isolated. (IV) does not give CO: reactions and gives the haloform reaction slowly. (III) is not readily hydrolysed, but hot AcOH containing a little H_2O and H_2SO_4 produces MeOAc. *n* and *d* of the products are given.

XXXIII. Passage of Cl_2 over CH:CBu^{α} in H_2O at 45±5° gives trans-*αβ-dichloro-*Δ^{α}*-n-hexene* (V) (20%), b.p. 55—57°/25 mm., *ααβ-trichloro*-n-*hexane* (VI) (20%), b.p. 90—93°/10 mm., *ααββ-tetrachloro*-n-*hexane* (VII) (28%), b.p. 108—110°/10 mm., and *CHCl*$_2$ *Bu*$^{\alpha}$ *ketone* (VIII) (20%), b.p. 63—65°/11 mm. In AcOH cis-*αβ-dichloro-*Δ^{α}-n-*hexene* (IX) (23%), b.p. 80—82°/25 mm., (VI) (18%), (VII) (7%), (VIII) (34%), and AcCl (20%) [produced with (VIII) by fission of OAc·CBu^{α}Cl·$CHCl_2$] are formed. In Ac_2O (IX) (5%), (VI) (12%), (VII) (26%), (VIII) (43%), and AcCl (100%) (produced by fission of the primary additive product, Ac_2O→CBu^{α}:CH→Cl_2) are formed. No oxygenated products are obtained in Bu^{γ}OH or MeOAc. In Bu^{γ}OH some Bu^{γ}OCl must be formed to act as source of HCl, the products being (V) (102%) and (VI) (23%). In MeOAc the products are (IX) (35%), (I) (7%), (VI) (19%), (VII) (28%), and *αααββ-pentachloro*-n-*hexane* (48%), b.p. 129—131°/10 mm. The factors influencing production of (V) and/or (IX) are obscure. The structures of (V) and (IX) are determined by dipole moments, which are 0·57 and 1·993 × 10^{-18} e.s.u., respectively. *n* and *d* of the products are given. R. S. C.

Solvolysis of *tert.*-butyl chloride. Solvolytic reactions and the Walden inversion. S. Winstein (J. Amer. Chem. Soc., 1939, **61**, 1635—1640).—Ingold's S_N1 mechanism for the reaction, RHal + R'OH → ROR' + HHal, is held to be inherently improbable, because, *inter alia*, the halogen ion split off would not protect the R^+ ion sufficiently to force reaction to occur at the back of the C. The solvent (H_2O) is considered to play an essential part in such reactions, the mechanism being: (*a*) $H_2O + \rangle C{\cdot}X \rightarrow H_2\overset{+}{O}{-}C\langle + X^-$; (*b*) $\rangle C{\cdot}X + OH_2 \rightarrow C{-}\overset{+}{O}H_2 + X^-$; (*c*) $H_2O + \rangle C{\cdot}\overset{+}{O}H_2 \rightarrow H_2\overset{+}{O}{-}C\langle + OH_2$; (*d*) $\rangle C{-}\overset{+}{O}H_2 \rightarrow \rangle C{\cdot}OH + H^+$; (*e*) $H_2\overset{+}{O}{-}C\langle \rightarrow OH{\cdot}C\langle + H^+$. Reaction (*a*) involves reversal of configuration, whereas (*b*) involves its retention. (*c*) is racemisation. The rates and products of hydrolysis of Bu^{γ}Cl in aq. $COMe_2$ and aq. dioxan and of its alcoholysis (MeOH, EtOH) are accounted for by equations, based on fugacities, involving either 2 or 3 solvent mols. (cf. Olson *et al.*, A., 1938, I, 86; Bateman *et al.*, A., 1938, II, 304). Reaction is thus essentially multimol. (cf. Hammett *et al.*, A., 1938, II, 86, 87), the usual transition state being (*A*); solvent mol. (1) finds its place by attack away from the Cl; solvent mol. (2) becomes attached because of the tendency to form H–Cl linkings. Removal of mol. (2) results in inversion, and removal of mol. (1) results in retention of configuration. Formation of (*A*) accounts for the reaction (*c*). With very low concn. of H_2O



in, *e.g.*, $COMe_2$, reaction becomes bimol., the transition states for inversion and retention of configuration being (*B*) and (*C*), respectively. Other first-order reactions are briefly discussed from a similar viewpoint. Solvolysis of $CHPh_2Cl$ and CHPhMeCl is similar to that of Bu^{γ}Cl. R. S. C.

Peroxide effect in the addition of reagents to unsaturated compounds. XX. Addition of hydrogen bromide to Δ^{β}-butinene and β-bromo-Δ^{β}-butene. C. Walling, M. S. Kharasch, and F. R. Mayo (J. Amer. Chem. Soc., 1939, **61**, 1711—1713).—Abnormal addition to a non-terminal ethylenic linking is achieved by unsymmetrical distribution around it. (:$CMe)_2$ (prep. modified), b.p. 27·0—27·4°, m.p. —28° to — 27°, adds HBr (no solvent) only normally to give $CMeEtBr_2$, whether peroxides or antioxidants are present. With ascaridole in C_5H_{12} only abnormal addition occurs, giving $(CHMeBr)_2$. In AcOH presence of peroxides or antioxidants controls the results. The unsymmetrical loading occurs at the intermediate stage, CHMe:$CMeBr$. The effect of the presence and nature of the solvent is remarkable. R. S. C.

Treatment of neopentyl halides with mercury di-*p*-tolyl. F. C. Whitmore and E. Rohrmann (J. Amer. Chem. Soc., 1939, **61**, 1591—1592).—$CH_2Bu^{\gamma}Br$ and $Hg(C_6H_4Me\text{-}p)_2$ at 200° (20 hr.) react only very slightly, giving ~5% of olefines, mainly $CHMe{:}CMe_2$. $CH_2Bu^{\gamma}I$ also reacts very slightly (7—9%), but gives only 0·7% of olefines. $CH_2Bu^{\gamma}I$ and $HgCl_2$ in Et_2O–N_2 give 23·5% of *Hg dineopentyl*, m.p. 31—33°, b.p. 67—69°/3 mm., and some HgCl·CH_2Bu^{γ}. R. S. C.

Reaction of neopentyl chloride with sodium. F. C. Whitmore, A. H. Popkin, and J. R. Pfister (J. Amer. Chem. Soc., 1939, **61**, 1616—1617).—$CH_2Bu^{\gamma}Cl$ and Na (1 atom) give 36% of CMe_4, 25% of 1 : 1-dimethyl*cyclo*propane, b.p. 19·8°/740 mm., and 13% of $(CH_2Bu^{\gamma})_2$. R. S. C.

Preparation of neopentyl iodide and bromide. F. C. Whitmore, E. L. Wittle, and B. R. Harriman (J. Amer. Chem. Soc., 1939, **61**, 1585—1586).—

CH_2Bu^{γ}·OH, red P, and I give only 4—9% of iodide (cf. Ingold *et al.*, A., 1933, 262). $CH_2Bu^{\gamma}Cl$ (prep. in 30% yield from CMe_4 by Cl_2), b.p. 83·3°/740 mm., readily gives the Mg derivative, which with $HgCl_2$ in Et_2O yields 90% of MgCl·CH_2Bu^{γ}, m.p. 117—118°. With aq. I–KI this gives 92% of $CH_2Bu^{\gamma}I$, b.p. 132·6°/734 mm., stable, and with Br gives 82% of $CH_2Bu^{\gamma}Br$, b.p. 105°/732 mm. No rearrangement occurs. MgCl·CH_2Bu^{γ} and I in Et_2O give $CH_2Bu^{\gamma}I$ contaminated with the alcohol and hydrocarbons. $CH_2Bu^{\gamma}I$ is much less reactive than $Bu^{\alpha}I$. R. S. C.

Chemistry of vitamin-*E*. IX. Preparation of long-chain halides and ketones containing *iso*-pentane units. L. I. Smith, H. E. Ungnade, F. L. Austin, W. W. Prichard, and J. W. Opie (J. Org. Chem., 1939, **4**, 334—341).—The complete hydrogenation of geraniol requires a temp. of 200° and initial pressure 2550 lb. Reaction occurs in two well-defined stages. Citronellol, from which the allylic double linking is absent, is much more readily reduced completely (125°/1900 lb.) whilst farnesol requires 200°/2700 lb. for complete reduction. The only methods suitable for the conversion of these unsaturated and saturated alcohols into their halides involve the use of dry H halide. For allylic alcohols good yields are obtained when the alcohol is saturated with dry HBr or HCl, preferably in the presence of a drying agent and kept in the cold, whilst the higher saturated alcohols give the best yields of halides (bromides) by treatment with a current of dry HBr at 150° without a solvent. Aq. HBr adds to the double linking of allylic alcohols so that dihalides are the main product. For the alkylation of $CH_2Ac·CO_2Et$ with allylic halides dilution with light petroleum appears advantageous but with saturated halides the customary procedure may be followed. Hydrolysis of the esters to ketones is best effected with H_2O alone at 200° under high pressure of H_2. OEt·$[CH_2]_2$·Cl does not react with $CO(CH_2·CO_2Et)_2$, which with OEt·$[CH_2]_2$·I or preferably OEt·$[CH_2]_2$·Br gives a modest yield of *Et_2 ethoxyethylacetonedicarboxylate* (I), b.p. 108—114°/17 mm. *Et_2 perhydrogeranylacetonedicarboxylate* has b.p. 145—155°/0·1 mm. (I) and perhydrogeranyl bromide (II) give a non-uniform product. (II) is converted by successive treatments with Mg and OMe·CH_2Cl into *α-methoxy-δθ-dimethylnonane*, b.p. 94—94·5°/14·5 mm., obtained with greater difficulty but in somewhat better yield from tetrahydrogeranyl chloride; it is best cleaved by dry HBr to the C_{11} bromide. H. W.

Reaction steps in the conversion of βγ-diacetoxybutane into βγ-dibromobutane. S. Winstein and H. J. Lucas (J. Amer. Chem. Soc., 1939, **61**, 1581—1584).—Conversion of $(CHMe·OAc)_2$ into $(CHMeBr)_2$ by aq. HBr is shown to proceed by way of OAc·CHMe·CHMe·OH (I), OAc·CHMe·CHMeBr (II), and OH·CHMe·CHMeBr, by (*a*) isolating these intermediates from the reaction mixture and (*b*) synthesising them and showing them to react with aq. HBr in the desired direction and at the correct speeds. The step (I) → (II) is the only one at which inversion occurs, which explains why only one C is inverted during the whole series of changes. dl-threo- (III), b.p. 70·1°/13 mm., and dl-erythro-*γ-Bromo-β-acetoxybutane* (IV), b.p. 67·2°/13 mm., are obtained from the corresponding bromohydrins by Ac_2O. dl-erythro-*γ-Acetoxybutan-β-ol* (V), b.p. 79·2°/10 mm., is obtained from the *meso*-glycol by Ac_2O and a little H_2O or, with an inversion, from *trans*-βγ-epoxybutane (VI) by AcOH. *meso*-$(CHMeBr)_2$ is obtained from (IV) or (VI). *dl*-$(CHMeBr)_2$ is obtained from (III) or (V) (both sources). Reaction mechanisms are discussed. Conversion of $(CHMe·OAc)_2$ into $(CHMeBr)_2$ by HBr in AcOH involves much inversion, but the reaction mechanism is obscure. R. S. C.

Intramolecular reaction between neighbouring substituents of vinyl polymerides. P. J. Flory (J. Amer. Chem. Soc., 1939, **61**, 1518—1521).—Statistical analysis shows that when the X of polymerides, $[CH_2·CHX·CH_2·CHX]_n$ (I), interact to form rings, 13·53% of the X become isolated; 86·47% is thus the theoretical limit of the reaction. If the polymeride is a random mixture of (I), $[CH_2·CHX·CHX·CH_2]_n$, and $[CHX·CH_2·CH_2·CHX]_n$ units, and if reaction of αδ-substituents is impossible, 18·40% of the substituents become isolated. R. S. C.

Retention of configuration in the reaction of γ-bromobutan-β-ols with hydrogen bromide. S. Winstein and H. J. Lucas (J. Amer. Chem. Soc., 1939, **61**, 1576—1581).—*trans*-, b.p. 53·5°/742 mm., and *cis*-βγ-Epoxybutane (I), b.p. 59·7°/742 mm., give *erythro*- (II), b.p. 53·1°/13 mm. (3 : 5-dinitrobenzoate, m.p. 85°; α-naphthylurethane, m.p. 133°), and *threo*-γ-bromobutan-β-ol (III), b.p. 50·5°/10 mm. (3 : 5-dinitrobenzoate, m.p. 109°; α-naphthylurethane, m.p. 103°), respectively. (III) is also obtained from *cis*-Δ^{β}-butene by NHBrAc. Aq. K_2CO_3 reconverts (III) into (I). 48% aq. HBr at 0° converts (II) and (III) into pure *meso*- and *dl*-$(CHMeBr)_2$, respectively. Reaction mechanisms to explain the retention of configuration are discussed. R. S. C.

Hydrogenation of a higher secondary alcohol by nickel catalysts containing manganese, zinc, or thorium. K. Kino (J. Soc. Chem. Ind. Japan, 1939, **42**, 188B).—Hydrogenation (Ni) of the alcohol obtained by reducing stearone removes the OH slowly at 200°, rapidly at 250°. The reaction is accelerated by Th, but not by Zn or Mn. A. Li.

Catalytic dehydration of C_6—C_8 aliphatic alcohols. S. Goldwasser and H. S. Taylor (J. Amer. Chem. Soc., 1939, **61**, 1751—1761).—When passed over Al_2O_3 (various samples give the same results) at 398°, *n*-C_6H_{13}·OH (I) gives mainly Δ^{α}-*n*-hexene, CH_2:$CMePr^{\alpha}$, and $CHMe$:$CHPr^{\beta}$; $CHEt_2·CH_2·OH$ (II) gives mainly Δ^{α}- and Δ^{γ}-*n*-hexene, $CHMe$:$CMeEt$, CH_2:CEt_2, and $CHEt$:CMe_2; $CHPr^{\alpha}_2$·OH (III) gives mainly Δ^{γ}-*n*-hexene, CH_2:$CEtPr^{\alpha}$, and $CHPr^{\alpha}$:CMe_2; $CHMeBu^{\beta}·CH_2·OH$ (IV) gives mainly $CHMe$:$CH·CHMeEt$, $CHPr^{\beta}$:CMe_2, and $CHMe$:$CMePr^{\beta}$; $CHPr^{\beta}_2$·OH (V) gives mainly $CHEt$:$CHPr^{\beta}$, $CHPr^{\beta}$:CMe_2, and $CHMe$:$CMePr^{\beta}$; $CHEtBu^{\alpha}·CH_2·OH$ (VI) gives mainly $CHBu^{\alpha}$:CMe_2, $CHMe$:$CMeBu^{\alpha}$, $CHEt$:$CMePr^{\alpha}$, and Δ^{γ}-*n*-octene. The numerous secondary decomp. products are identified, their origin as secondary products being proved by their formation in larger amounts with longer times of contact. Much tar is also formed, the amount

increasing with the amount of alcohol recovered, *i.e.*, with increasing rate of passage; it is formed in competition with the dehydration, showing that the alcohol is more strongly adsorbed than the olefines and flushes the latter off the surface. The ease of dehydration is (II)>(III)>(I)>(IV)>(V). This order is not connected with the no. of H attached to the C·OH and is unintelligible if dehydration is from a CH_2 next to the C·OH; moreover, it correlates exactly with the no. of other H available sterically. The primary products are precisely accounted for if elimination of H_2O gives a *cyclo*propane derivative as labile intermediate, all the expected products from fission of the ring being found; moreover, they accord with the view that the ease of removal of H is from CH > CH_2 > Me. ThO_2 gives similar results, but ring-fission tends to occur more at one place. Cr_2O_3 causes also dehydrogenation, leading to aromatic products. The apparatus is a modification of that previously described (A., 1939, II, 305). R. S. C.

Spectrographic and chemical examination of some unsaturated alcohols and their dehydration products. I. β-Methylpentane-βδ-diol. G. Dupont and (Mlle.) M. Darmon. **II. Mesityl oxide and alcohol derivatives.** G. Dupont and (Mlle.) M. L. Menut (Bull. Soc. chim., 1939, [v], **6**, 1208—1214, 1215—1220).—I. Spectrographic examination and selective hydrogenation ($NaNH_2$) are used to determine the constitution of the unsaturated products. OH·CMe_2·CH_2Ac is hydrogenated (Cu chromite) at 110—120° to β-methylpentane-βδ-diol, b.p. 192° (Raman spectra), which when distilled with NH_2Ph,HBr gives β-methyl-Δ^{α}-penten-δ-ol (I), b.p. 128—130°, a mixture (II), b.p. 75·5—76·5°, of *cis*- and *trans*-β-methyl-$\Delta^{\alpha\gamma}$-pentadiene, and a little β-methyl-$\Delta^{\beta\delta}$-pentadiene (cf. Diels *et al.*, A., 1929, 819; Bacon *et al.*, A., 1937, II, 395). (II) is hydrogenated (Raney Ni or Pt) to a mixture of *cis*- and *trans*-δ-methyl-Δ^{β}-pentene. (II) and CHMe:CH·CHO give 5-aldehydo-2 : 4-dimethyl-Δ^{1}-*cyclo*hexene, b.p. 90—91°/20 mm. (semicarbazone, m.p. 182°), which with $COMe_2$ gives an isomeride, b.p. 134—135°/15 mm., of ionone (Raman spectra examined). (I) is hydrogenated to β-methylpentan-δ-ol (III), b.p. 128—130°.

II. Mesityl oxide (III), CHAc:CMe_2, from the dehydration (I, HBr, or $CuSO_4$) of OH·CMe_2·CH_2Ac, contains some isomeride, CH_2Ac·CMe:CH_2, the amount varying with the method of prep. (III) and MgMeBr afford mainly OH·CMe_2·CH:CMe_2 and ~20% of OH·CMe·CH_2·CMe:CH_2 (Raman spectra examined), readily dehydrated by NH_2Ph,HBr to CMe_2:CH·CMe:CH_2, b.p. 93—95°, hydrogenated ($NaNH_2$) to $CHPr^{\beta}$:CMe_2, b.p. 83—84°. Pondorff reduction of (III) gives, through a boric ester, b.p. 130°/15 mm., a mixture of CMe_2:CH·CHMe·OH, with ~20% of CH_2:CMe·CH_2·CHMe·OH, hydrogenated to (III). β-Methyl-Δ^{β}-penten-δ-ol is dehydrated (NH_2Ph,HBr) to β-methyl-$\Delta^{\alpha\gamma}$-pentadiene. A. T. P.

Reactions relating to carbohydrates and polysaccharides. LVI. Synthesis of higher polyoxyethylene glycols. R. Fordyce, E. L. Lovell, and H. Hibbert. **LVII. Synthesis of 90-membered and 186-membered oxyethylene glycols.** R. Fordyce and H. Hibbert (J. Amer. Chem. Soc., 1939, **61**, 1905—1910, 1910—1911; cf. A., 1938, II, 39).—LVI. Addition of $(CH_2$·$OH)_2$ to Na (1 atom) in MeOH at 40°, removal of the MeOH, and heating with $(CH_2Cl)_2$ (1·1 mol.) at 95° gives 48% of *hexaoxyethylene glycol* (I), OH·$[CH_2$·CH_2·$O]_6$·H, m.p. 2·1°, b.p. 185—185·7°/0·015 mm. The cryst. *salt*, OH·$[CH_2]_2$·ONa, + $(CH_2$·$OH)_2$, and CPh_3Cl in dioxan at 70° give *β-triphenylmethoxyethyl alcohol*, m.p. 116—116·5°, constituting a proof of structure. $SOCl_2$ in C_5H_5N at 45° converts (I) into the *dichloride*, m.p. −12·4°, b.p. 168—169°/0·1 mm., which with the K_1 salt of (I) in light-petroleum (b.p. 100—110°), first at 65°, then at 135°, and finally at 175°, gives *octadecaoxyethylene glycol* (II), OH·$[CH_2$·CH_2·$O]_{18}$·H, m.p. 23·8°. The *dichloride* (prep. therefrom by $SOCl_2$ at 65°), m.p. 22·9°, of (II) with the K_1 salt of (II) [as for (II), but at 135°] gives *dotetracontaoxyethylene glycol* (III), OH·$[CH_2$·CH_2·$O]_{42}$·H, m.p. 33·8°. The derived *dichloride* has m.p. 33·4°. The purity of (I), (II), and (III) is proved by the regularity of *n* and, particularly, by the long flat portion of the cooling curve and the abrupt termination thereof.

LVII. The Na salt of (III) and dichloride of (I) give *nonacontaoxyethylene glycol* (IV), OH·$[CH_2$·CH_2·$O]_{90}$·H, birefringent, m.p. 40·6°, the Na salt of which with the dichloride of (I) gives the *glycol* (V), OH·$[CH_2$·CH_2·$O]_{186}$·H, m.p. 44·1°. The purity of (IV) and (V) is shown by cooling curves. R. S. C.

Reactions relating to carbohydrates and polysaccharides. LVIII. Relation between chain length and viscosity of polyoxyethylene glycols. R. Fordyce and H. Hibbert. **LIX. Precipitability of pure hemicolloidal polyoxyethylene glycols.** E. L. Lovell and H. Hibbert (J. Amer. Chem. Soc., 1939, **61**, 1912—1915, 1916—1920; cf. preceding abstract).—LXVIII. Staudinger's equation, $\eta_{sp}/c = K_mM$, is shown to hold for the pure glycols, OH·$[CH_2$·CH_2·$O]_n$·H (n = 6, 18, 42, 90, and 186), except for low n. For low n, particularly, it is better replaced by $\eta_{sp}/c = K_mM + \beta$, β being the η_{sp}/c intercept on the graph. The relations between K_m and the mol. wt. (M) for the pure glycols and for Staudinger's mixed polyoxyethylene oxides are similar, but not identical, the difference being due to the non-homogeneity of the latter.

LIX. The relation between the "precipitability" (Schulz, A., 1937, I, 510) of the above glycols and n is determined for MeOH–Et_2O and dioxan–Et_2O, and a new quant. equation is postulated. The log of the solubility (%) ∝ % Et_2O in the MeOH–Et_2O. The glycol (n = 186) behaves abnormally and indicates that pptn. may not always provide a regularly graded series of products. R. S. C.

***d*-Arabitol in *Fistulina hepatica*.**—See A., 1939, III, 733.

Tritylation experiments in the sugar alcohol series. M. L. Wolfrom, W. J. Burke, and S. W. Waisbrot (J. Amer. Chem. Soc., 1939, **61**, 1827—1829).—*l*-Fucitol with CPh_3Cl in C_5H_5N at 60°, followed by Ac_2O at 45°, gives *l-fucitol* 1-CPh_3 *ether*

2 : 3 : 4 : 5-*tetra-acetate*, m.p. 152°, $[\alpha]_D^{30}$ −18° in $CHCl_3$ (also obtained from the *l*-fucitol CPh_3 ether of Valentin, A., 1932, 42), converted by HBr–AcOH into l-*fucitol* 1-*bromide* 2 : 3 : 4 : 5-*tetra-acetate* (I), m.p. 142—143°, $[\alpha]_D^{30}$ −9·8° in $CHCl_3$, and by H_2O in hot AcOH into l-*fucitol* 2 : 3 : 4 : 5-*tetra-acetate*, m.p. 92—94°, $[\alpha]_D^{30}$ −15° in $CHCl_3$, which with HBr–AcOH gives (I) and with Ac_2O gives the *penta-acetate*, m.p. 127°, $[\alpha]_D^{30}$ +20·5° in $CHCl_3$. Dulcitol and CPh_3Cl (2 mols.) in C_5H_5N give the 1-CPh_3, m.p. 83°, and 1 : 6-$(CPh_3)_2$ *ether* (II), m.p. 183—184°; (II) is isolated as its *compound* (III), +$2C_5H_5N$,HCl, m.p. 182—184°, and thence as *solvate* (IV), +EtOH, m.p. 183—184° (sinters at 80°), from which the EtOH is removed by heating at 110°/vac. over P_2O_5. With Ac_2O–C_5H_5N at 0°, (III) or (IV) gives *dulcitol* 1 : 6-$(CPh_3)_2$ *ether* 2 : 3 : 4 : 5-*tetra-acetate*, m.p. 237—238°, which with HBr–AcOH gives the 1 : 6-*dibromide* 2 : 3 : 4 : 5-*tetra-acetate*, m.p. 197—198°. With PhCHO and $ZnCl_2$, (II) gives *dibenzylidenedulcitol* 1 : 6-$(CPh_3)_2$ *ether*, m.p. 233—234°. Xylitol with CPh_3Cl, followed by Ac_2O, in C_5H_5N at room temp. gives *xylitol* 1 : 5-$(CPh_3)_2$ *ether* 2 : 3 : 4-*triacetate*, m.p. 206°. *d*-Mannitol in C_5H_5N with CPh_3Cl at 90°, followed by Ac_2O at 0°, gives d-*mannitol* 1-CPh_3 *ether* 2 : 3 : 4 : 5 : 6-*penta-acetate*, m.p. 163—164°, $[\alpha]_D^{30}$ +35·5° in $CHCl_3$. R. S. C.

Substituted ethers derived from ethylene chlorohydrin. S. P. Lingo with H. R. Henze (J. Amer. Chem. Soc., 1939, **61**, 1574—1576; cf. A., 1939, II, 299).—Saturating a mixture of $CH_2Cl{\cdot}CH_2{\cdot}OH$ and RCHO with HCl at <0° gives $CH_2Cl\,CH_2Cl{\cdot}CH_2$ *ether*, b.p. 46°/10 mm., $(CH_2Cl{\cdot}CH_2)_2$ *ether* (prep. from paracetaldehyde), b.p. 51°/10 mm., $CH_2Cl{\cdot}CH_2$ α-*chloro*-n-*propyl*, b.p. 60°/10 mm., and -n-*butyl ether*, b.p. 71°/10 mm., all unstable, which with CuCN, $Hg(CN)_2$, or AgCN (gives no carbimide) (not NaCN or KCN) in C_6H_6 yield $CH_2{\cdot}CN\ CH_2Cl{\cdot}CH_2$ *ether*, b.p. 109—110°/27·5 mm., $CH_2Cl{\cdot}CH_2$ α-*cyano-ethyl*, b.p. 91°/10 mm., -n-*propyl*, b.p. 97·5°/6 mm., and -n-*butyl ether*, b.p. 105·5°/4·5 mm. With MgRHal in Et_2O these give *Me* β-*chloroethoxymethyl ketone*, b.p. 72—73°/8 mm. (*semicarbazone*, m.p. 103°), β-*chloroethoxymethyl Et*, b.p. 82°/5 mm. (*semicarbazone*, m.p. 92·5°), *Pr*$^{\alpha}$, b.p. 88·5—90°/4 mm., *Bu*$^{\alpha}$, b.p. 88·2—89°/2 mm., n-*amyl*, b.p. 96·2—97°/2·5 mm., and iso*amyl ketone*, b.p. 99·5—100·5°/2·5 mm., *Ph* β-*chloroethoxymethyl ketone*, m.p. 26·1°, b.p. 152—155°/4·5 mm. (*semicarbazone*, m.p. 119·5—120°), *Me*, b.p. 70—72°/4 mm., and *Et* α-β′-*chloroethoxyethyl ketone*, b.p. 71°/3·5 mm. (*semicarbazone*, m.p. 104°), α-β′-*chloroethoxyethyl Pr*$^{\alpha}$ *ketone*, b.p. 87·5—88·3°/3 mm. (*semicarbazone*, m.p. 127°), and *Me* β-*iodoethoxymethyl ketone*, b.p. 90—92°/4 mm. 5-β-*Chloroethoxymethyl*-5-iso*amyl*-, m.p. 152·5°, 5-*phenyl*-5-β-*chloroethoxymethyl*-, m.p. 159·8°, 5-*ethyl*-5-α-β′-*chloroethoxyethyl*-, m.p. 168·8°, and 5-α-β′-*chloroethoxyethyl*-5-n-*propyl*-, m.p. 140·5°, *-hydantoin* (but no other hydantoins) were also obtained. B.p. of the ketones and m.p. are corr. *n* and *d* are given. R. S. C.

Preparation of ethyl hypochlorite. H. T. Comastri (Anal. Asoc. Quím. Argentina, 1939, **27**, 41—44).—The instability of EtOCl is attributed to the presence of HCl. After treatment with ice-cold dil. $NaHCO_3$ saturated with NaCl it will keep for several hr. F. R. G.

Sulphurous esters and chlorosulphites. P. Carré and D. Libermann (Bull. Soc. chim., 1939, [v], **6**, 1255).—The observations of Gerrard (A., 1939, II, 97) were recorded previously by the authors (A., 1933, 696). J. W. S.

Hydrolysis of α- and β-glycerophosphates. M. C. Bailly (Compt. rend., 1939, **208**, 1820—1822).—Na α- and β-glycerophosphate are hydrolysed without isomerisation (cf. A., 1939, I, 205) by boiling H_2SO_4 at p_H 3·62, the β- twice as rapidly as the α-form. Below p_H 3 isomerisation accompanies hydrolysis. J. L. D.

***X*-Ray and thermal examination of the glycerides. VI. Symmetrical mixed triglycerides $CH(O{\cdot}CO{\cdot}R')(CH_2{\cdot}O{\cdot}COR)_2$ (continued).** T. Malkin and M. L. Meara (J.C.S., 1939, 1141—1144).—The following symmetrical triglycerides have been prepared by the methods used previously (A., 1939, II, 97), and all exist in four solid modifications, vitreous, α, β′, and β, the m.p. of which are in the order given: β-*decodimyristin* (16°, 37°, 40°, 43·5°), β-laurodipalmitin (34°, 47°, 50°, 53·5°), β-myristodistearin (47°, 56°, 59°, 62·5°), β-*myristodidecoin* (3°, 21°, 30°, 34°), β-palmitodilaurin (I) (19°, 35°, 42·5°, 45·5°), β-*stearodimyristin* (II) (33°, 47°, 53°, 55·5°), β-decodipalmitin (20°, 42°, 48°, 51·5°), β-laurodistearin (36°, 52°, 58°, 60·5°), β-*palmitodidecoin* (6°, 27°, 36°, 40°), β-stearodilaurin (21°, 38°, 43°, 47°), β-*stearodidecoin* (5°, 34°, 40°, 44·5°), and β-decodistearin (30°, 47°, 53°, 57°). In contrast to other glycerides, the long spacings of the β forms of all except (I) and (II) correspond with twice the length of a single mol., but the side spacings do not suggest any fundamental difference in structure. J. D. R.

Autoxidation of organic sulphur compounds. M. Delépine (Bull. Soc. chim., 1939, [v], **6**, 1234—1236; cf. A., 1922, i, 914).—The results obtained (*loc. cit.*) are confirmed, *i.e.*, that action ceases very soon, with a permanent arrest in autoxidation. Experiments performed in 1912, with S compounds, *e.g.*, OMe·CS·SMe, MeCS·OEt, in air or O_2, are further examined; after 26 years in the tubes, similar results are obtained. A. T. P.

Structural identity of polysulphones prepared by peroxide catalysis and under the influence of ultra-violet light. C. S. Marvel and W. H. Sharkey (J. Amer. Chem. Soc., 1939, **61**, 1603).—On irradiation with ultra-violet light for ~1 week Δ^{α}-pentene combines with SO_2; the polysulphone formed in this way is identical with that formed in presence of peroxide catalysts. W. R. A.

***pp′*-Diaminodiphenylmethane as a reagent for the identification of monobasic, saturated, aliphatic acids.** A. W. Ralston and M. R. McCorckle (J. Amer. Chem. Soc., 1939, **61**, 1604—1605).—$(p\text{-}NH_2{\cdot}C_6H_4)_2CH_2$ and RCO_2H, when heated to boiling, give *pp′*-di(acet-, m.p. 227—228°, *-di*(*propion*-, m.p. 212—213°, *-di*-(n-*butyr*-, m.p. 197—198°, *-di*-(n-*valer*-, m.p. 188—189°, *-di*-(n-*hex*-, m.p. 185—186°,

-di-(n-*hept-*, m.p. 183—184°, *-di-*(n-*oct-*, m.p. 182—183°, *-di-*(n-*non-*, m.p. 176—177°, *-di-*(n-*dec-*, m.p. 178—179°, *-di-*n-(*undec-*, m.p. 175—176°, *-di*(*laur-*, m.p. 174—175°, *-di-*(n-*tridec-*, m.p. 172—173°, *-di*(*myrist-*, m.p. 170—171°, *-di-*(n-*pentadec-*, m.p. 167—168°, *-di*(*palmit-*, m.p. 167—168°, *-di*(*margar-*, m.p. 164—165°, and *-di-*(*stear-*, m.p. 164—165°, *-amido*)*diphenylmethane*, which are useful for characterising the acids. The lower members give good depressions of the m.p. when mixed. R. S. C.

Xanthates of metals of group VI. L. Malatesta (Gazzetta, 1939, **69**, 408—416).—$(NH_4)_2MoO_4$ and $OEt{\cdot}CS_2K$ treated in H_2O with SO_2 give molybdenyl tetraethylxanthate, new m.p. 118·5° (slight decomp.) (cf. Montequi, A., 1930, 1028) ($3C_5H_5N$ additive product), which with aq. KCN in $COMe_2$ gives $Mo_2O_3(CN)_4,4H_2O$ and $KCS_2{\cdot}OEt$; with solid KCN in $COMe_2$, K molybdocyanides are formed. *Molybdenyl tetra-methyl-*, decomp. 100—120°, *-n-propyl-*, m.p. 89—91° (slight decomp.), *-isopropyl-*, m.p. 114°, *-n-butyl-*, m.p. 75°, *-isobutyl-*, m.p. 106—107·5° (slight decomp.), *-isoamyl-*, m.p. 105° (decomp.), and *-cyclohexyl-xanthate*, m.p. 121° (decomp.), are prepared similarly. $UO_2(NO_3)_2$ and $OR{\cdot}CS_2K$ give *uranyl di-methyl-*, *-ethyl-* (easily hydrolysed), *-isoamyl-*, and *-isopropyl-xanthate*, and similar products, all of which decompose at 50—60°. Similar derivatives of W are not obtained. E. W. W.

Preparation of acrylic acid esters. P. P. Kobeko, M. M. Koton, and F. S. Florinski (J. Appl. Chem. Russ., 1939, **12**, 313—316).—Esters of $CH_2{:}CH{\cdot}CO_2H$ are prepared as follows: $CH_2{:}CH{\cdot}CHO$ (+Br) → $CH_2Br{\cdot}CHBr{\cdot}CHO$ (+HNO_3) → $CH_2Br{\cdot}CHBr{\cdot}CO_2H$ (+ ROH) → $CH_2Br{\cdot}CHBr{\cdot}CO_2R$ (+Zn) → $CH_2{:}CH{\cdot}CO_2R$ (R = Bu, *iso*amyl). R. T.

Preparation of derivatives of the higher fatty acids. E. Ochiai and M. Shimizu (J. Pharm. Soc. Japan, 1938, **58**, 302—303).—An attempt to prepare derivatives of stearic acid having p_H 5—8 in aq. solution. The following are described: *stearylquinine* (*Pt* salt, m.p. 217° decomp.; *hydrochloride*, m.p. 69°, p_H 2·5), *stearyltropine*, m.p. 49·8° (*picrate*, m.p. 96·8°; *perchlorate*, m.p. 94·5°; *hydrochloride*, m.p. 144°, p_H 4·3), heptadecylamine hydrochloride, p_H 4·8, *stearhydrazide*, m.p. 114°. S. H. H.

Lipins of tubercle bacilli. LVII. Mycolic acids of avian tubercle bacillus wax. R. J. Anderson and M. M. Creighton (J. Biol. Chem., 1939, **129**, 57—63).—α- (I), $C_{38}H_{74}O_3$, m.p. 69—70°, $[\alpha]_D$ +5·6° in $CHCl_3$ (*Br*-derivative, 22·4% Br, m.p. 47—49°), and β- (II), $C_{88}H_{174}O_3$, m.p. 60—61°, $[\alpha]_D$ +5·5° in $CHCl_3$ (*Br*-derivative, 22·9% Br, m.p. 43—49°), *-mycolic acid* have been obtained from the avian tubercle bacillus wax. These acids differ from the corresponding acids from human tubercle bacilli in not containing OMe-groups. (I) decomposes on heating at 1 mm. to form a branched-chain pentacosanoic acid, $C_{25}H_{50}O_2$, m.p. 78—79°, in 25% yield, whereas (II) similarly yields *n*-tetracosanoic acid (21%). The non-volatile residues from (I) and (II) are separable into highly unsaturated fractions of varying solubility in Et_2O and mol. wt. 1000—1100 (Rast). P. G. M.

Resonance reaction. II. P. Neogi and K. L. Mondal (J. Indian Chem. Soc., 1939, **16**, 239—240). —Maleic acid is converted into fumaric and citraconic into mesaconic in presence of MnO_2 by a "resonance reaction" (A., 1930, 550). W. R. A.

***cis–trans*-Isomerisation with boron fluoride.** C. C. Price and M. Meister (J. Amer. Chem. Soc., 1939, **61**, 1595—1597).—BF_3 in CCl_4 or BF_3,Et_2O equilibrates *cis-* and *trans*-stilbene (93·1% of *trans*), probably by forming a complex, $^+CHPh{\cdot}CHPh{\rightarrow}BF_3^-$ (cf. Price *et al.*, A., 1938, II, 478). $AlCl_3$ in the Friedel–Crafts reaction and H^+ in the isomerisation of olefines form similar complexes. Et_2 maleate is unaffected by BF_3, probably because the latter forms complexes with the CO_2Et rather than with the C:C. R. S. C.

Hydroxylation of unsaturated substances. V. Catalytic hydroxylation of unsaturated substances with functional groups. N. A. Milas, S. Sussman, and H. S. Mason (J. Amer. Chem. Soc., 1939, **61**, 1845—1847; cf. A., 1938, II, 1).—H_2O_2–$Bu^{\gamma}OH$–OsO_4 converts Et crotonate into $Me{\cdot}[CH{\cdot}OH]_2{\cdot}CO_2Et$ (56%), Et_2 maleate into Et_2 *meso*tartrate (41%), Et_2 fumarate into Et_2 *r*-tartrate (58%), mesityl oxide into β-methyl-*n*-pentane-βγ-diol-δ-one (23%), b.p. 104—110°/16 mm. [p-*nitrophenylhydrazone*, m.p. 251—253° (decomp.)], $CH_2{:}CH{\cdot}OAc$, $(CH_2{:}CH)_2O$, or $CH_2{:}CHBr$ into $OH{\cdot}CH_2{\cdot}CHO$ (60, 96, 12·5%), and oleic acid into ιc-dihydroxystearic acid. $CHPh{:}CH{\cdot}CH_2{\cdot}OH$ gives 12·2% of $OH{\cdot}CHPh{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$ (I), an *ether* of (I), $C_{18}H_{22}O_5$, m.p. 155·5—156° (*tetrabenzoate*, m.p. 118—119°), and (?) another *ether* (*tetrabenzoate*, m.p. 217°), but is mostly converted into PhCHO and $OH{\cdot}CH_2{\cdot}CHO$. R. S. C.

M.p. curve of esters of the dihydroxystearic acid from castor oil. S. Ishikawa and E. Kuroda (Sci. Rep. Tokyo Bunrika Daigaku, 1939, **3**, 265—271).—Me 9ι-dihydrostearate, m.p. 110° (corr., Berl), is hydrolysed and the acid is esterified by the requisite alcohol and $PhSO_2Cl$ to the *Et*, m.p. 106°, *Pr*$^{\alpha}$, m.p. 100·6°, *Bu*$^{\alpha}$, m.p. 93·0°, n-*amyl*, m.p. 93·7°, n-*hexyl*, m.p. 92·2°, n-*heptyl*, m.p. 94·3°, n-*octyl*, m.p. 93·4°, n-*nonyl*, m.p. 95·4°, n-*decyl*, m.p. 94·9°, n-*dodecyl*, m.p. 95·6°, n-*tetradecyl*, m.p. 96·6°, n-*hexadecyl*, m.p. 97·4°, and n-*octadecyl*, m.p. 98·2°, ester. H. W.

Synthesis of *n*-eicosanedicarboxylic acid, $CO_2H{\cdot}[CH_2]_{20}{\cdot}CO_2H$, and *n*-docosanedicarboxylic acid, $CO_2H{\cdot}[CH_2]_{22}{\cdot}CO_2H$. S. Shiina (J. Soc. Chem. Ind. Japan, 1939, **42**, 147B; cf. A., 1937, II, 483).—$CO_2Et{\cdot}[CH_2]_{18}{\cdot}CO_2Et$ is converted via the glycol, di-iodide, and dicyanide into $CO_2H{\cdot}[CH_2]_{20}{\cdot}CO_2H$, m.p. 126·9—127·1° ($Me_2$, m.p. 71—71·2°, and Et_2 ester, m.p. 61—61·2°), which by similar reactions yields the glycol, m.p. 105·3—105·5°, di-iodide, m.p. 71·9—72·1°, and $CO_2H{\cdot}[CH_2]_{22}{\cdot}CO_2H$, m.p. 126·9—127·1° ($Me_2$, m.p. 75·0—75·2°, and Et_2 ester, m.p. 65·9—66·1°). A. Li.

Structure of vinyl polymerides. III. Polymeride from α-angelicalactone. C. S. Marvel and C. L. Levesque (J. Amer. Chem. Soc., 1939, **61**, 1682—1684; cf. A., 1938, II, 255).—BF_3,Et_2O (0·4

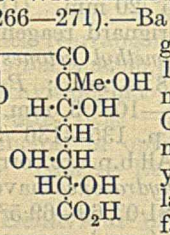
c.c.) (but not peroxides) in CS_2 (40 c.c.) converts α-angelicalactone (15 g.) into a *polymeride* (I), in which

$$\begin{matrix}CMe{=}C\text{—}\\ O\cdot CO\cdot CH_2\end{matrix}\left[\begin{matrix}\text{—}CMe{=}C\text{—}\\ O\cdot CO\cdot CH_2\end{matrix}\right]_n\text{—}H \quad (I.)$$

n is 7—8 as judged by the mol. wt. in $COPh_2$ and titration of residual C:C by Br in CCl_4. 75% of the lactone groups appear from the following evidence to be retained. (I) dissolves slowly in aq. NaOH and undergoes 84% reaction with NH_3–dioxan at 150—160° to give a lactam and ~90% reaction with LiPh to give a polyalcohol. Since BF_3 is a *trans*-esterifying reagent, some of the $CH_2\cdot CO_2H$ are expected to become isolated and the above reactions are consistent with the head-to-tail structure of (I). In presence of Cu chromite at 250°/400 atm., (I) absorbs twice the calc. amount of H_2 and gives only 70% of polymeric product, this having a lower mol. wt.; the reaction is explained on the basis of (I) as due to fission of C·O linkings in O·C·C·C·O leading to some units of types ·CHMe·CH($CH_2\cdot CO_2H$)· and ·CHMe·CH($CH_2\cdot CH_2\cdot OH$)·. Hydrogenation at 175°/400 atm. leads to absorption of 0·84±0·05 mol. of H_2, which agrees with the val. (0·75) calc. by statistical analysis (Flory, A., 1939, II, 401) for C·O fission allowing C·O linkings to become isolated; little C·C cleavage occurred at this temp. Isomerisation to β-angelicalactone prior to polymerisation would give structures not containing O·C·C·C·O and is thus excluded. Ultra-violet light gives a more mobile polymeride of lower mol. wt. R. S. C.

Reduction of *dl*-erythronolactone to *dl*-erythrose. J. W. E. Glattfeld and B. D. Kribben (J. Amer. Chem. Soc., 1939, **61**, 1720—1725).—*dl*-Erythronolactone with Ac_2O–HCl or AcCl gives the *lactone diacetate*, m.p. 52·5—53°, and with KOH or NaOH in MeOH gives *K* or *Na* dl-*erythronate*. The K salt with AcCl gives dl-*erythronic acid triacetate* (74%), an oil (*Ca* salt), which with $SOCl_2$ (must be pure) gives the *acid chloride*, b.p. 114—116°/2 mm. H_2–Pd–$BaSO_4$ in xylene reduces and partly deacetylates this, giving dl-*erythrose diacetate* (I) (20%), b.p. 126—129°/2 mm. Hydrolysis of (I) gives *dl*-erythrose (identified as phenylosazone), but 2 : 4-$(NO_2)_2C_6H_3\cdot NH\cdot NH_2$ gives a *substance* (? the *diacetyltriazine*), m.p. 172—173°. R. S. C.

Tetrahydroxyadipic acid. O. Votoček and O. Wichterle (Coll. Czech. Chem. Comm., 1939, **11**, 266—271).—Ba δ-ketorhamnohexonate and aq. HCN give a *lactonic acid* (I), $C_8H_{12}O_8$, m.p. 198°, $[\alpha]_D$ −25·4° (and an oily epimeride), which gives the *Ba* salt, $C_8H_{12}O_9Ba,+2H_2O$, and by the usual methods an oily methylheptose, which yields a trace of an osazone. Distillation of (I) gives a pyrone. These facts and Hudson's rule indicate the formula shown for (I). R. S. C.



Relations between rotatory power and structure in the sugar group. XXXII. Rotations of the aldonic γ-lactones. C. S. Hudson (J. Amer. Chem. Soc., 1939, **61**, 1525—1528; cf. A., 1939, II, 300).—The rule of optical superposition applies to γ-aldolactones if they are divided into classes of the (*A*) ribose–aldonic and (*B*) xylonic–lyxonic pairs of epimerides. Data for class *B* are, however, scanty. This principle is not always in accord with the qual. lactone rule. It shows *D*-gulo-*L*-taloheptolactone to belong to class *A*. [α] of several unknown hepto- and octo-lactones are calc. *L*-Epirhamno- and β-*L*-fucohexolactone are probably δ-lactones (speed of mutarotation). *D*-Gluco-*D*-idoheptolactone behaves abnormally in solution. R. S. C.

Preparation of mannonolactones from seeds of date palm (*Phœnix dactylifera*). Effect on gastric mucin smears. K. J. Goldner and C. H. Rogers (J. Amer. Pharm. Assoc., 1939, **28**, 364—369).—The seeds contain 48·85% of mannan and 0·68% of galactan. The prep. from Ca mannonate of δ-, m.p. 159—165°, $[\alpha]_D^{20}$ +114·2° to +41·3° in H_2O (14 days), and γ-*lactone*, m.p. 151°, $[\alpha]_D^{20}$ +51·0° in H_2O, *Me*, m.p. 155°, *Et*, m.p. 161°, Pr^{β}, m.p. 169°, and Bu^{α} *mannonate*, m.p. 144°, and *mannoethanolamide*, m.p. 149—150°, $[\alpha]_D^{20}$ −14·4° in H_2O, is described. The efficiency of these substances in dissolving mucin and their non-toxicity indicate their applicability to dental cleaning preps. F. O. H.

Isolation of ketouronic acids as crystalline alkaloidal salts. J. P. Hart and M. R. Everett (J. Amer. Chem. Soc., 1939, **61**, 1822—1824).—1% aq. solutions of sugars are oxidised by Br at ~25°; after removal of the Br and HBr, the ketouronic acids are isolated as Ba salts and crystallised as brucine salts. *Brucine* l- (I) (from *d*-gulolactone), m.p. 165—166°, $[\alpha]_D^{25}$ −24·5°, and d-*fructo*-6-*uronate* (from *d*-mannose), m.p. 192—192·5° (decomp.), $[\alpha]_D^{25}$ −15·5°, l-*tagato*-6-*uronate* (from *d*-galactose), m.p. 189—189·5° (decomp.), $[\alpha]_D^{25}$ −17°, d-*xyloketouronate* (from *d*-xylose), m.p. 168—169°, $[\alpha]_D^{25}$ −9°, *l*-sorbo-6-uronate (from *d*-glucose), m.p. (anhyd.) 174—175° (decomp.) and (+2H_2O) 182° (decomp.), $[\alpha]_D^{25}$ −24°, and l-deoxy-*l*-fructo-6-uronate [with (I) from *l*-rhamnose], m.p. 128—129°, $[\alpha]_D^{25}$ −32° (all in H_2O), are thus obtained. The ketose structure of the acids is shown by their stability to Br. Naphthoresorcinol, orcinol, and Molisch tests of the salts are identical. R. S. C.

New water-soluble calcium salt, calcium gluconate-glucoheptonate. A. Salomon (Pharm. Weekblad, 1939, **76**, 914—917).—Ca gluconate-glucoheptonate, prepared by mixing solutions of Ca gluconate and Ca glucoheptonate or by neutralising a solution of the two acids with $Ca(OH)_2$, is very sol. in H_2O (50%) and 11·5% solutions (p_H ~7) are suitable for intravenous injection. S. C.

Structure of alginic acid. E. L. Hirst, J. K. N. Jones, and (Miss) W. O. Jones (Nature, 1939, **143**, 857).—High yields of *d*-mannuronic acid (I) are obtained by the action of MeOH–HCl on alginic acid (II). A partly degraded form of (II) of comparatively low mol. wt. has been isolated by means of the same reagent. With TlOEt and MeI it gives the corresponding fully methylated derivative, which, on hydrolysis (conc. HNO_3) and degradative oxidation, yields *meso*dimethoxysuccinic acid (III), indicating that in each of the (I) residues the Me groups were

attached at $C_{(2)}$ and $C_{(3)}$. This was confirmed as follows. Methylated (II) with MeOH–HCl under pressure gives the Me ester of 2 : 3-dimethylmannuronide, which on hydrolysis and oxidation (aq. Br) yields 2 : 3-dimethylmannosaccharic acid, which is oxidised by HIO_4 to $CHO{\cdot}CO_2H$ and the semialdehyde of (III). (II) appears to be composed of *d*-mannuronic anhydride residues linked glycosidically. In addition, (II) contains a chain of (I) residues in each of which the OH at $C_{(2)}$ and $C_{(3)}$ are free. The glycosidic linkage is either 1 : 5 or (probably) 1 : 4. Structural resemblances with cellulose and pectic acid are pointed out. L. S. T.

Condensation of acetaldehyde and vinyl acetate. C. S. Marvel, J. Harmon, and E. H. Riddle (J. Org. Chem., 1939, **4**, 252—255).—Successive addition of Na and vinyl acetate (I) to MeCHO gives *αγ-ethylidenedioxybutyl acetate*, b.p. 74—75°/6 mm. Under similar conditions (I) does not react with EtCHO, Pr$^{\alpha}$CHO, Pr$^{\beta}$CHO, or PhCHO. Reaction between MeCHO and (I) does not occur in presence of KOH–EtOH, $ZnCl_2$, $Ba(OH)_2$, $Mg(OMe)_2$, NaOEt, NaOPh, anhyd. Na_2CO_3, $SnCl_4$, AcOH + *p*-$C_6H_4Me{\cdot}SO_3H$, dry HCl, or dry *p*-$C_6H_4Me{\cdot}SO_3H$ in C_6H_6. H. W.

Synthesis of acetals of chloro- and bromoacetaldehyde. E. M. Filachione (J. Amer. Chem. Soc., 1939, **61**, 1705—1706).—Passage of Cl_2 into $CH_2{:}CH{\cdot}OAc$ in abs. EtOH or MeOH cooled in $COMe_2$–CO_2 gives Et_2 (83%), b.p. 53—54°/16 mm., or *Me$_2$ chloroacetal* (53%), b.p. 124·5—126·5°. At −10° air carrying Br gives Et_2 bromoacetal (68%), b.p. 62—63°/15 mm.; $CHCl_3$–Br, added to the MeOH solution at −40°, gives 46% of Me_2 bromoacetal, b.p. 48—51°/18 mm. Structures are proved by hydrolysis, identification of MeOH or EtOH, and oxidation (H_2O_2) of the aldehyde to the acid. R. S. C.

Aldehydic perfumes. II. Synthesis of pelargonaldehyde. S. Ishikawa and A. Miyata (Sci. Rep. Tokyo Bunrika Daigaku, 1939, **3**, 257—263).—The yield of pelargonaldehyde (I) obtained by ozonisation of oleic acid suspended in aq. $NaHSO_3$ with a little decahydronaphthalene as dispersing agent does not exceed 20%. Oxidation of Me 9ι-dihydroxystearate (II) with $Pb(OAc)_4$ in AcOH gives (I) in 50% yield accompanied by Me 7-aldehydo-octoate (2 : 4-*dinitrophenylhydrazone*, m.p. 67—68°). (I) is also obtained in very modest yield by heating (II) with sand at 650° in CO_2. H. W.

C_{10}, C_{12}, and C_{14} aldehydes from copra oil. R. Escourrou (Bull. Soc. chim., 1939, [v], **6**, 1173—1181).—Fatty acids (obtained by saponification of the oil) and PCl_3 give the corresponding chlorides, hydrogenated (Pt) under reduced pressure (not at atm.) to the aldehydes. Lauryl chloride, b.p. 141°/14 mm., at 300—320°/170—180 mm., affords undecane, b.p. 194—195°/760 mm.; at 200—205°/50 mm., lauraldehyde is formed, with some tricosane, $C_{23}H_{48}$ (mechanism of formation discussed). The use of Raney Ni at 160°/50 or 580 mm. gives no aldehyde. Hydrogenation (Pt) of myristyl chloride, b.p. 195°/45—47 mm., at 220—230°/60—65 mm. affords $Me{\cdot}[CH_2]_{12}{\cdot}CHO$ and tridecane, $C_{13}H_{28}$. Decoyl chloride, b.p. 115°/13 mm., at 200°/80—90 mm. gives decaldehyde, b.p. 207—210°/760 mm., and polymerised products. Octoyl chloride, b.p. 75—77°/8—10 mm., at 195°/80—90 mm. gives octaldehyde, b.p. 72°/20 mm., with some polymerisation. A. T. P.

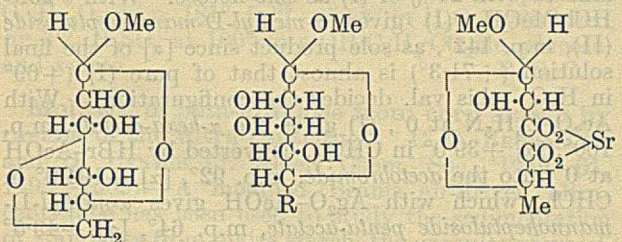
Reaction of methyl α-chloroethyl ketone with potassium cyanide. R. Justoni (Gazzetta, 1939, **69**, 378—391).—The product from $COMe{\cdot}CHMeCl$ (I) and aq. KCN is not $COMe{\cdot}CHMe{\cdot}CN$ (cf. Henry *et al.*, A., 1900, i, 537), nor a dimethyl*iso*oxazole (II) (cf. Youtz *et al.*, A., 1930, 93), but *αβ-oxido-α-methylbutyronitrile*, $\overset{O}{\overset{CHMe}{\diagdown\!\!\diagup}}CMe{\cdot}CN$, (III), b.p. 145°/755 mm. With *p*-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2$, (II) does not react, but (III) gives (*p*-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}N{:}CMe)_2$ (and similarly other derivatives of Ac_2). In EtOH, (I) and KCN also give (III), with $CHMeAc{\cdot}CN$ [which is, however, not obtained from (III) and Na or NaOEt (cf. *loc. cit.*)]. With liquid HCN, (I) gives *Me α-chloroethyl ketone cyanohydrin*, b.p. 120—123°/15 mm., which with aq. KOH yields (III), with a very small proportion of (I). With KOH–MeOH, (I) yields acetoin, of which the *cyanohydrin*, b.p. 120—123°/15—16 mm., with H_2SO_4 or P_2O_5 gives only slight traces of (III). E. W. W.

Keto-ethers. V. β-Chloro*iso*propoxymethyl ketones derived from propylene chlorohydrin. J. J. Spurlock and H. R. Henze (J. Org. Chem., 1939, **4**, 234—241).—$CH_2Cl{\cdot}O{\cdot}CMe_2Cl$ (I), b.p. 106—107°/146 mm., 160—161°/747 mm., is obtained by saturating $OH{\cdot}CHMe{\cdot}CH_2Cl$ and 36% CH_2O with HCl at 0° or from BzCl and $OH{\cdot}CHMe{\cdot}CH_2Cl$ at 145—155°. It is best converted into *β-chloro*isopropoxyacetonitrile (II), b.p. 98—99° (corr.)/15 mm., by treatment with CuCN in PhMe at 120° with purification by distillation in vac. Alternatively, propylene αβ-oxide is saturated with HCl and treated with CH_2O and again saturated with HCl, giving *di-(β-chloro*isopropyl) *formal*, b.p. 112·5—113·5°/11 mm., which is treated with BzCl, thereby yielding *β-chloro*isopropyl *benzoate*, b.p. 106—107°/2—3 mm., and (I), which is then treated with CuCN. Poorer yields of (II) are derived from (I) and $Hg(CN)_2$ in boiling C_6H_6 whereas (I) and KCN scarcely react. Crude (II) is transformed by EtOH and HCl into *Et β-chloro*isopropoxyacetate, b.p. 110—111°/19 mm., converted by conc. aq. NH_3 into *β-chloro*isopropoxyacetamide, m.p. 31·2° (corr.), which is dehydrated by P_2O_5 at 130° to (II), b.p. 104—105°/20 mm. (II) is transformed by the appropriate Grignard reagent into the following *β-chloro*isopropoxymethyl ketones; *Me*, b.p. 73—74°/4 mm.; *Et*, 77—78°/4 mm.; *Pr*, m.p. 95—96°/6 mm.; *Bu*, b.p. 101—102°/3 mm.; *amyl*, b.p. 109—110°/3 mm.; *Ph*, b.p. 135—136°/3 mm., CH_2Ph, b.p. 151—152°/4 mm. All b.p. are corr. The corresponding 2 : 4-*dinitrophenylhydrazones* have m.p. 120·5—121·5°, 85·5—86·5°, 80·5—81·0°, 69—69·5°, 91·5—92·5°, 181—182°, and 77—78° (corr.), respectively. The mol. refraction of these ketones is a better index of purity than is the parachor. H. W.

Stability of a higher ketone and a higher secondary alcohol towards heat. K. Kino (J. Soc. Chem. Ind. Japan, 1939, **42**, 187B).—Stearone (from commercial stearic acid), and the corresponding

carbinol (Na + BuOH), were heated at various temp., and the colour, m.p., mol. wt., and OH val. (after reduction in the former case) of the products recorded. Little decomp. occurs below 260°. A. Lr.

Oxidation of glucosides by lead tetra-acetate. R. C. Hockett and W. S. McClenahan (J. Amer. Chem. Soc., 1939, **61**, 1667—1671).—*cis*-Glycols of the sugar series are always attacked faster than are the *trans*-glycols by $Pb(OAc)_4$ (6·5 mols., equiv. to infinite excess since 13 mols. react no faster); 21 examples are cited. If the ether-aldehyde formed can yield a *cis*-glycol of type (*A*) by cyclic acetal formation, a second mol. of $Pb(OAc)_4$ is very rapidly consumed; if this is impossible, reaction slows down after 1 mol. has been used; examples are α-methyl-*d*-mannopyranoside (*B*) (R = CH_2·OH), which gives (*A*), and α-methyl-*l*-rhamnopyranoside (*B*) (R = Me) and α-



(*A*.) (*B*.) (*C*.)

methyl-*d*-mannopyranoside 6-CPh_3 ether (*B*) (R = CH_2·O·CPh_3), which cannot give (*A*). α-Methyl-*l*-fucoside gives the *Sr* salt (*C*), $+2H_2O$, $[\alpha]_D^{20}$ +29·8° in H_2O. R. S. C.

Behaviour of glucose dimethyl acetal towards carbohydrases. N. K. Richtmyer, M. Adams, and C. S. Hudson (J. Amer. Chem. Soc., 1939, **61**, 1833—1834).—Glucose Me_2 acetal is unaffected by top yeast, taka-diastase, emulsin, maltase, invertase, pancreatic or malt amylase. R. S. C.

Glucofuranosides and thioglucofuranosides. V. Hydrolysis of α-ethylthioglucofuranoside. E. Pacsu and E. J. Wilson, jun. (J. Amer. Chem. Soc., 1939, **61**, 1450—1454; cf. A., 1938, II, 473).—Hydrolysis of α-ethylthioglucofuranoside (improved prep.; tetra-acetate, $[\alpha]_D$ +150·0° in $CHCl_3$) by 0·01N-HCl at 98—100° gives about 50% of glucose and EtSH, partly directly and partly by way of β-*ethylthioglucofuranoside*, a syrup, $[\alpha]_D^{20}$ −104° in H_2O (*tetra-acetate*, a syrup, $[\alpha]_D^{20}$ −53·1° in $CHCl_3$), but much rearrangement to α- (I), $[\alpha]_D^{20}$ +261·4° in H_2O (*tetra-acetate*, m.p. 95°, $[\alpha]_D^{20}$ +194·1° in $CHCl_3$), and β-ethylthioglucopyranoside, a syrup, $[\alpha]_D$ −60° (tetra-acetate, $[\alpha]_D$ −25·6° in $CHCl_3$), also occurs. The principle of optical superposition does not apply to (I). Glucose Et mercaptal has $[\alpha]_D^{20}$ −37·4° in H_2O. R. S. C.

Behaviour of the dimethyl acetals of glucose and galactose under hydrolytic and glucoside-forming conditions. M. L. Wolfrom and S. W. Waisbrot (J. Amer. Chem. Soc., 1939, **61**, 1408—1411).—Complex changes of $[\alpha]$ of *d*-glucose and *d*-galactose Me_2 acetals with 0·05% HCl in MeOH or H_2O at 25° and determination of readily hydrolysable material during the reaction show that the very rapid initial hydrolysis is followed by formation of unstable non-pyranoid glucosides, which later slowly give the stable pyranosides. R. S. C.

Synthetic galactose 1-phosphate. H. W. Kosterlitz (Biochem. J., 1939, **33**, 1087—1093; cf. A., 1938, III, 933).—Tri(tetra-acetylgalactose) 1-phosphate, $[\alpha]_D^{17}$ +119·9° in MeOH (from acetobromogalactose and Ag_3PO_4), with MeOH–HCl at 25° for 8 hr. yields galactose 1-phosphate, which was isolated as the crude Ba and dibrucine salts; the latter afforded the K_2 salt ($+2H_2O$), $[\alpha]_D^{18}$ +108·2° in H_2O (anhyd. salt), which was converted into the *Ba* salt, $[\alpha]_D^{18}$ +92·7°. The ester appears to be α-galactopyranose 1-phosphate. F. O. H.

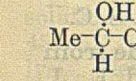
Glucofuranosides and thioglucofuranosides. VI. Preparation of dimethyl acetal and methyl-furanosides from *d*-fructose diethyl mercaptal. E. Pacsu (J. Amer. Chem. Soc., 1939, **61**, 1671—1675; cf. A., 1938, II, 432, also above).—*d*-Fructose Et_2 mercaptal (prep. from the penta-acetate modified to give a quant. yield) with $HgCl_2$–HgO in MeOH at −80° gives only d-*fructose* Me_2 *acetal* (I), m.p. 107—108°, $[\alpha]_D^{20}$ −45·6°, −63·0°, $[\alpha]_{6563}^{20}$ −35·6°, −50·0°, $[\alpha]_{5463}^{20}$ −53·6°, −76·1° in H_2O and MeOH, respectively (*penta-acetate*, m.p. 109°, $[\alpha]_D^{20}$ 0 in $CHCl_3$), but at room temp. gives also the cryst. and syrupy γ-methyl-fructosides of Purves and Hudson (A., 1934, 513). Invertase at p_H 4·5 and yeast at p_H 7 are without effect on (I), but yeast in unbuffered solution ferments it owing to prior hydrolysis by the acids of the yeast; (I) is extremely sensitive to acid. Acetal and pyranoside formation from mercaptals may be independent reactions, or both may proceed by way of an intermediate of type, >C(OR)·SR. R. S. C.

Formation of α-ethylthioglucopyranoside from glucose ethyl mercaptal. E. Pacsu and E. J. Wilson, jun. (J. Amer. Chem. Soc., 1939, **61**, 1930—1931).—Glucose Et_2 mercaptal and 22% HCl give α-ethylthioglucopyranoside (< 20% yield) without addition of glucose (cf. Brigl *et al.*, A., 1939, II, 299). The same product (15%) is obtained from glucose and EtSH in 22% HCl. The β-pyranoside is probably also formed. R. S. C.

Action of triphenylmethyl chloride on α-methyl-*D*-mannopyranoside. A. J. Watters, R. C. Hockett, and C. S. Hudson (J. Amer. Chem. Soc., 1939, **61**, 1528—1530).—α-Methyl-*D*-mannopyranoside is etherified preferentially at the primary OH by CPh_3Cl in C_5H_5N, giving the 6-CPh_3 *ether*, $+C_5H_5N$, m.p. 101—102°, $[\alpha]_D^{20}$ +23·45° in $CHCl_3$ ($CaCl_2$ *compound*, $+2{\cdot}5EtOH$, m.p. ~110—112° $[\alpha]_D^{20}$ +26·6° in MeOH), the structure of which is proved as follows. With Ac_2O–C_5H_5N at 0° it gives α-*methyl*-D-*mannopyranoside* 6-CPh_3 *ether* 2 : 3 : 4-*triacetate*, m.p. 130°, $[\alpha]_D^{20}$ +44·33° in $CHCl_3$, hydrolysed by cold HBr–AcOH to α-*methyl*-D-*mannopyranoside* 2 : 3 : 4-*triacetate*, m.p. 98°, $[\alpha]_D^{20}$ +55·54° in $CHCl_3$, which with MeI–Ag_2O (5 treatments) gives a syrupy 6-*Me ether*. Hot 2% HCl converts this into 6-methyl-*D*-mannose, $[\alpha]_D^{20}$ +15·3° in $CHCl_3$ [osazone = 6-methylglucosazone, m.p. 172° (lit., 177°), $[\alpha]_D^{20}$ −68·6° → −48·0° in EtOH in 48 hr.]. M.p. are corr. R. S. C.

Relations between rotatory power and structure in the sugar group. XXXIII. α- and β-Methylpyranosides of *L*-fucose (*L*-galactomethylose) and their triacetates. R. C. HOCKETT, F. P. PHELPS, and C. S. HUDSON (J. Amer. Chem. Soc., 1939, **61**, 1658—1660; cf. A., 1939, II, 405).—The calc. $[\alpha]$ of α-methyl-*L*-fucoside (I) (Hudson, A., 1925, i, 233) is confirmed by experiment (cf. Tadokoro *et al.*, J. Biochem. Japan, 1923, **2**, 461; Minsaas, A., 1932, 723). *L*-Fucose (prep. from *Ascophyllum nodosum* described) and hot 1% HCl–MeOH give α-, m.p. 154°, $[\alpha]_D^{20}$ −197° (triacetate, m.p. 67°, $[\alpha]_D^{20}$ −149·7° in $CHCl_3$), and β-methyl-*L*-fucoside, m.p. 121—123°, $[\alpha]_D^{20}$ +14·2° in H_2O (triacetate, m.p. 96—97°, $[\alpha]_D^{20}$ +7·1° in $CHCl_3$). R. S. C.

Cleavage of the carbon chains of some methylaldohexomethylopyranosides by oxidation with periodic acid. W. D. MACLAY, R. M. HANN, and C. S. HUDSON (J. Amer. Chem. Soc., 1939, **61**, 1660—1666).—Accepted structures are confirmed. α-Methyl-*L*-galactomethylopyranoside (Votoček's nomenclature) and HIO_4 afford *L'*-methoxy-*L*-methyldiglycolldialdehyde, $+H_2O$, m.p. 98—99·5°, $[\alpha]_D^{20}$ −141·4° (cf. Jackson *et al.*, A., 1937, II, 325), converted by Br–$SrCO_3$ into *Sr* L'-*methoxy*-L-*methyldiglycollate* (I), $+xH_2O$, $[\alpha]_D^{20}$ (anhyd.) +68·2°. α-Methyl-*D*-gluco-, $[\alpha]_D^{20}$ +152·7°, β-methyl-*L*-galacto-, and β-methyl-*D*-gluco-methylopyranoside give similarly D'-*methoxy*-D-*methyl*-, m.p. 98—99°, $[\alpha]_D^{20}$ +141·4°, D'-*methoxy*-L-*methyl*-, m.p. 100—101°, $[\alpha]_D^{20}$ +88·8°, and L'-*methoxy*-D-*methyl-diglycolldialdehyde*, m.p. 101—102°, $[\alpha]_D^{20}$ −88·8°, respectively, and thence the corresponding *Sr* salts, (II), $+xH_2O$, $[\alpha]_D^{20}$ −68·2°, (III), $[\alpha]_D^{20}$ −45·6°, and (IV), $[\alpha]_D^{20}$ +45·7°. Hydrolysis of (I) and (III) yields $H_2C_2O_4$ and *L*-lactic acid (V), dextrorotatory (Zn salt, $+2H_2O$, $[\alpha]_D^{20}$ −7·7° to −7·9°); that of (II) and (IV) gives $H_2C_2O_4$ and *D*-lactic acid (Zn salt, prepared also from morphine *D*-lactate). Changes of $[\alpha]$ during HIO_4-oxidation are recorded. $[\alpha]$ are in H_2O. R. S. C.


(V.)

Conversion of *d*-glucose into *d*-idose. W. H. G. LAKE and S. PEAT (J.C.S., 1939, 1069—1074).—4 : 6-Dimethyl-2 : 3-anhydro-β-methylmannoside when heated with NaOMe–MeOH yields 2 : 4 : 6-*trimethyl*-β-*methyl*-d-*idopyranoside* (I), m.p. 75°, $[\alpha]_D^{14}$ −61·0° in $CHCl_3$, converted by aq. H_2SO_4 into 2 : 4 : 6-*trimethyl*-d-*idose* (a syrup), $[\alpha]_D^{18}$ +26·6° in H_2O, +8·0° in $CHCl_3$, which with aq. Br gives *trimethyl*-d-*idono*-δ-*lactone*, $[\alpha]_D^{17}$ −47·5° in $CHCl_3$, −15·4° in H_2O. From this, with liquid NH_3, 2 : 4 : 6-*trimethyl*-d-*idonamide*, $[\alpha]_D^{17}$ −20·0° in $CHCl_3$, is formed. Methylation of (I) (Ag_2O–MeI) yields *tetramethyl*-β-*methyl*-δ-*idopyranoside*, b.p. 125°/0·02 mm., $[\alpha]_D^{14}$ −68·5° in $CHCl_3$, −49·0° in H_2O, −77·3° in MeOH, hydrolysed by aq. H_2SO_4 to *tetramethyl*-d-*idopyranose* (II) (a syrup), $[\alpha]_D^{15}$ +14·5° in MeOH, +22·0° in H_2O, which on distillation at 130°/0·008 mm. gives *octamethyldi*-d-*idopyranose*, m.p. 102°, $[\alpha]_D^{19}$ +90·2° in $CHCl_3$, +95·0° in MeOH, +103° in H_2O, which on hydrolysis with 0·1N-H_2SO_4 regenerates (II). Oxidation of (II) with aq. Br yields *tetramethyl*-d-*idono*-δ-*lactone*, m.p. 91°, $[\alpha]_D^{16}$ −52·6° in $CHCl_3$, $[\alpha]_D^{13}$ −32·0° in H_2O, which on oxidation with HNO_3 followed by treatment of the acids with NH_2Me gives *l*-dimethoxysuccinmethylamide and *i*-trimethoxyxyloglutaromethylamide. J. D. R.

Synthesis of *D*-mannoheptulose; preparation of some of its derivatives. E. D. MONTGOMERY and C. S. HUDSON (J. Amer. Chem. Soc., 1939, **61**, 1654—1658).—The pulp (21 kg.) of the fruit of *Persea gratissima*, Gaertn., yields *D*-mannoheptulose (I) (315 g.), perseitol (75 g.), a non-reducing gum (400 g.), and a syrup (310 g.) (cf. LaForge, A., 1917, i, 118). In aq. 0·05N-$Ba(OH)_2$, *D*-manno-*D*-galaheptose gives [Lobry de Bruyn rearrangement; $[\alpha]$ >68·6° → +25·4° (in these and other cases $[\alpha]_D^{20}$)] a mixture, which after removal of aldoses by Br–$Ba(OBz)_2$ affords (I) (25%), m.p. 152°, $[\alpha]$ +29·2° in H_2O, and *D*-glucoheptulose (13%), m.p. 170—174°, $[\alpha]$ +66·9° in H_2O; in hot C_5H_5N it gives 72% of aldoses with 21% of (I) as sole ketose. With 0·25N-HCl–MeOH, (I) gives α-*methyl*-D-*mannoheptuloside* (II), m.p. 142°, as sole product since $[\alpha]$ of the final solution (+71·3°) is almost that of pure (I) (+69° in H_2O; this val. decides the configuration). With Ac_2O–C_5H_5N at 0°, (I) gives the α-*hexa-acetate*, m.p. 100°, $[\alpha]$ +39·0° in $CHCl_3$, converted by HBr–AcOH at 0° into the *acetobromide*, m.p. 92°, $[\alpha]$ +104·0° in $CHCl_3$, which with Ag_2O–MeOH gives α-*methyl*-D-*mannoheptuloside penta-acetate*, m.p. 64°, $[\alpha]$ +49·5° in $CHCl_3$, obtained also from (II) by Ac_2O–C_5H_5N at 0° and hydrolysed to (II). Hydrolysis of (II) by 0·005N-HCl at 98° is very rapid (*k* 0·050), but (II) is nevertheless a pyranoside (*a*) because it is formed equally, although very rapidly, at 20° and the b.p., and (*b*) because of its optical relations to *D*-mannose derivatives. R. S. C.

Periodic acid oxidation of αα-trehalose E. L. JACKSON and C. S. HUDSON (J. Amer. Chem. Soc., 1939, **61**, 1530—1532).—The structure of αα-trehalose is confirmed by oxidation by HIO_4 (4 mols. consumed) to 2 HCO_2H and D'D'-*oxydi*-(D-*hydroxymethyldiglycollaldehyde*), a syrup, converted by Br and $SrCO_3$ in H_2O into *Sr*$_2$ D'D'-*oxydi*-(D-*hydroxymethyldiglycollate*) (54%), $+6H_2O$, $[\alpha]_D^{20}$ (anhyd.) −24·0° (*c* 0·29), −52·8° (*c* 0·91) in H_2O, and the free acid, $[\alpha]_D^{20}$ +71·3° in H_2O, from which by hydrolysis and oxidation (Br) gives $H_2C_2O_4$ and 65% of Ca *D*-glycerate. R. S. C.

Cleavage of cellobiose and celtrobiose by emulsin. N. K. RICHTMYER and C. S. HUDSON (J. Amer. Chem. Soc., 1939, **61**, 1834—1835).—Cellobiose is hydrolysed 6·8 times as fast as is celtrobiose (I) by sweet almond emulsin, the difference being due to the same steric reason as for lactose–neolactose (Helferich *et al.*, A., 1939, II, 99). Hydrolysis of (I) by emulsin, but not by maltase, confirms its β-glucosidic structure. R. S. C.

2 : 4 : 6-Trimethyl-β-phenyl- and -benzyl-*D*-glucoside. N. K. RICHTMYER (J. Amer. Chem. Soc., 1939, **61**, 1831—1832).—β-Phenyl-*D*-glucoside (isolated or prepared *in situ* from its tetra-acetate) and Me_2SO_4–NaOH at 95° give 2 : 4 : 6-*trimethyl*-β-*phenyl*-D-*glucoside*, m.p. 108—109°, $[\alpha]_D$ −57·5° in $CHCl_3$ (with an isomeride, m.p. 105—106°), hydrolysed by hot 5% HCl to 2 : 4 : 6-trimethyl-*D*-glucose (I). β-Benzyl-*D*-glucoside gives similarly its 2 : 4 : 6-*Me*$_3$

derivative, m.p. 94—95°, $[\alpha]_D^{20}$ −49·1° in $CHCl_3$, also hydrolysed to (I). R. S. C.

Flavonol glucoside of *Calystegia japonica*, Chois. G. Hukuti (J. Pharm. Soc. Japan, 1939, **59**, 85—86).—Extraction of the leaves and stems of *C. japonica*, Chois, with MeOH gives *campherol-3-rhamnoglucoside*, $C_{27}H_{30}O_{15},2H_2O$, m.p. 220—224°, in 0·03% yield. It is hydrolysed by dil. H_2SO_4 to campherol, glucose, and rhamnose and transformed by CH_2N_2 followed by dil. H_2SO_4 into 3-hydroxy-5 : 7 : 4′-trimethoxyflavone, m.p. 151°. H. W.

Isolation of monotropitoside from *Gaultheria Cumingiana*, Vidal. M. Yasue and T. Sasaki (J. Pharm. Soc. Japan, 1938, **58**, 219).—Extraction of the leaves and twigs of this plant with 50% MeOH, treatment with $Pb(OAc)_2$, etc. yields *monotropitoside*, $C_{19}H_{26}O_6$, m.p. 181°, $[\alpha]_D^{30}$ −58·8° in H_2O, hydrolysed by 3% H_2SO_4 at 100° to *o*-OH·C_6H_4·CO_2Me, glucose, and xylose. R. S. C.

Mol. wt. of beta-amylose from corn starch by means of the ultra-centrifuge. C. O. Beckmann and Q. Landis (J. Amer. Chem. Soc., 1939, **61**, 1495—1503).—A modified Beams air-driven ultra-centrifuge has been used to study the sedimentation of β-amylose from maize starch, the granules of which were disrupted by dry grinding for 168 hr. and dispersed in H_2O. The β-amylose thus obtained is of various particle sizes, and mol. wts. range from 17,000 to 225,000. ~50% of the material has a sedimentation const. of $4·0 \times 10^{-13}$ (mol. wt. 31,000—60,000), whilst the vals. for the whole material range from 1·30 to $>12 \times 10^{-13}$. In the fractionation of ground maize β-amylose by MeOH a light fraction is obtained which is easily pptd. and retrograded. This anomalous behaviour is explained in terms of particle shape and hydration. α-Amylose from maize starch has a sedimentation const. of $\sim 6000 \times 10^{-13}$. W. R. A.

Mol. wt. of α-amylodextrin (erythro-granulose) from potato starch. C. O. Beckmann and Q. Landis (J. Amer. Chem. Soc., 1939, **61**, 1504—1507).—The mol. wts. of α-amylodextrins, prepared by three different methods involving the action of β-amylase on potato starch, vary from 8600 to 29,100. The heterogeneity of the dextrins is discussed. They are more spherical in shape than is β-amylose. W. R. A.

Constitution of laminarin. Isolation of 2 : 4 : 6-trimethylglucopyranose. V. C. Barry (Sci. Proc. Roy. Dublin Soc., 1939, **22**, 59—67; cf. A., 1938, III, 631).—Treatment of the dried comminuted fronds of *Laminaria cloustoni* with aq. $H_2C_2O_4$ (0·25%) for 3 days gives laminarin (I), $[\alpha]_D^{15}$ −12·8° in H_2O. An aq. solution of (I) and dil. HCl slowly deposits an insol. form, the difference in physical properties being thought to be due to the size of the colloidal particles. Acetylation of (I) gives the *triacetate*, $[\alpha]_D^{13}$ −52·0° in $CHCl_3$ (hydrolysed by 5% MeOH–HCl to α-methylglucoside), methylation of which (Me_2SO_4 + 45% KOH, 7 treatments) gives *trimethyl-laminarin*, $[\alpha]_D^{18}$ −4·39° in $CHCl_3$, hydrolysed by 2% MeOH–HCl to 2 : 4 : 6-trimethylglucopyranose. It is suggested that (I) consists of a chain of β-glucopyranose (1 : 3 linkings) units bent into spiral form. S. H. H.

***tert.*-Alkyl primary amines, CRR′R″·NH_2. I. Ethoxymethyldiallylcarbinylamine and some analogues.** B. B. Allen and H. R. Henze (J. Amer. Chem. Soc., 1939, **61**, 1790—1794).—OR·CH_2·CN and MgR′Cl give an additive product, which with CH_2:CH·CH_2·MgBr (I) yields OR·CH_2·CR′(CH_2·CH:CH_2)·NH_2. R′ may also be allyl. The amines do not give the carbylamine reaction, but their structure is proved by Hofmann degradation of a diallyl compound and synthesis of some of the products. OR·CH_2·CN (R = Me, Et, or Pr^β) (1 mol.) and (I) (2 mols.) in Et_2O give ~60% yields of *δ-amino-δ-methoxy-*, b.p. 187·5—188°/753 mm., *-δ-ethoxy-* (II), b.p. 196—197°/755 mm., and *-δ-isopropoxy-*, b.p. 203—204·5°/753 mm., *-$\Delta^{\alpha\zeta}$-heptadiene*. Addition of (I) to the product from MgPr^{a}Br and OEt·CH_2·CN gives *δ-amino-δ-ethoxymethyl-Δ^α-heptene* (III) (60·7%), b.p. 197—198°/753 mm. Hydrogenation (PtO_2; AcOH) of (II) or (III) gives *δ-amino-δ-ethoxymethyl-*n*-heptane* (IV), b.p. 198°/754 mm. (*picrate*, m.p. 123·5—124·5°). MeI and 40% aq. KOH convert (II) and (IV) into *trimethyl-δ-ethoxymethyl-$\Delta^{\alpha\zeta}$-heptadien-δ-yl-*, m.p. 100·5—101·5° (decomp. at higher temp.), and *trimethyl-δ-ethoxymethyl-*n*-heptyl-ammonium iodide*, decomp. 132·5—133·5°, converted at 150—180°/25—27 mm. into *δ-ethoxymethyl-$\Delta^{\alpha\gamma\zeta}$-heptatriene*, b.p. 71—72° (uncorr.)/16—17 mm., and *-Δ^γ-heptene*, b.p. 173·5—175°/740 mm., 72—73° (uncorr.)/17 mm., respectively. Hydrogenation (Pt-black; $COMe_2$) of both these final products yields *δ-ethoxymethyl-*n*-heptane*, b.p. 170—171° (uncorr.)/740 mm., also obtained from $CHPr^a_2$·MgBr and CH_2Cl·OEt in Et_2O. OEt·CH_2·CO_2Et (prep. from OEt·CH_2·CN in Pr^aOH by HCl), b.p. 173·5°/748 mm., and MgPr^{a}Br (2 mols.) give 94·6% of *δ-ethoxymethyl-*n*-heptan-δ-ol*, b.p. 200—201°/752 mm., which with conc. HCl gives the corresponding *chloride*, b.p. 94—95° (uncorr.)/25 mm.; conversion thereof into (III) could not be achieved. Temp. are corr. *n*, *d*, and *γ* of the products are given, and [*M*] and the parachors calc. R. S. C.

Crystal structure of glucosamine [and α-chitosamine].—See A., 1939, I, 457.

Action of periodic acid on α-amino-alcohols. B. H. Nicolet and L. A. Shinn (J. Amer. Chem. Soc., 1939, **61**, 1615).—HIO_4 oxidises substances containing *cis*-CX·CX, in which X = OH or NH_2. Thus, serine gives 95% of CH_2O and (judged by consumption of HIO_4) NH_3 and CHO·CO_2H (slowly further oxidised to CO_2 and HCO_2H). Qual. results with other NH_2-acids are reported. $NH([CH_2]_2$·OH$)_2$ rapidly gives $4HCO_2H$, but NEt_2·$[CH_2]_2$·OH does not react. R. S. C.

Polyiodides in alcoholic solutions of iodine and hexamethyl-αγ-diaminopropan-β-ol iodide. M. Covello (Annali Chim. Appl., 1939, **29**, 187—189; cf. A., 1937, II, 8).—Ultra-violet absorption spectra indicate the presence of dissociable complexes in 0·05M. and 0·02M. solutions of the propanol with 4, 6, and 8I per mol. F. O. H.

Guanidomalonic acid.—See A., 1939, III, 707.

Phosphoserine and its enzymic hydrolysis.— See A., 1939, III, 721.

Reaction between organic sulphur compounds and hydrogen peroxide. XVIII. Action of neutral hydrogen peroxide on thiocarbamides. Synthesis of aminoiminomethanesulphinobetaines. R. KITAMURA (J. Pharm. Soc. Japan, 1939, **59**, 33—36).—Gradual addition of H_2O_2 to $CS(NH_2)_2$ in 70% EtOH gives formamidinesulphinobetaine, decomp. 127—128°; *methyl-*, decomp., 95—97°, *propyl-*, decomp. 152—153°, and *diallyl-*, decomp. 89—91°, *-formamidinesulphinobetaine* are obtained from the requisite substituted thiocarbamides. All are unstable and are transformed by KOH and H_2O_2 at room temp. into the corresponding carbamides. H. W.

Action of aldehydes on thiol-amino-compounds. L. GENEVOIS and P. CAYROL (Bull. Soc. chim., 1939, [v], **6**, 1223—1230; cf. Schubert, A., 1936, 824).—Neutral solutions of equimols. of cysteine (I) and CH_2O (at p_H 4) give the compound, cysteine–formaldehyde (1 to 1 mol.) (stable at p_H 4 to p_H 7), m.p. ~65° (hygroscopic), decomposed by I. MeCHO, EtCHO, and PrCHO act similarly but not completely, and PhCHO much less readily. (I) (1 mol.) reacts with ketones, *e.g.*, $COMe_2$, $AcCO_2H$, or furfuraldehyde, only in large excess, *e.g.*, 20 mols. of $COMe_2$; the equilibrium is discussed. Between p_H 3 and 7, (I) acts amphoterically, similarly to other NH_2-acids. $CO_2H{\cdot}CH(NH_2){\cdot}[CH_2]_2{\cdot}CO{\cdot}NH{\cdot}CH(CH_2{\cdot}SH){\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2H$ reacts only with a large excess of CH_2O, *e.g.*, 200 mols. (reaction complete at p_H 7·5); MeCHO reacts less readily, and ketones not at all. A definite relationship between NH and SH is essential for positive reaction. Thiolacetic or thiosuccinic acid does not react even with a very large excess of aldehydes or ketones. A. T. P.

Electrolytic reduction and determination of oxidised glutathione. J. S. DOHAN and G. E. WOODWARD (J. Biol. Chem., 1939, **129**, 393—403).—Oxidised glutathione (I) is completely reduced electrolytically in an acid medium using a Hg cathode. The reduced (I) is determined by the sp. glyoxalase method or iodometrically. No oxidised (I) was found in sulphosalicylic acid extracts of blood or tissue but when added it was completely recovered by electrolytic reduction and only partly by reduction with Zn. E. M. W.

Halogenoacetylcarbamides. I. A. PEARL and W. M. DEHN (J. Amer. Chem. Soc., 1939, **61**, 1377—1378).—$CH_2Cl{\cdot}COCl$ and $CO(NH_2)_2$, first at room temp. and then at 100°, give chloroacetylcarbamide, m.p. 190—191° (lit., decomp. 160°, m.p. 180°), sternutatory. *Dichloroacetylcarbamide* (prep. from $CHCl_2{\cdot}COCl$), m.p. 149—150°, is also sternutatory and with NaI in $COMe_2$ gives *di-iodoacetylcarbamide*, m.p. 192—193°. $CCl_3{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2$ gives similarly *tri-iodoacetylcarbamide*, m.p. 74—75°, unstable in air. *Dibromoacetylcarbamide*, m.p. 180—181°, is prepared from $CHBr_2{\cdot}COBr$. R. S. C.

Dimorphism of α-bromo*iso*valerylcarbamide. A. WATANABE (J. Pharm. Soc. Japan, 1938, **58**, 145—149; cf. Ichikawa, A., 1936, 1237).—Cryst. form and physical consts. are compared for the α- (plates or scales) and β-form (needles or prisms), m.p. 153—154°; the α- at 120—130° gives the β-form. A. T. P.

Characteristic reaction of dithio-oxamide with ferrous iron. G. NILSSON (Analyst, 1939, **64**, 501).—A deep blue colour is produced when excess of cold alkaline aq. dithio-oxamide reacts with a Fe^{II} salt, or with a Fe^{III} salt in presence of a reducing agent. Metallic Fe does not react with the alkaline reagent unless rendered cathodic for a few sec., after which it dissolves with production of a blue colour. E. C. S.

Hydrolysis of guanidine by boiling potassium hydroxide solution. G. LAUDE (Compt. rend., 1939, **208**, 1848—1850; cf. A., 1938, I, 202, and following abstract).—The rate of hydrolysis of equimol. amounts of guanidine, creatine, creatinine, and arginine is the less the greater is the mol. wt. J. L. D.

Curves showing formation of ammonia by boiling alkaline solutions of guanidine and proteins. G. LAUDE (Compt. rend., 1939, **208**, 1691—1692).—Rates of production of NH_3 by alkaline hydrolysis of guanidine, creatine, arginine, and the albumin of egg, blood, and wheat are examined (cf. A., 1937, II, 357; 1938, I, 202). J. L. D.

Co-ordination by methyl *iso*nitrile. Structure of β-tetramethyl ferrocyanide. H. M. POWELL and G. B. STANGER (J.C.S., 1939, 1105—1106).—The β form of Me_4 ferrocyanide (Hartley, J.C.S., 1913, **103**, 1196) is shown by *X*-ray analysis to be the *trans* six-co-ordinated compound with four MeNC mols. attached to Fe by linkings of the type found in metallic carbonyl compounds. J. D. R.

Isomerisation of *cyclo*hexane and methyl-*cyclo*pentane. A. L. GLASEBROOK and W. G. LOVELL (J. Amer. Chem. Soc., 1939, **61**, 1717—1720).—$AlCl_3$, activated by H_2O or HCl, equilibrates *cyclo*hexane and methyl*cyclo*pentane (I) to mixtures containing 12·5% of (I) at 25°, rising to 25·6% at 77·4° (cf. Nenitzescu *et al.*, A., 1933, 941). Thermodynamic consts. are calc. R. S. C.

Dehydration of *trans*-2-methyl*cyclo*hexanol. C. C. PRICE (J. Amer. Chem. Soc., 1939, **61**, 1847—1849).—*trans*-2-Methyl*cyclo*hexanol and P_2O_5 at any temp. between 140° and 230° give a mixture (*A*) of 1- (35—50% of the mixture) and 3-methyl-Δ^1-*cyclo*hexene (structures determined by oxidation), although Vogel's C_7H_{12} and C_7H_{14} (A., 1938, II, 268, 354, 436; 1939, II, 304) resemble 1-ethyl*cyclo*pentene and ethyl-*cyclo*pentane, respectively, in physical properties. (*A*) is reduced (H_2, Raney Ni, EtOH), best after distillation with EtOH, to methyl*cyclo*hexane (no change in physical properties during 1 month). R. S. C.

Catalytic cyclisation of paraffin hydrocarbons in presence of platinised charcoal. B. A. KAZANSKI and A. F. PLATE (J. Gen. Chem. Russ., 1939, **9**, 496—502).—The following products are obtained by passing the hydrocarbon over Pt–C at 305—310°; from *n*-hexane, C_6H_6; from β-methylhexane, PhMe; from γ-methylheptane, PhEt and *o*- and *p*-xylene; from δ-methylheptane, *m*-xylene; from δ-methyl-

octane, PhPr and *m*-C_6H_4MeEt. Di*iso*amyl passed over Ni–Al_2O_3 catalyst at 350° yields up to 25% of unidentified aromatic products. R. T.

Synthesis and properties of β-phenyloctane, ε-phenylnonane, and η-phenyltridecane. A. D. Petrov, A. D. Baidanov, N. N. Zakotin, and P. I. Suntzov (J. Gen. Chem. Russ., 1939, **9**, 509—512).—Mg hexyl bromide and COPhMe yield β-*phenyloctan*-β-*ol*, b.p. 136—137°/12 mm., dehydrated by heating in presence of I to β-*phenyl*-Δ^{β}-*octene*, b.p. 121—122°/10 mm., which with H_2 (Ni catalyst) gives β-*phenyloctane*, b.p. 125—127°/18 mm., not solidifying at −80°. ε-*Phenylnonan*-ε-*ol*, b.p. 130—132°/7—8 mm., from $MgBu^aBr$ and EtOBz, similarly yields ε-*phenyl*-Δ^{δ}-*nonene*, b.p. 117—121°/6 mm., hydrogenated to ε-*phenylnonane*, b.p. 126—127°/12 mm. η-*Phenyltridecan*-η-*ol*, b.p. 165—170°/8 mm., η-*phenyl*-Δ^{ζ}-*tridecene*, b.p. 153—154°/8 mm., and η-*phenyltridecane*, b.p. 183—184°/20° mm., not solidifying at −78°, are obtained analogously. The η of the saturated hydrocarbons varies little with change in temp. R. T.

Rearrangement of 4-*tert*.-butyl-*m*-xylene with aluminium chloride. L. I. Smith and H. O. Perry (J. Amer. Chem. Soc., 1939, **61**, 1411—1412).—1 : 3 : 4-$C_6H_3Me_2Bu^{\gamma}$, b.p. 113—114°/28 mm., 210—214°/760 mm. [oxidised by $KMnO_4$ to 1 : 3 : 4-$C_6H_3(CO_2H)_3$], prepared from 1 : 3 : 4-$C_6H_3Me_2$·MgI by $Bu^{\gamma}Cl$, is converted by $AlCl_3$ at 100° into 1 : 3 : 5-$C_6H_3Me_2Bu^{\gamma}$ (cf. Baddeley *et al.*, A., 1935, 612) and may thus be an intermediate in the reaction of *m*-xylene and $Bu^{\gamma}Cl$ in presence of $AlCl_3$. R. S. C.

Trinitrotriphenylmethide ion as a secondary and primary base.—See A., 1939, I, 472.

Beryllium chloride in organic reactions. H. Bredereck, G. Lehmann, C. Schönfeld, and E. Fritzsche (Ber., 1939, **72**, [*B*], 1414—1429).—In its behaviour towards org. chemicals $BeCl_2$ shows a close analogy to $AlCl_3$ but usually requires a somewhat higher temp. Reactions which require only a slight activation, *e.g.*, hydrocarbon syntheses with labile halogen compounds, proceed very smoothly whereas difficulty is experienced when stable compounds are involved. The ketone synthesis appears to take place less readily with $BeCl_2$ than with $AlCl_3$. It is assumed that the primary substance in the change is an additive compound of the metallic halide and the org. partner which should not be too stable. Such stability is more likely to be met with in the Be derivatives by reason of the smaller ionic radius of the metal and hence more drastic conditions are necessary subsequently. The yields with $BeCl_2$ and $AlCl_3$ are somewhat similar but variations occur in both directions and final judgment cannot be pronounced until the optimal conditions for each change have been established. In cases where mol. amounts are required the advantage lies with $BeCl_2$ by reason of its smaller mol. wt. but economically $AlCl_3$ remains unchallenged. The following reactions are described in detail: C_6H_6 and CH_2PhCl to CH_2Ph_2 (60%), *o*- and *p*-$C_6H_4(CH_2Ph)_2$; PhMe and CH_2PhCl to CH_2Ph·C_6H_4Me-*p* and *benzyl*-p-*methylbenzylbenzene*, b.p. 234—236°/12 mm.; *m*-xylene and CH_2PhCl to phenylxylylmethane and (*phenylxylyl*)*benzylmethane*, b.p. 240—245°/14 mm.; CH_2PhCl and *s*-$C_6H_3Me_3$ to phenylmesitylmethane, m.p. 36°, and *phenyl*-2 : 4 : 6-*trimethylphenylbenzylmethane*, b.p. 238—244°/12 mm., m.p. 76°; C_6H_6 and $CHPhCl_2$ to $CHPh_3$ (yield 28·5%) and a little CH_2Ph_2; PhMe and $CHPhCl_2$ to *phenyl*-p-, b.p. 218—220°/12 mm. (yield 73%), and (?) -o-, b.p. 286—289°/12 mm., -*ditolylmethane*; $CHPhCl_2$ and $NPhMe_2$ to leucomalachite-green (yield 54·2%); PhMe and EtBr to *p*-C_6H_4MeEt (yield 47%) and $C_6H_3MeEt_2$, b.p. 195—200°/760 mm.; PhMe and AcCl to *p*-C_6H_4MeAc (yield, 80%); AcCl and C_6H_6 to COPhMe (yield 33%); C_6H_6 and CH_2Ph·OH to CH_2Ph_2 (yield 58%) and $C_6H_4(CH_2Ph)_2$, or with less $BeCl_2$ to CH_2PhCl (yield 57%) which is thus an intermediate in the production of CH_2Ph_2 by this method; $CHPh_2$·OH and $BeCl_2$ at 100—110° afford $CHPh_2Cl$ in 77% yield; CH_2Ph·OH and PhMe to CH_2Ph·C_6H_4Me and phenyltolylbenzylmethane; $COMe_2$ and $BeCl_2$ at 150° to mesityl oxide (yield 27%) and phorone (yield 12%); COMeEt and $BeCl_2$ to γ-methyl-Δ^{γ}-hepten-ε-one, b.p. 167—168° (yield 30%); COPhMe to $C_6H_3Ph_3$ and dypnone; PhCHO and PhMe to phenyldi-*p*-, b.p. 193°/3 mm., and -*o*- (I), b.p. 270°/3 mm., -tolylmethane [MeOBz and *o*-C_6H_4Me·MgBr give *phenyldi*-o-*tolylcarbinol*, m.p. 107—108°, which is reduced to (I), m.p. 104—105°]; CH_2Cl·CO_2Ph and $BeCl_2$ at 130—140° to *o*- and *p*-OH·C_6H_4·CO·CH_2Cl; *p*-C_6H_4Me·OBz to 2 : 5 : 1-OH·C_6H_3Me·COPh, m.p. 84° (yield 69%); *p*-C_6H_4Me·OAc and $BeCl_2$ to 2 : 5 : 1-OH·C_6H_3Me·COMe, converted by HNO_3 (*d* 1·2) at 100° into 3-*nitro*-2-*hydroxy*-5-*methylacetophenone*, m.p. 132° (*Na* salt). $CPh_2{:}CH_2$ is converted by $BeCl_2$ in C_6H_6 at 110—120° into its dimeride, m.p. 142°, in ~90% yield. C_2H_4 gives the highest yields of distillable polymerisate at 200°/initial pressure 110 atm. At higher temp. carbonisation increases. All fractions are unsaturated; *n*- and *iso*-hexane, hexene, pentanes, pentenes, and butenes have been identified. C_3H_6 at 155—165°/30 atm. gives volatile hydrocarbons (15·3%), benzines (20·7%), light oils (39·3%), and heavy and lubricating oils (24·7 %). All fractions are unsaturated. The gases contain unchanged C_3H_6, butene (II), and *iso*butene (III). At 200° (III) yields ~80% of benzines consisting mainly of di*iso*butene and isomeric octenes with some tri*iso*butene and its isomerides. Very little saturated hydrocarbon is present. A tetrameric iso*butene*, b.p. 101—102°/4 mm., has been identified. The gases contain unchanged (III), C_3H_6, and (II). *iso*Hexene, *iso*pentane, and *iso*hexane are present in the volatile distillate. In glass vessels > half of the polymerisate is a yellow, viscous material, not volatile at 360°/vac.; the material of the autoclave appears to have a proper, catalytic influence. *iso*Hexene at ~200°/20—30 atm. gives benzines (54%) consisting of C_8 with some C_{12} hydrocarbons, *n*- and *iso*-hexane, and *iso*pentane. BeO has moderate catalytic activity whereas BeF_2 and Be_2OF_2 have very little effect. BeO appears to accelerate polymerisation rather than cracking, isomerisation, or hydrogenation. Anthracene and phenanthrene are cracked by $BeCl_2$ to tetrahydronaphthalene, alkyl-benzenes and -naphthalenes, or, under other conditions, to unidentified cryst. compounds. Attempts to crack an aromatic

coal-tar oil were unsatisfactory, only small amounts of benzenoid hydrocarbons being obtained. H. W.

Resonance and physical and chemical properties of diphenyl types. M. Calvin (J. Org. Chem., 1939, **4**, 256—261).—The requirement that the four linkings extending from a double linking $^{1}_{2}>C=C<^{3}_{4}$ must be coplanar is applied to the contributing resonating states of diphenyls. Discussion of the effect of non-*o*-substituents on the rate of racemisation of certain diphenyls leads to the prediction that 2 : 2′-dibromo-4-nitro-4′-aminodiphenyl should be resolvable and have a racemisation half-life >10 min. Consideration of the effect of the possibility or impossibility of conjugated resonating states on the absorption spectrum of substituted diphenyls brings the prediction that certain non-resolvable tetra-*o*-substituted diphenyls should show the conjugated absorption spectrum whereas other tetra-*o*-substituted diphenyls in which the coplanar arrangement of the rings is impossible should have an absorption spectrum very similar to the uncoupled parts. The existence of optically active derivatives of 9 : 9′-diphenanthryl and of 9-*cyclo*hexenylphenanthrene is foretold and the relationship between the contributing resonating states and the reactivity towards a diene condensation is discussed. H. W.

Reaction between hexabromobenzene and magnesium phenyl bromide. T. A. Geissman and R. C. Mallatt (J. Amer. Chem. Soc., 1939, **61**, 1788—1790).—C_6Br_6 and MgPhBr give (on hydrolysis) small yields of 1 : 2 : 4 : 5-$C_6H_2Br_4$ and -$C_6H_2Ph_4$ and much tar, the $C_6H_2Br_4$ being formed from $C_6Br_4(MgBr)_2$ and the $C_6H_2Ph_4$ from $C_6Ph_4(MgBr)_2$, *i.e.*, by independent mechanisms. Carbonation gives 2 : 3 : 5 6-*tetraphenylterephthalic acid*, m.p. >320° (block) (*Me*$_2$ ester, m.p. 280°). C_6Br_6 is unchanged by Mg + MgI_2, indicating no reaction (above) with Mg or Mg + $MgBr_2$. A large excess of MgPhBr doubles the yield of $C_6H_2Ph_4$. C_6Br_6 and LiPh give only polymeric material. C_6Br_6 and MgPhI give 7·9% of $C_6H_2Ph_4$ and much tar. R. S. C.

Reaction between maleic anhydride and vinylhydrindenes. R. T. Arnold (J. Amer. Chem. Soc., 1939, **61**, 1405—1406).—Gradual addition of conc. H_2SO_4 to hydrindene, 30% aq. CH_2O, and conc. HCl at 60° gives 5-*chloromethylhydrindene* (57% yield), b.p. 110—112°/4 mm., converted by $(CH_2)_6N_4$ in 60% EtOH into hydrindene-5-aldehyde, b.p. 135—138°/23 mm., which with $CH_2(CO_2H)_2$ and piperidine at 60° yields β-5-*hydrindenylacrylic acid* (I), m.p. 161—162°. α-5-*Hydrindenylethyl alcohol* [prep. from acetohydrindene (II) by Na–EtOH], b.p. 133°/10 mm., with HCO_3H or PhNCO gives polymerides, but with C_5H_5N–$SOCl_2$ gives a chloride, converted by KOH–EtOH into 5-*vinylhydrindene* (III), b.p. 95—100°/10 mm., which is obtained also from (I) in 5% yield by thermal decomp. in presence of quinol or Cu–quinoline. MgMeI and (II) give a carbinol, converted by dry HCl at 0° into the chloride, which with KOH–EtOH at 60° yields 5-iso*propenylhydrindene*, b.p. 84°/2 mm. This and (III) are polymerised by maleic anhydride in xylene at 100°, showing that either the ethylenic linkings of the hydrindene ring are not "fixed" by the C:C or that the rate of polymerisation exceeds that of addition. R. S. C.

Photosensitive nitro-compounds. VI. Certain nitronaphthalene derivatives substituted in the *o*- or *p*-positions with sulphur-containing radicals. N. N. Voroshcov, V. V. Kozlov, and I. S. Travkin (J. Gen. Chem. Russ., 1939, **9**, 522—525).—1 : 2-NO_2·$C_{10}H_6$·NH_2 diazotised in aq. H_2SO_4 and then treated with SO_2 (Cu-bronze catalyst) yields 1-*nitronaphthalene*-2-*sulphinic acid*, m.p. 119·5°. 2 : 1-NH_2·$C_{10}H_6$·SO_3H is converted (Sandmeyer with $NaNO_2$) into 2-*nitronaphthalene*-1-*sulphonic acid*. R. T.

Phenanthrene syntheses with 2 : 3-dimethyl-Δ²-*cyclo*hexenone. E. Bergmann and A. Weizmann (J. Org. Chem., 1939, **4**, 266—269).—The crude condensation product of CH_2Ac·CO_2Et and $(CH_2O)_3$ is heated with NaOEt–EtOH at 85—115° and the product is acidified with AcOH, thus giving *Et* 3-*methyl*-Δ²-cyclo*hexenone*-4-*carboxylate*, b.p. 160—165°/35 mm., 108°/1 mm., which is converted by NaOMe and MeI in MeOH into *Et* 2 : 3-*dimethyl*-Δ²-cyclo*hexenone*-4-*carboxylate*, b.p. 158—161°/21 mm., 104—110°/1 mm., transformed by 10% KOH–EtOH into 2 : 3-*dimethyl*-Δ²-cyclo*hexenone* (I), b.p. 53—65°/1·5 mm. CH_2Ph·CH_2·MgCl and (I) afford 3-β-*phenylethyl*-1 : 2-*dimethyl*-Δ$^{1:3}$-cyclo*hexadiene*, b.p. 155°/6 mm., converted by $SnCl_4$ in C_6H_6 saturated with HCl at 0° into 1 : 2-*dimethyl*-3 : 4 : 9 : 10 : 11 : 12-*hexahydrophenanthrene*, b.p. 105—107°/0·02 mm., 150—160°/29 mm., which is dehydrogenated (Se at 330°) to 1 : 2-dimethylphenanthrene, m.p. 142—143°, usually accompanied by some 1 : 2-*dimethyl*-9 : 10-*dihydrophenanthrene*, b.p. 115—120°/2 mm. *m*-OMe·C_6H_4·MgBr reacts violently with $(CH_2)_2O$, giving *m*-anisylethyl alcohol, b.p. 105—110°/1 mm., transformed by $SOCl_2$ and $NPhMe_2$ (C_5H_5N gives inconst. results) into *m*-*anisylethyl chloride*, b.p. 85—87°/1·5 mm., 128—130°/14 mm., also obtained from *m*-OMe·C_6H_4·MgBr and *p*-C_6H_4Me·SO_3·CH_2·CH_2Cl, *m*-OMe·C_6H_4·$[CH_2]_2$·MgCl and (I) yield 3-β-m-*anisylethyl*-1 : 2-*dimethyl*-Δ$^{1:3}$-cyclo*hexadiene*, b.p. 145—147°/0·8 mm., cyclised (as above) to 7-*methoxy*-1 : 2-*dimethyl*-3 : 4 : 9 : 10 : 11 : 12-*hexahydrophenanthrene*, b.p. 135°/0·07 mm. This is dehydrogenated to 7-methoxy-1 : 2-dimethylphenanthrene (*picrate*, m.p. 149°) and 7-*methoxy*-1 : 2-*dimethyl*-9 : 10-*dihydrophenanthrene*, b.p. ~150°/1 mm. H. W.

Syntheses in the 1 : 2-benzanthracene and chrysene series. L. F. Fieser and W. S. Johnson (J. Amer. Chem. Soc., 1939, **61**, 1647—1654).—Some benzanthracene and chrysene derivatives are synthesised. Formation of benzanthracene or chrysene derivatives by ring-closure sometimes depends on the condensing agent used. When the product obtained from 8-keto-3 : 4 : 5 : 6 : 7 : 8-hexahydro-1 : 2-benzanthracene (I) and MgEtBr is dehydrated by heating, it gives 88·5% of 8-*ethyl*-3 : 4 : 5 : 6-*tetrahydro*-1 : 2-*benzanthracene*, m.p. 65—67°, b.p. ~185°/1 mm., dehydrogenated by S at 210—255° (followed by Zn dust) to 8-*ethyl*-1 : 2-*benzanthracene*, double m.p. 78—79° and 82·5—83° (*picrate*, m.p. 149·5—150°). Heating with S at 230—255° (not PtO_2 in $C_{10}H_8$)

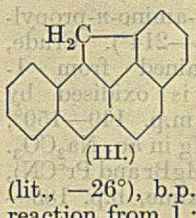
and subsequent distillation converts (I) into 8-*hydroxy*-1 : 2-*benzanthracene* (45%), m.p. 151·3—151·8° (*acetate*, m.p. 133—133·6°), which with NH_3 and $NaHSO_3$ in aq. dioxan at 190—200° yields 8-*amino*-1 : 2-*benzanthracene* (26%), m.p. 201·7—202·3° (decomp.). *Me* γ-*keto*-γ-9 : 10-*dihydro*-2-*phenanthryl*-*butyrate* (prep. from the acid by HCl–MeOH), m.p. 77—78°, and MgMeI (≯ slight excess) in boiling Et_2O–C_6H_6 give 53% of γ-9 : 10-*dihydro*-2-*phenanthryl*-Δ^{β}-*pentenoic acid* (II) (? mixed stereoisomerides), m.p. 117—125° [a probably pure acid had m.p. 137—138° (decomp.)], but at a lower temp. 32% of (II) is obtained with 35% of γ-9 : 10-*dihydro*-2-*phenanthryl*-γ-*valerolactone* (III), m.p. 61·5—63° (clear at 70°). (III) is obtained also from (II) by hot 10% H_2SO_4 and with boiling aq. alkali gives the γ-*OH-acid*, m.p. 95—97° (decomp.). Reduction of (III) by Zn–alkali or Zn–Hg–HCl was unpromising, but H_2–PtO_2 in AcOH reduces (II) readily to γ-9 : 10-*dihydro*-2-*phenanthryl*-n-*valeric acid*, m.p. 77·5—78·5°, converted by HF in 81·5% or by PCl_5 in C_6H_6, followed by $AlCl_3$, in 64% yield into 8-*keto*-5-*methyl*-3 : 4 : 5 : 6 : 7 : 8-*hexahydro*-1 : 2-*benzanthracene* (IV), m.p. 127·9—128·4°. This is converted into 5-methyl-1 : 2-benzanthracene (49·5% yield) by heating with Zn–Hg in PhMe–AcOH–HCl–H_2O, removing unchanged ketone chromatographically (Al_2O_3), and dehydrogenating with S at 200—255°. Condensation of (IV) with MgMeI (excess) in C_6H_6 and dehydration at 250° gives a mixture, from which 5 : 8-*dimethyl*-3 : 4-*dihydro*-1 : 2-*benzanthracene*, m.p. 82·2—82·8° [absorption spectrum very similar to that of 20-methyl-6 : 7-dihydrocholanthrene; max. at 2715 (log ε 4·72) and 3090 A. (log ε 4·13)], separates; the residue is converted by S, first at 210—215° and then at 235°, into 5 : 8-*dimethyl*-1 : 2-*benzanthracene*, m.p. 131·2—131·4° and then 134·4—134·7° (*picrate*, m.p. 174·5—175°). 8-Methyl-1 : 2-benzanthracene, $POCl_3$, and NPhMe·CHO in *o*-$C_6H_4Cl_2$ at 100° give 8-*methyl*-1 : 2-*benzanthracene*-10-*aldehyde* (42%), m.p. 151·5—152°, the *hydrazone*, m.p. 181—181·5° (decomp.), of which with EtOH–NaOEt at 195—208° yields 8 : 10-*dimethyl*-1 : 2-*benzanthracene*, m.p. 145·5—146·5° (*picrate*, m.p. 165·5—166°). Me γ-2-phenanthrylbutyrate (prep. from the 9 : 10-H_2-ester, b.p. ~230°/4—5 mm., by S at 235—255°), b.p. ~240°/4 mm., yields the derived acid (V), m.p. 134—135·5°, which with HF gives 78% of 8-*keto*-5 : 6 : 7 : 8-*tetrahydro*-1 : 2-*benzanthracene* (VI), m.p. 117·5—118·5°; MgMeCl etc. then yields 8-*methyl*-5 : 6-*dihydro*-1 : 2-*benzanthracene*, m.p. 80—80·6° [*picrate*, m.p. 151—152° (decomp.)], and thence (S at 205—245°) 8-methyl-1 : 2-benzanthracene. However, $ZnCl_2$ in Ac_2O–AcOH cyclises (V) in 51% yield to 4-keto-1 : 2 : 3 : 4-tetrahydrochrysene (VII); 85% H_2SO_4 at 100° gives 23% of (VII); PCl_5–C_6H_6, followed by $AlCl_3$, gives 35% of (VI) and 17·5% of (VII), or in $PhNO_2$ mainly (VI) with very little (VII). MgMeCl, followed by dehydration, converts (VII) into a H_2-derivative (90%), which with S at 215—245° gives 4-*methylchrysene*, m.p. 151—151·5° (*picrate*, red and unstable orange *forms*, m.p. 137·5—138°). M.p. are corr.

R. S. C.

Photo-oxides of carcinogenic hydrocarbons. J. W. Cook, R. Martin, and E. M. F. Roe (Nature, 1939, **143**, 1020).—Passage of O_2 through a 0·05% solution of 9 : 10-dimethyl-1 : 2-benzanthracene in CS_2 exposed to the light of a 200-w. gas-filled lamp gives a photo-oxide (I), m.p. 193—194°. Photo-oxides (m.p. in parentheses) have been obtained equally readily from 5 : 9 : 10- (212—213°) and 6 : 9 : 10-*trimethyl*- (II) (205—206°), 5 : 6 : 9 : 10-*tetramethyl*-1 : 2-*benzanthracene* (III) (228—229°), and 9 : 10-dimethyl-1 : 2 : 5 : 6-dibenzanthracene (222—223°). (II) has m.p. 157—158°, and (III), m.p. 132—133°. The ultra-violet absorption spectrum of (I) shows bands similar to those of a *meso*-H_2-derivative of 1 : 2 : 5 : 6-dibenzanthracene, with ~ half their intensities. Irradiation (Hg arc) of a C_6H_{14} solution of (I) causes decomp. and the spectrum of the parent hydrocarbon reappears. The spectrum of 9 : 10-dihydroxy-9 : 10-dimethyl-9 : 10-dihydro-1 : 2-benzanthracene shows bands of the same order of intensity as the photo-oxide, but shifted ~180 A. towards the far ultra-violet. 1 : 2-Benzanthracene, but not 1 : 2 : 5 : 6-dibenzanthracene and 3 : 4-benzpyrene, gives indications of the formation of a photo-oxide.

L. S. T.

Synthesis of 1′ : 9-methylene-1 : 2-benzanthracene and related hydrocarbons. L. F. Fieser and J. Cason (J. Amer. Chem. Soc., 1939, **61**, 1740—1745).—Acenaphthene and AcOH or AcCl in HF give 1- (I) (29%), m.p. 114—114·5° [*picrate*, m.p. 114·5—115°; $C_6H_3(NO_2)_3$ *derivative*, m.p. 113·5—114°], and 3-acetoacenaphthene, m.p. 69—69·5° (picrate, orange and yellow *forms*, m.p. 97—97·5°), both stable in HF. KOCl in aq. dioxan at 60° oxidises (I) to 1-acenaphthoic acid (95·5%), m.p. 254—256°, which with $Na_2Cr_2O_7$–AcOH at 90—95° give 2-*carboxy*-1 : 8-*naphthalic anhydride*, m.p. 297·5—298·5° (*Me* ester, m.p. 191—192°), and with $SOCl_2$ gives 1-*acenaphthoyl chloride*, m.p. 110—111° (with $AlCl_3$ in C_6H_6 gives a substance, decomp. >200°), and thence by NH_3 in aq. dioxan the *amide*, m.p. 227—228°. With MgPhBr this gives 1-*benzoylacenaphthene* (II), m.p. 91·5—92°, b.p. 210—215°/1 mm., obtained also from Mg 1-acenaphthyl iodide and PhCN. Pyrolysis of (II) at 425° gives 1′ : 9-*methylene*-1 : 2-*benzanthracene* (III) (13%), m.p. 122·7—123·1° [*picrate*, m.p. 141·5—142°; $C_6H_3(NO_2)_3$ *derivative*, m.p. 162·5—163°], 1 : 2 : 3-$C_6H_3MeI{\cdot}NO_2$ and H_2–PtO_2 in AcOH give 1 : 2 : 3-$C_6H_3MeI{\cdot}NH_2$, m.p. 40—40·6° (lit., 41—42°); for prep. of 1 : 3 : 2-C_6H_3MeClI (IV), m.p. 27·3—27·6° (lit., —26°), b.p. 123—123·5°/14 mm., by the diazo-reaction from 1 : 2 : 3-$C_6H_3MeI{\cdot}NH_2$ it is best (74·5% yield) to omit isolation of the amine. Grignard reactions of (IV) with CO_2, 2-$C_{10}H_7{\cdot}COMe$, or 2-$C_{10}H_7{\cdot}CN$ give poor yields of indefinite materials, probably owing to steric hindrance of the I.



(III.)

1 : 2 : 3-$C_6H_3Me_2{\cdot}NH_2$ (prep. in 92% yield from the NO_2-compound by Fe–H_2O or H_2–catalyst), b.p. 98—100°/11 mm., gives (diazo-reaction) 40% of 1 : 2 : 3-$C_6H_3Me_2{\cdot}CN$, b.p. 105—107°/11 mm., which with 1-$C_{10}H_7{\cdot}MgBr$ in Et_2O–C_6H_6 and later in hot C_6H_6 yields 89% of 3-*o*-*xylyl* α-$C_{10}H_7$ *ketone*, b.p. 190—195°/1 mm. Pyrolysis thereof with a little Zn dust

at 425—430° yields 5- and 8-methyl-1 : 2-benzanthracene (V) and 1 : 2-benzanthracene. 3-o-*Xylyl* β-$C_{10}H_7$ *ketone* (similarly prepared), m.p. 62—63°, gives a mixture, from which (V) is separable with difficulty. 2-*Aceto*-1 : 8-*naphthalic anhydride*, m.p. 219—219·3°, is obtained by oxidation ($Na_2Cr_2O_7$–AcOH) of (I). M.p. are corr. R. S. C.

New syntheses of the red hydrocarbon rubicene. V. I. Chmelevski and I. J. Postovski (J. Gen. Chem. Russ., 1939, **9**, 620—624).—Mg and boiling fluorenone give rubicene, in 11% yield. 9 : 10-Dihydroxy-9 : 10-diphenyl-9 : 10-dihydroanthracene with $AlCl_3$ and MnO_2 (30 min. at 100°) affords rubicene in 4% yield. R. T.

Naphthylaminoalkanes. F. F. Blicke and C. E. Maxwell (J. Amer. Chem. Soc., 1939, **61**, 1780—1782).—$C_{10}H_8$ derivatives of benzedrine and similar types have only slight pressor activity (dogs) and produce tolerance and cross-tolerance for ephedrine. When 1-$C_{10}H_7$·CH_2Cl and $(CH_2)_6N_4$ are heated in $CHCl_3$ and the product is distilled with conc. HCl and EtOH, there is obtained 1-$C_{10}H_7$·CH_2·NH_2, b.p. 200—205°/30 mm. (hydrochloride, new m.p. 260—262°). 1-$C_{10}H_7$·MgBr with MeCN in Et_2O, followed by aq. HCl, gives 1-$C_{10}H_7$·COMe, b.p. 145—147°/6 mm., the oxime, new m.p. 134—135°, of which with Na–EtOH yields 1-$C_{10}H_7$·CHMe·NH_2, b.p. 141—142°/5 mm. {hydrochloride, m.p. 236—237° [lit., 220—221° (decomp.)]}. 2-$C_{10}H_7$·CMe:N·OH, m.p. 142—143°, yields similarly 2-$C_{10}H_7$·CHMe·NH_2, b.p. 172—174°/29 mm. [hydrochloride, m.p. 279—280° (lit., 199—200°)]. 1-$C_{10}H_7$·COEt (prep. from 1-$C_{10}H_7$·MgBr and EtCN), b.p. 171—172°/12 mm., gives the oxime, new m.p. 55—57°, and thence 1-α-amino-*n*-propylnaphthalene, b.p. 148—149°/10 mm. (*hydrochloride*, m.p. 281—282°). 1-$C_{10}H_7$·CH_2Cl and $CHNa(CO_2Et)_2$ in C_6H_6 give 1-$C_{10}H_7$·CH_2·$CH(CO_2Et)_2$, b.p. 199—201°/3 mm., converted by MeI and Na–EtOH into *Et*$_2$ *α-naphthylmethylmethylmalonate* (I), m.p. 51—52°, b.p. 207—209°/2 mm., which with KOH in 60% KOH gives the malonic *acid*, m.p. 172—173° (decomp.); heating at 175—180° then yields β-1-*naphthyl*isobutyric *acid* (II), m.p. 91—92°, the *amide*, m.p. 134—135°, of which with NaOBr at 70—80° gives 1-β-amino-*n*-propylnaphthalene (*hydrochloride*, m.p. 213—214°). Crude, oily 1-$C_{10}H_7$·CH:CMe·COMe, obtained from 1-$C_{10}H_7$·CHO, COMeEt, and HCl, is oxidised by NaOBr to 1-$C_{10}H_7$·CH:CMe·CO_2H, m.p. 149—150°, which is reduced to (II) by 4% Na–Hg in aq. Na_2CO_3. 1-$C_{10}H_7$·$COPr^a$ (prep. from 1-$C_{10}H_7$·MgBr and Pr^aCN), b.p. 155—157°/3 mm., gives the oxime, b.p. 185—187°/8 mm., and thence 1-α-amino-*n*-butylnaphthalene, b.p. 142—143°/4 mm. (*hydrochloride*, m.p. 281—282°). (I) affords 5-α-*naphthylmethyl*-5-*methylbarbituric acid*, m.p. 127—128°. R. S. C.

Thio-acyl derivatives of primary amines (synthesis of acyclic carbocyanine dyes). I. L. Knunianz and L. V. Razvadovskaja (J. Gen. Chem. Russ., 1939, **9**, 557—570).—CH_2Ph·NH·CSMe and MeI at 0° yield the *hydriodide*, m.p. 104—106° (decomp. by aq. K_2CO_3), of *thioacetbenzylamide* S-*Me ether*, SMe·CMe:N·CH_2Ph, b.p. 115—118°/4 mm., the *methiodide*, m.p. 120°, of which is condensed with $CH(OEt)_3$ or the anilanilide of CO_2H·CH_2·CHO or of glutaconaldehyde in boiling Ac_2O to the *dyes*, CHR:CHR′, R·[CH:CH]$_2$·R′, or R·[CH:CH]$_3$·R′ [R = CH_2Ph·NMeI:C(SMe)·; R′ = CH_2Ph·NMe·C(SMe):CH·], and with *p*-NMe_2·C_6H_4·CHO to give the *dye*, CH_2Ph·NMeI:C(SMe)·CH:CH·C_6H_4·NMe_2-*p*.

NHMeAc and P_2S_5 in C_6H_6 (70 min. at the b.p.) followed by MeI yield *thioacetmethylamide* S-*Me ether*, b.p. 132—133°, the *methiodide* of which is condensed as above, to yield the corresponding dyes [R = NMe_2I:C(SMe)·, R′ = NMe_2·C(SMe):CH·]. The absorption spectra (in EtOH) of the dyes are given. The sensitising action of the dyes on photographic emulsions is similar to that of the corresponding thiazoline dyes. R. T.

Quenching of fluorescence and photothermal decomposition of aniline.—See A., 1939, I, 404.

Diazotisation and nitrosation of amines. IV. General interpretation of the reaction. J. C. Earl and N. G. Hills (J.C.S., 1939, 1089—1092; cf. A., 1939, II, 207).—Decomp. of 0·15N-aq. $NHMe_2$,HNO_2 at 5° is accelerated by HCl or H_2SO_4, the rate being a max. with 0·5 mol. of acid. The conductivity during nitrosation of 0·01M-aq. NHPhMe at 5° falls with time; if HCl is present, an initial fall is followed by a rise, the amount of which increases with the amount of HCl (0·1—0·3 mol.). NHPhMe,HNO_2 disappears from H_2O in presence of acids at a regular rate, increased by increasing the concn. of acid. These and previous results are explained as due to a primary reaction, OH·N:O + NHR_2 → $(OH)_2N$·NR_2. The reported third-order rate for similar reactions is reconciled with this reaction by considering the effects of ionic dissociation on the various systems involved. R. S. C.

Separated auxo-enoid systems. VI. Coloration of nitrobenzyl derivatives of aromatic amines. V. A. Ismailski and V. I. Stavrovskaja (J. Gen. Chem. Russ., 1939, **9**, 647—662).—The coloration of nitrobenzyl derivatives of aromatic amines is ascribed to interaction between the NO_2·C_6H_4·CH_2· and ·NHPh groups. Similar relations between structure and intensity of coloration are found as for the analogous nitro-azo-compounds. R. T.

Preparation of nuclear-substituted dimethylanilines. D. P. Evans and R. Williams (J.C.S., 1939, 1199—1200).—Alternate addition, in portions, of Me_2SO_4 (in total a slight excess) and 30% NaOH (to keep the solution alkaline to phenolphthalein) to nuclear-substituted anilines gives the dimethylaniline or its methosulphate in 40—94% yield; the *tert.* amine is readily obtained from the methosulphate by treating the derived methiodide with NaOH in boiling C_5H_{11}·OH or, less well, by treating with Ag_2O and heating the methohydroxide.

o-OPh·C_6H_4·NH_2 gives o-*phenoxydimethylaniline*, m.p. 34·5°, b.p. 161—162°/13 mm., and *o*-OPh·C_6H_4·NMe_3·OH. 2-*Dimethylaminodiphenyl*, b.p. 145·5°/11 mm., and p-*phenoxydimethylaniline*, b.p. 185°/13 mm., m.p. 34°, are described. R. S. C.

Substituted acetylenes and their derivatives. XXXIV. Addition of arylamines to alkinenes. J. A. Loritsch and R. R. Vogt (J. Amer. Chem. Soc., 1939, **61**, 1462—1463; cf. A., 1939, II, 400).—NH_2Ph adds to *n*-C_5H_{11}·C:CH (I) or Δ^{γ}-octinene in presence of HgO and Et_2O,BF_3 to give N-*α-methyl-n-hexylideneaniline*, b.p. 88—90°/4 mm., and the *anil*, CPrBu:NPh, b.p. 95—97/4 mm., respectively. A *by-product*, $C_{20}H_{33}N$, b.p. 138—141°/4 mm., is obtained in the former reaction. The structure of the anils is proved by acid hydrolysis to NH_2Ph and the ketone. NHPhEt and (I) give N-*ethyl*-N-*α-methylene-n-hexylaniline*, b.p. 92—94°/4 mm. (hydrolysed to COMe·C_5H_{11} and NHPhEt), and a *by-product*, $C_{22}H_{37}N$, b.p. 146—149°/4 mm. $NPhEt_2$ does not add to (I). R. S. C.

Naphthalene series. VIII. Preparation of 4-nitro-1-naphthylamine and of an azo-dye derived therefrom. N. N. Voroshcov and V. V. Kozlov (J. Gen. Chem. Russ., 1939, **9**, 587—589).—1 : 4-NH_2·$C_{10}H_6$·NO is oxidised ($KMnO_4$) to 1 : 4-NH_2·$C_{10}H_6$·NO_2, m.p. 196°, the diazo-derivative of which when coupled with *m*-$C_6H_4(OH)_2$ yields a bluish-red *azo*-dye. R. T.

Phenyl- and naphthyl-urethanes and the corresponding disubstituted carbamides. P. Jannke (J. Amer. Pharm. Assoc., 1939, **28**, 360—364).—Formation of $CO(NHAr)_2$ (I) during prep. of phenyl- and naphthyl-urethanes is discussed with reference to the work of Sherk (A., 1921, i, 239, 240). Solubility data (EtOH and $C_2H_4Cl_2$) for the urethanes of thymol, carvacrol, and thymoquinol and for $CO(NHPh)_2$ and $CO(NH·C_{10}H_7\text{-}\alpha)_2$ indicate that $C_2H_4Cl_2$ is a suitable solvent for separating the urethane and corresponding (I). F. O. H.

Derivatives of sulphanilamide.—See B., 1939, 884, 885.

Nitration of 3 : 3′-dichloroazoxybenzene and reduction of some of the products. H. E. Bigelow and W. H. Steeves (Canad. J. Res., 1939, **17**, B, 160—165).—Reduction of *m*-$C_6H_4Cl·NO_2$ with Na_3AsO_3 in NaOH yields 3 : 3′-dichloroazoxybenzene (I), which with boiling HNO_3 (*d* 1·45) gives a mixture of 3 : 3′-*dichloro*-6-*nitro*- (II), m.p. 116°, -4-*nitro*- (III), m.p. 145°, -2-*nitro*-, m.p. 112°, -5-*nitro*-, m.p. 105°, and -4 : 6-*dinitro-azoxybenzene*, m.p. 157°. Reduction of (II) with Sn–HCl gives *m*-$C_6H_4Cl·NH_2$ (IV) and 4 : 1 : 2-$C_6H_3Cl(NH_2)_2$; similarly (III) gives (IV) and 2 : 1 : 4-$C_6H_3Cl(NH_2)_2$. With fuming HNO_3, (I) gives 3 : 3′-*dichloro*-2 : 4 : 6-*trinitroazoxybenzene*, m.p. 165° [also formed from (II) or (III) with fuming HNO_3], and an *isomeride*, m.p. 182°. Reduction of (III) with Na_3AsO_3 yields the corresponding *tetrachloroazobisazoxybenzene*, m.p. 210°, and a small quantity of *tetrachlorotrisazoxybenzene*, m.p. 195°. Reduction of (II) gave a Cl-free *substance*, exploding at 275° (hydrochloride, m.p. 178°). J. D. R.

Structure and absorption spectra of azo-dyes. W. R. Brode (Proc. Sixth Conf. Spectros., 1938, 128—133).—The absorption spectra of a series of halogen-substituted benzeneazophenols have been investigated. It has been found that an increase in mol. wt. is usually accompanied by a decrease in frequency of the absorption bands which is approx. ∝ increase in mol. wt., but varies with position of substitution. Substitution in the *p′*-position by NO_2, Me, or halogen causes a max. in the magnitude of the absorption bands in all solvents. Halogen substitution in the *oo′*-positions causes a very marked decrease in the magnitude of the absorption bands in all solvents. In *op′*-disubstituted compounds, the *p′*-substituent exerts a greater effect on the frequency of the absorption max. in EtOH, the *o*-substituent having more effect on the extinction of the band. Br has a greater extinction effect than Cl. The principal absorption bands of the compounds in NaOH consist of two overlapping bands which may be due to two forms of vibration of the mol. in equilibrium. Cl-derivatives appear to exist in four equilibrium levels and Br-derivatives in six. An investigation of the formation of the chelate ring between *o*-hydroxyazo-dyes and metallic salts has been carried out by studying the absorption spectra of the complexes and of a series of related compounds possessing certain structural units in common with the complexes. The Cu complex of 3-benzeneazo-*p*-cresol exists in azoid, $C_6H_3Me\langle^{N:NPh}_{O\text{-}M\cdot}$, and quinoid, $C_6H_3Me\langle^{N—NPh}_{O\rightarrow M\leftarrow}$, forms in equilibrium. The structures of *o*-OH·C_6H_4·CHO (I) and of the Schiff's bases formed from PhCHO and *o*-OH·C_6H_4·NH_2, and from (I) and NH_2Ph have been investigated. A. J. M.

Action of mixed organo-magnesium compounds on benzaldehydeacylphenylhydrazones. Preparation of α-acyl-β-alkylphenylhydrazines. P. Grammaticakis (Compt. rend., 1939, **208**, 1910—1912; cf. A., 1937, II, 287).—CHPh:N·NAcPh (I) with MgEtBr gives N-*acetyl*-N-*phenyl*-N′-*α-phenylpropylhydrazine*, b.p. 182—184°/<1 mm. (*phenylcarbamyl* derivative, m.p. 153°), and a little CHPh:N·NHPh (II). (I) or benzaldehydecarbamylphenylhydrazone (III) with MgMeI gives (II) almost entirely. (I) or (III) with MgPhBr gives mainly (II) as well as products of interaction of (II) with MgPhBr [*β-benzyhydrylphenylhydrazine*, m.p. 77°, CPh_2:N·NHPh, CPh_2:NH, NH_2Ph, CPh_2:NPh, and small amounts of $(CHPh_2)_2$]. CHPh:N·NBzPh (IV) with MgPhBr gives N-*benzoyl*-N-*phenyl*-N′-*benzhydryl-hydrazine*, m.p. 145°, as well as CPh_2:NH, NHPhBz, CPh_3·OH, and (II). (IV) with MgMeI or MgEtI gives mainly N-*benzoyl*-N-*phenyl*-N′-*α-phenylethyl*-, b.p. 195°/<1 mm., or -N′-*α-phenylpropyl-hydrazine*, b.p. 198°/<1 mm., as well as small amounts of (II), CPhAlk:NH, and NHPhBz. Benzaldehydephenylcarbamylphenylhydrazone (V) with MgMeI, MgEtBr, and MgPhBr gives, respectively, N-*phenylcarbamyl*-N-*phenyl*-N′-*α-phenylethyl*-, m.p. 144°, -N′-*α-phenylpropyl*-, m.p. 102°, and -N′-*benzhydryl-hydrazine*, m.p. 214°. In each case 1 : 3 : 4-*triphenyl*-1 : 2 : 4-*triazol*-5-*one*, m.p. 224°, is formed by intramol. oxidation of (V). J. L. D.

Germicidal action and chemical constitution of isomeric xylenols and monohalogenated derivatives. K. Heicken (Angew. Chem., 1939,

52, 263—265).—The results of Lockemann *et al.* (A., 1933, 707) are corr. *o*-3-, *o*-4-, *m*-2-, *m*-4-, *m*-5-, and *p*-xylenol are mono-chlorinated (SO_2Cl_2–AcOH), -brominated (Br–AcOH), and -iodinated (I–aq. NH_3–KI). The following are new or disputed: 5-*chloro*-m-2-, m.p. 83° (cf. Busch *et al.*, A., 1929, 1432); 6-bromo-*o*-3-, m.p. 91° (cf. Short *et al.*, A., 1936, 720); 6-*iodo*-o-3-, m.p. 86° (6 : ?-I_2-derivative, m.p. 84·5°); 5-*iodo*-o-4-, m.p. 67·5°, -m-2-, m.p. 105°, and -m-4-, b.p. 123—124°/16 mm.; 2-*iodo*-m-5-, m.p. 131° [2 : 4 : 6-I_3-derivative, m.p. 177° (darkening)]; 5-*iodo*-p-2-, m.p. 97·5° (3 : 5-I_2-derivative, m.p. 61·5°) *-xylenols*. The Cl- and Br-derivatives of *o*-3-, *m*-5-, and *p*-xylenols are 50—70 times, and of *o*-4-, *m*-2-, and *m*-4-xylenols are 15—20 times, as strong as PhOH towards *B. coli* and *S. pyogenes aureus*. A. T. P.

Steric hindrance in ketone–phenol condensations. Synthesis of *cyclo*alkenylphenols and *cyclo*alkylcoumarans. J. B. Niederl and V. Niederl (J. Amer. Chem. Soc., 1939, **61**, 1785—1788).—Alkylidenediphenols are not obtained from phenols, 2-alkyl*cyclo*hexanones (*A*), and HCl in AcOH or from *m*-C_6H_4Alk·OH (*B*) and *cyclo*hexanone (I) (cf. A., 1939, II, 175). (*A*) and (*B*) give coumarans. *m*-Cresol and (I) give (2—3 weeks) at room temp. 1-5′-*hydroxy*-*o*-*tolyl*-Δ^1-cyclo*hexene* (12—15%), m.p. 65° [aryloxyacetic acid *derivative*, m.p. 160° (*Br*-derivative, m.p. 150°); *phenylurethane*, m.p. 114°; *acetate*, b.p. 155—157°/12 mm.]. *m*-C_6H_4Et·OH and (I) give 1-4′-*hydroxy*-2′-*ethylphenyl*-Δ^1-cyclo*hexene* (15%), m.p. 55° [aryloxyacetic acid *derivative*, m.p. 117° (*Br*-derivative, m.p. 146°); *phenylurethane*, m.p. 134°; *acetate*, b.p. 169—174°/12 mm.]. PhOH and 2-methyl*cyclo*hexanone (II) give 1-p-*hydroxyphenyl*-2-*methyl*-Δ^1-cyclo*hexene* (III) (55—60%), m.p. 144° [aryloxyacetic acid *derivative*, m.p. 136° (*dibromide*, m.p. 104°); *phenylurethane*, m.p. 160; *acetate*, b.p. 161°/10 mm.; *benzoate*, m.p. 72°]. *o*-Cresol and (II) give 1-6′-*hydroxy*-m-*tolyl*-2-*methyl*-Δ^1-cyclo*hexene* (IV) (45—50%), m.p. 86° [aryloxyacetic acid *derivative*, m.p. 113° (*dibromide*, m.p. 107°); *phenylurethane*, m.p. 134°; *acetate*, b.p. 172—174°/12 mm.; *benzoate*, m.p. 69°]. *m*-Cresol or *m*-C_6H_4Et·OH with (II) and HCl in AcOH at 80° (reaction is too slow at room temp.) gives 1 : 5-*dimethyl*- (~40%), b.p. 139—141°/12 mm., or 1-*methyl*-5-*ethyl*- (~30%), b.p. 146—148°/12 mm., -1 : 2-*tetramethylenecoumaran*, respectively. The structure of (III) and (IV) is proved by conversion of the dibromides named by N-NaOH at room temp. into p-1′ : 2′-*dihydroxy*-2′-*methyl*cyclo*hexylphenoxy*-, m.p. 130°, and 5-1′ : 2′-*dihydroxy*-2′-*methyl*cyclo*hexyl*-*o*-*tolyloxy*-*acetic acid*, m.p. 140°, respectively (proof of 2 *tert.* Br), which with HCl in aq. EtOH undergo the pinacolone rearrangement, yielding *p*-2′-keto-1′-methyl*cyclo*hexylphenoxy- and 5-2′-keto-1′-methyl*cyclo*hexyl-*o*-tolyloxy-acetic acid (2 : 4-*dinitrophenylhydrazone*, m.p. 87°), respectively. R. S. C.

Sulphonic esters of 4 : 4′-dihydroxydiphenyl. S. E. Hazlet (J. Amer. Chem. Soc., 1939, **61**, 1921).—4 : 4′-*Dihydroxydiphenyl dibenzenesulphonate*, m.p. 148°, di-*p*-toluenesulphonate, m.p. 187—188°, *di*-o-, m.p. 191—192°, -m-, m.p. 216—217°, and -p-*nitro*-, m.p. 231°, and *di*-p-*bromo*-*benzenesulphonate*, m.p. 201—202°, are prepared. R. S. C.

Mono- and di-esters of pyrogallol. A. von Wacek and F. K. J. Travnicek (Österr. Chem.-Ztg., 1939, **42**, 281—286).—Pyrogallol carbonate and AcCl in C_5H_5N give *pyrogallol* 1-*acetate* 2 : 3-*carbonate*, m.p. 121°, hydrolysed by H_2O at 75° to *pyrogallol* 1-*acetate*, m.p. 85°. With BzCl–C_5H_5N, first at room temp. and then at 80°, this gives *pyrogallol* 1-*acetate* 2 : 3-*dibenzoate* (~10%), m.p. 124°. Similarly are prepared *pyrogallol* 1-*benzoate* 2 : 3-*carbonate*, m.p. 141°, and 1-*benzenesulphonate* 2 : 3-*carbonate*, m.p. 93°, hydrolysed by boiling H_2O to the 1-*benzoate*, m.p. 133°, and 1-*benzenesulphonate*, m.p. 121°. 1-*Carbobenzyloxypyrogallol* 2 : 3-*carbonate* (prep. in $NPhMe_2$), m.p. 74°, in aq. $COMe_2$ at 60° gives 1-*carbobenzyloxypyrogallol*, m.p. 110°, which with AcCl in $NPhMe_2$ gives 1-*carbobenzyloxypyrogallol* 2 : 3-*diacetate*, m.p. 105°, and thence (H_2–Pd-black; $COMe_2$) *pyrogallol* 1 : 2-*diacetate*, m.p. 115°. R. S. C.

Catalytic synthesis of anisole and *p*-tolyl methyl ether. S. Ishikawa and M. Matsuhashi (Sci. Rep. Tokyo Bunrika Daigaku, 1939, **3**, 249—255).—PhOMe is obtained in 48% yield by passing PhOH and MeOH over ThO_2 at 400°; addition of CeO_2 or use of a carrier brings no advantage. At 500° Ph_2O and xanthene (I) are also formed; under like conditions (I) is produced from PhOH or Ph_2O and CH_2O. Similarly *p*-cresol and MeOH afford *p*-C_6H_4Me·OMe, $(C_6H_4Me)_2O$, and 2 : 7-*dimethylxanthene*, m.p. 168·2° (corr., Berl), oxidised by HNO_3 to 2 : 7-*dimethylxanthone*, m.p. 173·4° (corr., Berl). H. W.

Phthalic esters as alkylating agents. H. King and E. V. Wright (J.C.S., 1939, 1168—1170).—Salts (best, K salts) of phenols with alkyl phthalates (I) (1 mol.) at 190—200° give good yields of the alkyl ethers. In many cases both alkyls of part of (I) are utilised. Thus are obtained PhOMe (75), PhOEt (66), PhOBu (76), *o*-OMe·C_6H_4·OR (R = Me 78, Et 84, and Bu, m.p. 17—18°, 80%). KOPh and *o*-OMe·C_6H_4·OK with MeOBz give PhOMe (63) and *o*-$C_6H_4(OMe)_2$ (57%), respectively. *p*-OK·C_6H_4·NHMe with *o*-$C_6H_4(CO_2Me)_2$ at 200—210° gives *p*-OMe·C_6H_4·NMe_2 and *phthal*-p-*anisylimide*, m.p. 162°, with *o*-$C_6H_4(CO_2Et)_2$ gives *p*-methylethylaminophenetole (*picrate*, m.p. 125°; hygroscopic hydrochloride) and *phthal*-p-*phenetylimide*, m.p. 204—205°, but with *o*-$C_6H_4(CO_2Bu)_2$ gives p-*butoxymethylaniline*, b.p. 154—155°/16 mm. (*picrate*, m.p. 98°). R. S. C.

Chemistry of vitamin-*E*. Chloromethylation of polymethylquinols and their derivatives; cleavage of quinol ethers. L. I. Smith, H. E. Ungnade, J. W. Opie, W. W. Prichard, R. B. Carlin, and E. W. Kaiser (J. Org. Chem., 1939, **4**, 323—333).—3 : 6 : 2 : 4 : 5-$(OMe)_2C_6Me_3$·CH_2Cl (I), new m.p. 67—68°, is condensed with CH_2Ac·CO_2Et and the product is hydrolysed (NaOH) to α-3 : 6-*dimethoxy*-2 : 4 : 5-*trimethylphenylbutan*-γ-*one*, m.p. 78—78·5° (*semicarbazone*, m.p. 108—109°). This could not be satisfactorily demethylated by NH_2Ph,HBr at 225—227°, boiling HI (*d* 1·50) and AcOH, 40% HBr, or AcOH saturated with HBr. 3 : 6 : 2 : 4 : 5-$(OMe)_2C_6Me_3$·CH_2·OAc, m.p. 65—66°, from (I) and KOAc in boiling AcOH, is hydrolysed to the corre-

sponding alcohol (II), m.p. 120—121°, which is oxidised (CrO_3 in AcOH) to the aldehyde (III), m.p. 83·5—84·5°; (I) and $(CH_2)_6N_4$ in boiling aq. EtOH give impure (II). $AlCl_3$ in boiling light petroleum demethylates (III) to 6-*hydroxy*-3-*methoxy*-2 : 4 : 5-*trimethylbenzaldehyde*, m.p. 88—89°, with probably 3 : 6-*dihydroxy*-2 : 4 : 5-*trimethylbenzaldehyde*, possibly two modifications, yellow, m.p. 129—131°, and orange, m.p. 147—148°, obtained in poor yield from trimethylquinol (IV), $Zn(CN)_2$, and HCl in Et_2O. 3 : 6-*Diethoxy*-ψ-*cumene*, b.p. 102—103°/2 mm., m.p. 34—35°, obtained from the quinol, Et_2SO_4, and KOH in boiling MeOH, is converted successively into 3 : 6-*diethoxy*-2 : 4 : 5-*trimethylbenzyl chloride*, m.p. 86—87°, the *acetate*, m.p. 113·5—114·5°, and the *alcohol*, m.p. 112—113°, which is oxidised to the phototropic 3 : 6-*diethoxy*-2 : 4 : 5-*trimethylbenzaldehyde*, m.p. 99—100°. Dealkylation occurs even less readily than with the corresponding $(OMe)_2$-compounds. (IV) and CH_2PhCl in presence of alkali or C_5H_5N give a difficultly separable mixture (mainly of *C*-CH_2Ph compound and unchanged material) also obtained from the MgBr salt in Et_2O. 3 : 6-*Dibenzyloxy*-ψ-*cumene*, m.p. 72·5—73·5°, is obtained in small yield from the quinol and CH_2PhCl in boiling $COMe_2$ containing K_2CO_3. (IV) is converted by the successive action of NaOEt and $CH_2Br{\cdot}CO_2Me$ followed by hydrolysis into 3 : 6-dicarboxymethoxy-ψ-cumene, m.p. 205—206°, which appears to be unaffected by successive treatments with $SOCl_2$ and $AlCl_3$ in C_6H_6 but is transformed by warm 95% H_2SO_4 into 4-*carboxymethoxy*-3 : 5 : 6-*trimethylcoumaranone*, m.p. 211—213°. Similarly 3 : 6-di-α-carboxyethoxy-ψ-cumene is obtained as an oil. ψ-Cumoquinol diacetate (pure), 40% CH_2O, and HCl are maintained at 10—20° while a fairly rapid stream of HCl is passed, after which the mixture is warmed to 25° and saturation is continued, thus giving 3 : 6-*diacetoxy*-2 : 4 : 5-*trimethylbenzyl chloride*, m.p. 150—151°, often accompanied by a by-product, m.p. 225—227°. With $CHAcNa{\cdot}CO_2Et$ in C_6H_6 it affords *Et* 3 : 6-*dihydroxy*-2 : 4 : 5-*trimethylbenzylacetoacetate*, m.p. 135—136° (decomp.). H. W.

Pyrogallol–acetone condensation products. A. von Wacek and K. Kratzl (Österr. Chem.-Ztg., 1939, **42**, 286—289).—No CMe_2 derivative could be obtained directly from pyrogallol, but the appropriate 1-derivatives with $COMe_2$ and P_2O_5 in $COMe_2$ give 2 : 3-iso*propylidene*pyrogallol 1-*Me ether*, b.p. 113—115°/17 mm. (hydrolysed by 20% H_2SO_4 to pyrogallol 1-Me ether), 1-*benzoate*, m.p. 78°, and 1-*benzenesulphonate*, m.p. 84°. Pyrogallol 1-acetate gives an impure 2 : 3-*CMe*$_2$ derivative (I), b.p. 123—128°/12 mm., hydrolysed by 5% KOH at room temp. to 1 : 2-iso*propylidene*pyrogallol (II), m.p. 89—90° (no $FeCl_3$ reaction), whence (I) is obtained pure (m.p. 47—48°) by hot Ac_2O. The *homologue*, 1 : 2 : 3-$OMe{\cdot}C_6H_3{<}^{O_2CMeEt}_{O}$, b.p. 129—132°/12 mm., is similarly obtained. (II) is termed *gallacetonin*, and its derivatives are named accordingly. R. S. C.

Synthesis of diphenyl ethers containing methoxy- and ethoxy-groups. H. King (J.C.S., 1939, 1165—1168).—*o*-$OEt{\cdot}C_6H_4{\cdot}OH$ (1·5), *o*-$C_6H_4Br{\cdot}OEt$ (1), KOH (1·5 mols.), and a little Cu-bronze at 190—200° give *di*-o-*phenetyl ether*, m.p. 53°, b.p. 140—145°/0·5 mm. o-*Anisyl* o-*phenetyl ether*, m.p. 91—92°, b.p. 150°/0·6 mm., is similarly prepared. 4 : 3 : 1-$OH{\cdot}C_6H_3(OMe){\cdot}CO_2H$ (Ac derivative, m.p. 144°) is obtained in nearly 86% yield from 4 : 3 : 1-$OAc{\cdot}C_6H_3(OMe){\cdot}CHO$ by $KMnO_4$–$COMe_2$, followed by 2N-NaOH at room temp. 4 : 5 : 3 : 1-$OH{\cdot}C_6H_2Br(OMe){\cdot}CO_2H$, m.p. 231° (lit. 221°), and Et_2SO_4 in 2N-NaOH at 90° give 5-*bromo*-3-*methoxy*-4-*ethoxybenzoic acid*, m.p. 141—142°, and its *Et* ester (I), m.p. 25—26°, b.p. 197°/15 mm. With KOPh (1·5 mols.) and a little Cu powder at 180—190°, followed by MeOH–KOH, (I) gives 5-*carboxy*-3-*methoxy*-2-*ethoxydiphenyl ether* (II), m.p. 116—117°, and, by debromination, 4 : 3 : 1-$OEt{\cdot}C_6H_3(OMe){\cdot}CO_2H$. 4-*Acetoxy*-3-*ethoxybenzaldehyde* (prep. from the OH-aldehyde by Ac_2O and N-KOH), m.p. 48—49°, with $KMnO_4$ in $COMe_2$ gives 4-*acetoxy*-, m.p. 152—153°, hydrolysed to 4-*hydroxy*-3-*ethoxybenzoic acid*, m.p., 164—165°. Br–AcOH then gives 5-*bromo*-4-*hydroxy*-3-*ethoxybenzoic acid* (III), +3 or $2H_2O$, m.p. 207°, and 2 : 4-*dibromo*-6-*ethoxyphenol*, m.p. 110°. Me_2SO_4–2N-NaOH converts (III) into *Me* 5-*bromo*-4-*methoxy*-3-*ethoxybenzoate* (IV), m.p. 77—78°, less of the corresponding *acid*, m.p. 183—184°, and a small amount of *Me* 5-*bromo*-4-*hydroxy*-3-*ethoxybenzoate*, m.p. 111—112°. With KOPh (1·5 mols.) and Cu powder at 180°, (IV) gives 5-*carboxy*-2-*methoxy*-3-*ethoxydiphenyl ether* (V), double m.p. 117—118° and 134° (sometimes 134° only), and 4-*methoxy*-3-*ethoxybenzoic acid*, m.p. 165°. With Cu powder in boiling quinoline, (II) and (V) give CO_2 and 3-*methoxy*-2-*ethoxy*-, m.p. 33—34°, b.p. 155°/2 mm., and 2-*methoxy*-3-*ethoxy*-*diphenyl ether*, m.p. 23°, b.p. 138—141°/0·5 mm., respectively. R. S. C.

Constitution of rhapontin. S. Kawamura (J. Pharm. Soc. Japan, 1938, **58**, 83—85).—Rhapontin from Turkey rhubarb root is a glucoside of *rhapontigenin*, identified as 3 : 5 : 3′-*trihydroxy*-4′-*methoxystilbene* (I), m.p. 190—191°, the *tribenzoate*, m.p. 142°, of which is oxidised by CrO_3–AcOH to benzoyl *iso*vanillic (II) and dibenzoylresorcylic acids. With O_3 in AcOH, (I) gives *iso*vanillin and α-resorcaldehyde. With Pt–H_2 it gives *dihydrorhapontigenin* (3 : 5 : 3′-*trihydroxy*-4′-*methoxydibenzyl*), m.p. 135—136° (*tribenzoate*, m.p. 106—107°). With Ac_2O and with NaOAc–Ac_2O, (I) gives *triacetates*, m.p. 114° and 128°, regarded as *cis–trans* isomerides. Since rhapontin benzoate with CrO_3 gives (II) and a Na_2CO_3-insol. substance, the glucose mol. is presumably attached to a resorcinol-O atom. E. W. W.

Preparation and behaviour of mixed diacyl derivatives of *o*-aminophenol containing a carboaryloxy radical and the *p*-toluenesulphonyl group. L. C. Raiford and J. R. Shelton (J. Org. Chem., 1939, **4**, 207—219).—*o*-$NH_2{\cdot}C_6H_4{\cdot}OH$ and 3 : 5 : 1 : 4-$NH_2{\cdot}C_6H_2BrMe{\cdot}OH$ (I) have been converted into mixed diacyl derivatives in which one of the radicals was invariably *p*-$C_6H_4Me{\cdot}\dot{S}O_2$. When the other radical was $\cdot CR{:}\dot{O}$, $OR{\cdot}\dot{C}{:}O$ or $Ar{\cdot}\dot{C}{:}O$ isomerides were obtained when the acyls were introduced in different orders and no migration was observed. When the second radical was $OAr{\cdot}\dot{C}{:}O$ isomeric mixed compounds were again formed but

under these conditions the products may suffer further change. Thus, the *N*-*p*-toluenesulphonyl derivative of each base reacts with $ClCO_2Ph$ to give the expected $O{\cdot}CO_2Ph$ derivative. That formed from the first base loses PhOH immediately to give the corresponding *N*-*p*-toluenesulphonylbenzoxazolone; with the second base both diacyl derivatives and the substituted benzoxazolone are obtained. Acylations are effected by the method of Einhorn and Hollandt or by that of Groenvik. Where these methods are unsatisfactory good results are obtained by treatment of the aminophenol with $NPhMe_2$ and the acid chloride in dioxan. The following derivatives of o-$NH_2{\cdot}C_6H_4{\cdot}OH$ appear new: N-*benzoyl*-O-p-*toluenesulphonyl*-, m.p. 109—110°; O-*benzoyl*-N-p-*toluenesulphonyl*-, m.p. 141°; N-*carbethoxy*-O-p-*toluenesulphonyl*-, m.p. 72—74°; O-*carbethoxy*-N-p-*toluenesulphonyl*-, m.p. 128—130°. (I) gives the following derivatives: N-p-*toluenesulphonyl*- (II), m.p. 171—172°; N-*acetyl*-O-p-*toluenesulphonyl*-, m.p. 131—132°; O-*acetyl*-N-p-*toluenesulphonyl*-, m.p. 150—151·5°; N-*benzoyl*-O-p-*toluenesulphonyl*-, m.p. 149—151°; O-*benzoyl*-N-p-*toluenesulphonyl*-, m.p. 163—164°; N-*carbethoxy*-O-p-*toluenesulphonyl*-, m.p. 124·5—125°, hydrolysed to 5-bromo-6-hydroxy-3-methylphenylurethane, m.p. 83°; O-*carbethoxy*-N-p-*toluenesulphonyl*-, m.p. 140—142°. *o*-Aminophenyl *p*-toluenesulphonate and $ClCO_2Ph$ afford o-*carbophenoxyaminophenyl* p-*toluenesulphonate*, m.p. 114°, which gives only a dark oil when hydrolysed with KOH–EtOH. 2-*p*-Toluenesulphonamidophenol and $ClCO_2Ph$ in C_5H_5N or according to Schotten–Baumann yield unchanged material and a little 2-*p*-toluenesulphonylbenzoxazolone, m.p. 141—142°. (II) and $ClCO_2Ph$ in C_5H_5N afford unchanged material and *Ph* 5-*bromo*-3-p′-*toluenesulphonamido*-p-*tolyl carbonate* whereas in warm dioxan containing $NPhMe_2$ the product is 6-bromo-2-*p*-toluenesulphonyl-4-methylbenzoxazolone, m.p. 175—176°. Under various conditions 5-bromo-3-amino-*p*-tolyl *p*-toluenesulphonate and $ClCO_2Ph$ afford the *diacyl* derivative, m.p. 129—131°, and (by loss of PhOH) 1 : 3-*di*-(5-*bromo*-6-p-*toluenesulphonoxy*-3-*methylphenyl*)*uretidone*, m.p. 208—209°, hydrolysed to the $(OH)_2$-compound, $\begin{matrix}NR{\cdot}CO\\CO{\cdot}NR\end{matrix}$ (R = 2 : 5 : 3-$OH{\cdot}C_6H_2MeBr$·), m.p. 170° (decomp.).

H. W.

Relationships between constitution and action of derivatives of *p*-aminophenol. C. Rohmann and K. Friedrich (Ber., 1939, **72**, [*B*], 1333—1339).—$NEt_2{\cdot}[CH_2]_2{\cdot}Cl$, HCl, and p-$NO_2{\cdot}C_6H_4{\cdot}ONa$ in xylene at 135—145° give *p*-nitrophenyl β-diethylaminoethyl ether, decomp. >240° (yield 67%), reduced by Fe and HCl with a little Pt as catalyst to the NH_2-derivative (I), which condenses with PhCHO in presence of $ZnCl_2$ to the :CHPh compound, reduced by Na and abs. EtOH at room temp. to *p*-benzylaminophenyl β-diethylaminoethyl ether (non-cryst. *dihydrochloride*). Condensation of (I) with the requisite aldehyde followed by reduction of the product gives the non-cryst. *dihydrochlorides* of *p*-ethylamino-, *p*-propylamino-, and *p*-*n*-butylamino-phenyl β-diethylaminoethyl ether. The compounds do not disturb the circulation and are non-irritant; they have a distinct local anæsthetising action.

H. W.

Synthesis of organic compounds containing radioactive sulphur. H. K. Alber (J. Franklin Inst., 1939, **228**, 177—181).—^{35}S is prepared as a by-product of bombardment of CCl_4 with neutrons (cyclotron), mixed with (added) ^{32}S, and used to prepare radioactive $(p$-$NO_2{\cdot}C_6H_4{\cdot}S)_2$ (I) from p-$C_6H_4Cl{\cdot}NO_2$, Na_2S, and S, and thence by Cl_2–H_2O radioactive p-$NO_2{\cdot}C_6H_4{\cdot}SO_2Cl$. When ordinary or radioactive (I) is heated on a micro-m.p. hot stage, some (? tetragonal) crystals melt at 134°, resolidify and remelt at 164—165°, whereas the remaining crystals melt at 178—179° (lit. m.p. between 170° and 180°); three cryst. modifications are present.

R. S. C.

Hydroxyaryl alkyl and aralkyl sulphides.—See B., 1939, 808.

Normal and abnormal reactions of the sodium derivatives of aromatic thiols with halogenonitro-naphthalenes and -benzenes. H. H. Hodgson and E. Leigh (J.C.S., 1939, 1094—1096).—Normal reactions of ArSNa with aromatic chloronitro-compounds support the explanation previously offered for the anomalous reactions (A., 1938, II, 406). PhSH and 2 : 1-$C_{10}H_6Cl{\cdot}NO_2$ in hot NaOH–EtOH give *Ph* 1-*nitro*-2-*naphthyl sulphide*, m.p. 58—58·5°. *Ph* 4-*nitro*-1-*naphthyl sulphide*, m.p. 105·5—106°, is similarly prepared. The appropriate naphthyl- or anthraquinonyl-thiol with 2 : 1- or 1 : 4-$C_{10}H_6Cl{\cdot}NO_2$ in hot NaOH–EtOH–H_2O yields α-, m.p. 107°, and β-$C_{10}H_7$ 1-*nitro*-2-*naphthyl sulphide*, m.p. 91°, α-, m.p. 127°, and β-$C_{10}H_7$ 4-*nitro*-1-*naphthyl sulphide*, m.p. 151°, 1-*nitro*-2-, m.p. 435° (decomp.; block), and (?) 4-*nitro*-1-*naphthyl* 1-*anthraquinonyl sulphide*, decomp. when heated, 1-*nitro*-2-, m.p. 384° (decomp.; block), and (?) 4-*nitro*-1-*naphthyl* 2-*anthraquinonyl sulphide*, m.p. 238° (block).

R. S. C.

Activity of the methylene group in the isomeric *p*-tolyl mononitrobenzyl sulphones and in *p*-tolyl 2 : 4-dinitrobenzyl sulphone. R. L. Shriner and S. O. Greenlee (J. Org. Chem., 1939, **4**, 242—251).—Interaction of p-$C_6H_4Me{\cdot}SO_2Na$ with the requisite nitrobenzyl halide in boiling EtOH affords p-*tolyl* o- (I), m.p. 131—132°, p- (II), m.p. 188—189°, and m- (III), m.p. 160—161°, -*nitrobenzyl sulphone* and p-*tolyl* 2 : 4-*dinitrobenzyl sulphone* (IV), m.p. 159—160°. (I) and (II) are converted by NaOEt into coloured salts which do not alkylate with MeI or couple with I but are brominated to p-*toluenesulphonyl*-o-, m.p. 116—117°, and -p-, m.p. 166—167°, -*nitrophenylmethyl bromide*, respectively. (I) in $PhNO_2$ is converted by the successive action of KOEt–EtOH and I into p-*toluenesulphonyl*-o-*nitrophenylmethyl iodide*, m.p. 145—146°. (III) does not undergo bromination in presence of NaOEt. (IV) in $PhNO_2$ is transformed by KOEt–EtOH into a purple, cryst. *salt* (V), $C_{14}H_{11}O_6N_2SK$, from which the initial material is regenerated on acidification and which is brominated to p-*toluenesulphonyl*-2 : 4-*dinitrophenylmethyl bromide*, m.p. 178—180°. The halogeno-compounds give only a slight ppt. when boiled with $AgNO_3$–EtOH but the halogen is readily removed when they are boiled with NaOAc in 80% EtOH or by reduction with Na_2S. MeI converts (V) into α-p-

toluenesulphonyl-α-2 : 4-*dinitrophenylethane*, m.p. 167—168°, in 63% yield. I and (V) give αβ-*di*-(p-*toluenesulphonyl*-2 : 4-*dinitrophenyl*)*ethane*, decomp. 375° (block). All these reactions indicate that the anion of the salt involved in these reactions is a carbanion and not one of the possible tautomeric *aci*-NO_2 structures. Boiling NaOH–EtOH converts *p*-nitrophenyl benzyl sulphone into 4 : 4′-*dibenzylsulphonylazoxybenzene*, m.p. 340—342°. *p*-$C_6H_4Me{\cdot}SO_2{\cdot}CH_2{\cdot}NO_2$ (VI) gives a nearly colourless *salt*, $C_7H_8O_4NSK$. Addition of Br to (VI) in NaOH yields *dibromonitro*-p-*toluenesulphonylmethane*, m.p. 127°. Attempts to condense (I), (II), (III), (IV), or (VI) with $Et_2C_2O_4$ in presence of NaOEt or KOEt were unsuccessful; they could not be condensed with PhCHO. H. W.

Functional aptitude of the methyl group. III. Derivatives of diphenyl sulphone. L. Chardonnens and J. Venetz (Helv. Chim. Acta, 1939, **22**, 853—868).—In suitable conjunction with NO_2, Me appears to be more strongly activated by $PhSO_2$ than by Bz but two $PhSO_2$ groups are ineffective. 3 : 4-$NO_2{\cdot}C_6H_3Me{\cdot}SO_2Cl$, m.p. 36°, is transformed by $AlCl_3$ and C_6H_6 at 70° into 3-*nitro*-4-*methyldiphenyl sulphone*, m.p. 117·5°, which is converted by PhCHO in presence of piperidine at 130° into 3-*nitro*-4-*styryldiphenyl sulphone*, m.p. 191—192° (*dibromide*, decomp. 217°), by *p*-$NMe_2{\cdot}C_6H_4{\cdot}CHO$ into 3-*nitro*-4-p-*dimethylaminostyryldiphenyl sulphone*, m.p. 177°, by *p*-$OMe{\cdot}C_6H_4{\cdot}CHO$ into 3-*nitro*-4-p-*methoxystyryldiphenyl sulphone*, m.p. 158°, and by *p*-$NO{\cdot}C_6H_4{\cdot}NMe_2$ in boiling EtOH containing anhyd. Na_2CO_3 into 2-*nitro*-4-*benzenesulphonylbenzald*-p′-*dimethylaminoanil*, m.p. 187—188°, hydrolysed by HCl to 2-*nitro*-4-*benzenesulphonylbenzaldehyde* (I), m.p. 133—134° (*phenylhydrazone*, m.p. 217°; *semicarbazone*, m.p. 259°). *p*-$C_6H_4Me{\cdot}SO_2Ph$ is converted by conc. H_2SO_4 and HNO_3 (*d* 1·5) at 0—10° into 3 : 3′-*dinitro*-, m.p. 150—151°, and by conc. H_2SO_4 and HNO_3 (*d* 1·52) at room temp. and then at 100° into 3 : 5 : 3′-*trinitro*-, m.p. 191—192°, -4-*methyldiphenyl sulphone*. (I) is converted by 1% NaOH in aq. $COMe_2$ into 6 : 6′-*dibenzenesulphonylindigotin*, m.p. >370° (block). Similarly, 3 : 3′-dinitro-4 : 4′-dimethyldiphenyl sulphone affords 3 : 3′-*dinitro*-4 : 4′-*distyryl*-, m.p. 276° (block), and -4 : 4′-*di*-p-*dimethylaminostyryl*-, m.p. 237°, -*diphenyl sulphone*. The *di*-p-*dimethylaminoanil*, m.p. 250—251° (hydrolysed by HCl–H_2O in presence of $CHCl_3$), of 3 : 3′-*dinitro*-4 : 4′-*diformyldiphenyl sulphone*, m.p. 191—192° (*disemicarbazone*, m.p. >330°), is prepared. From 5-nitro-2-methyldiphenyl sulphone are derived 5-*nitro*-2-*styryl*-, m.p. 233°, and -2-p-*dimethylaminostyryl*-, m.p. 264°, -*diphenyl sulphone* and 4-*nitro*-2-*benzenesulphonylbenzald*-p′-*dimethylaminoanil*, m.p. 232·5°, hydrolysed to 4-*nitro*-2-*benzenesulphonylbenzaldehyde*, m.p. 121—122° (*phenylhydrazone*, m.p. 255—256°). 2 : 4-Dibenzenesulphonyltoluene, m.p. 192—193°, is conveniently prepared by heating 1 : 2 : 4-$C_6H_3Me(SO_3H)_2$ with C_6H_6 and P_2O_5 at 180°, or by transforming *p*-$C_6H_4Me{\cdot}SO_2Ph$ by a mol. proportion of $ClSO_3H$ into $PhSO_2{\cdot}C_6H_3Me{\cdot}SO_3H$, which is heated with C_6H_6 and P_2O_5 at 180°; it does not condense with PhCHO. If *p*-$C_6H_4Me{\cdot}SO_2Ph$ is treated with a large excess of $ClSO_3H$ 4-*methyldiphenyl sulphone*-3 : 3′-*disulphonyl chloride*, m.p. 159°, appears to be formed. H. W.

Manufacture of di-*p*-aminophenyl sulphones.—See B., 1939, 808.

Identification of aromatic sulphones. C. A. Buehler and J. E. Masters (J. Org. Chem., 1939, **4**, 262—265).—Ph *p*-tolyl, *pp*′-ditolyl, *p*-chlorophenyl *p*-tolyl, and *p*-bromophenyl *p*-tolyl sulphone are oxidised (CrO_3 in glacial AcOH) to Ph *p*-carboxyphenyl, m.p. 266—268° (*Et* ester, m.p. 70—70·5°), di-*p*-carboxyphenyl, m.p. 358—363° (Et_2 ester, m.p. 156—156·5°), p-*chlorophenyl* p-*carboxyphenyl*, m.p. 274·1—275·3° (*Et* ester, m.p. 132—133°), and p-*bromophenyl* p-*carboxyphenyl*, m.p. 283·8—285·5° (*Et* ester, m.p. 133—134°), *sulphone*, respectively. The m.p. are high and insufficiently characteristic of the acids, which are therefore esterified by EtOH and conc. H_2SO_4. The $(NO_2)_2$-derivatives are obtained by the action of conc. HNO_3 and conc. H_2SO_4 at 60° on the sulphone and are highly characteristic. The following sulphones are described (all m.p. are corr.): di-*m*-nitrophenyl, m.p. 202·1—203·1°; ? m-*nitrophenyl* 2-*nitro*-p-*tolyl*, m.p. 151·7—152·7°; ? m-*nitrophenyl* 3-*nitro*-4-*ethylphenyl*, m.p. 137·7—138·8°; *m*-nitrophenyl 4-chloro-3-nitrophenyl, m.p. 146·6—147·6°; ? m-*nitrophenyl* 4-*bromo*-3-*nitrophenyl*, m.p. 162·1—163·1°; di-(2-nitro-*p*-tolyl), m.p. 164·2—165·2°; ? 2-*nitro*-p-*tolyl* 3-*nitro*-4-*ethylphenyl*, m.p. 116·4—117·4°; 4-chloro-3-nitrophenyl 2-nitro-*p*-tolyl, m.p. 151·2—151·7°; ? 4-*bromo*-3-*nitrophenyl* 2-*nitro*-p-*tolyl*, m.p. 160·1—161·1°; ? *di*-4-*bromo*-3-*nitrophenyl*, m.p. 235·3—237·3°. H. W.

Crystalline esters of vitamin-*A*.—See A., 1939, III, 601.

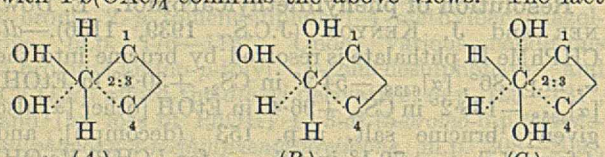
Resolution of phenylmethylcarbinol. E. Downer and J. Kenyon (J.C.S., 1939, 1156).—*dl*-CHPhMe H phthalate is resolved by brucine into the *l*-, m.p. 86°, $[\alpha]_{6438}$ −54·2° in CS_2, +30·2° in EtOH, $[\alpha]_{4358}$ −138·2° in CS_2, +96·4° in EtOH [other [α] also given; brucine salt, m.p. 153° (decomp.)], and *d*-form, $[\alpha]_{5461}$ +79·1° in CS_2. α for *l*-CHPhMe·OH, b.p. 93°/14 mm., for 5 λλ are recorded. R. S. C.

Dehydration of α-phenyl-β-propenyl glycol. Formation of aldehyde (hydrobenzoin change) and ketone. Y. Deux and D. Abragam (Compt. rend., 1939, **208**, 2084—2086; cf. Tiffeneau and Weil, A., 1937, II, 225; Deux, following abstract).—α-Phenyl-Δ$^{\gamma}$-pentene-αβ-diol (I) (1 part) in 30% H_2SO_4 (5 parts) when distilled in steam gives a volatile oil (*A*), b.p. 139—141°/13 mm.; fractional crystallisation of the derived semicarbazones shows the presence of CHMe:CH·CHPh·CHO (II) or CHEt:CPh·CHO (III), and benzyl propenyl ketone (IV). Reduction of (*A*) (H_2–catalyst) gives a product, oxidised by Ag_2O to $CHPhPr^{\alpha}{\cdot}CO_2H$ [from (II) or (III)] and $COPr^{\alpha}{\cdot}CH_2Ph$ [from (IV)]. (II) or (III) is formed as a result of a hydrobenzoin change, whereas (IV) results from a vinyl mechanism. The aromatic character of propenyl is thus less marked than that of vinyl. J. L. D.

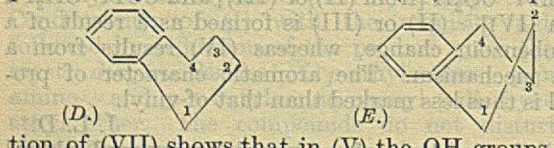
Dehalogenation of α-phenyl-β-propenyl glycol iodohydrin and isomerisation of the corre-

sponding oxide. Y. Deux (Compt. rend., 1939, **208**, 2002—2004; cf. A., 1939, II, 265).—CHPh:CH·CHEt·OH (from CHPh:CH·CHO and MgEtBr) with hot H_2SO_4 gives *α-phenyl-Δ^{αγ}-pentadiene* (I), b.p. 110—111°/14 mm., which with HgO and I in Et_2O–H_2O followed by treatment with $AgNO_3$ is converted into CHMe:CH·CHPh·CHO (II) or CHEt:CPh·CHO (III), b.p. 142—143°/14 mm. (*semicarbazone*, m.p. 166—167°), so that propenyl behaves like an aromatic radical. (II) or (III) with H_2–Raney Ni gives CHPhPr^{α}·CHO, oxidised to α-phenylvaleric acid, m.p. 53°. HOI adds to the double linking near Ph; dehalogenation is accompanied by a hydrobenzoin change. The chlorohydrin of (I) with powdered KOH gives *αβ-oxido-α-phenyl-Δ^{γ}-pentene*, b.p. 87—89°/4 mm., which under 20 mm. over kieselguhr at 250—300°, similarly gives (II) or (III). J. L. D.

2 : 3-Dihydroxy*trans*-decahydronaphthalenes and the configuration of tetrahydronaphthalene. K. Ganapathi (Ber., 1939, **72**, [*B*], 1381—1386; cf. A., 1938, II, 286, 496).—2 : 3-Diketo*trans*-decahydronaphthalene is reduced by Na–Hg to 2 : 3-dihydroxy-*trans*-decahydronaphthalene (I), m.p. 141°, by Hg–Al in moist Et_2O to the isomeride (II), m.p. 128—129°, and by Al–Hg in EtOH to a mixture of (II) and the isomeride (III), m.p. 166°. Δ^2-Octahydronaphthalene is oxidised by neutral $KMnO_4$ to (I) with a little (II) and by BzO_2H to an oxido-compound which is hydrolysed to (III). It follows therefore that (III) is *trans*-2 : 3-dihydroxy*trans*-decahydronaphthalene whereas (I) and (II) are *cis*-derivatives. (I) and (III) are unaffected by dry $COMe_2$ containing conc. H_2SO_4 whereas (II) is quantitatively isomerised to (III). (I), (II), and (III) have the configuration (*A*), (*B*), and (*C*), respectively. Titration of (I)—(III) with $Pb(OAc)_4$ confirms the above views. The fact



that among the 2 : 3-dihydroxydecahydronaphthalenes the formation of :CMe_2 derivatives is possible only when the two rings are united in the *cis* position to one another gives a ready method of determining the nature of the union of two rings of unknown configuration. The planar configuration of tetrahydronaphthalene is excluded by the Raman spectrum. The three 2 : 3-dihydroxytetrahydronaphthalenes have m.p. 135° (IV), 120° (V), and 140° (VI). The mixture of glycols obtained from 2 : 3-dibromotetrahydronaphthalene is converted by $COMe_2$ and 1% HCl into (IV) and the :CMe_2 derivative (VII) of (V). It appears therefore that (IV) is the *trans*-isomeride produced by the isomerisation of (VI). The production of (VII) shows that in (V) the OH groups lie in the same plane as the C atoms to which they are



united. The tetrahydronaphthalene ring, at any rate as far as its 2 : 3-$(OH)_2$-derivative is concerned, has the spatial configuration (*D*) and not (*E*). The *disemicarbazone* of *trans*-cyclohexane-1 : 2-diacetaldehyde has m.p. 160—162°. H. W.

Influence of the structure of bromo-derivatives of alkyl- and alkoxy-benzenes on the synthesis of pinacols by the Grignard method. T. W. Jezierski (Rocz. Chem., 1939, **19**, 307—316).—The following 9 : 10-dihydroxy-9 : 10-diaryl-9 : 10-dihydrophenanthrenes were synthesised from phenanthraquinone and MgRBr, under identical conditions (yields given in parentheses): aryl = o-*tolyl*, m.p. 151·5—152° (51%), *m*-tolyl (45%), *p*-tolyl (57%), 3 : 4-*dimethylphenyl*, m.p. 194·5—195° (23%), o-*anisyl*, m.p. 179—180° (43%), m-*anisyl*, m.p. 185·5—186·5° (48%), *p*-anisyl (47%), o-*phenetyl*, m.p. 196—197° (52%), m-*phenetyl*, m.p. 159—160° (39%), and *p*-phenetyl (44%); Mg *m*-4- and *p*-xylyl bromides do not give the expected derivatives. The above products are oxidised (CrO_3) to 2 : 2′-diaroyldiphenyls, viz., *di*-o-*toluoyl*, m.p. 134·5—135·5° (79%), -*m*-toluoyl (71%), -*p*-toluoyl (72%), -3 : 4-*dimethylbenzoyl*, m.p. 126—127° (52%), -o-*anisoyl*, m.p. 136—137° (84%), -m-*anisoyl*, m.p. 87—88° (90%), -*p*-anisoyl (83%), -o-*ethoxybenzoyl*, m.p. 142·5—143·5° (70%), -m-*ethoxybenzoyl*, m.p. 91·5—92·5° (82%), and *p*-ethoxybenzoyl (75%). R. T.

Oxidation of adrenaline by succinic acid. Inhibition by cocaine and sparteine. T. Wense (Z. physiol. Chem., 1939, **260**, 100—104; cf. Marquardt, A., 1939, III, 581).—Tests with luminol and a trace of hæmin show that aq. succinic (I) and fumaric acid contain peroxide which is probably responsible for the inactivation of adrenaline by solutions of these acids. The degree of luminescence is not increased by exposing the solutions of the acids to sunlight. The action of (I) is not increased by ergotamine. The oxidation of adrenaline by the solutions is inhibited by cocaine and sparteine. Sparteine (but not cocaine) also inhibits the autoxidation of adrenaline and the inactivation of adrenaline by MeCHO. Cocaine diminishes but sparteine increases the luminescence produced with luminol. W. McC.

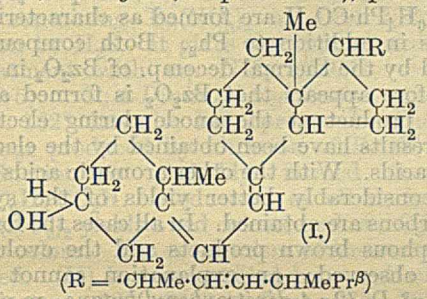
Biochemical reduction of a 1 : 2-benzanthracene derivative. A. Dansi and A. Vercellone (Ber., 1939, **72**, [*B*], 1457—1458).—1 : 2-Benzanthracene-10-aldehyde is reduced by fermenting yeast to 10-*hydroxymethyl*-1 : 2-*benzanthacene*, m.p. 173—174°. H. W.

[Sensitive test for ergosterol and differentiation of ergosterol and ergosteryl esters.] A. F. von Christiani and V. Anger (Ber., 1939, **72**, [*B*], 1482; cf. A., 1939, II, 316).—The indicated concn. of $Pb(OAc)_4$ is double that required. H. W.

Catalytic hydrogenation of cholesteryl acetate in acetic acid containing hydrochloric acid. T. Kawasaki (J. Pharm. Soc. Japan, 1939, **59**, 79—80).—Hydrogenation (Pt-black) of cholesteryl acetate in AcOH–38% HCl (34 : 1) gives, through the acetate, cholestanol, m.p. 140—141° when purified chromatographically (C_6H_6 solution; activated Al_2O_3); a small amount of cholestane is formed also (probably through cholesterylene). A. T. P.

Sitosterol complex. Isolation of α_3-sitosterol. S. Bernstein and E. S. Wallis (J. Amer. Chem. Soc., 1939, **61**, 1903—1904).—Wheat-germ oil yields α_1-, α_2-, and a little α_3- (I) -sitosterol (cf. Wallis *et al.*, A., 1937, II, 100). (I), $C_{29}H_{48}O$, m.p. 142—143°, $[\alpha]_D^{20}$ +5·2°, gives a benzoate, m.p. 173—175°, $[\alpha]_D^{20}$ +12·0°, 3 : 5-dinitrobenzoate, m.p. 210—211·5°, $[\alpha]_D^{20}$ +12·2°, and *acetate*, m.p. 152—153°, $[\alpha]_D^{20}$ +6·1° (all $[\alpha]$ in $CHCl_3$). R. S. C.

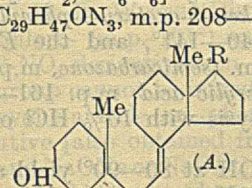
Dihydrotachysterol. F. von Werder (Z. physiol. Chem., 1939, **260**, 119—134; cf. Windaus *et al.*, A., 1933, 62).—The product (*A*) obtained by reduction (Na, EtOH) of tachysterol contains ~30% of the antirachitically inactive dihydrovitamin-D_2 (cf. Windaus *et al.*, A., 1932, 311), m.p. 65—66°, $[\alpha]_D^{19\cdot5}$ +10° (all rotations in $CHCl_3$) (benzoate, m.p. 70—71°, $[\alpha]_D^{22}$ +30°), separable as the allophanate, m.p. 184—186°, $[\alpha]_D^{19}$ +16°, and also obtained by similar reduction of vitamin-D_2. The fraction of (*A*) not, or only slightly, adsorbed on Brockmann's Al_2O_3 consists largely of *dihydrotachysterol* (I), m.p. 125—127°, $[\alpha]_D^{22}$ +97·5° (*propionate*, m.p. 97—98°, $[\alpha]_D^{22}$ +37°; n-*butyrate*, m.p. 62—63°), purified chro-



(R = ·CHMe·CH:CH·CHMePr$^\beta$)

matographically through the *acetate* (II), m.p. 108—110°, $[\alpha]_D^{23}$ +32·8°. (I) and its esters show characteristic absorption max. at 242, 251, and 261 mμ. (II) consumes 3 H_2 (Pt, 96% AcOH), does not react with $(CH\cdot CO)_2O$ in xylene at 135°, and is oxidised (CrO_3, aq. AcOH, room temp.) to the ketone, $C_{19}H_{32}O$, of Windaus *et al.* (A., 1936, 1247). The antirachitic activity of (I) is ~0·5% of that of vitamin-D_2; (I) possesses the highest calcification factor of any substance (derived from irradiated ergosterol) so far investigated. The limiting toxic dose (mouse) of (I) and (II) is 10 and 200 μg. respectively. H. B.

Constitution of dihydrovitamin-D_2 and -D_3. A. Windaus and C. Roosen-Runge (Z. physiol. Chem., 1939, **260**, 181—184).—Oxidation (O_3, AcOH) of the *allophanate*, m.p. 165°, $[\alpha]_D^{17}$ +61·3° in $CHCl_3$, of dihydrovitamin-D_3 (I) gives the same ketone, $C_{18}H_{32}O$, as is obtained from vitamin-D_3 (A., 1938, II, 58). Dihydrovitamin-D_2 (II) is oxidised [$Al(OBu^\beta)_3$, $COMe_2$, C_6H_6] to a ketone, the *semicarbazone*, $C_{29}H_{47}ON_3$, m.p. 208—210° (decomp.), of which shows the characteristic high absorption (max. at 270 mμ.) of an αβ-unsaturated ketone. (I) and (II) are, therefore, most probably (*A*) with R = ·CHMe·[CH_2]$_3$·Pr$^\beta$ and ·CHMe·CH:CH·CHMePr$^\beta$, respectively (cf. *loc. cit.*; von Reichel *et al.*, A., 1936, 603). H. B.



Sterols. XIV. Ketone cyanohydrins. S. Kuwada and M. Miyasaka (J. Pharm. Soc. Japan, 1938, **58**, 115—118; cf. A., 1937, II, 190).—Androsterone and *iso*androsterone afford *cyanohydrins*, decomp. 163° (*diacetate*, m.p. 183°) and 210° (*diacetate*, m.p. 144°), respectively. *trans*-Dehydroandrosterone cyanohydrin diacetate and MgMeI afford 17-methyl-$\Delta^{5:6}$-*trans*-androstene-3 : 17-diol, m.p. 197—199° (diacetate, m.p. 146°), identical with that from *trans*-dehydroandrosterone and MgMeI. *Cholestanone cyanohydrin*, decomp. 125—150°, and MgMeI give 3-*methyl*-, m.p. 147—148° [with a (?) stereoisomeride, m.p. 125°; both dehydrated (Ac_2O; $Bu^\beta CO_2H$; C_5H_5N–Ac_2O) to 3-methyl-$\Delta^{2 \text{ or } 3}$-cholestene], and 3-*acetyl-cholestan-3-ol*, m.p. 173° (purified through the *semicarbazone*, m.p. ~250°). A. T. P.

Œstradiol 3-CH_2Ph ether, m.p. 82—84°.—See B., 1939, 885.

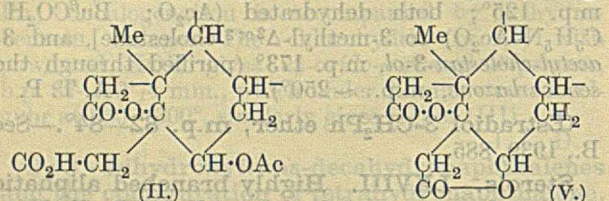
Sterols. LXVIII. Highly branched aliphatic esters of œstrone and α-œstradiol. R. E. Marker and E. Rohrmann (J. Amer. Chem. Soc., 1939, **61**, 1922—1923).—*Œstrone* 3-αα-*dimethylpropionate*, m.p. 164—166° [hydrogenated (PtO_2; EtOH–Et_2O) to α-*œstradiol* 3-αα-*dimethylpropionate*, m.p. 178—180°], and 3-ββ-*dimethyl*-n-*butyrate*, m.p. 148—150° (hydrogenated to α-*œstradiol* 3-ββ-*dimethyl*-n-*butyrate*, m.p. 127—129°), α-*œstradiol* 3 : 17-*bis*-αα-*dimethylpropionate*, m.p. 174—176°, and 3 : 17-*bis*-ββ-*dimethyl*-n-*butyrate*, m.p. 98—100°, are prepared. R. S. C.

Œstradiol 3-acylates.—See B., 1939, 885.

Sugar-cane wax. III. New constituents of unsaponifiable fraction. T. Mitui (J. Agric. Chem. Soc. Japan, 1939, **15**, 526—530; cf. A., 1938, II, 232).—The unsaponifiable fraction also contains α-*saccharostanediol* (I), $C_{29}H_{52}O_2$, m.p. 206° (*dibenzoate*, m.p. 160°; *di*-3 : 5-*dinitrobenzoate*, m.p. 171°), and β-*saccharostenone* (II), $C_{29}H_{48}O$, m.p. 106° (*oxime*, m.p. 163—165°; 2 : 4-*dinitrophenylhydrazone*, m.p. 206°; *tribromide*, m.p. 160·5°). (I) contains 2 OH whilst (II) contains 1 CO and 1 double linking. J. N. A.

Steroids and related compounds. IV. Stereochemical configuration of the cholestane-3 : 5 : 6-triols. B. Ellis and V. A. Petrow (J.C.S., 1939, 1078—1083; cf. A., 1939, II, 367).—The triol obtained from cholesterol by H_2O_2, now renamed cholestane-3 : 5 : 6-triol-*I*, is shown by the following and Criegee's evidence (A., 1933, 62) to be the 3(β) : 5(α) : 6(β)-triol. The isomeric cholestane-3 : 5 : 6-triol-*II* (new name) (obtained by $KMnO_4$ or OsO_4) is similarly shown to be the 3(β) : 5(β) : 6(β)-triol. The arguments are based on the rules of bromination and oxidative ring-fission for 3-keto-steroids being unaffected by the OH on $C_{(5)}$. 3 : 6-Diacetoxycholestan-5-ol with cold KOH–abs. EtOH gives 6-*acetoxycholestane*-3 : 5-*diol*, +H_2O, m.p. 132—133° or (anhyd.) 143—144°, $[\alpha]_D^{19}$ −26·4°, converted by BzCl–C_5H_5N into the known 3-benzoyloxy-6-acetoxycholestan-5-ol and by CrO_3 in AcOH at 100° (3 min.) into 6-*acetoxycholestan*-5-*ol*-3-*one* (I), m.p. 161—162°, $[\alpha]_D^{19}$ −10·2°, and the 6-*acetoxy-lactonic acid* (II), $C_{29}H_{46}O_6$, m.p. 217—218° (sinters at 185°), $[\alpha]_D^{20}$ −10·4°. $SOCl_2$–C_5H_5N, first at room temp.

and then boiling, or boiling Ac_2O dehydrates (I) to *6-acetoxy-*Δ^4*-cholesten-3-one* (III), m.p. 101·5°, $[\alpha]_D^{19}$ +36°, hydrolysed by 1% KOH–MeOH at room temp. to Δ^4*-cholesten-6-ol-3-one* (IV), m.p. 192° (known semicarbazone, m.p. 221°), which is oxidised by CrO_3 in C_6H_6–AcOH to the known Δ^4-cholestene-3 : 6-dione. HCl–EtOH converts (III) or (IV) into cholestane-3 : 6-dione, also obtained from (III) by 5% NaOMe–MeOH (excess). 0·5% KOH–EtOH converts (II) into the *dilactone* (V), $C_{27}H_{42}O_4$, m.p. 165° (sinters at 155°) (neutralises 2 KOH hot). With Br in AcOH at 35°, (I) gives *2-bromo-* (VI) (40%), m.p.



186°, $[\alpha]_D^{21}$ +3·6°, and a little 2 : 2-*dibromo-6-acetoxycholestan-5-ol-3-one*, m.p. 218° (decomp.), $[\alpha]_D^{19}$ +70·9° [obtained also by further bromination (presence of a trace of HBr) of (VI); with NaI in C_6H_6–EtOH liberates Br]. C_5H_5N is without effect on (VI), but 1·5% KOH–MeOH at 55—60° converts it into *cholestan-6-ol-3-one* 2 : 5-*oxide* (20—30%), m.p. 181—182° (stable to 10% HCl–EtOH; *acetate*, m.p. 84°, regenerates the oxide with 2·5% KOH–MeOH), which with CrO_3–AcOH gives *cholestane-3 : 6-dione* 2 : 5-*oxide*, m.p. 115—116° (*bis-2 : 4-dinitrophenylhydrazone*, m.p. 171°). Cholestane-3 : 5-diol-6-one belongs to the triol-*II* series, since CrO_3–AcOH oxidises it to coprostan-5(β)-ol-3 : 6-dione [= cholestan-5-ol-3 : 6-dione-*II*]. Partial CrO_3-oxidation of triol-*I* at room temp. gives a product, converted by boiling Ac_2O into 3-acetoxycholestan-5-ol-6-one (VII), m.p. 238°, $[\alpha]_D^{23}$ −56·2°. NaOMe–MeOH hydrolyses (VII) to cholestane-3 : 5-diol-6-one-*I* (VIII), and $SOCl_2$ in hot C_5H_5N dehydrates it to 3(β)-acetoxy-Δ^4-cholesten-6-one. Ac_2O–$KHSO_4$ at 100° or boiling Ac_2O converts (VII) into 3(β) : 5(α)-diacetoxycholestan-6-one, m.p. 169—170°, $[\alpha]_D^{22}$ −11°, hydrolysed to (VIII). M.p. are corr. $[\alpha]$ are in $CHCl_3$. R. S. C.

Chaulmoogryl chaulmoograte. T. Kariyone and T. Sugahara (J. Pharm. Soc. Japan, 1939, **59**, 18—20).—Reduction of chaulmoogra oil (I) by Na and EtOH gives a mixture separated by fractional distillation into hydnocarpyl alcohol, b.p. 136—142°/1 mm., m.p. 19°, $[\alpha]_D^{17}$ +56·27° (*phenylurethane*, m.p. 69°), and chaulmoogryl alcohol (II), b.p. 152—158°/1 mm., m.p. 23°, $[\alpha]_D^{17}$ +57·90°. When hydrogenated in presence of Ni, (I) affords *dihydrohydnocarpyl alcohol*, b.p. 155—165°/2 mm., m.p. 25° (*phenylurethane*, m.p. 72°), and dihydrochaulmoogryl alcohol, b.p. 155—160°/1·5 mm. Chaulmoogroyl chloride and (II) give *chaulmoogryl chaulmoograte*, m.p. 31°, $[\alpha]_D^{23}$ +55·40° in $CHCl_3$. H. W.

Derivatives of phenylacetonitrile. P. Jullien (Bull. Soc. chim., 1939, [v], 6, 1252—1254; cf. A., 1936, 1109).—$CH_2Ph{\cdot}CN$ and Et_2O–$NaNH_2$ followed by BuBr give a mixture of Bu_1 and Bu_2 derivatives, further treated similarly to give $CBu_2Ph{\cdot}CN$, b.p. 172—175°/25 mm., hydrolysed by KOH–EtOH at 100° (bath) to a little $CBu_2Ph{\cdot}CO{\cdot}NH_2$, m.p. 76°. Similarly prepared is $CPr^{\beta}_2Ph{\cdot}CN$ (I), b.p. 144—146°/25 mm., separated from $CHPr^{\beta}Ph{\cdot}CN$ (II) by treating with 85% H_2SO_4; (I) is unaltered and (II) gives the corresponding amide. $CH_2Ph{\cdot}CHPh{\cdot}CN$, m.p. 58°, and $(CH_2Ph)_2CPh{\cdot}CN$, m.p. 83°, are readily prepared. A. T. P.

Kolbe's electrosynthesis with aromatic acids; benzoic, phenylacetic, β-phenylpropionic, and phenoxyacetic acid. F. Fichter and H. Stenzl (Helv. Chim. Acta, 1939, **22**, 970—978).—Kolbe's electrosynthesis can be effected with various aromatic acids if C_5H_5N is used as solvent; the films which so frequently form on the anode during electrolysis of solutions in H_2O or MeOH are thereby dissolved. The difficulty of effecting Kolbe's electrosynthesis with aromatic acids depends on the sensitiveness of the aromatic nucleus towards anodic O. The use of C_5H_5N alone or in presence of MeOH prevents the evolution of O_2 at the anode. The new method has been applied successfully to $CH_2Ph{\cdot}CH_2{\cdot}CO_2H$, $CH_2Ph{\cdot}CO_2H$, $OPh{\cdot}CH_2{\cdot}CO_2H$, and with smaller yields to BzOH. With BzOH, 4-phenylpyridine and p-$C_6H_4Ph{\cdot}CO_2H$ are formed as characteristic by-products in addition to Ph_2. Both compounds are obtained by the thermal decomp. of Bz_2O_2 in C_5H_5N. It therefore appears that Bz_2O_2 is formed as intermediate product at the anode during electrolysis; similar results have been obtained by the electrolysis of fatty acids. With the other aromatic acids investigated, considerably better yields of the synthetic hydrocarbons are obtained. In all cases the formation of amorphous brown products and the evolution of CO are observed; an explanation cannot yet be given. *αδ-Di-(2 : 4-dinitrophenyl)butane*, m.p. 204—205°, is prepared. H. W.

Acetonephenylpyruvic [α-hydroxy-γ-keto-α-benzylvaleric] acid and its dehydration product. P. Cordier (Compt. rend., 1939, **209**, 49—51; cf. A., 1938, II, 60).—The acid is easily dehydrated in AcOH–HCl to (probably) *γ-keto-α-benzyl-*Δ^{α}*-pentenoic acid*, m.p. 94°, which when oxidised (NaOCl or NaOBr) gives benzyl-maleic (I) and -fumaric (II) acids (cf. A., 1928, 519). When excess of NaOHal is removed with $NaHSO_3$, more (II) is isolated, whereas As_2O_3 leads to (I). J. L. D.

Aldehydo-acids and aldo-enol-lactones. II. Synthesis of the γ-lactone of αγ-dihydroxy-β-phenyl-Δ^{β}**-butenoic acid (3-hydroxy-2-keto-4-phenyl-2 : 3-dihydrofuran). III. Certain specific properties of γ-aldo-enol-lactones and unsaturated aldehydo-acids.** M. M. Schemjakin (J. Gen. Chem. Russ., 1939, **9**, 484—490, 491—495).—II. $OH{\cdot}CH(OEt){\cdot}CO_2Et$ and $CH_2Ph{\cdot}CHO$ in Ac_2O (20 hr. at 140—145°) yield *2-keto-3-acetoxy-4-phenyl-2 : 3-dihydrofuran* (I), m.p. 140—141°, and the *Et* ester (II), b.p. 110—114°/3 mm. (*semicarbazone*, m.p. 167°), of *β-aldehydo-β-phenylacrylic acid*, m.p. 161—162° [also obtained by hydrolysis with 10% HCl of (I)].

III. (I) or (II) and 3% NaOH at 80—90° yield a *truxinic acid*, m.p. 195—196° (*Me* ester, m.p. 198—199°), differing from other known truxinic acids. R. T.

Naphthylacrylic acids and their derivatives. I. β-2-Naphthylcrotonic acids. A. Banchetti (Gazzetta, 1939, **69**, 398—405).—β-$C_{10}H_7$·COMe (I) and $CH_2Br·CO_2Et$ with Zn in boiling C_6H_6 give the *Et* ester (II), b.p. 210—215°/24 mm., of β-2-*naphthylcrotonic acid* (III), m.p. 169—170° (product, m.p. 140—150°, with Br_2), to which, with other substances, (II) is hydrolysed by KOH–EtOH. With conc. H_2SO_4, (II) gives (I), not an indone. Aq. $KMnO_4$–Na_2CO_3 oxidises (III) to (I). A solution of (III) in C_6H_6 exposed to ultra-violet light yields a *stereoisomeride*, m.p. 141—142°. Either this or (III) is reduced by Na–Hg in aq. NaOH to β-2-*naphthylbutyric acid*, m.p. 109—110°. E. W. W.

Chemistry and metabolism of phenylalanine. I. Nitration. R. J. Block and D. Bolling (J. Biol. Chem., 1939, **129**, 1—12).—The view that the violet colour formed in the colorimetric determination of phenylalanine (I) is due to a derivative of *diaci-o*-dinitrodihydrobenzene is confirmed by the prep. of diaci-3 : 4-*dinitro*-3 : 4-*dihydrophenylalanine* (II), m.p. 182—183° (decomp.), giving a negative ninhydrin reaction, by nitration of (I) with conc. H_2SO_4 containing $Ba(NO_3)_2$ at 100° followed by reduction by H_2S. It gives the typical violet colour on treatment with aq. NH_3, NaOH, or Na_2CO_3 (p_H ~9·5). 3 : 4-*Dinitrophenylalanine*, m.p. 155°, decomp. 182°, has also been prepared. The cherry-red colour produced by nitration of BzOH followed by reduction is probably formed from 2 : 5-$(NO_2)_2C_6H_3·CO_2H$. Reduction of all derivatives of p-$C_6H_4(NO_2)_2$ yields a red colour, and of o-$C_6H_4(NO_2)_2$ a violet colour. The mechanism of these reactions is discussed. (II) is accompanied by a red amorphous solid, decomp. 220—250° (softens ~65—70°), which may be 3 : 4-dinitro-3 : 4-dihydrobenzoic acid. P. G. M.

Azlactones. I. Preparation of α-benzamidocrotonic acid azlactone and the conversion of *allo*threonine into threonine. H. E. Carter, P. Handler, and D. B. Melville (J. Biol. Chem., 1939, **129**, 359—369).—*N*-Benzoyl-*dl*-threonine, *N*-benzoyl-*dl-allo*threonine, and their *O*-Me, O-*Ac*, m.p. 138—140° and 86—89°, respectively, and -Bz, new m.p. 158—159° and 179—180°, respectively, derivatives are converted into *α-benzamidocrotonic acid azlactone* (I), m.p. 95—96°, by the action of BzCl in C_5H_5N. NaOMe converts (I) into *N*-benzoyl-*O*-methylthreonine. The structure of (I) is confirmed by synthesis from hippuric acid and MeCHO, hydrolysis (N-HCl) to *α-benzamidocrotonic acid*, m.p. 193—195°, and $EtCO·CO_2H$, and reduction (H_2, PtO_2, AcOH) to $NHBz·CHEt·CO_2H$. E. M. W.

Derivatives of 4-chloro-3-nitrobenzonitrile. C. H. D. Witte (Diss., Leiden, 1939, 107 pp.).—*p*-Chloro- (m.p. 101°) and -bromo-benzonitrile give the 3-NO_2-derivatives on nitration and a second NO_2-group cannot be introduced directly. Nitration of *p*-cyano-anisole or -phenetole affords the 2-NO_2-derivative [also obtained from 3 : 4 : 1-$NO_2·C_6H_3Cl·CN$ (I) and NaOMe or NaOEt] and 2 : 6-*dinitro*-4-*cyano-anisole*, m.p. 114°, or -phenetole respectively. The appropriate amine and (I) give *N*-methyl- (*Ac* derivative, m.p. 92°), -ethyl- (*Ac* derivative m.p. 85°), -n-*propyl*-, m.p. 116° (*Ac* derivative, m.p. 102°), -n-*butyl*-, m.p. 69° (*Ac* derivative, m.p. 63°), -n-*amyl*-, m.p. 60°, -n-*heptadecyl*-, m.p. 82° (*Ac* derivative, m.p. 77°), and -β-*hydroxyethyl*- (II), m.p. 135° (N-*Ac* derivative, m.p. 130°), -2-*nitro*-4-*cyanoanilines*. N-n-*Heptadecyl*-2 : 4-*dinitroaniline*, m.p. 61° (*Ac* derivative, m.p. 70°), is obtained by interaction of $C_{17}H_{35}·NH_2$ and 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$. Nitration of (II) gives β-N-(2 : 6-*dinitro*-4-*cyanophenyl*)-N-*nitroaminoethyl nitrate*, m.p. 130°, also obtained by nitrating N-β-*hydroxyethyl*-2 : 6-*dinitro*-4-*cyanoaniline*, m.p. 116°, prepared from ethanolamine and (I). Nitration of NN′-*di*-(2-*nitro*-4-*cyanophenyl*)*ethylenediamine*, prepared from $(CH_2·NH_2)_2$ and (I), or NN′-*di*-(2 : 6-*dinitro*-4-*cyanophenyl*)*ethylenediamine*, m.p. 282°, obtained by replacement of OMe in corresponding anisole, gives NN′-*dinitro*-NN′-*di*-(2 : 6-*dinitro*-4-*cyanophenyl*)*ethylenediamine*, m.p. 204° (block), 212° (tube). (I) reacts with N_2H_4 and $NHMe·NH_2$ forming 2-nitro-4-cyanophenyl-hydrazine and -α-N-*methylhydrazine*, m.p. 130°, respectively. 2-*Nitro*-4-*cyanophenyl-hydrazones* and -*methylhydrazones* of the following are described, the respective m.p. being given in parentheses : $COMe_2$ (128°, 144°); COMeEt (139°, 124°); $COEt_2$ (129°, 125°); CH_2O (175°, 126°); MeCHO (179°, 110°); EtCHO (132°, 129°); Pr^nCHO (138°, 101°); PhCHO (225°, 183°); *o*- (255°, 218°), *m*- (272°, 209°), and *p*-$NO_2·C_6H_4·CHO$ (301°, 235°); *o*- (276°, 191°), *m*- (256°, 173°), and *p*-$C_6H_4Cl·CHO$ (253°, 193°); 3 : 4-CH_2O_2·$C_6H_3·CHO$ (279°, 176°); 4-hydroxy-3-methoxy- (304°, 225°), and -3-ethoxy-benzaldehyde (308°, 237°); furfuraldehyde (204°, 184°); 5-methyl- (199°, 169°) and 5-hydroxymethyl-furfuraldehyde (177°, —). (I) reacts with Na_2S_2 forming 2 : 2′-dinitro-4 : 4′-dicyanodiphenyl disulphide; the product obtained with Na_2S is indefinite. The taste of the various compounds is discussed. S. C.

Nitroamines. VIII. Nitroaminobenzoic acid. E. Macciotta (Gazzetta, 1939, **69**, 330—332).—*o*-$NH_2·C_6H_4·CO_2H$ with HNO_3 (*d* 1·52) in AcOH gives *o-nitroaminobenzoic acid* (deflagrates when heated) (*Na* and *Ag* salts), which in conc. H_2SO_4 rearranges to 3 : 2 : 1-$NO_2·C_6H_3(NH_2)·CO_2H$. *m*-$NH_2·C_6H_4·CO_2H$ similarly with HNO_3, followed by $Hg(OAc)_2$ gives Hg bis-*m*-nitroaminobenzoate. E. W. W.

Chloral-chlorosalicylamides and their methyl ethers. N. W. Hirwe and K. N. Rana (Ber., 1939, **72**, [*B*], 1346—1353; cf. A., 1939, II, 264).—In hydroxybenzamides the condensation with chloral is restricted partly by OH in the *ortho*- and completely by OH in the *meta*- or *para*-position. The condensation of methoxybenzamides is facilitated by OMe in the *ortho*-, *meta*-, or *para*-position. A negative group in position 3 (*o* to OH) in *o*-$OH·C_6H_4·CO_2H$ favours condensation, which is restricted by a similar group at $C_{(5)}$ (*p* to OH). The following are obtained by heating a mixture of amide and chloral under an air condenser until a clear solution is obtained : *chloral*-3-*chloro*- (I) [3-*chloro*-2-*hydroxybenz*-βββ-*trichloro*-α-*hydroxyethylamide*], m.p. 159—160°, -5-*chloro*- (II), m.p. 148—149° (decomp.), and -3 : 5-*dichloro*-, (III), m.p. 158—159° (decomp.), -*salicylamide*; *chloral*-3-

chloro-, m.p. 115—116°, *-5-chloro-* (IV), m.p. 157—158° (decomp.), and *-3 : 5-dichloro-*, m.p. 143—144°, *-2-methoxybenzamide*. Chlorination of chloralsalicylamide with Cl_2 (1 mol.) in AcOH at >20° gives mainly (I) with some (II) and 5-chlorosalicylamide, m.p. 226—227°; if two mols. of Cl_2 are used (III) is obtained. Similarly chloral-2-methoxybenzamide and Cl_2 (1 mol.) afford (IV), also obtained exclusively when more than 1 mol. of halogen is used. H. W.

Synthesis of homo*iso*vanillic acid. H. W. Bersch (Arch. Pharm., 1939, **277**, 271—286; cf. A., 1922, i, 569; Schöpf *et al.*, A., 1932, 1040).—O-*Carbethoxyisovanillin*, m.p. 58—59° [from *iso*vanillin (I), $ClCO_2Et$, and dil. NaOH], with $NaHSO_3$ followed by NaCN yields the *cyanohydrin*, m.p. 98° (sinters at 90°), which with MeOH–HCl and then H_2O gives Me 3-carbethoxyoxy-4-methoxymandelate. Successive chlorination ($SOCl_2$), reduction (H_2, PtO_2, C_5H_5N), and hydrolysis of this yields homo*iso*vanillic acid, new m.p. 127—129° [30—40% yield from (I)]. Several other methods were tried. Vanillin and BzCl in Et_2O with aq. KCN yields O-*benzoylvanillin cyanohydrin benzoate*, m.p. 146·5—147·5, reduced (Pd in tetrahydronaphthalene) to 4-*benzoyloxy*-3-*methoxyphenylacetonitrile*, m.p. 110°; O-*benzoyl*isovanillin *cyanohydrin benzoate* (oil) is similarly prepared (poor yield). (I) with $MeNO_2$ yields *ω-nitro*-3-*hydroxy*-4-*methoxystyrene*, m.p. 155—156° (sinters at 150°), reduced (H_2, Pd–C, C_5H_5N) to 3-*hydroxy*-4-*methoxyphenylacetaldoxime*, m.p. 146—147°. Acetylation (Ac_2O–conc. H_2SO_4) of (I) yields a mixture of the mono-, m.p. 86°, and *tri-acetate*, m.p. 117—118°. 3-*Benzyloxy*-4-*methoxybenzyl alcohol*, m.p. 70—71° (from *iso*vanillyl alcohol, CH_2PhCl, and MeOH–NaOMe), with $SOCl_2$ yields the *chloride*, m.p. 70—75°, which does not react normally with KCN. 3-*Nitro*-4-*methoxyphenyl-acetonitrile*, m.p. 86—87° (from the chloride and NaCN), is hydrolysed to the *-acetic acid*, m.p. 133—134° (sinters at 129°); reduction (H_2, Pd–C, EtOAc) of the nitrile and of the *Me*, m.p. 102°, and *Et*, m.p. 58—59°, esters of the acid yields respectively 3-*amino*-4-*methoxyphenylacetonitrile*, m.p. 40° (*hydrochloride*, m.p. 202°), and *Me*, b.p. 147—148°/1 mm. (*hydrochloride*, m.p. 190—191°), and *Et* 3-*amino*-4-*methoxyphenylacetate*, b.p. 150—152°/1 mm. [*hydrochloride*, m.p. 166—167° (turning brown)], none of which can be satisfactorily diazotised. α-Diethylamino-α-3 : 4-methylenedioxy- (cf. Knoevenagel, A., 1904, i, 982) and *-3-hydroxy*-4-*methoxyphenylacetonitrile* (similarly prepared), m.p. 83° (sinters at 78°), do not react with EtBr or MeI. A. Li.

Condensation of 4-nitro-*o*-tolunitrile with aromatic aldehydes. C. Candea and E. Macovski (Bull. Soc. chim., 1939, [v], **6**, 1182—1187; cf. A., 1938, II, 491).—4 : 1 : 2-NO_2·C_6H_3Me·CN (I) (unaffected by NaOMe–MeOH) and PhCHO or *o*-NO_2·C_6H_4·CHO in NaOMe–MeOH afford 4-*nitro-* (II), m.p. 263° (partial decomp.), or 4 : 2′-*dinitro*-2-*carbamylstilbene*, m.p. 228°. (I) and PhCHO with piperidine at 130—140° give 4-nitro-2-cyanostilbene, new m.p. 145° (unaffected by NaOMe). The latter and H_2O_2–MeOH, followed by aq. KOH to the boiling solution, give (II); (I) similarly affords 4 : 1 : 2-NO_2·C_6H_3Me·CO·NH_2, new m.p. 175°. The mechanism of reaction is discussed. A. T. P.

Hydrindene derivatives. II. Simple substitution products. J. Lindner, F. Schmitt, and B. Zaunbauer (Monatsh., 1939, **72**, 216—222).—Directions are given for the conversion of 4 and 5-aminohydrindene into the corresponding hydroxy-, acetoxy-, methoxy-, and cyano-hydrindenes; the acids and their amides are described. 5-*Acetoxyhydrindene*, m.p. 17—18°, and *hydrindene-4-carboxylic acid*, m.p. 155° (*amide*, m.p. 171·5°), appear new. H. W.

Synthesis of sphaerophorin. A. Hashimoto [with S. Koyama] (J. Pharm. Soc. Japan, 1938, **58**, 221—223).—Sphaerophorol, HCl, HCN, and $AlCl_3$ give *sphaerophorolaldehyde* (I), 3 : 5 : 1 : 2-$(OH)_2C_6H_2(C_7H_{15})$·CHO, m.p. 83° (p-*nitrophenylhydrazone*, m.p. 204°); its *OO*-$(CO_2Et)_2$-derivative by $KMnO_4$-oxidation and hydrolysis affords *sphaerophorolcarboxylic acid*, m.p. 140°. 5 : 1 : 3 : 2-OMe·C_6H_2Me(O·CO_2Et)·COCl and (I) in C_5H_5N give the *aldehyde* (p-*nitrophenylhydrazone*, decomp. 182°) corresponding with sphaerophorin (II); treatment with $ClCO_2Et$–C_5H_5N, oxidation by $KMnO_4$–$MgSO_4$–$COMe_2$, and hydrolysis by 4% NaOH–EtOH then gives (II), m.p. 137° (cf. A., 1934, 525). 3 : 1 : 5 : 2-OMe·C_6H_2Me(O·CO_2Et)·COCl and (I) afford similarly iso*sphaerophorin* (III), 5 : 1 : 3 : 2-OH·C_6H_2Me(OMe)·CO·O·C_6H_2(OH)(C_7H_{15})·CO_2H-1 : 3 : 5 : 4, m.p. 137° (CH_2N_2 gives trimethylsphaerophorin). R. S. C.

Orsellinic esters. F. Fuzikawa and H. Sengoku (J. Pharm. Soc. Japan, 1939, **59**, 91—92).—By heating lecanoric or gyrophoric acid with the requisite alcohol, *Pr*^{α}, m.p. 125—126°, *Pr*^{β}, m.p. 115°, *Bu*^{α}, m.p. 95°, *Bu*^{β}, m.p. 139°, iso*amyl*, m.p. 88°, *CH*$_2$*Ph*, m.p. 137—138°, and ·*CH*$_2$·*CH*$_2$*Ph*, m.p. 102—103°, *orsellinates* are obtained. H. W.

Lichen substances. XCIII. Thamnolic acid. Y. Asahina and M. Hiraiwa (Ber., 1939, **72**, [*B*], 1402—1404).—Thamnolic acid (I) loses CO_2 when warmed with an excess of NH_2Ph in EtOH–glycerol at 60° giving *decarboxythamnolanil*, m.p. 216° (decomp.), hydrolysed by 10% HCl in $COMe_2$ to decarboxythamnolic acid, new m.p. 225°, which is thus very readily obtained. The reaction is adapted to the microchemical detection of (I). *Hæmatommanil*, m.p. 206°, is considerably more stable in presence of an excess of NH_2Ph but is partly decomposed in boiling EtOH. (I) can also be detected by means of its Ba salt. Very probably (I) is identical with hirtellic acid. H. W.

Synthesis of 6-methoxydiphenyl ether-3 : 4′-diacetic acid. M. Tomita, M. Satomi, and T. Ikeda (J. Pharm. Soc. Japan, 1938, **58**, 127—130; cf. Kondo *et al.*, *ibid.*, 1933, **53**, 92; A., 1932, 1048).—6-Methoxydiphenyl ether-3 : 4′-dicarboxyl chloride and CH_2N_2–Et_2O afford the 3 : 4′-di(diazoketone) (I), m.p. 135°, converted by Ag_2O–H_2O–dioxan at 60° into 6-*methoxydiphenyl ether*-3 : 4′-*diacetic acid* (II), m.p. 173° [*diamide*, m.p. 194°, obtained from (I) and aq. NH_3–$AgNO_3$–dioxan at 60—65°, is hydrolysed

(EtOH–KOH) to (II)]. (I) and Ag_2O–EtOH at 60° give the Et_2 ester of (II). A. T. P.

Synthesis of methyl 3-bromohydrastate. S. Uyeo and M. Katayanagi (J. Pharm. Soc. Japan, 1939, **59**, 94—96).—7-Nitro-5 : 6-methylenedioxyhydrind-1-one is oxidised by 10% HNO_3 at 100° to 3-*nitrohydrastic* [3-*nitro*-4 : 5-*methylenedioxyphthalic*] *acid*, m.p. 236—237°, the Me_2 ester, m.p. 157—158°, of which is reduced (H_2, PtO_2, EtOAc) to Me_2 3-*aminohydrastate*, m.p. 92—93°; this is transformed (Sandmeyer) into Me_2 3-*bromohydrastate*, m.p. 150—151°, which readily forms Me_2 hydrastate when heated with Cu-bronze. H. W.

Chemiluminescence of hydrazides of carboxylic acids. E. S. Wasserman and G. P. Mikluchin (J. Gen. Chem. Russ., 1939, **9**, 606—619).—Hydrazides of the types R·CO·NH·NH_2 (R = Ph, *m*-NO_2·C_6H_4, CHPh:CH), (·CO·NH·NH_2)$_2$, and R(CO·NH·NH_2)$_2$ [where R = CH_2, ·CH(OH)·CH_2·, ·CH(OH)·CH(OH)·, ·CH(NH_2·CH_2)·], and [·CH(CO·NH·NH_2)$_2$]$_2$ do not exhibit chemiluminescence [hæmatin or $K_3Fe(CN)_6$ as activator], except when the radical R contains an NH_2-group. In the series (R·CO·NH·)$_2$ luminescence exists when R = CCl_3, *p*-NO_2·C_6H_4, or *o*-NH_2·C_6H_4, but not when R = H or Ph. Chemiluminescence is exhibited by (·CO·NH·)$_2$ and other cyclic hydrazides of the types R(·CO·NH·)$_2$, viz., malon-, naphthalic, 4-*nitronaphthalic*, m.p. >320°, *diphenic*, m.p. >310°, *o-carboxyphenylglycine*, m.p. >320°, 1-*amino*-2 : 5-*diphenylpyrrole*-3 : 4-*dicarboxylic*, m.p. >320°, 4-hydroxy- and 3-nitro-phthal-, 4-sulphophthal- (N_2H_4 salt, m.p. >310°), 3-nitro-*N*-phenylphthal-, and *N*-carbethoxymethylphthal-hydrazides.

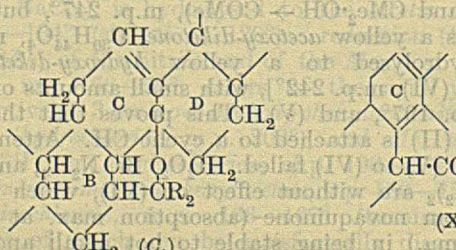
o-C_6H_4<CO·NH / NH·CO>, NH<CO·NH / CO·NH>, and *o*-C_6H_4<NH·CO / NH·CO> do not exhibit chemiluminescence. R. T.

Bile acid, $C_{27(28)}H_{46(48)}O_6$, m.p. 252—255°, $[\alpha]_D^{23}$ —30·58° in EtOH (Me ester, m.p. 94—96°), from shark bile, and keto-acid, m.p. 175°.—See A., 1939, III, 693.

Isomerides of 3 : 5 : 6-trihydroxycholanic acid. J. Hattori (J. Pharm. Soc. Japan, 1939, **59**, 12—16).—Treatment of Me Δ^3-3-hydroxycholenate (I), m.p. 145—146°, with 40% H_2O_2 in AcOH and subsequent acetylation yields *Me* α-5-*hydroxy*-3 : 6-*diacetoxycholanate* (II), m.p. 150—151°, $[\alpha]_D^{30}$ —42·4° in $CHCl_3$ {hydrolysed by alkali to α-3 : 5 : 6-*trihydroxycholanic acid*, m.p. 258—259° (decomp.), $[\alpha]_D^{28}$ —4·37° in EtOH [*Me* ester (III), m.p. 213—214°]}, and *Me* 3 : 5 : 6-*triacetoxycholanate* (IV), m.p. 193—193·5°, $[\alpha]_D^{30}$ —36·9° in $CHCl_3$, hydrolysed by alkali to 3 : 6-*dihydroxy*-5-*acetoxycholanic acid*, m.p. 239—240° (decomp.). This is transformed by Ag_2O and MeI into *Me* 3 : 6-*dihydroxy*-5-*acetoxycholanate*, m.p. 163·5—164·5°, and by MeOH–H_2SO_4 into *Me* β-3 : 5 : 6-*trihydroxycholanate*, m.p. 210—212°, which is acetylated to *Me* 5-*hydroxy*-3 : 6-*diacetoxycholanate*, m.p. 141—142·5°, $[\alpha]_D^{33}$ —46·9° in $CHCl_3$, hydrolysed by alkali to β-3 : 5 : 6-*trihydroxycholanic acid*, m.p. 236·5—237·5° (decomp.), $[\alpha]_D^{29}$ —3·92° in EtOH. (II) is converted by dry HCl in Ac_2O into (IV). The production of these isomerides depends on the configuration of the two OH at $C_{(5)}$ and $C_{(6)}$. Excess of BzO_2H in $CHCl_3$ converts (I) into *Me* α-3-*hydroxy*-5 : 6-*oxidocholanate* (V), m.p. 142·5—143·5°, $[\alpha]_D^{28}$ —52·5° in $CHCl_3$, which does not give a yellow colour with $C(NO_2)_4$ in $CHCl_3$ but gives a ppt. with digitonin in EtOH; it is acetylated to *Me* α-3-*acetoxy*-5 : 6-*oxidocholanate* (VI), m.p. 130—131°, $[\alpha]_D^{28}$ —47·4° in $CHCl_3$, and hydrolysed to α-3-*hydroxy*-5 : 6-*oxidocholanic acid*, m.p. 210—211° (decomp.). Fission of the oxide ring of (V) by AcOH leads to (II) whereas heating with H_2O or with 50% EtOH yields (III); with HCl–MeOH it affords Me 5-chloro-3 : 6-dihydroxycholanate, m.p. 220° (decomp.), which is also obtained similarly from (II). *Me* 5-*chloro*-6-*hydroxy*-3-*acetoxy*- (VII), m.p. 189—189·5°, and -3-*benzoyloxy*-, m.p. 186—188°, -*cholanate* are described. Scission of (V) with MeOH and conc. H_2SO_4 yields *Me* γ-3 : 5 : 6-*trihydroxycholanate*, m.p. 223—224° [*acid*, m.p. 211—212·5° (decomp.), $[\alpha]_D^{30}$ —12·8° in EtOH; 3-*acetate*, m.p. 134—135·5°, $[\alpha]_D^{18}$ —40·5° in $CHCl_3$]. C_5H_5N and $AgNO_3$ transform (VII) into (VI), which is transformed by AcOH into (II). H. W.

Quinovic acid. VI. H. Wieland, W. Schmitt, and A. Hrubesch [and, in part, K. Kraus]. **VII.** H. Wieland and H. Schlenk (Annalen, 1939, **539**, 219—241, 242—261; cf. A., 1936, 849).—VI. Evidence is presented that quinovic acid (I) is a derivative of (*A*). Pyroquinovic acid (II), $[\alpha]_D^{20}$ —61·3° in $CHCl_3$, is obtained from (I) in 70—80% yield at 280—300°/vac. Me pyroquinovate and MgMeI give a *dimethylcarbinol* (III), $C_{31}H_{52}O_2$, m.p. 187—188°, the 3-*acetate* (IV), m.p. 213°, of which with CrO_3–AcOH at 40° yields mainly a colourless *acetoxy-diketone* (V), $C_{32}H_{48}O_4$ (C:C·CH_2 → C:C·CO, and CMe_2·OH → COMe), m.p. 247°, but at 85° yields a yellow *acetoxy-diketone*, $C_{30}H_{44}O_4$, m.p. 267° [hydrolysed to a yellow *hydroxy-diketone*, $C_{28}H_{42}O_3$ (VI), m.p. 242°], with small amounts of an acid, m.p. 197°, and (V). This proves that the *b*-CO_2H of (II) is attached to a cyclic CH. Attempts to oxidise (V) to (VI) failed. H_2O_2, Br, N_2H_4, and *o*-$C_6H_4(NH_2)_2$ are without effect on (VI), which also differs from novaquinone (absorption max. at 405 and 455 mμ.) in being stable to hot alkali and in having an absorption max. at 270 mμ. These facts prove the presence of CO·C:C·CO in (VI). The yellow acid, $C_{29}H_{40}O_5$ [obtained from (II) by CrO_3 (*loc. cit.*) and from acetylpyroquinovic acid by oxidation, followed by hydrolysis and further oxidation], also has CO·C:C·CO, has an absorption max. at 268 mμ., and is probably (VII) (R = CO_2H). *Acetylpyroquinovoyl chloride* (prep. by $SOCl_2$ at room temp.), m.p. 170° (decomp.) [with NaOH in dioxan gives the acetoxy-acid, but with boiling N-MeOH–KOH (1—2 min.) gives the hydroxy-ester], with ZnPhCl in PhMe gives the *acetoxy-ketone*, m.p. 161°, hydrolysed (KOH–Pr^{α}OH) to the *hydroxy-ketone* (VIII), $C_{35}H_{50}O_2$,

m.p. 235°, and oxidised by CrO_3–AcOH at 85° to the yellow *acetoxy-triketone* [(VII) R = COPh], $C_{37}H_{48}O_5$, m.p. 213° (does not undergo the benzilic acid rearrangement with 10% KOH–EtOH). Anhydropyroquinovic acid (Me ester, $[\alpha]_D^{20}$ −30·5° in $CHCl_3$) and $KMnO_4$ in aq. $COMe_2$ give the yellow acid, $C_{29}H_{40}O_4$, m.p. 286° (decomp.) (A., 1931, 1158, m.p. 283°) [Me ester, m.p. 235—238° (*loc. cit.*, 245°)], which has CO·C:C·CO as in (VII) and an additional ethylenic linking in ring A due to dehydration of the CH_2·CH·OH. Zn dust reduces the Ac derivative of (VI) to a H_2-derivative, m.p. ~230° (CO·C:C·CO → CO·CH·CH·CO), readily reconverted into (VI) by air. This and the other reactions indicate that (VI) contains the grouping (*B*). The yellow acetoxy-, $C_{31}H_{44}O_6$, and hydroxy-acid, $C_{29}H_{42}O_5$, obtained by oxidising acetylpyroquinovic acid, are also reduced by Zn dust in AcOH to H_2-derivatives, m.p. 290—291° and 283—284°, respectively, which rapidly regenerate the yellow acids in alkali in air. Boiling Ac_2O converts (IV) into a *substance* (IX), $C_{33}H_{52}O_2$, m.p. 191° (absorption max. at <230 mμ.), which with O_3 in EtCl at 0° gives CH_2O; dehydration thus gives a CMe:CH_2 in (IX). BzO_2H converts (IX) into a *diepoxy*-derivative, m.p. 229°, and 7% KOH–MeOH gives the diunsaturated *alcohol*, $C_{31}H_{50}O$, m.p. 148—150°, b.p. 230° (bath)/high vac. When heated at 150°, (III) or the similar carbinol obtained from Me anhydroquinovate gives a triunsaturated *hydrocarbon*, $C_{31}H_{48}$, m.p. 156—157°. CrO_3 in AcOH–CO_2 oxidises (III) to a *triketone* (6%), $C_{28}H_{40}O_3$, m.p. 197·5°, which contains the features (*B*). LiPh and (VIII) give an oily diphenylcarbinol (with CrO_3 gives 30% of $COPh_2$),

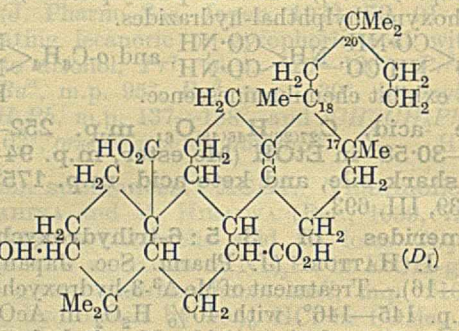


(*C*.)

(X.)

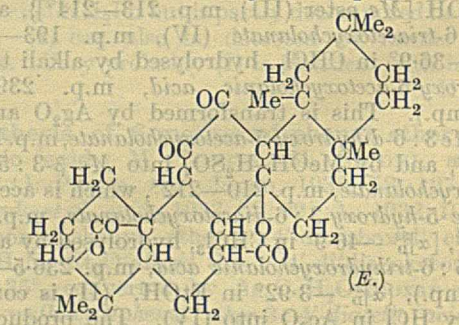
the acetate of which with Br–NaOAc in MeOH gives the *lactone* (*C*) (R = Ph), $C_{43}H_{54}O_2$, m.p. 235°; similarly, (IV) gives the *substance* (*C*) (R = Me), $C_{33}H_{52}O_3$, m.p. 164° (absorption max. at 230—236 mμ.). Me pyroquinovate and BzO_2H in $CHCl_3$ at 0° give the 13 : 14-*oxide*, $C_{30}H_{48}O_4$, m.p. 228° (*acetate*, m.p. 185—186°), converted by HCl–AcOH at 90°, followed by Ac_2O–C_5H_5N, into *Me pyroquinovadienate acetate*, m.p. 179°, which is hydrolysed by KOH–MeOH to pyroquinovadienic acid (X), $C_{29}H_{44}O_3$, $[\alpha]_D^{20}$ −41·6° in $CHCl_3$ (*Me* ester, m.p. 131·5°). Anhydropyroquinovic acid absorbs 2 O from BzO_2H, giving a *dioxidolactone*, $C_{29}H_{44}O_4$, m.p. 259°; the Me ester gives a *di*-, $C_{30}H_{46}O_4$, m.p. 286°, and *mono-oxido-ester* (XI), $C_{30}H_{46}O_3$, m.p. 189·5°. Fission of the lactone, $C_{29}H_{44}O_4$, by KOH in 50% MeOH, followed by esterification (CH_2N_2), gives a (?) *stereoisomeride* of (XI).

VII. Prep. of (X) (absorption max. at 247 mμ.; cf. quinochromin, 252 mμ.) from (I) by way of (II) is modified to give a 40% over-all yield. (X) and its Ac derivative absorb only 1 O from BzO_2H. With Br (1 mol.) and NaOAc in AcOH at −10°, (X) gives *pyroquinovatrienic acid* (XII), $C_{29}H_{42}O_3$, m.p. 244—245°, $[\alpha]_D^{20}$ −4·6° or −5·2° in $CHCl_3$ [*Me* ester, m.p. 197° (*acetate*, m.p. 144°)], and, sometimes, a (?) *acetoxy-lactone*, $C_{31}H_{44}O_5$, m.p. 325° (decomp.). The absorption max. at 269 mμ. shows (XII) to contain an aromatic ring (*C* or, less probably, *D*), and this is supported by oxidation by boiling, conc. HNO_3 to 1 : 2 : 3 : 4-$C_6H_2(CO_2H)_4$ and indifference to Br and H_2–catalyst. CrO_3 in cold AcOH converts (XII) into the corresponding *keto-acid*, $C_{29}H_{40}O_3$, m.p. 248°, $[\alpha]_D^{20}$ +18·8° in $CHCl_3$ (*Me* ester, m.p. 178°), or at 65° into an *acid*, $C_{27}H_{36}O_7$, m.p. 190—194° (decomp.). Tribenzoylquinovic acid (XIII) and $SOCl_2$, first at <0°, then at room temp., and finally at 100°, give *benzoylquinovoyl dichloride*, decomp. 200—204° [with hot MeOH gives Me_2 benzoylquinovate, m.p. 226° (lit. 235—236°)], which at ~210° and later 240—250° yields CO (80%), CO_2 (8%), and isomeric benzoyloxy-*compounds*, $C_{35}H_{46}O_2$, m.p. 269—271° (33%), $[\alpha]_D^{18}$ +41·6° to +45·3° in $CHCl_3$, and m.p. 191—193° (15%), $[\alpha]_D^{24}$ +65·7° in $CHCl_3$, hydrolysed to the *alcohols*, $C_{28}H_{42}O_2$, m.p. 261° and 192°, respectively; these give colours with $C(NO_2)_4$ and are shown by absorption max. at ~267 mμ. to contain an aromatic ring (formed under the isomerising influence of the HCl evolved). (I) is probably (*D*) and novaquinone



(*D*.)

(*E*), but, as these structures are not built up of isoprene residues, the Me at $C_{(17)}$, $C_{(18)}$, and $C_{(20)}$ may be replaced by Pr^β at $C_{(17)}$. However, the change of [α] from +116·5° in $CHCl_3$ for Me_2 quinovate to



(*E*.)

−61·1° in $CHCl_3$ for Me pyroquinovate and the difference in reactivity of the acids and esters towards

Br, $C(NO_2)_4$, etc. suggest that the ethylenic linkings may be in different places for the quinovic and pyroquinovic series. In Et_2O, (XIII) and $SOCl_2$ at 0° give *benzoylquinovoyl monochloride*, m.p. 197—198°, which with MeOH gives ? *Me*$_1$ *benzoylquinovate*, m.p. 211—212° (decomp.) [at 250°/vac. gives CO, a little CO_2, and a (?) quinovatrienol]. When melted, (I) gives + a trace of CO. Cl_2 and (I) in AcOH at room temp. give *trichloroquinovalactone* (XIV), $C_{30}H_{41}O_5Cl_3$, m.p. 287° (decomp.), $[\alpha]_D^{19}$ +23·1° in $CHCl_3$ [CH_2N_2 gives a *Me* ester, m.p. 302° (decomp.)], and a *Cl*$_3$*-acid*, $C_{30}H_{41}O_5Cl_3$, decomp. 324° (*Me*$_2$ ester, m.p. 206°); thus, (XIV) absorbs first 2 Cl, loses 1 HCl to form a monolactone, and has its CH·OH oxidised to CO, which then gives CCl_2. With boiling 8% KOH–MeOH (XIV) gives KCl and <50% of a *substance*, $C_{30}H_{42}O_7$, m.p. 275°, in which 2 Cl are replaced by OH and one is lost as HCl giving an ethylenic linking. With boiling C_5H_5N, (XIV) loses 1 Cl as HCl, giving a *substance*, $C_{30}H_{40}O_5Cl_2$, m.p. 282—285°. $AgNO_3$ in C_5H_5N at room temp. replaces 1 Cl by OH, and so gives a *substance*, $C_{30}H_{42}O_6Cl_2$, m.p. 285°. Zn dust in AcOH gives very slowly a poor yield of a *substance*, m.p. 253—255° (decomp.). Me quinovate, the OH-acid, $C_{29}H_{42}O_5$, and its ester absorb no O from BzO_2H, but quinochromin absorbs 1 O. Anhydroquinovic and novic acid have $[\alpha]_D^{20}$ +294° in $CHCl_3$–EtOH (1 : 2) and $[\alpha]_D^{18}$ +123° in $CHCl_3$, respectively. R. S. C.

Preparation of multiply unsaturated nitriles and aldehydes. II. G. Wittig and H. Hartmann (Ber., 1939, **72**, [*B*], 1387—1398).—Reaction does not occur between PhCHO and $CMe_2{:}C(CN)\cdot CO_2Me$ (I) at ~120° alone or in the presence of NH_2Ac or NEt_2Ac; NH_4OAc causes hydrolysis of (I) to $COMe_2$ and $CN\cdot CH_2\cdot CO_2Me$, which with PhCHO yields $CHPh{:}C(CN)\cdot CO_2Me$, m.p. 88—89°. In presence of piperidine and its acetate at 45°, PhCHO and (I) yield *Me α-cyano-δ-phenyl-β-methyl-*$\Delta^{\alpha\gamma}$*-pentadienate*, m.p. 111·5°, in 85% yield. $CHPh{:}CH\cdot CHO$, NH_4OAc, and (I) afford Me α-cyano-δ-phenyl-$\Delta^{\alpha\gamma}$-pentadienate, m.p. 143·5—144·5°. $CHPh{:}CH\cdot CHO$ and Me α-cyanosorbate in presence of piperidine and AcOH give *Me α-cyano-θ-phenyl-*$\Delta^{\alpha\gamma\epsilon\eta}$*-nonatetraenoate*, m.p. 168—169°, in 25% yield. This is hydrolysed by $Ba(OH)_2$–MeOH to the *acid*, m.p. 219—221°, which is decarboxylated by Cu powder at 180—200° to a mixture of stereoisomeric θ-phenyl-$\Delta^{\alpha\gamma\epsilon\eta}$-nonatetraenonitriles, of which a *form*, m.p. 146—149°, is obtained pure. Prolonged boiling of a mixture of β-ionone and $CN\cdot CH_2\cdot CO_2Me$ in AcOH containing NH_2Ac and NH_4OAc leads to *Me cyano-β-ionylideneacetate*, b.p. 171—172°/0·38 mm.; the non-cryst. acid is decarboxylated at 150° to *β-ionylideneacetonitrile*, b.p. 117—122°/1 mm., hydrolysed to β-ionylideneacetic acid, m.p. 125°. The reducibility of unsaturated nitriles $R\cdot[CH{:}CH]_n\cdot CN$ (*A*) decreases rapidly with increase of *n* when $SnCl_2$ and HCl in Et_2O are used. $CrCl_2$ in Et_2O–HCl or dioxan–HCl at 80°, $CrBr_2$ in Et_2O–HBr, VCl_2 or $TiCl_3$ in HCl–Et_2O are ineffective but much better results are obtained with $SnBr_2$ in HBr–Et_2O or HBr–dioxan at 55—60°, the yield of aldehyde from (*A*) being 73, 65, and 50% when $n = 0$, 1, and 2, respectively. A suitable apparatus is described. The method is not effective with $Ph\cdot[CH{:}CH]_3\cdot CN$. H. W.

Preparation of *m*-dialkylaminobenzaldehydes. W. Cocker and J. O. Harris (J.C.S., 1939, 1092—1094).—*m*-$NH_2\cdot C_6H_4\cdot CH(OMe)_2$ (I) in Et_2O with 1·5N-Na_2CO_3 and Et_2SO_4 at room temp. (7 days) gives m-*diethylaminobenzaldehyde*, b.p. 137—138°/6—7 mm. (*semicarbazone*, m.p. 165°; *azine*, m.p. 114—115°; 2 : 4-*dinitrophenylhydrazone*, m.p. 197—198°; *picrate*, m.p. 145·5—146°; *leuco-base*, m.p. 108·5—109·5°, of the crystal-violet analogue), which gives a *methiodide*, m.p. 167·5—168° (decomp.), but no ethiodide. 3N-Na_2CO_3, Pr^nI, and (I)–Et_2O, at room temp. for 21 days and then boiling for 4 days, give m-*di-n-propylaminobenzaldehyde*, b.p. 145—148°/5—6 mm. [*semicarbazone*, m.p. 172—172·5°; 2 : 4-*dinitrophenylhydrazone*, m.p. 207—208°; *picrate*, m.p. 136—137°; *methiodide*, m.p. 152°; *platinichloride*, m.p. 178° (decomp.)]. 1·5N-Na_2CO_3 and $CH_2{:}CH\cdot CH_2Br$ yield m-*diallylaminobenzaldehyde*, b.p. 131—132°/4 mm. [*semicarbazone*, m.p. 133·5—134°; 2 : 4-*dinitrophenylhydrazone*, m.p. 165—165·5°; *platinichloride*, m.p. 161° (decomp.), unstable in warm H_2O; *azine*, m.p. 70—71°; unstable, impure *picrate*, m.p. 108·5—109°], which gives no methiodide. 3N-Na_2CO_3 and CH_2PhBr give m-*dibenzylaminobenzaldehyde*, m.p. 59—60°, b.p. 230—231°/7 mm. (*semicarbazone*, m.p. 185—185·5°; *oxime*, m.p. 125—126°; 2 : 4-*dinitrophenylhydrazone*, m.p. 230—231°; *azine*, m.p. 167—167·5°; impure *platinichloride*, m.p. 124—125°), which gives no methiodide. The order of basicity of *m*-dialkylaminobenzaldehydes follows no accepted rules. Steric effects may influence the results. R. S. C.

γ-Substituted resorcinol derivatives. I. Synthesis of γ-resorcaldehyde. K. Nakazawa (J. Pharm. Soc. Japan, 1939, **59**, 57—59).—2 : 4 : 1-$(OH)_2C_6H_3\cdot CO_2H$ and $AlCl_3$–$Zn(CN)_2$–Et_2O, with HCl gas, give 3-*aldehydo*-2 : 4-*dihydroxybenzoic acid*, m.p. 195° (decomp.), converted by H_2O_2–aq. NaOH into pyrogallol-4-carboxylic acid, m.p. 221° (decomp.), or by boiling H_2O into γ-resorcaldehyde, m.p. 154° (oxime, m.p. 167°). A. T. P.

4-Methoxy-3-chloromethylbenzaldehyde. B. Reichert and K. auf dem Kampe (Arch. Pharm., 1939, **277**, 261—271; cf. A., 1937, II, 422).—4 : 3 : 1-$OMe\cdot C_6H_3(CH_2Cl)\cdot CHO$ (I) with $MeNO_2$ (EtOH–KOH) and $EtNO_2$ ($EtNH_2$) yields respectively β-*nitro-α-*(4-*methoxy*-3-*chloromethylphenyl*)-*ethylene*, m.p. 118°, and *-propylene*, m.p. 80°. Hydrolysis (dil. H_2SO_4) of (I) gives $OMe\cdot C_6H_3(CH_2\cdot OH)\cdot CHO$ (II) in 78% yield. (II) similarly yields β-*nitro-α-*(4-*methoxy*-3-*hydroxymethylphenyl*)-*ethylene*, m.p. 104—105° (*acetate*, m.p. 131—132°), and *-propylene*, m.p. 90°; reduction (H_2, Pd–C, C_5H_5N at 55°) of the former affords 4-*methoxy*-3-*hydroxymethylphenyl-acetaldoxime*, m.p. 119—120°, further reduced (H_2, PtO_2, EtOH–$H_2C_2O_4$ or Na–Hg + EtOH–AcOH) to the -ethylamine (*H oxalate*, m.p. 147—148°). (II) with $CH_2(CO_2H)_2$, C_5H_5N, and a trace of piperidine yields 4-*methoxy*-3-*hydroxymethylcinnamic acid*, m.p. 190—191°, reduced (H_2, Pd–C, 80% MeOH at 35°) to β-6-*methoxy*-m-*tolylpropionic acid*, m.p. 98—99° [*Me* ester (CH_2N_2), m.p. 45°]. Oxidation of (I) or (II) with dil. HNO_3 or of (II) with CrO_3 yields 4-*methoxy*isoph*thalaldehyde*,

m.p. 123—124° (*dioxime*, m.p. 170—172°), further oxidised ($KMnO_4$) to 4 : 3 : 1-OMe·$C_6H_3(CO_2H)_2$.
A. Li.

2 : 4-Dinitrophenylhydrazone, m.p. 198°, of *p*-hydroxyphenylpyruvic acid.—See A., 1939, III, 725.

Synthesis of substituted alicyclic methyl ketones. II. Hydroxymethyl ketones. W. A. Yarnall and E. S. Wallis (J. Org. Chem., 1939, 4, 284—288).—Attempts to condense *cyclo*hexanone (I) with $CH_2Cl·CHCl·CO_2Et$ in presence of NaOEt leads under all conditions to $CH_2{:}CCl·CO_2Et$. (I) does not condense with $OH·CH_2·CHCl·CO_2Et$.
$CH_2Cl·CHCl·CO_2H$ is obtained in 18% yield by addition of Cl_2 to $CH_2{:}CH·CH_2·OH$ and oxidation of the dichlorohydrin by HNO_3, or in 85% yield by passage of Cl_2 through $CH_2{:}CH·CHO$ at <−5° and treatment of the product with a mixture of conc. and fuming HNO_3 at 40—50°. Gradual addition of Mg *cyclo*hexyl chloride to a suspension of $CN·CH_2·OMgI$ (obtained from $OH·CH_2·CN$ and MgMeI) in Et_2O gives *cyclo*hexyl $CH_2·OH$ ketone, isolated as the 3 : 5-*dinitrobenzoate*, m.p. 110—111°. The 3 : 5-*dinitrobenzoates* of *cyclo*pentyl and 2-methyl*cyclo*pentyl $CH_2·OH$ ketones have m.p. 100° and 103°, respectively. 2-Methyl*cyclo*pentanone is reduced to the alcohol, which is converted in the usual manner into 2-*methyl*cyclo*pentyl chloride*, b.p. 122—124°/atm. pressure (some decomp.).
H. W.

Hydrogen fluoride as a condensing agent. VII. Acylation of aromatic compounds. J. H. Simons, D. I. Randall, and S. Archer. **VIII. Alkylation of benzene by esters.** J. H. Simons, S. Archer, and D. I. Randall (J. Amer. Chem. Soc., 1939, **61**, 1795—1796, 1821—1822; cf. A., 1939, II, 362).—VII. In HF at 80—100° PhMe with AcOH, Ac_2O, or AcCl gives *p*-$C_6H_4Me·COMe$, with BzOH or BzCl gives *p*-$C_6H_4Me·COPh$, and with Bu^aCO_2H gives *p*-$C_6H_4Me·COBu^a$; PhOH and AcOH give *p*-$OH·C_6H_4·COMe$; C_6H_6 and AcCl give COPhMe.
VIII. With HF in an excess of C_6H_6 at 80—100°, $Bu^\gamma OAc$ gives $PhBu^\gamma$ and COPhMe; $Pr^\beta OAc$ gives $PhPr^\beta$, COPhMe, and *p*-$C_6H_4Pr^\beta·COMe$; Bu^aOAc or *sec.*-BuO·$COPr^\beta$ gives PhBu-*sec.*; $CH_2Ph·OAc$ gives CH_2Ph_2. The reaction mechanism is discussed.
R. S. C.

Action of mixed organo-magnesium compounds on osazones. P. Grammaticakis (Compt. rend., 1939, **208**, 1998—2000; cf. A., 1937, II, 248, 287).—$COPh·CH{:}N·OH$ (1 mol.) with $NHPh·NH_2,HCl$ (2·2 mols.) in warm EtOH gives phenylglyoxalphenylosazone (I) (100%), which with MgPhBr in Et_2O gives *ω-phenylhydrazino-ω-phenylacetophenonephenylhydrazone* (II), m.p. 124°, and a small amount of $(·CPh{:}N·NHPh)_2$ (III). (I) with MgEtBr affords *ω-phenylhydrazino-ω-ethylacetophenonephenylhydrazone*, m.p. 123°. Glyoxalphenylosazone with MgPhBr similarly affords (II), (III), (I), and $CHPh{:}N·NHPh$. (I) does not react with MgMeI in Et_2O. (III) in boiling Et_2O/14 hr. with a large excess of MgMeI, MgEtBr, or MgPhBr forms no additive products. Cinnamaldehydephenylhydrazone with MgEtBr similarly affords *α-phenylhydrazino-α-styrylpropane*, b.p. 185—187°/<1 mm.
J. L. D.

Heterocyclic compounds containing nitrogen. XLIV. 2 : 2′-Dinitrodeoxybenzoin. P. Ruggli and A. Dinger (Helv. Chim. Acta, 1939, **22**, 908—911).—The product of the oxidation of *o*-$NO_2·C_6H_4·CH_2·CO·CO_2H$ by $CaOCl_2$ is shown to be 2 : 2′-dinitrodeoxybenzoin, m.p. 166° (lit. 160°). Hydrogenation (Raney Ni in EtOH–EtOAc–H_2O) of it yields 2-*o*-aminophenylindole, m.p. 153° (Ac derivative, m.p. 151—152°), and αβ-2 : 2′-diaminodiphenylethane, m.p. 67° (Ac_2 derivative, m.p. 250°).
H. W.

Influence of route chosen for an asymmetric synthesis on the configuration of the resulting enantiomorph. S. M. Partridge (J.C.S., 1939, 1201).—The formation of (+)- and (−)-$OH·CPhEt·COPh$ from (−)-$OH·CHPh·CO_2H$ (Roger, A., 1939, II, 111) and of (+)- and (−)-$OMe·C_6H_4·CMe(OH)·CO_2H$ (McKenzie *et al.*, A., 1932, 1037) is determined by the order in which the substituents are introduced and thus contradicts the conclusions of Roger.
R. S. C.

Rearrangement of α-hydroxy-carbonyl compounds. P. G. Stevens (J. Amer. Chem. Soc., 1939, **61**, 1714—1716).—Isomerism, $CH_2Ar·CO·CHAr'·OH \rightleftharpoons CH_2Ar·CH(OH)·COAr'$, is demonstrated, thus supporting Hibbert's theory of lignin formation. *α-Hydroxy-β-keto-γ-phenyl-α-p-chlorophenylpropane* (I), m.p. 125·5—126°, is prepared from *p*-$C_6H_4Cl·CO·CH(OH)·CHPh·CO_2H$ and from *p*-$C_6H_4Cl·CH(OH)·CN + CH_2Ph·MgCl$. *β-Hydroxy-α-keto-γ-phenyl-α-p-chlorophenylpropane* (II), m.p. 43—44°, is converted into (I) by Na_2CO_3 in hot 95% EtOH; the reverse transformation was effected in poor yield under narrow conditions. With strong alkali, (I) gives *p*-$C_6H_4Cl·CO_2H$ and *α-hydroxy-β-phenyl-α-p-chlorophenylpropionic acid* (III), m.p. 201—202°, the reaction mechanism being: (I) or (II) $\rightleftharpoons CH_2Ph·C(OH){:}C(OH)·C_6H_4Cl \rightarrow CH_2Ph·CO·CO·C_6H_4Cl$ (IV) + $CH_2Ph·CH_2·CO·C_6H_4Cl$ (not isolated); (IV) gives (III) by benzilic acid rearrangement or $C_6H_4Cl·CO_2H$ by cleavage. The structure of (III) is proved by synthesis from β-*p*-chlorobenzoyl-α-phenylethylene oxide by alkali and by oxidation to *p-chlorodeoxybenzoin*, m.p. 104·5—105·2°. H_2–PtO_2 in MeOH reduces *p*-$C_6H_4Cl·CO·CH{:}CHPh$ to *p*-C_6H_4Cl *β-phenylethyl ketone*, m.p. 75—76°, converted by Br–$CHCl_3$ into *p*-C_6H_4Cl *α-bromo-β-phenylethyl ketone*, m.p. 92—93°, which with Na_2CO_3 in aq. EtOH gives (II).
R. S. C.

Functional aptitude of the methyl group. II. Derivatives of benzophenone and benzil. L. Chardonnens and J. Venetz (Helv. Chim. Acta, 1939, **22**, 822—836).—Me in substituted benzophenones is activated if Bz is in the *para*- and NO_2 in the *ortho*-position but not if the placing of the substituents is reversed. 3-Nitro-4-methylbenzophenone (I) condenses with *p*-$NMe_2·C_6H_4·CHO$ in presence of piperidine at 155—160° to 3-*nitro*-4-*p-dimethylaminostyrylbenzophenone*, m.p. 180°. 3-*Nitro*-4-*p-methoxystyrylbenzophenone*, m.p. 156°, is obtained similarly. PhCHO and the requisite benzophenone afford 3 : 3′-*dinitro*-, m.p. 155—156°, 3 : 5-*dinitro*-, m.p. 129·5—130·5°, and 3 : 5 : 3′-*trinitro*-, m.p. 164·5°, *-4-styrylbenzophenone*. 3 : 3′-Dinitro-4-methylbenzophenone

and *p*-NO·C_6H_4·NMe_2 in boiling EtOH containing anhyd. Na_2CO_3 slowly afford 2-*nitro*-4-m′-*nitrobenzoylbenzald*-p″-*dimethylaminoanil*, m.p. 147—148°, and 2-*nitro*-4-m′-*nitrobenzoylbenzaldoxime* N-p-*dimethylaminophenyl ether*, m.p. 234°. *p*-NO·C_6H_4·NMe_2 and (I) yield 2-nitro-4-benzoylbenzald-*p*-dimethylaminoanil, m.p. 174—175°, and the corresponding *nitrone*, m.p. 217°. 3 : 5-Dinitro-4-methylbenzophenone appears to give exclusively 2 : 6-*dinitro*-4-*benzoylbenzald*-p-*dimethylaminoanil*, m.p. 157—158°. 5 : 2-NO_2·C_6H_3Me·CO_2H is transformed by the successive actions of $SOCl_2$ and C_6H_6–$AlCl_3$ into 5-*nitro*-2-*methylbenzophenone*, m.p. 79°, which is transformed by *p*-NO·C_6H_4·NMe_2 into 4-*nitro*-2-*benzoylbenzaldoxime* N-p-*dimethylaminophenyl ether*, m.p. 240°. 3 : 5 : 2-$(NO_2)_2C_6H_2Me$·CO_2H is transformed into 3 : 5-*dinitro*-2-*methylbenzophenone*, m.p. 88°, which yields 3 : 5-*dinitro*-2-*styrylbenzophenone*, m.p. 119—120°, with PhCHO and piperidine at 130°, and 2 : 4-*dinitro*-6-*benzoylbenzald*-p-*dimethylaminoanil*, m.p. 190—192°, with *p*-NO·C_6H_4·NMe_2 in boiling EtOH containing Na_2CO_3. 3 : 3′-Dinitro-4 : 4′-dimethylbenzophenone and PhCHO afford 3 : 3′-*dinitro*-4 : 4′-*distyrylbenzophenone*, m.p. 202—203°, whilst 3 : 3′-*dinitro*-4 : 4′-*diformylbenzophenonedi*-p-*dimethylaminoanil*, m.p. 200—201°, is obtained from *p*-NO·C_6H_4·NMe_2. 3 : 3′-Dinitro-4 : 4′-dimethylbenzil [*quinoxaline*, m.p. 179—180°, from *o*-$C_6H_4(NH_2)_2$] affords 3 : 3′-*dinitro*-4 : 4′-*distyrylbenzil*, m.p. 224° or 196—197° (*quinoxaline*, m.p. 207—208°). H. W.

Mechanism of reduction of conjugated systems with terminal carbonyl groups. Dienols obtained from unsaturated αδ-diketones. R. E. Lutz and W. G. Reveley (J. Amer. Chem. Soc., 1939, **61**, 1854—1859).—Reduction of COR·CH:CH·COR (I) catalytically or by metal is shown to occur by 1 : 6-addition, giving OH·CR:CH·CH:CR·OH (II) as primary product. When (I) (R = mesityl) is hydrogenated (Pt) in EtOH at 0° and the solution is filtered under N_2 and run into aq. or EtOH–I, the amount of (II) (R = mesityl) present is determined by the I consumed [(II) + 2I → (I)]; this amount depends on the time of manipulation and with short times rises to 93·7%; if the solution is kept, preferably after addition of a little piperidine as catalyst, ketonisation gives nearly 100% yields of (2 : 4 : 6-$C_6H_2Me_3$·CO·$CH_2)_2$ (III). The amount of (II) formed was checked (concordant results) by converting the (II) by $NaHSO_3$ in boiling 60% EtOH into the H_2O-sol. Na αδ-diketo-αδ-dimesitylbutane-β-sulphonate (*Pb* salt) and weighing the insol. (III). Zn dust in 1 : 1 AcOH–Et_2O at −5° to 0° gives a solution containing (I method) 61% of (II). Ketonisation of (II) (R = mesityl) in EtOH is very slow at 0°, but rises with increasing temp.; at 26—29° the half-life period is ~12 hr. at rest, but if the solution is disturbed, ketonisation is much more rapid. (II) (R = mesityl) could not be isolated. The amount of (II) (R = mesityl) obtained by hydrogenation at 0° was in 95% EtOH 91—94, dioxan–EtOH (4 : 1) 90, EtOAc 78, Pr^{β}_2O 60, C_6H_6 (at 5°) 54, *n*-C_6H_{14} 60, decahydronaphthalene 17, and AcOH–$EtCO_2H$ (63 : 37) ~40—50%. The dimagnesium enolate of (III) [prep. by heating with MgPhBr (excess) in di*iso*amyl ether at 110°] with I in 95% EtOH at 0° gives an excellent yield of *trans*-(I) (R = mesityl). OMgBr·CPh:CH·CPh:CPh·OMgBr [prep. from (:CHBz)$_2$ by MgPhBr] with I–EtOH gives CHBz:CPhBz (no CH_2Bz·CHPhBz) and 2 : 3 : 4 : 5-tetraphenylfuran (formed from the CHBz:CPhBz by the unused MgPhBr); this confirms the author's mechanism for addition of MgRHal to (I). Isolation of OH·CR:CH·CR:CR·OH (R = mesityl), m.p. 70—71°, and of four stable mono-enols, OH·CR:CR·CHR·COR, is announced without details. R. S. C.

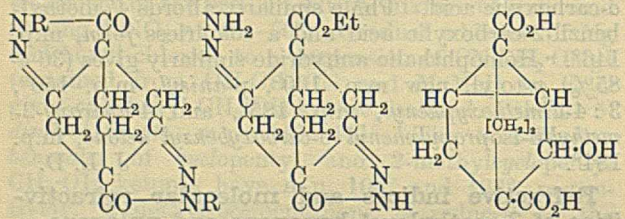
Synthesis of benzil-*o*-carboxylic and β-deoxybenzoin-*o*-carboxylic acids. B. Hoï (Compt. rend., 1939, **208**, 2082—2084).—Phthalonic anhydride, C_6H_6, and $AlCl_3$ at 80° afford a mixture of the yellow, m.p. 141·5°, and *colourless*, m.p. 125°, forms of benzil-*o*-carboxylic acid. PhMe similarly affords 4′-methylbenzil-2-carboxylic acid and a colourless *form*, m.p. 146°. Homophthalic anhydride similarly gives (30—85%) *p*-tolyl, new m.p. 160°, p-*anisyl*, m.p. 150°, 3 : 4-*dimethoxyphenyl*, m.p. 185°, and 4-*hydroxy*-2-*methyl*-5-iso*propylphenyl* o-*carboxybenzyl ketone*, m.p. 184°. J. L. D.

Refractive indices and molecular refractivities of 3-methyl*cyclo*hexanone and pulegone.—See A., 1939, I, 405.

Hydroaromatic series. VI. Addition of 6-methoxy-1-vinyl-3 : 4-dihydronaphthalene to Δ¹-*cyclo*pentenone and 4 : 4-dibromo-Δ¹-*cyclo*pentene-3 : 5-dione. E. Dane and K. Eder (Annalen, 1939, **539**, 207—212; cf. A., 1939, II, 318).—Δ²-*cyclo*Pentenyl acetate, b.p. 58—61°/20 mm., is best obtained, with some 1 : 2-*diacetoxy*cyclo*pentane*, b.p. 115—118°/20 mm., from *cyclo*pentene by $Pb(OAc)_4$ in AcOH at 50°. Δ²-*cyclo*Pentenol, b.p. 68—70°/40 mm., obtained therefrom, is oxidised by CrO_3 in dil. H_2SO_4 to Δ²-*cyclo*pentenone, b.p. 42°/10 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 165°). With butadiene in dioxan at 120—160°, this gives 4 : 7 : 8 : 9-tetrahydroindan-1-one, an oil (*dinitrophenylhydrazone*, m.p. 199°), and with 6-methoxy-1-vinyl-3 : 4-dihydronaphthalene (I) gives 1′-*keto*-7-*methoxy*-1 : 2 : 3 : 9 : 10 : 11-*hexahydro*cyclo*pentano*-3′ : 2′- or 2′ : 3′-1 : 2-*phenanthrene*, m.p. 141° (*dinitrophenylhydrazone*; HBr–AcOH gives a cryst. phenol, dehydrated by benzoquinone to a cryst. compound). 4 : 4-Dibromo-Δ¹-*cyclo*pentene-3 : 5-dione with butadiene or (I) in dioxan at 110—115° gives 2 : 2-*dibromo*-4 : 7 : 8 : 9-*tetrahydroindane*-1 : 3-*dione*, m.p. 92°, and 4′ : 4′-*dibromo*-3′ : 5′-*diketo*-7-*methoxy*-1 : 2 : 3 : 9 : 10 : 11-*hexahydro*cyclo*pentano*-1′ : 2′-1 : 2-*phenanthrene*, m.p. 166°, respectively. R. S. C.

***para*-Bridge formation with ethyl succinosuccinate. I. Formation of di*cyclo*-[1 : 2 : 2]-heptane, di*cyclo*-[2 : 2 : 2]-octane, and di*cyclo*-[3 : 2 : 2]-nonane systems.** P. C. Guha (Ber., 1939, **72**, [*B*], 1359—1373; cf. A., 1936, 1252).—The action of CH_2I_2, I, or Br on Et_2 sodiosuccinosuccinate (I) gives *Et*$_2$ 2 : 5-*dihydroxyterephthalate* (II), m.p. 133° (*Ac* derivative, m.p. 154°), identified by conversion by dil. HCl at 180° into quinol. CH_2Br_2 and (I) give a very small yield of *Et*$_2$ *di*cyclo-[1 : 2 : 2]-*heptane*-2 : 5-*dione*-1 : 4-*dicarboxylate*, b.p. 110°/1 mm. $COBr_2$

and (I) in C_6H_6 appeared to afford an *isomeride*, m.p. 132°, of (I) which gives a pale red colour with $FeCl_3$ in EtOH. $CHBr(CO_2Et)_2$ and (I) yield a product, m.p. 127—128°, which gives a blue-green colour with $FeCl_3$ and is not identical with (I) or (II). $(CH_2Br)_2$ and (I) give *Et*$_2$ *di*cyclo-[2 : 2 : 2]-*octane*-2 : 5-*dione*-1 : 4-*dicarboxylate* (III), m.p. 112° (*disemicarbazone*, m.p. 263—264°), which when heated with H_2O containing a few drops of HCl at 200°, or boiled with 50% H_2SO_4 or 18% HCl until a clear solution is obtained, is hydrolysed to the *dicarboxylic acid* (IV), m.p. 286° (*disemicarbazone*, m.p. 257°). This is partly decarboxylated at 270—280°/vac. to *di*cyclo-[2 : 2 : 2]-*octane*-2 : 5-*dionecarboxylic acid*, m.p. 216—217°. (IV) is readily re-converted into (III) by EtOH–HCl, which gives a *dioxime*, m.p. 210°, *mono-oxime*, m.p. 167°, is transformed by $NHPh{\cdot}NH_2$ into the



(V.) (VI.) (VII.)

pyrazolone compound [(V), R = Ph], m.p. 188—189°, by boiling NH_2Ph into the *dianilide*, m.p. 193°, and by N_2H_4,H_2O in EtOH into the *dipyrazolone* derivative [(V), R = H], m.p. 326°, and the *mono-pyrazolone* compound (VI), m.p. 204°, characterised by the formation of a *:CHPh* derivative, m.p. 281°. Boiling 10% KOH–EtOH transforms (III) into ββ′-*dicarboxysuberic acid*, m.p. 177—178°, which gives a mixture when esterified in the usual manner. Oxidation of (III) with $KMnO_4$ yields $(\cdot CH_2{\cdot}CO_2H)_2$, $H_2C_2O_4$, and an acid, m.p. 150°, which is not adipic acid; fuming HNO_3 gives $H_2C_2O_4$ and a trace of $(\cdot CH_2{\cdot}CO_2H)_2$. (III) is largely unchanged by Na and EtOH under CO_2. Reduction with Na–Hg in EtOH–AcOH leads to *Et*$_2$ *di*cyclo-[2 : 2 : 2]-*octane*-2 : 5-*diol*-1 : 4-*dicarboxylate*, b.p. 200—204°/3 mm., with H_2–PtO_2 activated by $FeCl_2$ in AcOH at 25°/2·5 atm. to the isomeric *diol diester*, b.p. 196—197°/5 mm., and by Zn–Hg and boiling dil. HCl to *di*cyclo-[2 : 2 : 2]-*octane*-1 : 4-*dicarboxylic acid*, m.p. 385° (*Et*$_2$ ester, b.p. 140—145°/3 mm.), and the *acid* (VII), m.p. 315° (*Et*$_2$ ester, b.p. 180—190°/4 mm.). Dry (I) and $Br{\cdot}[CH_2]_3{\cdot}Br$ at 170—175° give *Et*$_2$ *di*cyclo-[2 : 2 : 3]-*nonane*-2 : 5-*dione*-1 : 4-*dicarboxylate* (VIII), m.p. 132° (*disemicarbazone*, m.p. 227°), and a viscous yellow liquid, b.p. 180—190°/5 mm., which does not react with $FeCl_3$ and does not give a semicarbazone. Acid hydrolysis of (VIII) gives the *dicarboxylic acid*, m.p. 238° (*disemicarbazone*, m.p. 217°), readily re-esterified to (VIII). (VIII) and $NHPh{\cdot}NH_2$ give a *dipyrazolone* compound {cf. (V), R = Ph; $[CH_2]_3$ instead of $[CH_2]_2$}, m.p. 231—232°, and with N_2H_4,H_2O a *substance* {cf. (V), R = H; $[CH_2]_3$ instead of $[CH_2]_2$}, m.p. 321°. By the hydrolysis of (VIII) with 5% KOH–EtOH three *CO-dicarboxylic acids*, $C_{10}H_{14}O_5$, of the *cyclo*heptane series are obtained with m.p. 163°, 181° (*semicarbazone*, m.p. 220°), and 199° [*Et* ester, b.p. 195—205°/3 mm. (*semicarbazone*, m.p. 152°)], respectively. (VIII) is largely unchanged by Na–Hg in EtOH–AcOH but is reduced (Clemmensen) to *di*cyclo-[2 : 2 : 3]-*nonane*-1 : 4-*dicarboxylic acid*, m.p. >360°. H. W.

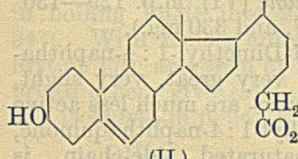
***para*-Bridge formation with ethyl succinosuccinate. II. Synthesis of dicarbethoxysuberic ester and its cyclisation to di*cyclo*-[2 : 2 : 2]-octanedione by double Dieckmann condensation.** P. C. Guha and C. Krishnamurthy (Ber., 1939, **72**, [*B*], 1374—1379).—*Et*$_2$ ββββ′β′-*tetracarbethoxysuberate*, m.p. 69°, is obtained from $(CH_2Br)_2$ and Et_2 sodiocarbethoxysuccinate or from $CH_2Br{\cdot}CO_2Et$ and Et_4 disodiobutane-ααδδ-tetracarboxylate. It is slowly hydrolysed by boiling HCl (1 : 1) to ββ′-*dicarboxysuberic acid*, m.p. 177—178° [*Et*$_4$ ester (I), b.p. 205°/2 mm.]. Gradual addition of (I) to mol. Na suspended in C_6H_6 at room temp. gives unidentified alkali-insol. material which yields a *semicarbazone*, m.p. 240—242° (decomp.), and a portion sol. in alkali which is hydrolysed and decarboxylated by HCl (1 : 1) to *di*cyclo-[2 : 2 : 2]-*octane*-2 : 5-*dione*, m.p. 205—206° (*disemicarbazone*, m.p. 244—245°). H. W.

***para*-Bridge formation with ethyl succinosuccinate. III. Resolution of di*cyclo*-[2 : 2 : 2]-octane-2 : 5-dione-1 : 4-dicarboxylic acid into its optical antipodes.** P. C. Guha and S. K. Ranganathan (Ber., 1939, **72**, [*B*], 1379—1380).—Crystallisation of the brucine salt of the *dl*-acid from boiling H_2O gives the normal *brucine* salt (I) ($+3H_2O$), $[\alpha]_D^{26\cdot5}$ −70·87° in H_2O, of d-*di*cyclo-[2 : 2 : 2]-*octane*-2 : 5-*dione*-1 : 4-*dicarboxylic acid*, m.p. 271°, $[\alpha]_D^{25}$ +23·85° in H_2O. Concn. of the mother-liquors from (I) with periodical removal of the salt which separates leaves a salt from which the l-*acid*, $[\alpha]_D^{28\cdot5}$ −23·24° in H_2O, is isolated. H. W.

Synthesis of substituted alicyclic methyl ketones. I. W. A. Yarnall and E. S. Wallis (J. Org. Chem., 1939, **4**, 270—283; cf. A., 1937, II, 294).—Addition of powdered NaOEt to *cyclo*hexanone and $CHMeCl{\cdot}CO_2Et$ affords *Et* α : 1-*oxido*-α-*cyclohexylpropionate*, b.p. 126—128°/19 mm., in 54% yield; the usual brown colour is avoided if the mixture is cooled to −80° and the yield is increased to 68%. In presence of Et_2O, anhyd. C_6H_6, or C_6H_6 + light petroleum the yields are 34, 47, and 54%, respectively. The use of an excess of α-halogeno-ester and condensing agent is advantageous, and $CHMeCl{\cdot}CO_2Et$ is superior to $CHMeBr{\cdot}CO_2Et$. *Et* α : 1-*oxido*-α-*cyclopentylpropionate*, b.p. 128°/25 mm., is prepared in poorer yield from *cyclo*pentanone. Excellent yields of the glycidic acids are obtained by hydrolysis of the esters with NaOH–EtOH, the Na salt being sometimes allowed to crystallise; when the acids are kept in solution before isolation small amounts of ketones are frequently formed. Pyrolysis of the acids at ordinary or reduced pressure gives low yields of ketones and appreciable amounts of resinous material. Attempts to obtain *cyclo*hexyl Me ketone (I) from Et α-hydroxy-α-1-chloro*cyclo*hexylpropionate by rearrangement under the influence of alkali show that the rate of re-formation of glycidic ester exceeds that of hydrolysis so that only traces of ketone are produced. α : 1-Oxido-α-*cyclo*hexylprop-

ionic acid and HCl yield α-hydroxy-α-1-chloro*cyclo*hexylpropionic acid, which when dissolved in aq. Na_2CO_3 and steam-distilled gives (I) in 29% yield and a mixture of acids which yields some (I) when pyrolysed. Much better results are secured by boiling the acid in C_5H_5N, whereby 75% yields of (I) are obtained but only 25% yields of *cyclo*pentyl Me ketone. Alternatively the glycidic acids are transformed into their Na salts, which are heated with an equiv. proportion of NaOH, thus giving 45—56% of ketone. By use of a large excess of $CHMeCl{\cdot}CO_2Et$ and NaOEt and prolonged boiling of the Et_2O solution, dehydroandrosterone (II) is almost completely converted into the non-cryst. glycidic ester, which is hydrolysed to a mixture from which acids, m.p. 183—185° and 240—244°, are isolated. The crude condensation mixture is dissolved in Et_2O and thoroughly washed; any propionates are removed at 50—70°/high vac. and unchanged (II) as its semicarbazone. The residual mixture of glycidic ester and androstenediol is hydrolysed by NaOH–EtOH and small amounts of Δ^5-pregnenolone (III) and Δ^5-*iso*pregnenolone are isolated as their semicarbazones, which are hydrolysed to the free ketones (separable by digitonin). Most attempts to improve the yield of (III) failed owing to the stability of the glycidic acid. Better results are, however, obtained when the acid is treated with HCl in dry Et_2O and the product is boiled in C_5H_5N; the ketones are isolated as their semicarbazones, which are hydrolysed to a cryst. product, m.p. 110—114°. This is brominated, oxidised, and debrominated to progesterone, identical with that obtained from stigmasterol. The possible formation of Δ^4-pregnenolone is mentioned. H. W.

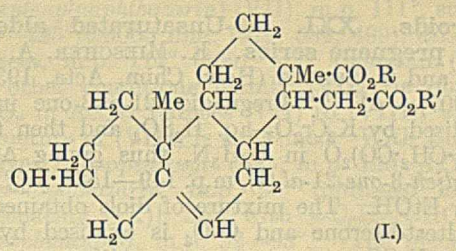
Δ^5-Norcholesten-3-ol-25-one, an oxidation product of cholesteryl acetate dibromide. J. Hattori (J. Pharm. Soc. Japan, 1938, **58**, 150—153). —Δ^5-Norcholesten-3-ol-25-one (I), m.p. 126—127° (sinters at 117°) [acetate, m.p. 139—140° (semicarbazone, decomp. 233—234°; oxime, m.p. 182°; dibromide, decomp. 125—126°); mono-oxime, m.p. 176—177°; monodinitrophenylhydrazone, m.p. 159—160°; dibromide, decomp. 130—131°], is isolated from the oxidation products of cholesteryl acetate dibromide by a method similar to that of Ruzicka *et al.* (A., 1937, II, 506). 3-Acetoxy-Δ^5-cholenic acid, m.p. 189° (corr.), and $SOCl_2$ give the chloride, converted by CH_2N_2 into the corresponding *diazoketone*, decomp. 158°. The latter and NH_3–$AgNO_3$–EtOH afford 3-*acetoxy*-Δ^5-*homocholenamide*, m.p. 200—204° (corr.), and thence 3-*hydroxy*-Δ^5-*homocholenic acid* (II), decomp. 217—219° (corr.) (sinters at 210°) (*Et* ester). The *acetate*, m.p. 188—191° (corr.), of (II) then gives, through the chloride and diazoketone (by HCl–Et_2O), the corresponding *CH_2Cl ketone*, m.p. 182—184°, converted by Zn–AcOH into the acetate, m.p. 137·5—138·5° (corr.), of (I). A. T. P.



(II.)

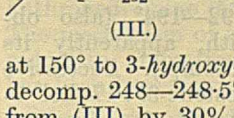
***trans*-Androsterone Me ether, m.p. 91°.**—See B., 1939, 885.

Sterols. XVI. Monoalkyl 3-hydroxy-$\Delta^{5:6}$-ætiobilienates. XVII. Synthesis of *trans*-dehydroandrosterone. S. Kuwada and K. Nakamura (J. Pharm. Soc. Japan, 1938, **58**, 254—256, 257—259).—XVI. Hydrolysis of Me_2 3-hydroxy-$\Delta^{5:6}$-ætiobilienate, m.p. 112°, for a short time with 0·2N-KOH–EtOH gives the Me_1 ester (I) (R = Me, R′ = H), m.p. 214·5—216·5°, $[\alpha]_D^{27}$ −75° [*acetate* (II), m.p. 168·5—169·5°]; prolonged treatment gives the *Et* ester (I) (R = Et, R′ = H), m.p. 176—177° (uncorr.), $[\alpha]_D^{28}$ −75·4° to −76·4° [*acetate*, m.p. 137·5—139°], previously believed to be a Me ester. 3-Hydroxy-$\Delta^{5:6}$-ætiobilienic acid with $MeOH–H_2SO_4$ gives the *Me* ester [(I), R = H, R′ = Me], m.p. 186·5—188°, $[\alpha]_D^{27}$ −55·9°, and with $CHMeN_2$ gives


(I.)

the Et_2 ester, m.p. 103·5—104·5°, hydrolysed by 0·2N-KOH–EtOH to (I) (R = Et, R′ = H), the identity of which with the previous prep. is proved by crystallographic and *X*-ray data.

XV. The acid chloride from (II) (prep. by $SOCl_2$) and CH_2N_2–Et_2O give the oily diazo-ketone, which with NH_3–$AgNO_3$ in EtOH yields β-*Me* 3-*acetoxy*-$\Delta^{5:6}$-α-*homocætiobilien*-α-*amide* (III), m.p. 165—166°. H_2SO_4–EtOH, followed by 0·2N-KOH–EtOH, then gives β-*Me* 3-*hydroxy*-$\Delta^{5:6}$-α-*homocætiobilienate*, m.p. 211—212°, hydrolysed by 15% KOH at 150° to 3-*hydroxy*-$\Delta^{5:6}$-α-*homocætiobilienic acid* (IV), decomp. 248—248·5°, which is also obtained directly from (III) by 30% KOH at 100° or 15% KOH at 150—160°. Boiling 10% KOH–EtOH converts (III) into 3-*hydroxy*-$\Delta^{5:6}$-α-*homocætiobilienamide*, decomp. 255—256°, hydrolysed to (IV) by H_2SO_4–EtOH. When the anhydride (prep. by Ac_2O) of (IV) is first heated at 250°/vac. for 10—15 min. and then distilled at 250—260°/high vac., it gives *trans*-dehydroandrosterone acetate. M.p. etc. are corr. R. S. C.


(III.)

Steroids. XXII. 17-Epimeric methylandrostenediols and methyltestosterone. K. Miescher and W. Klarer (Helv. Chim. Acta, 1939, **22**, 962—969).—The mother-liquors obtained in the prep. of 17-methylandrostenediol (I) by the action of MgMeI on *t*-dehydroandrosterone, after removal of unchanged ketone by $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$, afford 17-iso*methylandrostenediol* [17-*methyl*-Δ^5-*androstene*-3t : 17c-*diol*] (II), m.p. 203—204°, $[\alpha]_D^{21}$ −81° in EtOH, −84·5° in $CHCl_3$. (II) gives a 3-*monoacetate*, m.p. 160—161°, $[\alpha]_D^{21}$ −77° in EtOH, but does not yield a diacetate, whereas (I) is converted by boiling Ac_2O into 17-*methyl*-Δ^5-*androstene*-3t : 17t-*diol diacetate*, m.p. 145—146°, $[\alpha]_D^{21}$ −59° in EtOH. $Al(OPr^\beta)_3$ converts (II) in boiling PhMe–*cyclo*hexanone into 17-iso*methyl*-

testosterone [17-*methyl*-Δ^4-*androsten*-17c-*ol*-3-*one*] (III), m.p. 182—183°, $[\alpha]_D^{21}$ +66° in EtOH, +72° in $CHCl_3$ [*semicarbazone*, m.p. 220—222° (decomp.); 17-*methyltestosterone semicarbazone* has m.p. 226° (decomp.) or m.p. 270—272° (decomp.) in sealed tube]. 17-Methyltestosterone (IV) is transformed by Ac_2O–C_5H_5N at 130—140° into its acetate, m.p. 176—176·5°, $[\alpha]_D^{20}$ +69° in EtOH, whereas (III) gives resins in these circumstances and is unattacked under milder conditions. Distillation of (IV) with anhyd. $CuSO_4$ at 135—150°/0·01 mm. yields the *ketone*, $C_{20}H_{28}O$, m.p. 135—136°, $[\alpha]_D^{21}$ +137° in EtOH [*semicarbazone*, m.p. 230° (decomp.)], also obtained from (III). This is oxidised by OsO_4 to the *ketodiol*, $C_{20}H_{30}O_3$, m.p. 238°, $[\alpha]_D^{20}$ +51° in EtOH. H. W.

Steroids. XXI. αβ-Unsaturated aldehydes of the pregnene series. K. Miescher, A. Wettstein, and C. Scholz (Helv. Chim. Acta, 1939, **22**, 894—907).—$\Delta^{4:5\text{-}17:20}$-Pregnadien-21-ol-3-one in C_6H_6 is oxidised by $K_2Cr_2O_7$–aq. H_2SO_4 and then treated with $(\cdot CH_2\cdot CO)_2O$ in C_5H_5N, thus giving $\Delta^{4:5\text{-}17:20}$-*pregnadien*-3-*one*-21-*al* (I), m.p. 149—152°, $[\alpha]_D^{20}$ +139° in abs. EtOH. The mixture of diols obtained from 17-allyltestosterone and OsO_4 is oxidised by KIO_4 and aq. H_2SO_4 at room temp. to $\Delta^{4:5}$-pregnen-17-ol-3-on-21-al (II), m.p. 149—151° [dioxime, m.p. 215° (decomp.) (softens at 144°)], dehydrated in boiling AcOH containing Ac_2O to (I) [*disemicarbazone*, rapid decomp. >370°], also obtained from (II) by boiling in $EtCO_2H$ under N_2, or in *m*-xylene containing I, by sublimation at 145°/0·0001 mm., or by treatment with anhyd. $CuSO_4$ at 135°/0·001 mm. (I) is oxidised by air in PhMe at 100° to $\Delta^{4:5\text{-}17:20}$-*pregnadien*-3-*one*-21-*carboxylic acid*, m.p. 265—267° (decomp.) (*Me* ester, m.p. 152—154°). Boiling AcOH containing Ac_2O converts (II) into $\Delta^{4:16:20}$-21-*acetoxypregnatrien*-3-*one*, m.p. 192—194° [also obtained similarly from (I)], with, apparently its *stereoisomeride*, m.p. 262—264° (decomp.). Successive treatments of $\Delta^{5:6}$-17-allylandrostene-3*t*:17-diol 3-monoacetate (III) with Br in AcOH, O_3, Zn dust, and Girard's reagent lead to $\Delta^{5:6\text{-}17:20}$-3t-*acetoxypregnadien*-21-*al*, m.p. 185—187° (*semicarbazone*, m.p. 245—246°), also obtained by treating (III) successively with OsO_4 in Et_2O, Na_2SO_3 in boiling aq. EtOH, KIO_4, and H_2SO_4 in aq. MeOH, and Ac_2O–C_5H_5N at room temp. The presence of αβ-unsaturated :CO suffices for the positive but relatively slow and not particularly intense reduction of $AgNO_3$–NH_3. Other substituents except CHO or ketol do not cause any reduction. A suitable reagent for the detection of CHO is 1 : 4-$C_{10}H_6(OH)_2$, which gives a pronounced red colour with (II) but only a weak, non-sp. fluorescence with its precursor. αβ-Unsaturated 3-ketones with a double linking in the 17-side-chain give a red to violet-red colour with 1 : 4-O:$C_{10}H_6$:O. If CO is replaced by a βγ-unsaturated OH or an acyloxy-group at $C_{(3)}$ the colour is displaced towards shorter λ and becomes blue. When an alkyl residue constitutes the side-chain and the unsaturated :CO is also present in position 3 a green colour is formed which becomes blue in the case of the corresponding 3-OH-derivatives. Other compounds investigated give at most a feeble colour. H. W.

Intramolecular dehydrogenation of aromatic nuclei.—See B., 1939, 809.

Absorption spectra of naturally-occurring naphthaquinones and their derivatives.—See A., 1939, I, 402.

Chemistry of vitamin-*E*. VII. Preparation of quinones from methylphenols. L. I. Smith, J. W. Opie, S. Wawzonek, and W. W. Prichard (J. Org. Chem., 1939, **4**, 318—322).—The prep. of polymethylquinones is effected by coupling the requisite polymethylphenol with diazotised sulphanilic acid, reductive cleavage of the azo-compound, and oxidation of the NH_2-phenol followed by the removal of the quinone by steam-distillation or filtration. If certain precautions are taken pure quinones are obtained. Duroquinone, trimethylbenzoquinone, and *m*- and *p*-xyloquinone have been prepared in overall yields of 50—90% by the method, which fails when applied to the prep. of toluquinone. H. W.

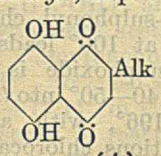
(A) Quinones having vitamin-*K* activity. L. F. Fieser, D. M. Bowen, W. P. Campbell, M. Fieser, E. M. Fry, R. N. Jones, B. Riegel, C. E. Schweitzer, and P. G. Smith. **(B) Synthesis of anti-hæmorrhagic compounds.** L. F. Fieser, D. M. Bowen, W. P. Campbell, E. M. Fry, and M. D. Gates, jun. (J. Amer. Chem. Soc., 1939, **61**, 1925—1926, 1926—1927).—(A) Vitamin-*K* activity of 2 : 3-dimethyl-1 : 4-naphthaquinone [absorption max. at 246 and 265 (log ε 4·2—4·3) and 330 mμ. (log ε 3·4)] is < 1/250 that of pure -K_1. Lomatiol and hydroxyhydrolapachol are active. *Diallyl*-1 : 4-*benzoquinone* (I), m.p. 16°, *diallylquinol* (II), m.p. 130—131° [obtained with an *isomeride* (III), m.p. 87—90°, from quinol diallyl ether; oxidation gives (I)], the *diacetate*, m.p. 111—112°, of (II), lapachol, hydrolapachol, *lomatiol Me ether*, m.p. 61·5—62°, and *lapachol Me ether*, m.p. 51·5—52°, have no, or only a trace of, activity. The oxido-reduction potential of -K_1 indicates that it is a 2 : 3-dialkyl-1 : 4-naphthaquinone. -K_1 may be 2-methyl- or 2 : (?6)-dimethyl-3-phytyl- and -K_2 2 : 3-difarnesyl-1 : 4-naphthaquinone. 2 : 1-CH_2:$CH\cdot CH_2\cdot C_{10}H_6\cdot OH$ is converted by way of the azo-compound and amine into 2-*allyl*-1 : 4-*naphthaquinone* (IV), m.p. 36—36·5°. 1 : 4-*Diallyloxynaphthalene*, m.p. 49·5—50°, with $NPhEt_2$ and Ac_2O gives 1 : 4-*diacetoxy*-2 : 3-*diallylnaphthalene* (V), m.p. 92·5—93°, which resists alkaline hydrolysis but with MgRHal and O_2 in Et_2O gives a *quinone* (VI), m.p. 129—130° (absorption max. at 245, 267, and 330 mμ.).

(B) 2 : 3-, 2 : 6-, and 2 : 7-Dimethyl-1 : 4-naphthaquinone have, respectively, very great, very slight, and definite -*K* activity. Benzo- are much less active than naphtha-quinones. 2-Allyl-1 : 4-naphthaquinone, which contains a βγ-unsaturated side-chain, is particularly active; (V) is inactive. The intense absorption bands of 2 : 3-dialkyl-1 : 4-naphthaquinones have general and fine structure similar to that of -K_1 and -K_2. These facts support the structures postulated for -K_1 and -K_2. 3-Hydroxy-2-Δ^a-heptenyl- and -2-*n*-heptyl-1 : 4-naphthaquinone are slightly active. 2 : 6 : 8-$C_{10}H_5Me_2\cdot O\cdot CH_2\cdot CH$:$CH_2$ is rearranged to 3 : 7-*dimethyl*-2-*allyl*-1-*naphthol*, b.p. 152—157°/2 mm., converted into the 4-NH_2-derivative and thence

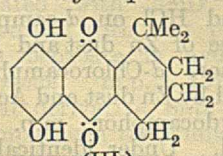
($FeCl_3$–$COMe_2$) into 2 : 6-*dimethyl*-3-*allyl*-1 : 4-*naphthaquinone*, m.p. 42—42·5°. Ag_2O oxidises (III) to an oily quinone, which adds $(CH_2{:}CMe)_2$ to give a product, converted by isomerisation and oxidation (CrO_3) into 6 : 7-*dimethyl*-2 : 3-*diallyl*-1 : 4-*naphthaquinone*, m.p. 69·5—70·7°. 6 : 7-*Dimethyl*-1 : 4-*naphthaquinone*, m.p. 118—119°, is similarly prepared. The adduct of 1 : 4-$O{:}C_6H_4{:}O$ and $(CH_2{:}CH)_2$ with $CH_2{:}CH{\cdot}CH_2Br$ and K_2CO_3 in $COMe_2$ gives 1 : 4-*diallyloxy*-5 : 8-*dihydronaphthalene*, m.p. 64—65°, rearranged in hot kerosene to 1 : 4-*dihydroxy*-2 : 3-*diallyl*-5 : 8-*dihydronaphthalene*, m.p. 108—109°, which with CrO_3–AcOH gives 2 : 3-*diallyl*-1 : 4-*naphthaquinone* (VII), m.p. 29—30°. (VI) is a quinone with 2 H more than (VII); more gentle cleavage of (V) by MgMeBr and oxidation by Ag_2O gives (VII). Absorption spectra of many of these quinones are given (T. J. Webb). The NaOEt–EtOH reaction for -K_1 is given by the allylnaphthaquinones (allyl group in quinone ring). R. S. C.

Constitution of vitamin-K_1. D. W. MacCorquodale, S. B. Binkley, S. A. Thayer, and E. A. Doisy (J. Amer. Chem. Soc., 1939, **61**, 1928—1929).—When hydrogenated catalytically, vitamin-K_1 absorbs 4 H_2 (3 H_2 to reduce the quinone ring; 1 H_2 to reduce the side-chain). The quinol diacetate from -K_1 with O_3 gives (?) $\zeta\kappa\xi$-trimethylpentadecan-β-one (semicarbazone, m.p. 66—67°). CrO_3 oxidises -K_1 to *o*-$C_6H_4(CO_2H)_2$ and (?) 2-*ethyl*-1 : 4-*naphthaquinonyl*-3-*acetic acid*, m.p. 210° (decomp.). -K_1 is thus probably 2-*ethyl*-3-*phytyl*-1 : 4-*naphthaquinone*. R. S. C.

Synthesis of alkannan and other alkylnaphthazarins. H. Brockmann and K. Müller (Annalen, 1939, **540**, 51—72; cf. A., 1936, 79).—Structures ascribed below are supported by absorption spectra, the main max. (mμ.) of which (in C_6H_6) are given in parentheses. Mixed products are separated by adsorption on acid-washed SiO_2 or CaC_2O_4. *p*-$C_6H_4(OMe)_2$, RCOCl, and $AlCl_3$ in boiling CS_2 give mixed acylquinol Me_1 and Me_2 ethers (40—50%), reduced by Zn–Hg–HCl–AcOH to the alkylquinol ethers. Thus are prepared 2-iso*butyrylquinol* *Me*$_2$, b.p. 160—165°/17 mm., 2-iso*butylquinol* *Me*$_2$, b.p. 131—134°/20 mm., 2-iso*valerylquinol* *Me*$_1$, b.p. 177—178°/18 mm., 2-iso*amylquinol* *Me*$_1$, b.p. 154—156°/18 mm., 2-γ-*methyl*-n-*valerylquinol* *Me*$_2$, b.p. 172—173°/7 mm., and 2-δ-*methyl*-n-*amylquinol* *Me*$_2$ *ether* (I), b.p. 168—170°/8 mm. (converted by $AlCl_3$ in boiling PhMe into 2-δ-*methyl*-n-*amylquinol*, m.p. 94°). With maleic anhydride (II) and $AlCl_3$–NaCl, first at 170° and then at 200° (1—2 min.), the appropriate ethers give *ethyl*-, m.p. 127°, n-*propyl*-, m.p. 98°, iso*butyl*-, m.p. 94°, and iso*amyl*-*naphthazarin* (*A*),



(*A*.)



(III.)

m.p. 89°, but (I) gives 1 : 1-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinizarin* (III), m.p. 83° (550, 512). 2 : 3-*Dimethylnaphthazarin* [prep. from 2 : 3-dimethylquinol (IV) and (II)], m.p. 174° (552, 513, 481), and CH_2N_2–Et_2O give a quinizarin *derivative*, $C_{14}H_{12}O_4N_2$, m.p. ~243—246° (496). With toluquinone or (IV), citraconic anhydride gives 2 : 6- (and/or 2 : 7-)*di*-, m.p. ~127° (560, 520, 485), or 2 : 3 : 6-*tri*-*methylnaphthazarin*, m.p. 165° (554, 516, 482), respectively. 2 : 3-Dihydronaphthazarin with an excess of $Bu^{\beta}CHO$ and HCl in warm AcOH gives a *di*iso*amylnaphthazarin*, m.p. 127° (562, 523, 487), and another *product*, but with 1 mol. of aldehyde gives in poor yield a *product*, $C_{25}H_{20}O_8$, m.p. 178°; with an excess of *iso*-$C_5H_{11}{\cdot}CHO$ (V) or *n*-$C_6H_{13}{\cdot}CHO$ it gives a *di*-(δ-*methyl*-n-*amyl*)-, m.p. 78°, or *di*-n-*heptyl*-*naphthazarin*, m.p. 114—115°, respectively. Naphthazarin (VI), (V), and conc. HCl in AcOH at 100° give mainly an amorphous product with some 1′-*dehydroalkannan* [2-δ-*methyl*-Δ^{α}-n-*pentenylnaphthazarin*] (VII), m.p. 111°, sublimes at 120—125°/0·0005 mm. (579, 534, 499), *diisobutylquinizarin*, m.p. 114° (469), and alkannan (VIII); under other conditions mainly (VIII) is obtained. H_2–PtO_2 in AcOH reduces (VII) to (VIII), whereby the structure of (VIII) is confirmed. With $Bu^{\beta}CHO$, (VI) gives Δ^{α}-iso*pentenyl*- (IX), m.p. 120—121°, and iso*amyl*-*naphthazarin*, m.p. 90° [obtained also by hydrogenating (IX)], and with *n*-$C_6H_{13}{\cdot}CHO$ gives *heptylnaphthazarin*, m.p. 92—93°. The mechanism of the aldehyde condensations is discussed. The alkyls of the dialkylnaphthazarins are probably in different rings. R. S. C.

Action of ammonia on anthraquinone in presence of reducing agents. I, II. H. Shingu (J. Soc. Chem. Ind. Japan, 1939, **42**, 173—174B).—Anthraquinone with NH_3 and $Na_2S_2O_4$ under pressure at 140—150° yields *meso*anthramine (I) (60% if 2 mols. of $Na_2S_2O_4$ are used), anthranol, dianthranol, and a N-containing ketodianthranyl (?) derivative, also produced, along with (I) (30%) and dihydrodianthronedi-imine (5%), from anthraquinol and NH_3. The mechanism of the reaction is discussed. Similar reductive amination of substituted anthraquinones has been investigated. A. Li.

Synthesis of hydroxyanthraquinone salts. II. Action of aqueous solutions of inorganic salts on hydroxyanthraquinones. G. Flumiani and V. Bajić (Monatsh., 1939, **72**, 368—372).—Addition successively of hydroxyanthraquinone (*A*) (0·2), $CuSO_4$ (0·2), and dil. H_2SO_4 (5—10 drops) to boiling H_2O (200 g.) gives the Cu salts (A., 1938, II, 237). Salts are formed only from OH in α-positions. Salts of the type, $Cu[(A) - H]_2$, are obtained in 20—70% yield from 1 : 2-di-, 1 : 2 : 6- and 1 : 2 : 7-tri-hydroxyanthraquinone, and of the type, $Cu_2[(A) - H]_2$, from 1 : 5- and (in aq. EtOH at 80°) 1 : 4-di- and 1 : 2 : 5 : 8-tetra-hydroxyanthraquinone. Salts are not obtained from 2-hydroxy-, 2 : 6- or 2 : 7-dihydroxy-anthraquinone. R. S. C.

Biochemistry of micro-organisms. LXII. Crystalline colouring matters of species in the *Aspergillus glaucus* series. II. J. N. Ashley, H. Raistrick, and T. Richards (Biochem. J., 1939, **33**, 1291—1303).—Rubroglaucin (A., 1934, 1263; 1937, II, 106) is a mixture of physcion (I) [4 : 5-dihydroxy-7-methoxy-2-methylanthraquinone], dimorphous, m.p. 203—204° (diacetate, new m.p. 186—187°), and the deep red *erythroglaucin* (II), $C_{16}H_{12}O_6$,

dimorphous, m.p. 205—206° [*triacetate*, m.p. 225°; *Me*$_3$ *ether* (III), m.p. 187—188°]. *Cynodontin Me*$_4$ *ether*, m.p. 233—234°, differs from (III), thus showing that (II), which is a tetrahydroxymethylanthraquinone Me_1 ether, is not a cynodontin Me_1 ether. In five of the species examined, (I) and (II) are accompanied by physcion anthranols *A*, m.p. ~260° (decomp.), and *B*, dimorphous, m.p. 181—182°; *B*, but not *A*, is obtained by reduction (Zn dust, AcOH) of (I) and both are oxidised (CrO_3–AcOH) to (I). These anthranols are probably 4 : 5-dihydroxy-7-methoxy-2-methyl-9- and -10-anthranols. Of the 17 species of *A. glaucus* examined, all give (I), (II) (except *A. mutabilis*), and flavoglaucin (except possibly *A. echinulatus*); 6 species give auroglaucin. H. B.

***d*-Neo*iso*menthol.** W. Hückel and H. Niggemeyer (Ber., 1939, **72**, [*B*], 1354—1358).—*l*-Piperitone is reduced (Pd–C in Pr$^{\beta}$OH) to a mixture of 70% of *d-iso*menthone and 30% of *l*-menthone, which is hydrogenated (Pt sponge in AcOH) to a mixture of *d*-neo*iso*menthol (I), (70%), *d*-neomenthol (II) (25%), and *l*-menthone (5%); *d-iso*menthol (III) does not appear to be present. When the mixture is treated with 70% of the theoretical quantity of 3 : 5-$(NO_2)_2C_6H_3$·COCl in C_5H_5N, nearly all of (II), which reacts very slowly, remains unaffected. The ester obstinately retains small amounts of *l*-menthyl dinitrobenzoate. It is therefore hydrolysed and the alcohol is purified through its *p*-nitro-, *p*-amino-, and *p*-benzamido-benzoate, thereby giving (I) with all the properties recorded by Read and Grubb (A., 1934, 528). Since, in acid solution, (I) is formed almost exclusively from *d-iso*menthone (IV), it follows that the vicinal substituents are in the *cis*-position to one another, thus confirming Read's view of the configuration of (I). This is further confirmed by the observation that d-*neo*iso*menthyl* p-*toluenesulphonate*, m.p. 66—67°, is as unstable as the ester of (II) whereas the esters of (III) and *l*-menthol are stable. In sign and magnitude [α] of (I), but not of (III), depends greatly on the solvent. Cautious oxidation of (I) with CrO_3 in AcOH gives almost homogeneous (IV), the oxime of which is reduced to the amine, which is purified through the hydrochloride, decomp. 258°, $[\alpha]_D^{20}$ +21·1° in H_2O. This is converted by HNO_2 into homogeneous (III), m.p. 83°, $[\alpha]_D^{20}$ +26·5° in EtOH (p-*toluenesulphonate*, m.p. 84·5°, $[\alpha]_D^{20}$ +5·88° in C_6H_6). *dl-iso*Menthol (p-*toluenesulphonate*, m.p. 64°) is most simply obtained by the hydrogenation (Ni at 140°/50—70 atm.) of thymol; the crude material is transformed into the *p*-nitrobenzoate, which is converted into the *p*-amino- and p-*benzamido*-, m.p. 119—120°, -*benzoate*, which is hydrolysed. H. W.

4-Methylbornylene and its hydration. A. I. Schavrigin (J. Gen. Chem. Russ., 1939, **9**, 516—521).—Dehydration by the xanthate method of 4-methylborneol or 4-methyl*iso*borneol (I) yields in both cases 4-methylbornylene; this yields chiefly (I) when hydrated by the methods of Bertram and Walbaum or of Kondakov. R. T.

Use of isotopes in chemical reactions. I. Mechanism of the Wagner–Meerwein rearrangement. Exchange of radioactive chlorine and of deuterium between camphene hydrochloride and hydrogen chloride. T. P. Nevell, E. de Salas, and C. L. Wilson (J.C.S., 1939, 1188—1199).—The conversion of camphene hydrochloride (I) into *iso*bornyl chloride (II) in presence of D radio-chloride proceeds in two steps, shown by comparing the speeds of rearrangement of Cl exchange and H exchange; the first step involves the rapid establishment of an ionic equilibrium by separation of Cl, and the second a relatively slow bimol. reaction between the org. ion and HCl. Experiments in pure $CHCl_3$ at 0° show that rearrangement is 1/15 as fast as Cl exchange. The difference between the mechanism for rearrangement and for H exchange is that interaction of the org. ion with HCl is much slower in the former case and much faster in the latter case than the preliminary halogen ionisation. The dissociation of (I) into camphene and HCl has no direct bearing on the rearrangement except in so far as it supplies the HCl necessary for the rearrangement when this has not been initially added. The bimol. reaction of the org. ion and HCl involves a Walden inversion and it follows that (II) has the *cis*-(*exo*-)configuration. It is concluded that D exchange involves one of the bridge heads; this process cannot involve a Walden inversion and therefore substitution of H by D proceeds with retention of configuration. F. R. S.

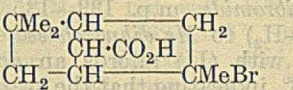
Action of acetic acid on α-pinene in presence of acetic anhydride and boron trioxide. I. Preparation of borneol. II. Identification of by-products. M. Imoto (J. Soc. Chem. Ind. Japan, 1939, **42**, 183—185B, 185—186B).—I. The influence of temp., quantity of AcOH and of catalyst, variation of reaction method, and the presence of dipentene or α-terpinyl acetate on the yields of bornyl and *iso*bornyl acetate is described.

II. Dipentene, camphene (?), α-terpinene, *p*-cymene, terpinolene, and α- and β-fenchyl acetates are by-products of the reaction. A. Li.

Camphor derivatives. III. Derivatives of camphor containing sulphur. T. Tukamoto (J. Pharm. Soc. Japan, 1939, **59**, 37—41).—π-*Thiol*-d-*camphor*, m.p. 94°, $[\alpha]_D^{22}$ +108·7°, is obtained in 21·7% yield by the reduction of *d*-camphor-π-sulphonyl chloride with powdered Sn and conc. HCl at 40—50° and subsequently at 100°, or in 11·4% yield by the use of Zn dust and AcOH under similar conditions. The *acetate*, m.p. 34°, *semicarbazone*, m.p. 219—220°, Hg derivative, blackens at ~260°, and the corresponding *disulphide*, m.p. 215°, are described. 10-Thiol-*d*-camphor, m.p. 66° (corresponding disulphide, m.p. 231°), is obtained in 40% yield by the action of Sn and HCl on *d*-camphor-10-sulphonyl chloride; the use of Zn dust and AcOH at 100° leads to *d*-camphor. *d*-Chlorocamphor π-sulphoxide is transformed by Zn dust and AcOH at 40—50° into *trans*-π-aldehydocamphor, m.p. 195—196°, with a little π-thiol. Under identical conditions chlorocamphor ω-sulphoxide (I) affords 10-*aldehydecamphor* (II), m.p. 205° (*semicarbazone*, m.p. 249°; identification by oxidation by $KMnO_4$ to ketopinic acid), and a little 10-thiol (III). With Zn dust and H_2O at 100° (I) affords some (II) but no (III). Thiocamphor

(IV), m.p. 118°, is prepared by treating camphoroxime in Et_2O with $NaNO_2$–20% H_2SO_4, whereby a mixture of camphorimine nitrate and pernitrosocamphor results, and this is converted by conc. aq. NH_3 into camphorimine, which with H_2S in C_6H_6 at 100° yields (IV). H. W.

[Reactions of] δ-fenchene-3-carboxylic acid. G. A. Nyman and E. Elomaa (Annalen, 1939, **539**, 266—275).—δ-Fenchene-3-carboxylic acid (I) (prep. from *dl-iso*fenchol-3-carboxylic acid modified to give a 68% yield) adds HBr in AcOH or H_2O to give *bromofenchanecarboxylic acid* [? (II)], m.p. 138—139°, and smaller amounts of an *isomeride*, m.p. 125·5°



(II.)

(decomp.), a pinacolinic rearrangement probably occurring. Removal of HBr from the Me ester by quinoline at 175—180° (followed by KOH–EtOH) or N-KOH–EtOH at 18° regenerates (I). Warm dil. NaOH, Na_2CO_3 at 50°, or Ag_2O at room temp. converts (II) into the corresponding *OH-acid*, m.p. 175—176°, which gives no lactone, is oxidised by HNO_3 (*d* 1·27) at 100° to an *acid*, $OH{\cdot}C_9H_{13}(CO_2H)_2$, m.p. 226·5°, and is converted by hot HCO_2H and subsequent distillation into (I) and a *OH-acid*, $C_{11}H_{18}O_3$, m.p, 213°, best obtained by boiling 18% HCl. R. S. C.

Triterpenes. L. Transformation of β-boswellic acid into α-amyrin. L. Ruzicka and W. Wirz (Helv. Chim. Acta, 1939, **22**, 948—951).—β-Boswellic acid has m.p. 236—238°, $[\alpha]_D$ +237° in $CHCl_3$. Acetyl-β-boswellic acid is converted by $SOCl_2$ at room temp. into *acetyl-β-boswellyl chloride*, m.p. 193°, which is reduced (Pd–$BaSO_4$ in PhMe) to the corresponding (impure) aldehyde (oxime, m.p. 226°), which gives a marked yellow colour with $C(NO_2)_4$. The *semicarbazone*, m.p. 281—284° (slight decomp.), is transformed by NaOEt–EtOH at 200° into α-amyrin, m.p. 185—187°, $[\alpha]_D$ +91·4° in C_6H_6 (acetate, m.p. 225—226°, $[\alpha]_D$ +83·3° in $CHCl_3$; benzoate, m.p. 193—194°). H. W.

Triterpene resinols and related acids. VII. D. E. Seymour, K. S. Sharples, and F. S. Spring (J.C.S., 1939, 1075—1078).—Oxidation (H_2O_2) of α-amyrenyl benzoate gives a compound, m.p. 302—304° (small amount), and *α-amyranonyl benzoate* (I), m.p. 205—206°, $[\alpha]_D^{19·5}$ +113·6° in $CHCl_3$, which is reduced (Na–$C_5H_{11}{\cdot}OH$) to *dihydroxy-α-amyrane*, m.p. 199—201°, $[\alpha]_D^{19·5}$ +70·5° in $CHCl_3$ (*diacetate*, m.p. 203—205°, $[\alpha]_D^{19·5}$ +90·0° in $CHCl_3$). Br and (I) yield iso-*α-amyrenonyl benzoate*, m.p. 205—206°, $[\alpha]_D^{19·5}$ +81·66° in $CHCl_3$, which when reduced (Na–$C_5H_{11}{\cdot}OH$) and treated with Ac_2O affords α-amyradienyl acetate, identical with that prepared from α-amyrenonol; the benzoate is hydrolysed (KOH) to iso-*α-amyrenonol*, m.p. 237—238°, $[\alpha]_D^{19·5}$ +72·11° in $CHCl_3$ (*Ac* derivative, m.p. 276·5°). This series of reactions emphasises the similarity in properties of the α- and β-amyrenols and points to a close structural resemblance of the unsaturated rings of these alcohols; the unsaturated centre of the α-isomeride is considerably less reactive than that of the β-isomeride. F. R. S.

Identity of pyrethrosin with chrysanthin and non-identity with geigerin. M. S. Schechter and H. L. Haller (J. Amer. Chem. Soc., 1939, **61**, 1607—1609).—Pyrethrosin (I) (preferred name) (Thoms, A., 1892, 349) is identical with chrysanthin (Rose *et al.*, A., 1938, II, 239) and chrysanthin (Chou *et al.*, A., 1934, 1007). (I), $C_{17}H_{22}O_5$, m.p. (from EtOAc) 201° or (from EtOH) 177—178°, $[\alpha]_D^{20}$ −30·5° in $CHCl_3$, −38·1° in abs. EtOH, reacts with 2 mols. of alkali forming AcOH and an acid, $C_{15}H_{26}O_7$, and gives no 2 : 4-dinitrophenylhydrazone. Geigerin (Rimington *et al.*, Onderstepoort J. Vet. Sci., 1936, **7**, 485) differs therefrom, having double m.p. (α-form) 78° and 189°, (β-form) 68° and 169°, $[\alpha]_D^{20}$ − 42·58° in $CHCl_3$, −60·23° in abs. EtOH, giving a 2 : 4-dinitrophenylhydrazone, reacting with 2 mols. of alkali to give an acid, $C_{15}H_{22}O_5$, and differing also in reactions with HCl, H_2SO_4, Br–$CHCl_3$, and $KMnO_4$. R. S. C.

Constituents of species of *Helenium*. II. Tenulin. E. P. Clark (J. Amer. Chem. Soc., 1939, **61**, 1836—1840; cf. A., 1936, 1574).—*Helenium macrocephalum* contains helenalin, which is a vermifuge, fish poison, and insecticide. Extraction of *H. tenuifolium*, *H. elegans*, or *H. badium* with $CHCl_3$ yields, often with difficulty and in variable yield, *tenulin* (I), $C_{17}H_{22}O_5$, m.p. 193—195°, $[\alpha]_D^{20}$ −21·6° in EtOH, which gives no reactions for OH, CO, CO_2H, or OR. H_2–PtO_2 reduces (I) in EtOAc to *dihydrotenulin*, m.p. (? + solvent) 182°, (anhyd.) 172° [*phenylhydrazone*, m.p. 248° (decomp.)]. Br in EtOAc gives a *dibromide* ["dibromotenulin,"] $C_{17}H_{22}O_5Br_2$, m.p. 124—125° (decomp.), and, from the mother-liquors, after 2—3 days "*bromotenulin*," $C_{17}H_{21}O_5Br$, m.p. 202—203° (decomp.). When heated at 300°, (I) evolves gas and yields *anhydrotenulin*, $C_{17}H_{20}O_4$, m.p. 172°. With NaOAc in boiling Ac_2O, (I) gives a *substance*, $C_{22}H_{26}O_5$, m.p. 240°. Alkali under various conditions converts (I) into an isomeride, iso*tenulin* (II), m.p. variable between 157° and 160—161° (obtained from *H. tenuifolium* by the method of Buehler *et al.*, A., 1938, III, 161), with (under some conditions) a *substance*, $C_{15}H_{20}O_4$, m.p. 255°. By the methods used for (I), (II) gives a H_2-derivative, m.p. 151° (*phenylhydrazone*, m.p. 219—220°), "*dibromo-*" [a *dibromide*], m.p. 135° (decomp.), and *bromo*-iso*tenulin*, m.p. 213° (decomp.). One lot of *H. tenuifolium* gave (I) and a *substance*, $C_{16}H_{22}O_5$, m.p. 233—234° (gives RI equiv. to 3·85% of OMe; H_2-, m.p. 192°, and two *Ac* derivatives, m.p. 163° and 193°). R. S. C.

Constitution of forsythin. II. S. Kunimine and S. Wada (J. Pharm. Soc. Japan, 1938, **58**, 182—185).—Nitration of *d*-forsythigenol Me ether (I) gives a $(NO_2)_2$-derivative, m.p. 180° [with HNO_3 affords 4 : 5 : 1 : 2-$(NO_2)_2C_6H_2(OMe)_2$], and 4 : 1 : 2-$NO_2{\cdot}C_6H_3(OMe)_2$. Hot MeOH–HCl converts (I) into pinoresinol Me_2 ether (II) [diastereoisomeric with, and also converted by MeOH–HCl into, (I)] and *d-epi*forsythigenol Me ether (III), m.p. 133—134° [$(NO_2)_2$-derivative, m.p. 230°]. Fission of the CH_2O_2 group of *d*-sesamin and subsequent methylation gives (I), (II), and a compound corresponding with (III). H. B.

Isolation of elemi resin acids. M. Mladenović (Monatsh., 1939, **72**, 350—353).—NH_3 in wet Et_2O ppts. some, but not all, of the NH_4 salts (cryst.) of the acids from elemi resin in a very pure state. No pptn. occurs in dry Et_2O. β-Elemonic and γ-elemic acid are completely pptd., and thus it is the neutral constituents which hinder pptn. from the resin. R. S. C.

Glycyrrhetic acid. K. Takeda (J. Pharm. Soc. Japan, 1938, **58**, 194—197).—Glycyrrhetic acid, m.p. 292—294°, $[\alpha]_D$ +160·3° in $CHCl_3$ (cf. lit.) [acetate, m.p. 314—317°; Me ester (I), m.p. 258°, $[\alpha]_D$ +154·8° in $CHCl_3$ (acetate, m.p. 301—303°; *dibromide*, decomp. 180—181°)], is obtained from K glycyrrhizate and 1% H_2SO_4 at 130—140°/3·5—4 atm. Oxidation (CrO_3–AcOH at 50—60°) of (I) gives *Me ketoglycyrrhetate*, m.p. 251° (*oxime*, m.p. 260°; *semicarbazone*, decomp. 250°), reduced [$Al(OPr^\beta)_3$ in PrOH–C_6H_6] to (I). S. H. H.

Sweet constituents of liquorice root. G. Kurono (J. Pharm. Soc. Japan, 1938, **58**, 220).—Me glycyrrhetinate and CrO_3–AcOH give *Me ketoglycyrrhetinate*, $C_{31}H_{46}O_4$ (*oxime*, m.p. 288·5°; *semicarbazone*, m.p. 254°). Glycyrrhetinic acid with Na in hot EtOH gives *dehydrohydroglycyrrhetinic acid*, $C_{30}H_{46}O_3$, m.p. 287° [*Me* ester, m.p. 272°; *acetate*, m.p. 261°; unsaturated to $C(NO_2)_4$], and, when distilled at 380—400°, gives a (?) *hydrosapotalene*, $C_{13}H_{20}$, b.p. 95—100°/2 mm., converted by Se into sapotalene. R. S. C.

Smilagenone: a correction. G. A. R. Kon, H. R. Soper, and A. M. Woolman (J.C.S., 1939, 1201).—Smilagenone, prepared on a larger scale (cf. A., 1936, 1386), has m.p. 187—189° (lit. 157°). o-*Bromobenzoates* have been found suitable for characterisation of smilagenin (m.p. 196—197°) and sarsasapogenin (m.p. 178—179°). F. R. S.

Identity of soja-sapogenol *B* with a new sterol ("sapogenol") from shoyu oil. K. Tsuda and T. Kazano (J. Pharm. Soc. Japan, 1939, **58**, 142).—Sapogenol, $C_{30}H_{50}O_3$, m.p. 258° (A., 1937, II, 417), is identical with soja-sapogenol *B*, m.p. 259° (Tsuda *et al.*, A., 1938, II, 24, 239). A. T. P.

Pittosapogenin, $C_{30}H_{50}O_7$, m.p. 308—310°, $[\alpha]_D^{20}$ +27·8° in $CHCl_3$ + MeOH (acetate, m.p. 252—254°), and compound, m.p. 51—52°, from *Pittosporum undulatum*.—See A., 1939, III, 638.

Saponins. III. Dissociation constant and potentiometric titration of sapoalbinic acid. R. Ruyssen and E. O. K. Verstraete (Natuurwetensch. Tijds., 1939, **21**, 125—136).—Sapoalbinic acid, obtained by dialysis of the saponins from soapwort, behaves like a monobasic org. acid, $\alpha = 7{\cdot}05 \times 10^{-5}$ in concns. 1·25—10% from concn.–p_H and κ measurements. The results deviate at lower and higher concns. in the latter case owing to aggregation. The equiv. is const. over a wide range of concns. at 1545. Conductometric methods cannot be used for standardising solutions of saponin acids. Direct titration with indicators (phenolphthalein) of the saponin acid and the sapogenin obtained by hydrolysis shows that the CO_2H occurs only in the saponenin part of the mol. S. C.

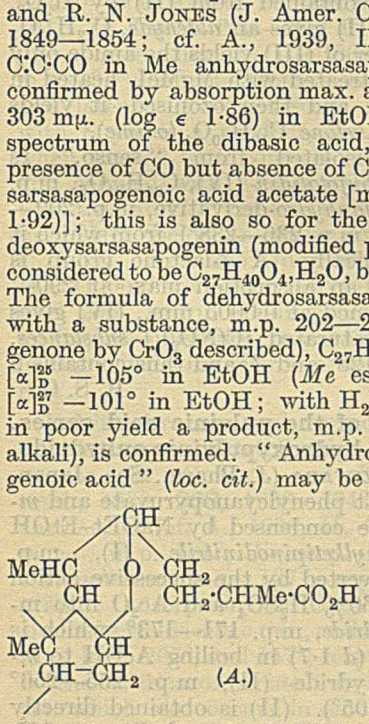
Sapogenins. V. Bassic acid. VI. Quillaic acid. D. F. Elliott and G. A. R. Kon (J.C.S., 1939, 1124—1129, 1130—1135).—V. *Bassic acid* (I), $C_{30}H_{46}O_5$, has been isolated from several species of *Bassia* and is shown to be an acid of the triterpene series; it has m.p. 316°, $[\alpha]_D$ +82·4° in C_5H_5N [(+H_2O), from EtOAc; (+MeOH) from MeOH; (+BuOH) from BuOH], and forms a *Me* ester (II), m.p. 212°, $[\alpha]_D$ +64° in $CHCl_3$. Dehydrogenation (Se) of (I) gives sapotalene (1 : 2 : 7-$C_{10}H_5Me_3$), 2 : 7-$C_{10}H_6Me_2$, 1 : 8-dimethylpicene (small amount), and (?) 1 : 2 : 5 : 6-$C_{10}H_4Me_3$·OH (small amount). Br and (II) yield a *dibromide*, m.p. 133—135°, and (II) is reduced (PtO_2–H_2) to *Me dihydrobassate*, m.p. 172—173°. $COMe_2$ with (II) affords an *acetonyl* derivative, m.p. 205°, indicating that the two OH involved in its formation must be in the 1 : 3 position; one of these OH must be primary since oxidation (Cu) of (II) gives CH_2O and a neutral diketone, $C_{30}H_{44}O_4$ (2 : 4-*dinitrophenylhydrazone*, m.p. 184°). With Ac_2O, (II) forms *triacetylbassic acid* (+H_2O), m.p. 117° (*Me* ester, m.p. 95—96°), and with Br–AcOH gives a *Br lactone*, m.p. 220°. The two OH, CO_2H, and a double bond in (I) occupy positions similar to those of other sapogenins but there is another OH and a reactive double bond the positions of which still remain to be determined. A partial formula for the compound is suggested.

VI. Quillaic acid (II), m.p. 292—293°, $[\alpha]_D$ +56·1° in C_5H_5N, is $C_{30}H_{46}O_5$ and not $C_{29}H_{44}O_5$ (cf. Windaus *et al.*, A., 1927, 42); it forms a Me ester, m.p. 222—223°, $[\alpha]_D$ +40·5° in C_5H_5N. Hydrogenation (H_2–PtO_2) of (III) gives *dihydroquillaic acid*, m.p. 315—316°, $[\alpha]_D$ +32° in C_5H_5N, formed by the reduction of the CO, and the *Me* ester, m.p. 269—270°, affords an *acetonyl* derivative, m.p. 256—259°, indicating the presence of 1 : 3-$(OH)_2$. The H_2-acid is unsaturated since it gives a saturated *triacetyl-lactone*, m.p. 247—249°. With AcOH–HBr, (III) forms a *diacetyl-lactone*, m.p. 260°, $[\alpha]_D$ −21·5° in $CHCl_3$, deacetylated to *quillaic lactone*, m.p. 315°, and oxidised (H_2CrO_4–AcOH) to an *acid*, $C_{33}H_{46}O_6$, m.p. 380° (*Me* ester, m.p. 375°), and its *Ac* derivative, m.p. 278—280°; the formation of these products indicates that (III) is an aldehyde. The C_{30} acid is further oxidised (H_2CrO_4) to a neutral *compound*, $C_{29}H_{42}O_4$, m.p. 296—297°, $[\alpha]_D$ −83·5° in $CHCl_3$ (*semicarbazone*, m.p. 301—302°; 2 : 4-*dinitrophenylhydrazone*, m.p. 298—299°), and several acids, one of which has m.p. 290—291° and gives a *Me* ester, m.p. 206°. Oxidation (H_2CrO_4) of (III) yields a neutral compound, $C_{29}H_{40}O_5$, m.p. 256—260°. These results show that (III) contains CH(OH)·C·CHO, doubtless situated in ring A; the position of the second OH has not yet been determined, but it is shown that it cannot be in rings A or C. (III) is probably a hydroxygypsogenin. F. R. S.

Constituents of the leaves of certain *Leucadendron* species. II. Degradation experiments with leucodrin. W. S. Rapson (J.C.S., 1939, 1085—1089).—Dibromoleucodrin (I) gives a series of derivatives analogous to those of leucodrin (II), and it appears as if its acidity is due to the presence

of halogen in the *m*-positions. $COMe_2$ and (I) afford iso*propylidenedibromoleucodrin*, m.p. 257° (*Ac*$_2$ derivative, m.p. 218—221°), which with CH_2N_2–MeOH yields the *Me ether*, sinters 175—176°, hydrolysed to *dibromoleucodrin Me ether*, m.p. 179—180°. MeI–Ag_2O with (I) gives a *Me*$_4$ *ether*, m.p. 136·5—137·5°. The action of $Pb(OAc)_4$ on (II) and various derivatives gives CH_2O but no other recognisable product. Acetyliso*propylideneleucodrin* Me ether is hydrolysed to *monoacetyl-leucodrin Me ether*, m.p. 102—103°, and methylated followed by hydrolysis to iso*propylideneleucodrin Me*$_2$ *ether*, m.p. 123·5—124·5°. *Leucodrin Me*$_4$ *ether*, m.p. 123—124°, cannot be degraded with $KMnO_4$ but with HNO_3 gives *nitroleucodrin Me*$_4$ *ether*, m.p. 162—163°, which with more conc. acid affords a *dilactonic acid*, $C_{18}H_{19}O_{11}N$, m.p. 139—140·5° (*Et* ester, m.p. 169·5—170·5°). Bromination of the Me_4 ether yields *bromoleucodrin Me*$_4$ *ether*, m.p. 158·5—159·5°, which with NH_3 does not form a dihydroxydiamide. Oxidation (H_2O_2) of the Me ether of (II) gives anisylsuccinic acid. The presence of $\geqslant C{\cdot}CH[C_6H_4{\cdot}OH(p)]{\cdot}CH_2{\cdot}C\leqslant$ in (II) seems certain. F. R. S.

Sarsasapogenin. IV. Sarsasapogenoic acid and related compounds. L. F. Fieser, E. M. Fry, and R. N. Jones (J. Amer. Chem. Soc., 1939, **61**, 1849—1854; cf. A., 1939, II, 31).—Presence of C:C·CO in Me anhydrosarsasapogenoate acetate is confirmed by absorption max. at 243 (log ϵ 4·13) and 303 mμ. (log ϵ 1·86) in EtOH. The absorption spectrum of the dibasic acid, $C_{27}H_{40}O_7$, indicates presence of CO but absence of C:C·CO, as does that of sarsasapogenoic acid acetate [max. at 281 mμ. (log ϵ 1·92)]; this is also so for the acid, obtained from deoxysarsasapogenin (modified prep.), and previously considered to be $C_{27}H_{40}O_4,H_2O$, but now $C_{27}H_{42}O_4,H_2O$. The formula of dehydrosarsasapogenoic acid (prep. with a substance, m.p. 202—209°, from sarsasapogenone by CrO_3 described), $C_{27}H_{40}O_5$, m.p. 164—165°, $[\alpha]_D^{25}$ −105° in EtOH (*Me* ester, m.p. 125—126°, $[\alpha]_D^{27}$ −101° in EtOH; with H_2–PtO_2 in AcOH gives in poor yield a product, m.p. ~200°; unstable to alkali), is confirmed. "Anhydrotetrahydrosarsasapogenoic acid" (*loc. cit.*) may be



(*A.*)

(*A*). Tschesche and Hagedorn's formula for sarsasapogenin (cf. *loc. cit.*) is held to account for the effects of acid, whilst Marker's formula (A., 1939, II, 276) does not accommodate the results of oxidation and the evidence in its favour is largely negatived by the following results. Octahydro-2 : 2′-difuryl [prep. from 2 : 2′-difuryl by H_2–Raney Ni at 150°, but not by H_2–PtO_2 or H_2–Pd–C (cf. Kondo *et al.*, J. Pharm. Soc. Japan, 1935, **55**, 142)], b.p. 77—80°/13 mm., reacts slowly with Br and a little HBr in AcOH, and (unless freshly purified) reduces SeO_2 and absorbs H_2 (PtO_2; HCl–EtOH), and suffers fission of one ring by HCl–AcOH at 88° giving a glycol (*bis*-3 : 5-*dinitrobenzoate*, cryst.). Tetrahydro-furoamide, m.p. 65—76° b.p. 135—138°/10 mm., and MgMeCl give 2-acetotetrahydrofuran, b.p. 52·3—54·8°/10 mm. (2 : 4-*dinitrophenylhydrazones*, orange, m.p. 122—124°, and yellow, m.p. 135—136°), which is unstable to alkali. R. S. C.

Sterols. LXVII. Sarsasapogenin derivatives. Bromo-compounds. R. E. Marker and E. Rohrmann (J. Amer. Chem. Soc., 1939, **61**, 1921—1922).—Sarsasapogenin (I) and Br in AcOH containing a trace of HBr give *bromosarsasapogenin*, $C_{27}H_{43}O_3Br$, decomp. ~125°, which is oxidised by CrO_3 in 80% AcOH to *bromosarsasapogenone*, m.p. 191° (decomp.), also obtained by brominating sarsasapogenone, which, however, with more Br gives *dibromosarsasapogenone*, m.p. 190° (decomp.). Reduction of bromosarsasapogenin acetate by Na–C_5H_{11}·OH or –EtOH gives (I), by H_2–PtO_2 in AcOH at 70°/3 atm. gives di- and by Zn–Hg–HCl gives tetra-hydrosarsasapogenin. Boiling C_5H_5N or $AgNO_3$–C_5H_5N at 25° has no effect on (II). R. S. C.

***allo*Strophanthidin.** E. Bloch and R. C. Elderfield (J. Org. Chem., 1939, **4**, 289—297).—Evidence is adduced in favour of the view that the isomerisation involved in the allomerisation of cymarin consists in an inversion of one of the asymmetric centres of the strophanthidin mol., probably at $C_{(14)}$ but possibly at $C_{(17)}$. *allo*Strophanthidin is oxidised by $KMnO_4$ in $COMe_2$ at 5° to allo*strophanthidinic acid*, $C_{23}H_{32}O_7$, m.p. 247°, $[\alpha]_D^{22}$ +39·2° in MeOH, the *Me* ester, m.p. 263—265°, of which is converted by CrO_3 in AcOH into *Me* allo*strophanthidonate*, m.p. 258°, $[\alpha]_D^{20}$ +20·1° in C_5H_5N (*Me strophanthidonate* has m.p. 161—162°, $[\alpha]_D$ +26° in C_5H_5N). This is transformed by boiling MeOH–10% HCl into *Me monoanhydro*allo*strophanthidonate*, m.p. 138—145°, $[\alpha]_D^{20}$ +118° in C_5H_5N. *Dianhydro*allo*strophanthidin*, m.p. 172—175°, $[\alpha]_D^{20}$ −123·1° in C_5H_5N, obtained by the action of EtOH–HCl on dianhydro*allo*strophanthidin oxidoethylal, is rapidly converted by conc. HCl into a *Cl*-derivative, m.p. 165°, transformed by NH_3 in boiling EtOH into dianhydro*allo*strophanthidin. *allo*Strophanthidin is converted by HCl (*d* 1·19) at 0° into an unstable *Cl*-derivative, $C_{23}H_{31}O_5Cl$, m.p. 175°, transformed by NH_3–EtOH into *anhydro*allo*strophanthidin*, m.p. 205°, $[\alpha]_D^{20}$ +119° in EtOH (3-*Bz* derivative, m.p. 252°; *oxime*, m.p. 182°). H. W.

Amber. V. L. Schmid and W. Hosse (Monatsh., 1939, **72**, 290—302).—Amber is extracted with EtOH. The extract is partly sol. in light petroleum and the dissolved portion is pptd. from the solution by MeOH. After treatment with Na_2CO_3 the material is purified chromatographically (Al_2O_3 in C_6H_6). The *substance*, m.p. 140°, $[\alpha]_D^{17\cdot5}$ +58° in C_6H_6, thus obtained is hydrolysed by KOH–MeOH to a resin *acid*, $C_{25}H_{40}O_4$, m.p. 136—139°, $[\alpha]_D^{17}$ +29° in C_6H_6 (*Me* ester, m.p. 125—127°; *Ac* derivative, m.p. 96—98°), and a resin *alcohol* (I), $C_{25}H_{36}O_2$, m.p. 117°, $[\alpha]_D^{18}$ +45·7° in C_6H_6 (*acetate*, m.p. 55—56°), which slowly gives a yellow colour with $C(NO_2)_4$ and is dehydrogenated by Se at 260—280° and then at 350° to 1 : 2 : 5-$C_{10}H_5Me_3$ and pimanthrene (II). The portion of amber which remains in Et_2O after removal of the acids when purified chromatographically gives two fractions, m.p. 110—130°, $[\alpha]_D^{18}$ +34·7° in C_6H_6 and $[\alpha]_D$ +26·7° in C_6H_6, respectively, the former of which is dehydrogen-

ated by Se to agathaline and (II). Either fraction when hydrolysed by alkali gives a resin *acid*, m.p. 130—135°, $[\alpha]_D^{19}$ +47·2° in C_6H_6 (*Me* ester, m.p. 120°; *Ac* derivative, m.p. 98°, $[\alpha]_D^{18}$ +52·8° in C_6H_6), and an alcohol, m.p. 113—115°, $[\alpha]_D^{19}$ +45·7° in C_6H_6 (acetate, m.p. 56—58°, $[\alpha]_D^{18}$ +62·6° in $COMe_2$), which slowly affords a yellow colour with $C(NO_2)_4$ and does not depress the m.p. of (I). H. W.

Amber. VI. Acids occurring in amber. L. Schmid [with T. Lenzer and E. Blum] (Monatsh., 1939, **72**, 311—321).—Prep. of amorphous succinoabietinolic (I), $OH{\cdot}C_{35}H_{50-52}O_3{\cdot}CO_2H$, m.p. 125—128°, $[\alpha]_D^{17}$ +26·34° in EtOH, and succoxyabietic acid (II), m.p. ~92—95°, $[\alpha]_D^{18}$ +16° in EtOH, from amber is described (cf. Schmid *et al.*, A., 1933, 831). (I) gives a *Ag* salt, sensitive to light, contains 2 active H, cannot be acetylated, gives no CO-reactions, is unaffected by H_2–PtO_2 in AcOH, and thus does not contain CO·C:C. It gives a *Me* ester, m.p. 82—85°, hydrolysed by 5% KOH–MeOH to a different *acid*, m.p. 121—124°, which is also obtained from (I) by alkali. (II) is a mixture; methylation does not stop at the CO_2H. With Se at 260—350°, (II) gives $(CH_2{\cdot}CO_2H)_2$ and 1 : 2 : 5-$C_{10}H_5Me_3$, but (I) gives also pimanthrene. As (I) and (II) are very sensitive to O_2, all the products hitherto isolated from amber may be decomp. products. R. S. C.

Acid, m.p. 133°, isomeric with marindinin, from *Piper methysticum*.—See A., 1939, III, 734.

Gibberellin-*A*, m.p. 194—196°, and -*B*, m.p. 245—246° (decomp.), $[\alpha]_D$ +36·13° in MeOH, from rice fungus.—See A., 1939, III, 627.

Neutral substance, $C_{16}H_{26}O$, m.p. 190°, from *Asclepias syriaca*, L.—See A., 1939, III, 639.

Constitution of crystalline constituent of the bark and leaves of *Abies mariesii*, Mast. I. T. Takahashi (J. Pharm. Soc. Japan, 1938, **58**, 273—276).—Warm EtOAc extracts from the bark and leaves a *compound* (I), $C_{30}H_{44}O_3$, m.p. 255°, $[\alpha]_D^{12}$ −96·93° in $CHCl_3$ [amorphous *tetrabromide*, m.p. ~130° (decomp.)], which is a lactone and contains OMe and :CHMe. It is reduced (H_2, Pt-black, EtOAc) to a H_2-derivative, m.p. 225°; in Et_2O, H_4-, m.p. 206—207°, and H_8-, m.p. 191—193°, -derivatives result. Hydrolysis (0·5N-EtOH–KOH) of (I) gives an amorphous *OH-acid* (II), $C_{29}H_{45}O_2{\cdot}CO_2H,H_2O$, m.p. 85—90° (decomp.) (K salt), another *acid*, m.p. ~120° (decomp.), and a neutral *substance*, m.p. 122—123°. Hot Ac_2O converts (II) into (I); Br–AcOH gives a *tetrabromide*, m.p. ~125° (decomp.), whilst NH_2OH affords a *compound*, $C_{30}H_{49}O_4N_3$, m.p. 186°, insol. in cold 20% H_2SO_4 or 30% KOH. Boiling 2% EtOH–HCl converts (I) into an *isomeride*, m.p. 215°, whilst 0·5N-EtOH– or 0·05N-MeOH–H_2SO_4 gives an *isomeride*, m.p. 24° (? 224°). Oxidation of (I) with CrO_3 (≡ 3·8 O_2) in AcOH at 55—60° affords an amorphous OMe-free *acid*, $C_{20}H_{32}O_3$, m.p. ~130° (decomp.), and a diketonic *OMe-lactone*, $C_{28}H_{38}O_5$, m.p. 218—221° [*dioxime* (+ NH_2OH), m.p. ~130° (decomp.); *dibromide*, m.p. 145—150° (decomp.), whence it is inferred that (I) contains 2 double linkings]. Oxidation ($KMnO_4$ ≡ 3 O_2) of (I) gives $H_2C_2O_4$ and a *OMe-lactone*, $C_{28}H_{42}O_4$, m.p. 90—95° (decomp.), which is further oxidised by CrO_3 (1·5 mols.) in AcOH to an *acid*, $C_{20}H_{30(32)}O_5$, m.p. 135—140° (decomp.); $KMnO_4$ (≡ 5·8 O_2) in AcOH at ~70° oxidises (I) to a *OMe-acid*, $C_{28}H_{42}O_5$, m.p. 215° (? Ac_1 derivative, m.p. 242—243°). H. B.

Constituents of "senso." VII. New constituent of native toad poison: F_3-bufotalin. H. Kondo and S. Ohno (J. Pharm. Soc. Japan, 1938, **58**, 102—103).—In addition to compounds previously described (cf. A., 1938, II, 197), toad poison contains F_3-*bufotalin*, $C_{24}H_{32}O_5$, m.p. 243—245°. (Cf. A., 1939, II, 382.) E. W. W.

Constituents of "senso." VIII. Ozonisation of acetyl-ψ-deacetylbufotalin. IX. Cinobufotalidin, a substance accompanying cinobufagin. H. Kondo and S. Ohno (J. Pharm. Soc. Japan, 1938, **58**, 232—234, 235—237).—VIII. The δ-lactone structure of ψ-deacetylbufotalin is confirmed by conversion of its Ac derivative by O_3 in $CHCl_3$ into CH_2O, HCO_2H, and $H_2C_2O_4$ [proof of $CR\langle^{CH:C(OH)}_{CH\text{——}O}\rangle CO$] with an *α-keto-aldehyde* (I), $C_{23}H_{34}O_6$, and an *α-keto-acid* (II), $C_{23}H_{34}O_7$. With $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$, (I) gives a *triazine*, and with AcO_2H, followed by H_2O_2, gives an amorphous *acid* (III), $C_{20}H_{32}O_5$, also obtained from (II) by H_2O_2. When kept in acid, (II) gives an *aldehyde*, $C_{22}H_{34}O_5$ (*oxime*). The Me ester of (III) yields the amide only incompletely; when treated with MgMeI, heated in xylene at 100—120°, and then ozonised, it yields $COMe_2$ and the cyclic *ketone*, $C_{19}H_{30}O_4$ (*oxime*).

IX. Cinobufagin, isolated from "senso," is accompanied by *cinobufotalidin* (IV), $C_{24}H_{34}O_6$, m.p. 217° (decomp.) (*acetylanhydro*-derivative, m.p. 209—210°; *p-nitrobenzoate*, m.p. 236—238°), from which it is separated mechanically. A δ-lactone group is indicated in (IV) by an absorption max. at 290—300 mμ. When sublimed at 0·0005 mm., (IV) gives 2 H_2O and two unsaturated $[C(NO_2)_4]$ *substances*, $C_{24}H_{30}O_4$, m.p. 125—128° and ?, and thus contains 2 *tert.* OH. R. S. C.

Lichen pigments of the pulvinic acid series. V. Synthesis of *m*-hydroxypulvinic anhydride. M. Asano and S. Fuziwara (J. Pharm. Soc. Japan, 1939, **59**, 83—85).—Et phenylcyanopyruvate and *m*-$OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}CN$ are condensed by NaOEt–EtOH to m-*methoxydiphenylketipinodinitrile* (I), m.p. 207·5° (decomp.), converted by the successive action of AcOH in boiling 60% H_2SO_4 and Ac_2O into m-*methoxypulvinic anhydride*, m.p. 171—173°, which is demethylated by HI (*d* 1·7) in boiling AcOH to *m*-hydroxypulvinic anhydride (II), m.p. 255—256° (acetate, m.p. 202—205°). (II) is obtained directly from (I) by the action of HI (*d* 1·7) in boiling AcOH. H. W.

Components of resins. XIII. Constitution of hinokiol. G. Fukui and T. Chikamori (J. Pharm. Soc. Japan, 1939, **59**, 86—91).—Methylhinokiol is oxidised with CrO_3 and the resulting ketone is reduced (Clemmensen or Wolff–Kishner) to a yellow liquid, b.p. 170—173°/3 mm., which is dehydrogenated (Se) to methoxyretene (I), m.p. 80°. Reduction of hinokione (II) (Clemmensen) and dehydrogenation of the product yields hydroxyretene (II), m.p. 179—

180°, methylated to (I). The OH of (II) is that which was originally present in hinokiol as ·CH_2·OH. $K_3Fe(CN)_6$ is without action on (III). Dehydrogenation of hinokiol (IV) with Cu powder affords (II). (IV) is therefore at diterpene alcohol with a phenolic nucleus. Application of the isoprene rule leads to a modification of the formula of (IV) from $C_{19}H_{28}O_2$ to $C_{20}H_{30}O_2$. Hence (IV) is a dihydroxydimethyloctahydroretene, the nucleus and side-chains of which are derived from four isoprene residues. In addition to (IV) and hinokinin, cuprescus resin yields (II). H. W.

Constitution of clerodin, the active bitter principle of *Clerodendron infortunatum*. II. H. N. Banerjee (Trans. Bose Res. Inst., 1936—1937, 75—88; cf. A., 1938, II, 288).—The following reactions of clerodin are described. Reduction (H_2–Pt in *cyclo*hexane–AcOH, or Zn + AcOH) yields *dihydroclerodin*, m.p. 115° (decomp., shrinks at 80°). MgMeI in amyl ether gives 1 mol. of CH_4 per mol. 10% H_2SO_4 at 100° yields the compound obtained (*loc. cit.*) by hydrolysis with EtOH–KOH. Cold conc. HCl removes the Ac group, giving a *compound*, $C_{11}H_{15}OCl$, m.p. >360°, containing no active H. Fusion with KOH at 200° yields an amorphous substance (decomp. 360; unaffected by CH_2N_2), further fusion of which at 250—300° affords an acid, m.p. 90—91°, equiv. wt. 104. Zn dust at 250—360° in a current of H_2 yields first a green liquid (I) (C 90·0, H 10·0%) [picrate, m.p. 131°; nitrate (containing N 8·2%), m.p. 88°], and later a brown, viscous oil. Dehydrogenation with S yields a product, b.p. 200°/20 mm., which when treated with conc. HNO_3, reduced, diazotised, and coupled with β-$C_{10}H_7$·OH yields a scarlet dye, whilst Se at 170° yields (I). Oxidation with $KMnO_4$ in $COMe_2$ yields an aromatic monobasic *acid* (II), $C_{13}H_{16}O_4$, m.p. 265° (decomp.); HNO_3 gives CO_2, $H_2C_2O_4$, and a NO_2-derivative (C 61·2, H 7·1, N 7·2%), m.p. 206°, sol. in alkali, whilst CrO_3 yields (II) and an impure substance, m.p. 117—120°, $[\alpha]_D$ −21°. It is concluded that clerodin contains an unsaturated ring. A. Li.

Echinochrome and spinochrome. Methoxy-derivatives. Distribution. Associated pigments. R. Glaser and E. Lederer (Compt. rend., 1939, **208**, 1939—1942).—Excess of echinochrome (I) (cf. A., 1938, II, 448) with CH_2N_2 gives *mono-*, m.p. 191°, *di-*, m.p. 161°, and *tri-methoxyechinochrome*, m.p. 137°, separated by chromatographic adsorption on $CaCO_3$. Spinochrome (II) similarly yields *mono-*, *di-*, and *tri-methoxyspinochrome*, m.p. 176°, 265°, and 147°, respectively. The pigment in the ovaries of *Arbacia æquituberculata* is mainly (I), which also occurs in small amounts [with (II)] in the violet scales of *Strongylocentrotus lividus*. In the former iso*echinochrome*, m.p. 247°, and an unidentified pigment are also found. The latter contains (II) together with brown pigments which give colour reactions with $FeCl_3$. J. L. D.

Scission of hydrofuran and hydropyran rings with acetic anhydride. R. Paul (Bull. Soc. chim., 1939, [v], **6**, 1162—1173; cf. A., 1939, II, 274). Orientation of the unsaturated OAc compounds (*loc. cit.*) is determined by identifying the R·CHO after treating the ozonide with Zn (+$AgNO_3$). 2-Methyltetrahydropyran and Ac_2O–$ZnCl_2$ at 200° give αε-diacetoxyhexane, b.p. 125—127°/14 mm., and α-*acetoxy*-Δ^δ-*hexene*, b.p. 73°/20 mm. (gives MeCHO). 2-Propyltetrahydropyran similarly gives αε-*diacetoxyoctane*, b.p. 153—155°/20 mm., and a mixture, b.p. 96—97°/14 mm., of α-acetoxy-Δ^δ- and -Δ^ϵ-octene (gives EtCHO + PrCHO). 2-Butyltetrahydropyran affords a mixture, b.p. 117°/20 mm., of α-acetoxy-Δ^δ- and -Δ^ϵ-nonene. 2-Phenyltetrahydropyran gives mainly Ph_2 (*loc. cit.*). Tetrahydrofuran and Ac_2O–$ZnCl_2$ at 230° (8 hr.) give αδ-*diacetoxybutane*, b.p. 229—230°, or 108°/10 mm., and a fraction, b.p. 160—165°/10 mm. 2-Ethyltetrahydrofuran, at 200°, affords αδ-*diacetoxyhexane*, b.p. 123—125°/14 mm., and α-acetoxy-Δ^δ- + -Δ^γ-hexene, b.p. 72—73°/20 mm. (gives MeCHO + EtCHO). 2-Butyltetrahydrofuran gives αδ-*diacetoxyoctane*, b.p. 142—158°/13 mm., and a mixture, b.p. 94—95°/13 mm., of α-acetoxy-Δ^δ- (88%) and -Δ^γ-octene (22%); amyltetrahydrofuran affords αδ-diacetoxynonane and a mixture, b.p. 117—118°/20 mm., of α-acetoxy-Δ^δ- and -Δ^δ-nonene. 2-Benzyltetrahydrofuran (at 190°) gives αδ-*diacetoxy*-ε-*phenylpentane*, b.p. 196—197°/16 mm., and a mixture, b.p. 153—158°/14 mm., of α-acetoxy-ε-phenyl-Δ^γ- and -Δ^δ-pentene (hydrogenated to α-*acetoxy*-ε-*phenylpentane*, b.p. 153°/12 mm.). A. T. P.

Action of hydroxymethylamides on ethyl pyromucate. G. B. Marini (Gazzetta, 1939, **69**, 340—344).—*o*-$C_6H_4(CO)_2N$·CH_2·OH added to Et pyromucate (I) in conc. H_2SO_4 gives 5′-*carbethoxyfurfurylphthalimide*, m.p. 118°, hydrolysed (NaOH–EtOH) to 5′-*carboxyfurfurylphthalamic acid*, m.p. 204°. With NHBz·CH_2·OH, (I) gives 5′-*carbethoxy-*, m.p. 106°, hydrolysed to 5′-*carboxy-benzfurfurylamide*, m.p. 180°, and with CH_2Cl·CO·NH·CH_2·OH, 5-*carbethoxychloroacetfurfurylamide*, m.p. 90°, hydrolysed by HCl to 5-*carboxyfurfurylamine hydrochloride*, m.p. 245° (*platinichloride*, m.p. 202°). E. W. W.

Aldehyde-acids and aldo-enol-lactones. I. Condensation of aconic acid with aldehydes and ketones. M. M. Schemjakin and I. A. Redkin (J. Gen. Chem. Russ., 1939, **9**, 442—446).—Aconic acid condenses with aldehydes in presence of $NHEt_2$, at 105°, to yield *benzylidene-*, m.p. 201—202°, *m-nitrobenzylidene-*, not melting at 290°, and *furfurylidene-aconic acid*, not melting at 290°. R. T.

Vitamin-*E*. IV. Synthesis of tocopherols. V. Direct allylation of phenols and quinols. VI. Addition of dienes to phenols and quinols. L. I. Smith, H. E. Ungnade, H. E. Hoehn, and S. Wawzonek (J. Org. Chem., 1939, **4**, 298—304, 305—310, 311—317).—IV. Passage of HBr into phytol containing anhyd. Na_2SO_4 at 0° gives phytyl bromide (I), which decomposes when kept at room temp. and cannot be distilled since it is largely converted at 75° into phytadiene (II). (I) when heated with trimethylquinol (III) affords some (II) and r-α-*tocopherol*, b.p. 140°/10^{-6} mm. (*allophanate*, m.p. 157—160°), which readily oxidises when exposed to air. Its absorption spectrum is nearly indistinguishable from that of natural α-tocopherol. p-*Xylotocopherol*, b.p. 145—150°/10^{-6} mm., when pyrolysed at 355—360° under CO_2 gives a mixture of quinols. m-*Xylotocopherol*,

b.p. 120—130°/10^{-6} mm., could not be obtained pure. These tocopherols have vitamin-*E* activity.

V. Allyl bromide (V) is less, and geranyl bromide more, reactive than γγ-dimethylallyl bromide (V) or (I) towards polylalkylphenols and quinols. (IV), (V), and (I) react with quinol in a sealed tube at 100—150° without solvent or catalyst. $ZnCl_2$ and C_6H_6 or light petroleum may be used but the yield and quality of the product are not improved. The optimum temp. is 100—150°; the pure materials must be thoroughly mixed to a paste and the tube heated in a vertical position. The following are described: 5-hydroxy-2 : 4 : 5 : 7-tetramethylcoumaran, m.p. 130·5—131·5° (*acetate*, m.p. 72·5—73·5°), also obtained by reducing 5-hydroxy-2 : 4 : 5 : 7-tetramethylcoumarone (H_2–Raney Ni at 200°/2600 lb.); 6-*hydroxy*-2 : 2 : 5 : 7 : 8-*pentamethylchroman*, m.p. 94—94·5° (*acetate*, m.p. 92·5—93·5°); 2 : 3 : 5-*trimethylphenyl allyl ether*, b.p. 59·2°/0·1 mm.; 2 : 3 : 5-*trimethyl*-6-*allylphenol*, m.p. 49·5—50·5°; 2 : 4 : 6 : 7-*tetramethylcoumaran*, b.p. 142—144°/29 mm.

VI. The condensation between dienes and phenols leading to chromans has been extended to certain quinols and to *p*-OH·C_6H_4·OMe. Under proper conditions these substances give good yields of chromans but, unless the conditions are carefully regulated, mixtures result. *p*-$C_6H_4(OH)_2$ does not react under any of the conditions tried; *p*-OH·C_6H_4·OMe and (III) react readily but 2 : 5-dimethylquinol does not. 2 : 3 : 5-$C_6H_2Me_3$·OH and isoprene in AcOH saturated with HCl at 0° give a *phenol*, $C_{14}H_{20}O$, m.p. 84—86°, and 2 : 2 : 5 : 7 : 8-*pentamethylchroman*, m.p. 40—41° (also obtained by use of $ZnCl_2$ as catalyst). *p*-OH·C_6H_4·OMe and dimethylbutadiene in AcOH saturated with HCl at 0° afford 6-*methoxy*-2 : 2 : 3-*trimethylchroman*, b.p. 50—53°/10^{-6} mm., whilst isoprene gives 6-*methoxy*-2 : 2-*dimethylchroman*, b.p. 74—80°/0·1 mm., and γ-*chloro*-α-o-*hydroxy*-m-*methoxyphenylbutane*, b.p. 83—90°/0·1 mm. (III) and isoprene in AcOH containing $ZnCl_2$ at 100° give 6-*hydroxy*-2 : 2 : 5 : 7 : 8-*pentamethylchroman*, m.p. 94—94·5° [*acetate*, m.p. 92·5—93·5°; allophanate, m.p. 209—211·5° (decomp.)]. (II) and (III) in boiling AcOH–HCO_2H afford α-tocopherol, apparently contaminated with a liquid of high b.p. H. W.

Vitamin-*E*. X. Reaction between quinones and metallic enolates. IX. L. I. Smith and W. W. Prichard (J. Org. Chem., 1939, 4, 342—350). —Addition of 1 : 3 : 5 : 2-$C_6H_2Me_3Ac$ followed by trimethylbenzoquinone (I) to MgEtBr in Et_2O gives 3 : 6-*dihydroxy*-2 : 4 : 5-*trimethylphenylacetomesitylene*, m.p. 148—148·5° (yield 90%) (*diacetate*, m.p. 169—170°), which does not give ketonic derivatives. It could not be converted into the corresponding coumarone by loss of H_2O. When refluxed with HCl in MeOH, EtOH, or AcOH it appears to give the *Me ether*, m.p. 158—159°, *Et ether*, m.p. 160—161·5°, and *acetate*, m.p. 149·5—150·3°, of the corresponding enol. When warmed with H_2SO_4 it gives only tarry products. CH_2Br·CO·CMe_2·CO_2Et could not be converted into the enolate by MgPhBr, Mg mesityl bromide, or CdPhCl, the product invariably failing to condense with the quinone. Et_2 β-keto-αα-dimethylglutarate does not condense with (I) in presence of $Mg(OMe)_2$ and, although it reacts with Na, the product gives only a red oil with (I). CN·CH_2·CO·CMe_2·CO_2Et with $Mg(OMe)_2$ affords a cryst. enolate, which gives only a non-cryst. product with (I). $CHBu^{\beta}(CO_2Et)_2$ reacts readily with (I) in presence of NaOEt or $Mg(OEt)_2$ but Bu^{β} is lost and the product is 5-*hydroxy*-2-*carboethoxy*-4 : 6 : 7-*trimethylisocoumaranone*, m.p. 111—112° (*acetate*, m.p. 101—103°). This is transformed by hot AcOH saturated with HCl into 5-*hydroxy*-4 : 6 : 7-*trimethylisocoumaranone*, m.p. 195—196° (*acetate*, m.p. 166—167°). H. W.

Vitamin-*E*. XI. Introduction of the *p*-hydroxy-group into chromans and coumarans. L. I. Smith, H. H. Hoehn, and H. E. Ungnade (J. Org. Chem., 1939, 4, 351—357).—2 : 2 : 5 : 7 : 8-Pentamethylchroman (I) couples very slowly with diazotised *p*-NH_2·C_6H_4·SO_3H so that only traces of the N_2 compound can be prepared. HNO_3 in AcOH readily transforms (I) into 6-nitro-2 : 2 : 5 : 7 : 8-pentamethylchroman, m.p. 125—125·5°, which is very inert and could not be reduced by Sn and HCl or by H_2 in presence of Pt at 45 lb. pressure; it is attacked by Na and $Bu^{\alpha}OH$, giving a non-cryst. product with a marked phenolic reaction. Br in CCl_4 converts (I) into 6-*bromo*-2 : 2 : 5 : 7 : 8-*pentamethylchroman*, m.p. 69—70°, which is mixed with EtBr and dropped on to Mg; the product is transformed by O_2 into 6-hydroxy-2 : 2 : 5 : 7 : 8-pentamethylchroman, m.p. 94—94·5°, in poor yield. Similarly 5-bromo- is converted into 5-hydroxy-2 : 4 : 6 : 7-tetramethylcoumaran, which with alkali at 300° gives 2 : 3 : 5-$C_6H_2Me_3$·OH. H. W.

Vitamin-*E*. XII. Preparation of chromans by action of Grignard reagents on dihydrocoumarins. L. I. Smith, H. E. Ungnade, and W. W. Prichard (J. Org. Chem., 1939, 4, 358—362). —Under any of the conditions used the first isolable product of the action of MgEtBr on dihydrocoumaran is α-*hydroxyphenyl*-γ-*ethylpentan*-γ-*ol*, m.p. 71—72°, usually accompanied by and readily cyclised (boiling AcOH–20% H_2SO_4) to 2 : 2-*diethylchroman*, b.p. 128·5—128·9°/12 mm. Similarly MgPhBr affords the corresponding carbinol and 2 : 2-*di*-n-*propylchroman*, b.p. 153—154°/15 mm., but no ketone. 6-Hydroxy-5 : 7 : 8-trimethyl-3 : 4-dihydrocoumarin gives the unstable carbinol, readily cyclised to 6-hydroxy-2 : 2 : 5 : 7 : 8-pentamethylchroman. H. W.

Synthesis of 4-methylcoumarin derivatives, using metallic chlorides as condensing agent. Z. Horii (J. Pharm. Soc. Japan, 1939, **59**, 59—60).—*m*-$C_6H_4(OH)_2$, 1 : 2 : 3- or 1 : 3 : 5-$C_6H_3(OH)_3$ with CH_2Ac·CO_2Et, using $FeCl_3$, $SnCl_4$, or $TiCl_4$ as condensing agent, gives 7-hydroxy-, 7 : 8- and 5 : 7-dihydroxy-4-methylcoumarin, respectively. High yields are claimed in most cases. A. T. P.

Dibenzfuran. XI. Substituents in the 4-position. H. Gilman and P. R. Van Ess. **XII. Metalation of bromo-derivatives.** H. Gilman, H. B. Willis, and J. Swislowsky (J. Amer. Chem. Soc., 1939, **61**, 1365—1371, 1371—1373; cf. A., 1939, II, 276).—XI. Some 4-substituted dibenzfurans are prepared. Structures are proved by synthesis of any isomerides previously unknown. 3-Hydroxydibenz-

furan (I) (prep. in 56—75% yield from 3-bromodibenzfuran, $CuSO_4$, Cu turnings, Cu bronze, and aq. NaOH in a steel bomb at 240°) and Br–AcOH give *4-bromo-3-hydroxydibenzfuran*, m.p. 123—123·5° [*Me ether* (II), m.p. 117—118°], and traces of the 2-Br-derivative (isolated as the Me ether). *3-Methoxydibenzfuran* [prepared from (I) by Me_2SO_4–NaOH], m.p. 46—47°, b.p. 164—165°/6 mm., and Br–AcOH give *2-bromo-3-methoxydibenzfuran* (III) (33%), m.p. 171—172°, and (II). 2-Bromo-3-acetamidodibenzfuran (prep. in 16·4% yield by bromination) and, best (96%), KOH–EtOH give the 3-NH_2-compound, the diazonium salt from which with boiling, aq. $CuSO_4$ affords 13% of *2-bromo-3-hydroxydibenzfuran*, m.p. 143—144° [Me ether = (III)]. CH_2:CH·CH_2Br, (I), and K_2CO_3 in $COMe_2$ give 72—82% of *3-allyloxydibenzfuran*, b.p. 178—180°/4 mm., rearranged by heating at 220—230° to *3-hydroxy-4-allyldibenzfuran* (IV), m.p. 83°, b.p. 173°/5 mm., which gives (Me_2SO_4) the *Me ether*, m.p. 67—68°, obtained also from the Mg derivative of (II) by CH_2:CH·CH_2Br. Hot KOH–MeOH converts (IV) into *3-hydroxy-4-propenyldibenzfuran*, m.p. 94—95°. The Grignard reagent from (III) and CH_2:CH·CH_2Br (excess) yield *3-methoxy-2-allyldibenzfuran*, b.p. 158—159°/4 mm. Passage of O_2 over the Grignard reagent from (II) and $MgBu^aBr$ in Et_2O–C_6H_6 gives 71% of *4-hydroxy-3-methoxydibenzfuran*, m.p. 111—111·5°, unstable in alkali, decomposed by HI, and converted by MeI–K_2CO_3–$COMe_2$ into 3 : 4-*dimethoxydibenzfuran*, m.p. 79°. The Grignard reagents of (II) and (III) with CO_2 yield *3-methoxydibenzfuran-4-*, m.p. 156—157° (*Me* ester, m.p. 99·5—100°), and *-2-carboxylic acid*, m.p. 206—207° (*Me* ester, m.p. 122·5°), respectively. *p*-OMe·C_6H_4·OK and 1 : 4 : 2-$C_6H_3Br_2$·NO_2 at 170° give 4-bromo-2-nitro-4′-methoxydiphenyl ether (crude), reduced by $SnCl_2$ to the amine, the diazonium chloride of which, when added to boiling 50% H_2SO_4, yields *3-bromo-6-methoxydibenzfuran*, m.p. 92·5° (debrominated by Pd–$CaCO_3$ to 3-methoxydibenzfuran). *4-Bromo-1-hydroxydibenzfuran* (V) (prepared by Br–AcOH from the OH-compound), m.p. 151·5—152°, gives the *Me ether*, m.p. 97—97·5°, obtained in 86% yield from 1-methoxydibenzfuran by Br–AcOH and converted [method as for (II)] into *4-hydroxy-1-methoxydibenzfuran*, m.p. 155°, which with HI and a little red P gives 1 : 4-*dihydroxydibenzfuran*, m.p. 217—218° (decomp.), and with Me_2SO_4–NaOH gives 1 : 4-*dimethoxydibenzfuran*, m.p. 78·5°. 1-Aminodibenzfuran (prep. in 56·7% yield by a modified Hofmann reaction) and Ac_2O in C_6H_6 give the Ac derivative, which with Br–AcOH yields *4-bromo-1-acetamidodibenzfuran*, m.p. 228°, and thence *4-bromo-1-aminodibenzfuran*, m.p. 119—120°; the diazonium salt thereof with aq. $CuSO_4$ affords (V), and with HPO_2 gives *4-bromodibenzfuran* (VI), m.p. 67°. Conc., aq. NH_3 and CuBr at 230—240° convert (VI) into *4-aminodibenzfuran*, m.p. 74° (*Ac* derivative, m.p. 205°). By Grignard reactions (VI) affords *4-hydroxydibenzfuran*, m.p. 140—140·5° (1- or 3-*Br*-derivative, m.p. 178°), and *dibenzfuran-4-carboxylic acid*, m.p. 232—233°, the *Me* ester, m.p. 63°, of which gives the 7-(?2-)NO_2-ester, m.p. 216°, and thence a *NO_2-acid*, m.p. 297—298°, decarboxylated by Cu bronze in quinoline to 2-nitrodibenzfuran. 1 : 4 : 2-$(OMe)_2C_6H_3$·MgBr and $MgBu^aBr$ with O_2 give 43% of 2 : 5-*dimethoxyphenol*, b.p. 134—135°/15 mm. (*benzoate*, m.p. 73·5°), the K salt of which with *o*-C_6H_4Br·NO_2 at 170° yields *2-nitro-2′ : 5′-dimethoxydiphenyl ether*, b.p. 190—193°/3 mm., and thence ($SnCl_2$) the *2-NH_2-ether*, m.p. 72°, b.p. 183—185°/4 mm., which gives a phenol and not a dibenzfuran by diazotisation and treatment with H_2SO_4.

XII. 1-Bromodibenzfuran and $LiBu^a$, first in Et_2O and then in C_6H_6, give a Li derivative, converted by CO_2 into dibenzfuran-1-carboxylic acid (57·5% of pure acid), which is not obtained by the Grignard process. 3 : 7-Dibromodibenzfuran gives similarly up to 72% of the 3 : 7-dicarboxylic acid and some (?) dibutyldibenzfuran. 2-Bromodibenzfuran (VII) gives a 5 : 1 mixture of dibenzfuran-1- and -2-carboxylic acid; the 1-acid probably arises by reaction of Li 2-dibenzfuryl with (VII) to give Li 2-bromo-1-dibenzfuryl (and dibenzfuran), which then reacts with dibenzfuran to give Li 1-dibenzfuryl and regenerate (VII). R. S. C.

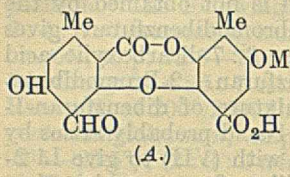
Methylation of hydroxyflavanols. Quercitin, gossypetin, and herbacetin. P. S. Rao and T. R. Seshadri (Current Sci., 1939, **8**, 255—256).—Pentamethylquercitin, hexamethylgossypetin, m.p. 170—172°, and *O*-pentamethylherbacetin, m.p. 156—158°, are obtained exclusively and in good yield by methylation (Me_2SO_4–NaOH–$COMe_2$) of the appropriate Ac derivative, using the method previously reported (A., 1939, II, 385). F. N. W.

3-Hydroxyflavanone derivatives. I. New synthesis. Y. Kimura (J. Pharm. Soc. Japan, 1939, **58**, 123—127; cf. A., 1937, II, 70).—2-Hydroxy-4 : 6-dimethoxyacetophenone and 10% aq. NaOH–EtOH at 10—20°, with *p*-OMe·C_6H_4·CHO, 3 : 4 : 1-$(OMe)_2C_6H_3$·CHO, 3 : 4 : 5 : 1-$(OMe)_3C_6H_2$·CHO, or piperonaldehyde, respectively, afford *2-hydroxy-4 : 6 : 4′-trimethoxy-*, m.p. 121°, *-4 : 6 : 3′ : 4′-tetramethoxy-*, m.p. 117°, *-4 : 6 : 3′ : 4′ : 5′-pentamethoxy-*, m.p. 146°, and *-4 : 6-dimethoxy-3′ : 4′-methylenedioxyphenyl α-methoxystyryl ketone*, m.p. 112—113°, converted by aq. HCl–EtOH into *3-hydroxy-5 : 7′ : 4′-trimethoxy-*, m.p. 158—159°, *-5 : 7 : 3′ : 4′-tetramethoxy-*, m.p. 176°, *-5 : 7 : 3′ : 4′ : 5′-pentamethoxy-*, m.p. 168—169°, and *-5 : 7-dimethoxy-3′ : 4′-methylenedioxy-flavanone*, m.p. 142°, respectively. A. T. P.

Pigments of the flavone series. V. Diosmin, a constituent of dahlia flowers. T. Nakaoki (J. Pharm. Soc. Japan, 1938, **58**, 197—201).—The white flowers of *D. variabilis* contain apigenin (~2·5%), luteolin (~0·2%), and luteolin Me_1 ether rhamnoglucoside (I) (~0·5%). (I) is identical with diosmin (Oesterle *et al.*, A., 1925, i, 1438) and is shown to be 5 : 3′-dihydroxy-4′-methoxyflavone-7-rhamnoglucoside. S. H. H.

Lichen substances. XCII. Psoromic acid. III. Y. Asahina and S. Shibata (Ber., 1939, **72**, [*B*], 1399—1402).—Hypoparellic acid Me_2 ether is transformed by $SOCl_2$ or conc. H_2SO_4 into 2 : 4 : 6-*trimethoxy-3 : 5 : 8-trimethylxanthone* (I), m.p. 187°, which does not react with CO: reagents under the usual conditions, has a blue fluorescence in Et_2O, gives a yellow solution in conc. H_2SO_4 which becomes

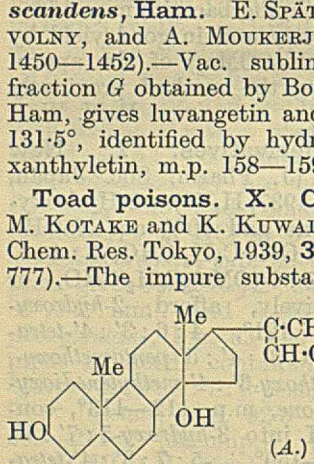
colourless when diluted with H_2O, and has an ultraviolet absorption spectrum resembling that of gentisein. It is a xanthone derivative since it is transformed by P_2S_5 and K_2S in xylene at 105—110° into 2 : 4 : 6-*trimethoxy*-3 : 5 : 8-*trimethylxanthione*, m.p. 159·5°, which is converted by NH_2OH,HCl and NaOAc into 2 : 4 : 6-*trimethoxy*-3 : 5 : 8-*trimethylxanthion-oxime*, m.p. 231° (decomp.). $NaNH_2$ and (I) in xylene at 150—180° afford 2′ : 4 : 5-trimethoxy-3 : 6 : 3′-trimethyldiphenyl ether, m.p. 110°; identical with decarboxylated (I). Since energetic reduction of (I) gives deoxyhypopsalazinol Me_3 ether, it is 2-carboxy-4 : 6 : 3′-trimethoxy-5 : 2′ : 5′-trimethyldiphenyl ether, and psoromic acid is *A*. Hypoparellic acid is converted by conc. H_2SO_4 at room temp. into 4 : 6-*dihydroxy*-2-*methoxy*-3 : 5 : 8-*trimethylxanthone*, m.p. 319° (decomp.) after becoming discoloured at ~280°, whilst (I) with Br–AcOH gives a *Br*-derivative, m.p. 264°, transformed by $SOCl_2$ into 7-*bromo*-2 : 4 : 6-*trimethoxy*-3 : 5 : 8-*trimethylxanthone*, m.p. 233°. H. W.



(*A*.)

Isolation of xanthyletin from *Luvunga scandens*, Ham. E. Späth, P. K. Bose, E. Dobrovolny, and A. Moukerjee (Ber., 1939, **72**, [*B*], 1450—1452).—Vac. sublimation of the coumarin fraction *G* obtained by Bose *et al.* from *L. scandans*, Ham, gives luvangetin and xanthyletin, m.p. 131—131·5°, identified by hydrogenation to tetrahydroxanthyletin, m.p. 158—159°. H. W.

Toad poisons. X. Constitution of bufalin. M. Kotake and K. Kuwada (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1939, **36**, 106—111; cf. A., 1934, 777).—The impure substance, m.p. 227°, obtained after removal of cinobufagin and cinobufotalin is the *acetate* (I), m.p. 229—231°, of bufalin (*A*), $C_{24}H_{34}O_4$, m.p. 235—236°, which, with conc. HCl yields *anhydrobufalin*, m.p. 204·5—206° (*acetate*, m.p. 151—152°), and, in AcOH, with CrO_3 in aq. H_2SO_4 a *ketone*, $C_{24}H_{32}O_4$, m.p. 226—227°. With Pd–H_2, (I) in EtOH gives *tetrahydroacetylbufalin*, m.p. 182—185°. W. McC.

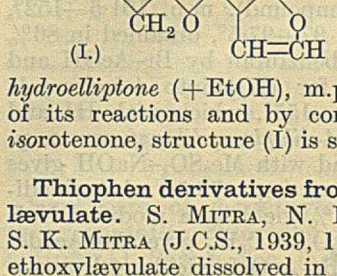


(*A*.)

Synthesis of diphenylene dioxide derivatives. XIII. 2 : 6-Di-(α-hydroxy-γ-piperidinopropyl)-diphenylene dioxide. XIV. β-Piperidinoalkyldiphenylene dioxide. M. Tomita (J. Pharm. Soc. Japan, 1939, **58**, 130—132, 133—136; cf. A., 1932, 1048).—XIII. 2 : 6-Diacetyldiphenylene dioxide and $(CH_2O)_2$ + piperidine hydrochloride in C_5H_{11}·OH (cf. Kamp *et al.*, A., 1936, 1390; Mannich *et al.*, A., 1922, i, 351; 1923, i, 43) afford 2 : 6-*di*-(β-*piperidinopropionyl*)*diphenylene dioxide* (I), m.p. 138° (*hydrochloride*, m.p. 231°). (I) and Na–Hg in EtOH give a N-free substance, m.p. >300°; catalytic reduction (PtO_2–EtOH at room temp.) of (I) gives 2 : 6-*dipropionyl*-, m.p. 241° (*dioxime*, m.p. 235°) [also obtained from diphenylene dioxide (II), EtCOCl, and $AlCl_3$], and 2 : 6-*di*-(α-*hydroxy*-γ-*piperidinopropyl*)-*diphenylene dioxide*, m.p. 120°. (II), Cl·$[CH_2]_2$·COCl, and $AlCl_3$ give 2 : 6-*di*-β-*chloropropionyldiphenylene dioxide*, m.p. 211°, converted by piperidine into (I).

XIV. 2 : 6-Dimethyldiphenylene dioxide and CH_2Cl·COCl–$AlCl_3$ afford the 3 : 7-*di*(*chloroacetyl*) derivative, m.p. 248°, converted into the 3 : 7-*di*(*piperidinoacetyl*) compound, m.p. 163—165° (*hydrochloride*, $+2H_2O$, m.p. >300°), and thence by Na–Hg into 3 : 7-*di*-(α-*hydroxy*-β-*piperidinoethyl*)-2 : 6-*dimethyl diphenylene dioxide*, m.p. 211°. Similarly prepared are: [from (II)] 2 : 6-*di*-(α-*bromopropionyl*)-, m.p. 213°, -*di*-(α-*piperidinopropionyl*)-, m.p. 185—186°, and -*di*-(α-*hydroxy*-β-*piperidinopropyl*)-*diphenylene dioxide*, m.p. 215° (analysis not good); 2 : 6-*di*-(α-*bromoisovaleryl*)-, m.p. 196°, and -*di*-(α-*piperidinoisovaleryl*)-, m.p. 161° (some loss of piperidine); and -*di*-(α-*bromoisobutyryl*)-*diphenylene dioxide*, m.p. 160—167° (impure; loses Br on crystallisation). The last-named and piperidine give a substance, $C_{20}H_{16}O_4$, m.p. 255°. A. T. P.

Active principles of leguminous fish-poison plants. II. Isolation of *l*-elliptone from *Derris elliptica*. S. H. Harper (J.C.S., 1939, 1099—1105).—Quick extraction (5% KOH) of an ethereal extract of *D. elliptica* (var. Sarawak creeping) affords rotenone and l-*elliptone* (I), $C_{20}H_{16}O_6$, m.p. 160°, $[\alpha]_D^{20}$ +55° in $COMe_2$, −18° in C_6H_6 (α-*oxime*, m.p. 222°; β-*oxime*, m.p. 236°; *monoacetate*, m.p. 200°). Racemisation of (I) with NaOAc–EtOH gives dl-*elliptone*, m.p. 176—177°, $[\alpha]_D$ ±0° in C_6H_6 (α-*oxime*, m.p. 259°; β-*oxime*, m.p. 261°; *monoacetate*, m.p. 202°), identical with Buckley's substance of m.p. 183° (B., 1936, 1117), of which (I) is the precursor. NaOAc and I with (I) yield dehydroelliptone, m.p. 264°, $[\alpha]_D$ ±0°, Reduction of (I) with H_2–PtO_2 affords successively l-*dihydro*-, m.p. 159°. $[\alpha]_D^{20}$ −97° in $COMe_2$, and l-*tetrahydro-elliptone* (+EtOH), m.p. 217° $[\alpha]_D^{20}$ +61° in $COMe_2$ (*diacetate*, m.p. 140—142°); similar reduction of the *dl*-compound gives dl-*tetrahydroelliptone* (+EtOH), m.p. 205°. From a study of its reactions and by comparison with those of *iso*rotenone, structure (I) is suggested. F. R. S.



(I.)

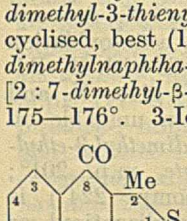
Thiophen derivatives from ethyl β-carbethoxylævulate. S. Mitra, N. K. Chakrabarty, and S. K. Mitra (J.C.S., 1939, 1116—1117).—Et β-carbethoxylævulate dissolved in the appropriate alcohol, saturated with HCl, with H_2S gives the *Me*, b.p. 125°/5 mm., *Et*, b.p. 150°/5 mm., and *Pr*$^{\alpha}$ *ether*, b.p. 135°/5 mm., of Et 5-hydroxy-2-methylthiophen-3-carboxylate. These are hydrolysed to 5-*methoxy*-, m.p. 128°, -*ethoxy*-, m.p. 122° (*Ba* salt), and -n-*propoxy*-2-*methylthiophen*-3-*carboxylic acid*, m.p. 75°, dealkylated to the 5-OH-*acid* (I), m.p. 160°. These acids condense with aromatic aldehydes (EtOH–HCl) to form dithienylarylmethanes: *di*-(5-*ethoxy*-3-*carboxy*-2-*methyl*-4-*thienyl*)-*phenylmethane*, m.p. 233°, and -4′-*hydroxy*-3′-*methoxyphenylmethane*, m.p. 235°, and *di*-(5-n-*propoxy*-, m.p. 232° (decomp.), and *di*-(5-*methoxy*-3-*carboxy*-2-*methyl*-4-*thienyl*)*phenylmethane*, m.p. 250°

(decomp.). Condensation of (I) with aldehydes gives yellow dyes: 5-*keto*-4-*benzylidene*-, m.p. 166°, -4-*o*-*nitrobenzylidene*-, m.p. 184° (decomp.), -4-*o*-*methoxybenzylidene*-, m.p. 152°, -4-*ethylidene*-, m.p. 124°, and -4-*cinnamylidene*-2-*methyl*-4 : 5-*dihydrothiophen*-3-*carboxylic acid*, m.p. 204°. F. R. S.

Thiophen series. XLV. 5-Hydroxy-2-methylthiophen (thiotenol). W. STEINKOPF and F. THORMANN (Annalen, 1939, **540**, 1—7).—5-Hydroxy-2-methylthiophen (I) (prepared by distilling $COMe\cdot[CH_2]_2\cdot CO_2H$ and P_2S_5 in CO_2), m.p. −23·5° to 22·5°, b.p. 94—96°/15 mm., gives a *benzoate*, m.p. 47—47·5°, and the known acetate, but condenses as a ketone with aldehydes. With PhCHO and HCl in abs. EtOH at room temp., it gives 57% of 5-*keto*-4-*benzylidene*-2-*methyl*-4 : 5-*dihydrothiophen*, m.p. 85—86°. Cryst. $FeCl_3$ in boiling EtOH gives *bis*-3-*keto*-2-*methyl*-4 : 5-*dihydro*-4-*thienylidene* ["*bis*-(2-*methylthiophen*)-4-*indigo*"], m.p. 188—190°, sublimes at 14 mm. With acenaphthenequinone and HCl–AcOH at 100°, it gives 7-*keto*-8-5′-*keto*-2′-*methyl*-4′ : 5′-*dihydro*-4′-*thienylidene*-7 : 8-*dihydroacenaphthene* [*acenaphthene*-(1)-2-*methylthiophen*-(4)-*indigo*], m.p. 164°. With 3 : 4-dibromothiophen-2 : 5-dialdehyde (II) in HCl–AcOH at 100°, it gives 3 : 4-*dibromo*-2 : 5-*di*-(5′-*keto*-2′-*methyl*-4′ : 5′-*dihydro*-4′-*thienylidenemethyl*)*thiophen* [3 : 4-*dibromo*-2 : 5-*thioxylidenebis*-3′-(5′-*keto*-2′-*methyl*-4′ : 5′-*dihydrothiophen*)], m.p. 232—234°. 3 : 4-*Dibromo*-2 : 5-*di*-(2′-*keto*-1′ : 2′-*dihydro*-1′-*thionaphthenylidenemethyl*)*thiophen* [3 : 4-*dibromo*-2 : 5-*thioxylidenebis*-1′-(2′-*keto*-1′ : 2′-*dihydrothionaphthen*)], cryst., is obtained from (II) and 2-hydroxythionaphthen in boiling HCl–AcOH. With *p*-$C_6H_4(CHO)_2$ in boiling HCl–AcOH, (I) gives *xylylidenebis*-4′-(5′-*keto*-2′-*methyl*-4′ : 5′-*dihydrothiophen*), *o*-$C_6H_4\left(CH{:}C<\begin{matrix}CH{:}CMe\\CO\text{-}S\end{matrix}\right)_2$, m.p. 167—168°, and very little 5-*keto*-4-p-*aldehydobenzylidene*-2-*methylthiophen*, m.p. 277—279°. The C_4H_3S is strongly bathochromic compared with Ph.

R. S. C.

Thiophen series. XLVI. Derivatives of 2 : 5-thioxen [2 : 5-dimethylthiophen]. W. STEINKOPF, T. BARLAG, and H. J. VON PETERSDORFF (Annalen, 1939, **540**, 7—14).—2 : 5-Dimethylthiophen, *o*-$C_6H_4(CO)_2O$, and $AlCl_3$ in $PhNO_2$ at 0—5° give 62% of 3-*o*-*carboxybenzoyl*-2 : 5-*dimethylthiophen*, m.p. 127—128° (*Et* ester, b.p. 152—153°/high vac., does not give an amide; 4-*Br*-derivative, m.p. 186°), reduced by Zn in boiling AcOH–H_2O (4 : 1) to α-2 : 5-*dimethyl*-3-*thienylphthalide* (64%), m.p. 154°, and cyclised, best (18%) by $AlCl_3$–NaCl at 140°, to 2 : 5-*dimethylnaphtha*-1′ : 4′-*quinonylo*-2′ : 3′-3 : 4-*thiophen* [2 : 7-*dimethyl*-β-*thionaphthanthrenequinone*] (I), m.p. 175—176°. 3-Iodo-2 : 5-dimethylthiophen and Cu bronze at 245—250° give *di*-2 : 5-*dimethyl*-3-*thienyl*, b.p. 142—144°/9 mm., purified by conversion into the 4 : 4′-*diacetoxymercuri*-derivative, m.p. 233—234°, and regeneration therefrom by 18% HCl at 100°. 5-Acetyl-2-methyl- or 3-acetyl-2 : 5-dimethyl-thiophen with isatin and KOH in aq. EtOH at 110° yield 2-2′-*methyl*-5′-, m.p. 227—228° (*Me* ester, m.p. 91—92°, b.p. 176—178°/high vac.), and 2-2′ : 5′-*dimethyl*-3′-*thienylquinoline*-4-*carboxylic acid*, m.p. 214—215° (*Me* ester, m.p. 79—80°), decarboxylated by soda-lime at ~360° to 2-2′-*methyl*-5′-, m.p. 122—123° (*picrate*, m.p. 192—194°), and 2-2′ : 5′-*dimethyl*-3′-*thienylquinoline*, an oil, respectively. 2-2′-*Thienylquinoline*, m.p. 132—133° (*picrate*, m.p. 194—195°), is similarly obtained from the 4-carboxylic acid.



(I.)

R. S. C.

Thiophen series. XLVII. Phenyl 2-thienyl diketone and its oximes. W. STEINKOPF and, in part, G. BOKOR (Annalen, 1939, **540**, 14—24).—Addition of $C_5H_{11}\cdot O\cdot NO$ to CH_2Ph 2-thienyl ketone and NaOEt in EtOH at <0° gives *Ph* 2-*thienyl diketone* Bz-syn-*mono-oxime* (I), m.p. 88°, the *benzoate*, m.p. 111—113°, of which is converted by hot, dil.

$Ph\cdot\underset{OH\cdot N}{C}\cdot CO\cdot C_4H_3S$ (I.) $\quad Ph\cdot\underset{C_4H_3S\cdot CO\cdot N}{C}\cdot OBz$ (III.) $\quad Ph\cdot\underset{N\cdot OH}{C}\cdot CO\cdot C_4H_3S$ (IV.)

NaOH–EtOH into PhCN and thiophen-2-carboxylic acid (II) and is thus (III). H_2SO_4–EtOH rapidly or HCl–AcOH–Ac_2O slowly converts (I) at room temp. into PhCN and (II). Boiling, conc. H_2SO_4 (short treatment) or HCl–EtOH at room temp. converts (I) into the Bz-anti-*mono-oxime* (IV), m.p. 144°, the *benzoate*, m.p. 139—140°, of which regenerates (IV) with alkali and is thus the normal benzoate. Hot, conc. H_2SO_4 hydrolyses (I) or (IV) into *Ph* 2-*thienyl diketone* (V), m.p. 65—65·5°, which is yellow when melted and thereafter when cooled in Et_2O–CO_2, but becomes colourless again when recrystallised. When (I) is treated with NaOEt–EtOH and benzoin, the reaction, $(OK\cdot\dot{C}Ph{:})_2 + (V) \rightarrow OK\cdot\dot{C}Ph\cdot COPh + OK\cdot\dot{C}Ph\cdot CO\cdot C_4H_3S$ [or $COPh\cdot\dot{C}(OK)\cdot C_4H_3S$], occurs, since subsequent oxidation gives (V) (47·6), Bz_2 (52·4), BzOH (77·64), and (II) (22·36%). With *o*-$C_6H_4(NH_2)_2$ at 125°, (V) gives 2-*phenyl*-3-2′-*thienylquinoxaline*, m.p. 128°. With NH_2OH,HCl and aq. NaOH, (I) gives *Ph* 2-*thienyl* anti-*diketoxime* (VI), m.p. variable, 193—195° (*diacetate*, m.p. 173·5—175·5°), and some syn-*diketoxime* (VII), m.p. 173—175° [*diacetate*, m.p. 165—166° after sintering; obtained also from (VI) by NH_2OH,HCl and aq. NaOH or by conc. HCl at 60—65°]; hydrolysis of the diacetates regenerates the

$Ph\cdot\underset{N\cdot OH}{C}\text{————}\underset{OH\cdot N}{C}\cdot C_4H_3S$ (VI.) $\quad Ph\cdot\underset{OH\cdot N}{C}\text{—}\underset{N\cdot OH}{C}\cdot C_4H_3S$ (VII.)

original dioximes. 2-*Cyanothiophen*, m.p. 51·5°, is obtained in ~70% yield from 2-ω-oximinoacetylthiophen by AcCl at 0° (less well by Ac_2O) and converted by conc. HCl into 2-thienylglyoxylic acid (80% yield), m.p. ($+H_2O$) 52—53°, (anhyd.) 91·5°. Passage of CH_2O into Mg 2-thienyl iodide in Et_2O (apparatus described) gives 66% of 2-hydroxymethylthiophen, b.p. 94·5—96°/12 mm. R. S. C.

Synthesis of thianthren (diphenylene disulphide) derivatives. Friedel–Crafts reaction with thianthren. Synthesis of 2 : 8-di-(α-hydroxy-β-piperidinoethyl)thianthren. M. TOMITA (J. Pharm. Soc. Japan, 1939, **58**, 139—141; cf. A., 1939, II, 442).—Thianthren (I) (Friedel–Crafts) affords 2 : 8-*di*(*chloroacetyl*)- (II), m.p. 177°, and thence -*di*(*piperidinoacetyl*)-, m.p. 129° (*hydrochloride*, m.p. 260°), and

2 : 8-*di*-(α-*hydroxy*-β-*piperidinoethyl*)-*thianthren*, m.p. 208°. (I) and AcCl–$AlCl_3$ give 2 : 8-*diacetylthianthren*, m.p. 157°, oxidised [as is (II) also] by CrO_3–AcOH to *diphenylenedisulphone*-2 : 8-*dicarboxylic acid*, m.p. >300°, obtained also by similar oxidation of 2 : 6-dimethylthianthren, m.p. 126°. A. T. P.

Phenoxthionine and thianthren derivatives. II. Synthesis of phenoxthionine and thianthren oxide derivatives. M. Tomita and T. Ikeda (J. Pharm. Soc. Japan, 1938, **58**, 231—232).—Phenoxthionine 10-oxide or 10 : 10-dioxide or thianthren 9 : 9 : 10 : 10-tetraoxide does not undergo the Friedel–Crafts reaction with $CH_2Cl{\cdot}COCl$. H_2O_2 converts 2 : 8-dichloroacetylphenoxthionine into the 10 : 10-*dioxide*, m.p. 224—229°, and 2 : 6-dichloroacetylthianthren into the 9 : 9 : 10 : 10-*tetraoxide*, m.p. 209—213°. With piperidine, these products give N- and Cl-free substances of high m.p., stated to be polymerised vinyl ketones. R. S. C.

Synthesis of phenoxthionine derivatives. I. Friedel–Crafts reaction with phenoxthionine. Synthesis of 2 : 8-di-(α-hydroxy-β-piperidinoethyl)phenoxthionine. M. Tomita (J. Pharm. Soc. Japan, 1939, **58**, 136—139).—Phenoxthionine and $CH_2Cl{\cdot}COCl$–$AlCl_3$ afford 2 : 8-*di*(*chloroacetyl*)- (I), m.p. 193°, and thence, with piperidine, 2 : 8-*di*(*piperidinoacetyl*)-, m.p. 105°, and (Na–Hg) 2 : 8-*di*-(α-*hydroxy*-β-*piperidinoethyl*)-*phenoxthionine*, m.p. 133°. (I) and Zn–Hg give 2 : 8-*diethylphenoxthionine* (II), m.p. 205—206°, also obtained from the 2 : 8-Ac_2 derivative (III), m.p. 175° (prepared by Friedel–Crafts reaction), similarly. $(4\text{-}C_6H_4Ac)_2O$ similarly affords 4 : 4′-*diethyldiphenyl ether*, b.p. 161—163°, converted by S–$AlCl_3$ into (II). (II) is oxidised (CrO_3) to 2 : 8-*diethylphenoxthionine* 10-*dioxide* (IV), m.p. >300° (Me_2 ester, m.p. 204—208°). $(4\text{-}C_6H_4Me)_2O$, S, and $AlCl_3$ afford 2 : 8-dimethylphenoxthionine, m.p. 73—74° (cf. Hilditch *et al.*, J.C.S., 1911, **99**, 408), oxidised (CrO_3) to (IV). A. T. P.

Oximinopyrroles. XI. Transformation products of 3-oximino-2 : 5-dimethylpyrrole. T. Ajello and S. Cusmano (Gazzetta, 1939, **69**, 207—214).—2 : 5-Dimethylpyrrole (new prep. from $COMe{\cdot}[CH_2]_2{\cdot}COMe$ and NH_4OAc in boiling AcOH, followed by treatment with aq. NH_3 and extraction with Et_2O) with NaOEt–EtOH and $C_5H_{11}{\cdot}O{\cdot}NO$ gives the *Na* salt (I) of 3-oximino-2 : 5-dimethylpyrrole. When (I) is acidified and the product steam-distilled or extracted with Et_2O, 3-acetyl-5-methyl*iso*oxazole (cf. Angelico and Calvello, A., 1904, i, 448; Schmidt and Widmann, A., 1909, i, 525) [*oxime*, m.p. 117° (*Bz* derivative, m.p. 180°); *semicarbazone*, m.p. 238—239°; *azine*, m.p. 156—158°] is formed. E. W. W.

Studies in the pyrrole series. I. Synthesis of certain *N*-alkyl-substituted 2 : 5-dimethylpyrrole-3(4)-carboxylic acid esters. N. M. Timoschevskaja (J. Gen. Chem. Russ., 1939, **9**, 406—408).—$CH_2Ac{\cdot}CHAc{\cdot}CO_2Et$ and NH_2R in EtOH yield Et 1 : 2 : 5-trimethyl-, 2 : 5-dimethyl-1-ethyl, m.p. 25—26°, -1-n-*propyl*-, b.p. 144°/4 mm., m.p. 44·5°, and -1-n-*butyl*-*pyrrole*-3-*carboxylate*, b.p. 162—163°/4 mm. R. T.

Imidoporphyrins. VI. 2-Methyl-3 : 4-diethyl- and 3 : 4-diethyl-pyrrole. Curtius degradation of Et 2-methyl-3 : 4-diethylpyrrole-5-carboxylate. H. Fischer, H. Guggemos, and A. Schäfer (Annalen, 1939, **540**, 30—50; cf. A., 1939, II, 288).—Numerous pyrrole, pyrromethene, and imidoporphyrin derivatives are synthesised. 3-*Acetyl*-5-*benzeneazo*-, m.p. 143° (*hydrochloride*, m.p. 134°), and -5-p-*sulphobenzeneazo*-2-*methyl*-4-*ethylpyrrole*, decomp. 222°, prepared by coupling, do not give the 5-aminopyrrole when hydrogenated (PtO_2). N_2H_4–NaOEt–EtOH converts 3-acetyl-2-methyl-4-ethylpyrrole into 2-methyl-3 : 4-diethylpyrrole (I), b.p. 104—106°/11 mm., and some 1-*amino*-2-*methyl*-3 : 4-*diethylpyrrole*, m.p. 68°, b.p. 140°/11 mm. (*picrate*, m.p. 170°); H_2–Raney Ni at 180°/200 atm. gives 70% of (I) and some of a *substance*, b.p. 76—77°/11 mm. (*picrate*, m.p. 115°). H_2–Raney Ni similarly reduces Et 3-acetyl-2-methyl-4-ethylpyrrole-5-carboxylate to Et 2-methyl-3 : 4-diethylpyrrole-5-carboxylate (II) (42%), m.p. 75°, obtained also with some *Et* 2-*methyl*-3 : 4-*diethylpyrrole*-1-*carboxylate*, an oil [readily converted into (I)], from (I) by $ClCO_2Et$. Photo-oxidation of (I) in Et_2O gives an oil, from which H_2O_2 yields 2-*hydroxy*-3 : 4-*diethylpyrrole*-5-*carboxylic acid*, m.p. 124°. SO_2Cl_2 (3 mols.) and (II) give an oily Cl_3-derivative, hydrolysed by boiling H_2O to 2-*carbethoxy*-3 : 4-*diethylpyrrole*-5-*carboxylic acid*, decomp. 264°, which with 10% NaOH at 160° yields 3 : 4-*diethylpyrrole*, b.p. 83°/10 mm. [PhN_2-derivative, decomp. 222° (*picrate*, decomp. 182°); gives no picrate or 2-CHO derivative], unstable in air. N_2H_4,H_2O and (II) at 150° give the *hydrazide*, m.p. 163° (obtained similarly from the 1-CO_2Et-derivative), which with $NaNO_2$ in AcOH at 0—5° yields 2-*methyl*-3 : 4-*diethylpyrrole*-5-*carboxylazide* (III), decomp. 98°. 1 mol. of SO_2Cl_2 in Et_2O converts (III) into an unstable Cl_1-derivative, which with MeOH at 35° gives 2-*methoxymethyl*-3 : 4-*diethylpyrrole*-5-*carboxylazide*, decomp. 58°. 2 mols. of SO_2Cl_2 in Et_2O yield 2-*dichloromethyl*-3 : 4-*diethylpyrrole*-5-*carboxylazide*, decomp. 97°, converted by MeOH containing a little H_2O into 2-*formyl*-3 : 4-*diethylpyrrole*-5-*carboxylazide*, decomp. 68°, and by $CH_2Ph{\cdot}OH$ in boiling xylene into N-2-*formyl*-3 : 4-*diethyl*-5-*pyrryl*-O-*benzylurethane*, decomp. 205° (*azine*, m.p. 198°). 3 mols. of SO_2Cl_2 with (III) in Et_2O gives an oily Cl_3-derivative, which reacts violently with MeOH to give N-2-*carbomethoxy*-3 : 4-*diethyl*-5-*pyrryl*-O-*methylurethane*, m.p. 113°. Boiling MeOH or $CH_2Ph{\cdot}OH$ in boiling xylene converts (III) into *urethanes*, (IV) $C_{11}H_{18}O_3N_2$, decomp. 119°, and $C_{17}H_{22}O_3N_2$, decomp. 136°, respectively, which are probably auto-oxidation products, give no picrates, and yield oils with H_2–Pd-black. In 50% AcOH at 100° (III) gives N_2 and 5-*amino*-2-*methyl*-3 : 4-*diethylpyrrole*, an unstable oil (*picrate*, m.p. 182°); 5-*amino*-2 : 4-*dimethyl*-3-*ethylpyrrole* [5-*aminocryptopyrrole*] (*picrate*, m.p. 201°; *picrolonate*, darkens at 200°, decomp. 224°) is analogously obtained; it cannot be diazotised or acylated. A hygroscopic by-product obtained in the treatment of Et 3-acetyl-2 : 4-dimethylpyrrole-5-carboxylate with N_2H_4–NaOEt (A., 1929, 1463) has m.p. 60° and is 1-*aminocryptopyrrole*. The 1-NH_2-derivatives obtained in such reactions are formed by ring-fission of the pyrroles to diketones, followed by

condensation thereof with N_2H_4. Et 2-bromomethyl-3 : 4-diethylpyrrole-5-carboxylate (improved prep.), decomp. 120—121°, in a little boiling MeOH gives *Et*$_2$ 3 : 4 : 3′ : 4′-*tetraethylpyrromethene*-5 : 5′-*dicarboxylate*, m.p. 98°, converted by boiling 50% KOH into a dicarboxylic acid, which with Br–AcOH affords 5 : 5′-*dibromo*-3 : 4 : 3′ : 4′-*tetraethylpyrromethene*, m.p. 163° (hydrobromide). With NH_3–EtOH at 140°, this gives *octaethyl*-βδ- (or αγ-)*di-imidoporphyrin* (V), m.p. 291° (absorption max. at 6232 and 5411 A.; removed from Et_2O by 20% HCl), which is also obtained with a little *octaethyl*-αγ- (βδ-)*di-imidoporphyrin* (absorption max. 6132, 5580, and 5326 A.; removed from Et_2O by 11% HCl) from (IV) and NHPh·NH_2 at 180—240°. With AgOAc or KOAc in boiling AcOH or, much less well, with NaOMe at 160—165°, 5-bromo-5′-methyl-3 : 4 : 3′ : 4′-tetraethylpyrromethene hydrobromide gives 5-*hydroxy*-5′-*methyl*-3 : 4 : 3′ : 4′-*tetraethylpyrromethene*, m.p. 230°, converted by Br–AcOH into a violet, cryst. *product*, $C_{35}H_{46}O_3N_4$. 3-Bromo-2-formyl-4-methyl-5-pyrryl-*O*-ethylurethane and cryptopyrrole in hot HBr–H_2O–MeOH yield 3-*bromo*-4 : 3′ : 5′-*trimethyl*-4′-*ethylpyrromethene*-5-*ethylurethane*, decomp. 154—155°. 2-Formyl-4-methyl-3-ethyl-5-pyrryl-*O*-ethylurethane with cryptopyrrole in aq. HBr–AcOH or opsonic acid in aq. HBr–HCO_2H gives 4 : 3′ : 5′-*trimethyl*-3 : 4′-*diethylpyrromethene*-5-*O*-*benzylurethane*, m.p. 140° (unstable hydrobromide), and *CH*$_2$*Ph* 4 : 3′-*dimethyl*-3-*ethylpyrromethene*-5-*carbaminate*-4′-*propionic acid hydrobromide*, m.p. 203—204°, respectively. R. S. C.

Reactions with amyl nitrite. II. T. Ajello (Gazzetta, 1939, **69**, 315—322).—2 : 3 : 5-Triphenylpyrrole with C_5H_{11}·O·NO (I) in Et_2O gives 4-*nitro*-2 : 3 : 5-*triphenylpyrrole* (II), m.p. 192—194°, reduced (Al in 30% KOH) to the 4-NH_2-compound, to which the *Me ether*, m.p. 195°, of (II) is also reduced by Zn–AcOH. 2 : 5-Diphenylpyrrole and (I) give a *substance*, $C_{16}H_{12}O_3N_2$ (?), m.p. 300°, and 3-*nitro*-2 : 5-*diphenylpyrrole* (III), m.p. 174°, reduced as above to the NH_2-compound, to which the *Me ether* is also reduced. With (I), oximino-di- and -tri-phenylpyrrole give (II) and (III), respectively. E. W. W.

Local anæsthetics from β-2-piperidylethyl alcohol. L. A. Walter and R. J. Fosbinder (J. Amer. Chem. Soc., 1939, **61**, 1713—1714).—2-β-Hydroxyethylpiperidine hydrochloride and the appropriate acid chloride (1 mol.) in hot, dry $CHCl_3$ give β-2-*piperidylethyl* benzoate, m.p. 189—191° (lit., 182—183°), p-, m.p. 209—210°, m-, m.p. 170—172°, and o-*nitro*-, m.p. 148—150°, p-, m.p. 249—251°, m-, m.p. 177—180°, and o-*amino*-, m.p. 209—211°, p-*ethoxy*-, m.p. 146—148°, 3-*nitro*-, m.p. 150—155° and 3-*amino*-4-*ethoxy*-*benzoate*, m.p. 173—175°, and *cinnamate*, m.p. 180—182°. The *N*-*phenylurethane* has m.p. 200—202°. A few pharmacological data are given. 2-β-Hydroxyethylpiperidine is best (15—20%) obtained from α-picoline (1) and 40% CH_2O (2 parts by wt.) at 120°, followed by Na–EtOH. Li picolinyl with $(CH_2)_2O$ or MeCHO gives 40% of 2-γ-hydroxy-*n*- and 2-α-hydroxy*iso*-propylpyridine, readily reduced to the piperidinyl alcohols. M.p. are corr. R. S. C.

E E (A., II.)

Catalytic transformations of heterocyclic compounds. XII. Conversion of tetrahydropyran into piperidine, *N*-ethylpiperidine, and tetrahydrothiopyran. J. K. Juriev, E. J. Pervova, and V. A. Sazonova. **XIII. Synthesis of pyrrolidine and thiophan by catalytic dehydration of butane-αδ-diol in presence of ammonia or hydrogen sulphide.** J. K. Juriev and N. G. Medovschtschikov (J. Gen. Chem. Russ., 1939, **9**, 590—594, 628—630).—XII. Tetrahydropyran passed in a stream of NH_3 over Al_2O_3 at 360—430° gives piperidine (I) in 20% yield; *N*-ethylpiperidine is prepared analogously, with NH_2Et, and tetrahydrothiopyran (II) with H_2S. (I) and H_2S at 415° (Al_2O_3 catalyst) yield (II).

XIII. $(OH·CH_2·CH_2)_2$ and NH_3 or H_2S at 400° similarly give pyrrolidine (35% yield) or thiophan (63% yield). R. T.

Hydrogenation of hydroxy-amides. J. D. D'Ianni and H. Adkins (J. Amer. Chem. Soc., 1939, **61**, 1675—1681).—Hydrogenation of α-, γ-, δ-, and ε-OH-amides gives mainly NH_2-alcohols, better in presence of Cu chromite at 250—260° than of Raney Ni at 225°. β-OH-amides are reduced and dehydrated. More complex cases are also studied. *Lactopiperidide*, b.p. 128—129°/7 mm., with H_2–Cu chromite and H_2–Ni, respectively, gives β-piperidino-*iso*propyl alcohol (51, 27%), αβ-dipiperidinopropane (10, 0%) (*picrate*, m.p. 171—172°), OH·CHMe·CH_2·OH (10, 18%), piperidine (I) (10, 38%), and 1-*n*-propylpiperidine (4, 0%). β-*Hydroxybutyropiperidide* (prep. from the Et ester at 200°), b.p. 118—123°/7 mm., with H_2–Cu chromite gives 1-*n*-butylpiperidine (78) and (I) (12%), but with H_2–Ni gives n-*butyropiperidide* (86%), b.p. 105—109°/7 mm., and (I) (12%). γ-Hydroxy-*n*-valeropiperidide with H_2–Cu chromite or –Ni, respectively, gives ε-*piperidinopentan*-β-*ol* (79, 15%), b.p. 107°/6 mm. (*picrate*, m.p. 97—98°), αδ-*dipiperidino*-n-*pentane* (6, 0%), b.p. 118—119°/1 mm. (*dipicrate*, m.p. 168—169°), (I) (7, 44%), and γ-valerolactone (0, 58%). δ-*Hydroxy*-n-*hexopiperidide*, b.p. 135—140°/1 mm., with H_2–Cu chromite or –Ni, respectively, gives ζ-*piperidino*-n-*hexan*-β-*ol* (76, 34%), b.p. 123—125°/7 mm. (*picrate*, m.p. 86—89°), αε-*dipiperidino*-n-*hexane* (6, 0%), b.p. 122—123°/0·5 mm. (*dipicrate*, m.p. 166—167°), (I) (4, 29%), and δ-hexolactone (0, 15%). ε-*Hydroxy*-n-*heptopiperidide*, b.p. 145—148°/0·5 mm., with H_2–Cu chromite gives η-*piperidino*-n-*heptan*-β-*ol* (60%), b.p. 105—106°/1 mm. (*picrate*, m.p. 62—64°), αζ-*dipiperidino*-n-*heptane* (14%), b.p. 127—130°/1 mm. [*dipicrate*, m.p. 203—205° (decomp.)], heptane-αζ-diol (26%), and (I) (9%). *n*-Hexopiperidide is largely unchanged by H_2–Raney Ni, giving *n*-C_6H_{13}·OH (5), (I) (7), and 1-*n*-hexylpiperidine (6%). NN-*Di*-n-*amylmalonamide*, b.p. b.p. 146°, with H_2–Cu chromite gives 1-*n*-amylpyrrolidone (32), $NH(C_5H_{11})_2$ (30), succin-*n*-amylimide (14), NN-*di*-n-*amylsuccinamide* (12), b.p. 180—181°, 1-*n*-amylpyrrolidine (II) (9), and NH_2·C_5H_{11}-*n* (7%); NN-*di*-n-*amyltartaramide*, b.p. 194—195°, gives $NH(C_5H_{11}$-*n*$)_2$ (20), (II) (11), and NH_2·C_5H_{11}-*n* (8%); 5-phenyl-2 : 4-dimethyl-4-oxazolidone gives mandelamide (35), OH·CHPh·CH_2·OH (29), CH_2Ph·CH_2·OH (3), and $NHPr^{\beta}_2$ (47%). *Muco-*

dipiperidide (344 g.), b.p. 231° (decomp.), with H_2–Cu chromite at 250° (less well at 225—235° or with Raney Ni at 175—200°) suffers fission only between $C_{(\beta)}$ and $C_{(\gamma)}$, giving (I) (23), 1-ethyl- (10), 1-*n*-butyl- (7·5), 1-β-hydroxyethyl-. (7), 1-acetyl- (4·2), and ζ-hydroxy-*n*-hexyl-piperidine (11·5), αβ-dipiperidinoethane (12), αδ-dipiperidino-*n*-butane (44) (*dipicrate*, m.p. 185—186°), αζ-dipiperidino-n-hexane (12·5), *αζ-dipiperidino-*n*-hexan-β-ol* (22), b.p. 125—130°/1 mm. (*dipicrate*, m.p. 138—139°; *dihydrochloride*, m.p. 189—191°), *αζ-dipiperidino-*n*-hexane-βε-diol* (16), b.p. 150—160°/1 mm. (*dipicrate*, m.p. 170—173°), and adipdipiperidide (11 g.). Boiling (I) with $OH{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2Et$ or $OH{\cdot}CMe_2{\cdot}CO_2Et$ gives mainly *β-β′-hydroxybutyroxybutyropiperidide*, b.p. 105—110°/1 mm., and *α-α′-hydroxyisobutyroxyisobutyropiperidide*, b.p. 108—108·5°/1 mm., respectively. R. S. C.

1-Azadi*cyclo*-[1 : 3 : 3]-nonane. V. Prelog, S. Heimbach, and R. Seiwerth (Ber., 1939, **72**, [*B*], 1319—1325).—$CH_2(CO_2Et)_2$, NaOEt, and $OPh{\cdot}[CH_2]_3{\cdot}Br$ in boiling EtOH afford Et_2 γ-phenoxypropylmalonate, b.p. 207—208°/7 mm., converted by prolonged boiling with $OPh{\cdot}[CH_2]_3Br$ and NaOEt in EtOH into Et_2 *di-γ-phenoxypropylmalonate*, b.p. 245—250°/0·01 mm., m.p. 42—43·5°; the corresponding *acid*, m.p. 123—123·5°, is decarboxylated at 180—200° to *αη-diphenoxyheptane-δ-carboxylic acid*, m.p. 65°, the *Et* ester, b.p. 248°/0·05 mm., of which is reduced by Na–abs. EtOH to *αη-diphenoxy-δ-hydroxymethylheptane*, b.p. 255°/0·3 mm.; this with 68% HBr at 100° gives *αη-dibromo-δ-bromomethylheptane*, b.p. 170—175°/0·03 mm., which does not yield a *tert.* base when heated with NH_3–MeOH. Et nicotinoylacetate hydrochloride is reduced (PtO_2 according to Bruce in EtOH) to *Et* β-3-*piperidylpropionate* (I), b.p. 141—142°/10 mm. (yield 33·5% varying greatly with quality of catalyst). 3-β-*Piperidylpropionic acid hydrochloride* has m.p. 229°. Na and boiling EtOH reduce (I) to *γ-3-piperidylpropanol*, b.p. 154°/10 mm., whence 3-*γ-bromopropylpiperidine hydrobromide*, m.p. 154°, transformed by 0·1N-NaOH at 50° into 1-*azadi*cyclo-[1 : 3 : 3]-*nonane* (II), b.p. ~175°, m.p. 114° (*hydrochloride*, volatilises without melting at >350°; *platinichloride*, m.p. 226°; *picrate*, m.p. 283°; *picrolonate*, m.p. 231°; *methiodide*, m.p. 351°). *Et αη-diethoxyheptane-δ-carboxylate*, b.p. 166—168°/22 mm., is reduced by Na and abs. EtOH to *αη-diethoxy-δ-hydroxymethylheptane*, b.p. 158—161°/15 mm., converted by PBr_3 and C_5H_5N into *αη-diethoxy-δ-bromomethylheptane*, b.p. 153°/11 mm. This with KCN in EtOH–H_2O gives *αη-diethoxy-δ-cyanomethylheptane*, b.p. 171—172°/12 mm., hydrolysed to *ε-ethoxy-α-γ′-ethoxypropylhexoic acid*, b.p. 206°/12 mm., which is converted through the azide into *αη-diethoxy-δ-aminomethylheptane*, b.p. 150—151°/10 mm. The corresponding hydrobromide and 67% HBr at 100° afford *αη-dibromo-δ-aminomethylheptane hydrobromide*, m.p. 159°, converted by 0·1N-NaOH at 50° into (II) in 79% yield. All m.p. are corr. H. W.

Hydrogenations in the pyridine series. P. Karrer (Annalen, 1939, **539**, 297—298).—Concerning priority (cf. Mumm *et al.*, A., 1939, II, 339). R. S. C.

Polarisation in heterocyclic rings with aromatic character. E. Ochiai (J. Pharm. Soc. Japan, 1939, **59**, 20—28).—Examination of the literature of heterocyclic compounds from the electronic viewpoint shows that, as with isocyclic compounds, the chemistry of heterocyclic compounds can be divided into rings of alicyclic and aromatic character. The heterocyclic rings of alicyclic type can be considered in accordance with that of aliphatic derivatives and those of aromatic character can be treated in the same manner as C_6H_6 derivatives if the following hypotheses are accepted. The development of aromatic character in heterocyclic rings is due to the presence of six-membered rings with three conjugated double linkings or of five-membered rings which contain at least one hetero-atom (O, S, Se) or radical (NH) with a lone pair of electrons and two double linkings. Gradual differences are observed in the intensity of the aromatic character of aromatic heterocyclic rings. The most important underlying factor is the polar effect of the hetero-atoms, particularly of those with a lone pair of electrons. The chemical reaction of the heterocyclic ring of aromatic character is greatly influenced by the polar effect of the hetero-atoms of the rings. Substituents which are present exert their polar effect. It is therefore possible that the substitution of hetero-rings which are devoid of substituents occurs in the same manner as the reaction of substitution products of C_6H_6 which are similarly polarised. Thus pyrrole and PhOH, C_5H_5N and $PhNO_2$ have many properties in common. These four hypotheses are in good agreement with the behaviour of compounds with one ring and one hetero-atom. Detailed consideration is given to polarisation in the furan, thiophen, and pyrrole rings and in the C_5H_5N ring. H. W.

Pyrid-2-one-5-sulphonamide and certain derivatives. C. Naegeli, W. Kündig, and H. Brandenburger (Helv. Chim. Acta, 1939, **22**, 912—924).—2-Chloropyridine-5-sulphonamide is converted by 10% NaOH at 110° into *pyrid-2-one-5-sulphonamide*, m.p. 269—271°, in 88% yield, which is not increased by the addition of Cu powder or $CuSO_4$; aq. Na_2CO_3 or $NaHCO_3$ is without action. 2-Chloropyridine-5-sulphonyl chloride and 33% NH_2Me in $COMe_2$ afford *2-chloropyridine-5-sulphonmethylamide*, m.p. 111—112°, transformed by boiling 10% NaOH containing Cu powder into *pyrid-2-one-5-sulphonmethylamide*, m.p. 188—190°. The following are analogously obtained: *2-chloropyridine-*, m.p. 115—117°, and *pyrid-2-one-*, m.p. 212—214°, *-5-sulphondimethylamide*; *2-chloropyridine-*, m.p. 86—87°, and *pyrid-2-one-*, m.p. 163·5—165°, *-5-sulphondiethylamide*; *2-chloropyridine-*, m.p. 78°, and *pyrid-2-one-*, m.p. 159—160°, *-5-sulphonallylamide*; *2-chloropyridine-*, m.p. 90—92°, and *pyrid-2-one-*, m.p. 178°, *-5-sulphon-*n*-butylamide*; *pyrid-2-one-5-sulphonanilide*, m.p. 214—215°; *2-chloropyridine-*, m.p. 116—118°, and *pyrid-2-one-*, m.p. 169—172°, *-5-sulphon*cyclo*hexylamide*; *2-chloropyridine-*, m.p. 131—132°, and *pyrid-2-one-*, m.p. 236—238°, *-sulphonpiperidide*; *pyrid-2-one-5-sulphonmorpholide*, m.p. 262—264°; *2-chloropyridine-*, m.p. 197°, and *pyrid-2-one-*, m.p. 282°, *-5-sulphon-*p*-nitroanilide-*, *pyrid-2-one-5-sulphon-*p′*-aminoanilide*, m.p. 246°; N^4*-pyrid-2′ one-5′-*, m.p. 250—252°, N′-*2″-pyridyl-*

N^4-2′-*chloropyridine*-5′-, m.p. 266°, and N′-2″-*pyridyl*-N^4-*pyrid*-2′-*one*-5′-*sulphonyl*-5′-, m.p. 301—302°, -*sulphonylsulphanilamide*; 2-(*pyrid*-2′-*one*-5′-*sulphonamido*)*pyridine*-5-*sulphonamide*, m.p. 295° (incipient decomp.); 2-2′-*Chloropyridine*-5′-*sulphonamidopyridine*, m.p. 235—236°, and 2-(NN-*di*-2′-*chloropyridine*-5′-*sulphon*)*amidopyridine*, m.p. 197—199°, are described. 2-2′-*Ethoxypyridine*-5′-*sulphonamidopyridine* and 2-*butoxypyridine*-5-*sulphonallylamide* have m.p. 180° and 67—68°, respectively.

H. W.

Indoline aldehydes.—See B., 1939, 809.

Synthesis of nitrogen ring compounds. XII. Synthesis of quinoline derivatives. II. Synthesis of 6 : 7-dimethoxyquinoline. S. Sugasawa, K. Kakemi, and T. Tsuda (J. Pharm. Soc. Japan, 1938, **58**, 80—82).—3 : 4 : 1-$(OMe)_2C_6H_3$·$[CH_2]_2$·CO_2H with HNO_3–AcOH at 40—50° gives 6-*nitro*-3 : 4-*dimethoxyhydrocinnamic acid*, m.p. 188°, reduced catalytically in EtOH at 2 atm. to 6 : 7-*dimethoxyhydrocarbostyril* (I), m.p. 136° (not obtained by action of HN_3 on 5 : 6-dimethoxyhydrindone), identified by its prep. by reduction of 6-nitro-3 : 4-dimethoxycinnamic acid. With P_2S_5 and K_2S in xylene at 90—95°, (I) gives 6 : 7-*dimethoxyhydrothiocarbostyril*, m.p. 151°, reduced electrolytically in 20% EtOH–H_2SO_4 (Pb anode; 1 amp. per sq. cm.; 25—35°) to 6 : 7-*dimethoxy*-1 : 2 : 3 : 4-*tetrahydroquinoline* (*hydrochloride*, m.p. 196°; *NO*-derivative, m.p. 137°; *Bz* derivative, m.p. 102°). This is dehydrogenated (method : Hoshino and Takiura, A., 1936, 863) to 6 : 7-*dimethoxyquinoline* [*hydrochloride*, m.p. 232° (decomp.); *picrate*, m.p. 251—252° (decomp.)].

E. W. W.

[Attempted] Ullmann reaction with nitrogenous heterocyclic compounds. M. Tomita and H. Watanabe (J. Pharm. Soc. Japan, 1938, **58**, 223—230).—Condensation of 7-hydroxy-6-methoxy-2-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline (I) with 8-bromo-6 : 7-dimethoxy-2-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline (II) by KOMe and Cu catalysts, first at 180° and then at 220°, failed, giving unchanged (I) and, by debromination of (II), the Me ether of (I). 3 : 4 : 1-OMe·C_6H_3(O·CH_2Ph)·CH:CH·NO_2 [prep. in 75% yield from 3 : 4 : 1-OMe·C_6H_3(O·CH_2Ph)·CHO and $MeNO_2$ by NH_2Me,HCl and Na_2CO_3 at room temp.], m.p. 123—124°, is reduced electrolytically to 3 : 4 : 1-OMe·C_6H_3(O·CH_2Ph)·$[CH_2]_2$·NH_2, the hygroscopic formate, m.p. 146—149° (decomp.), of which at 180—200°/vac. yields the N-*CHO* derivative, m.p. 57—63°. With $POCl_3$ in hot PhMe this gives 7-*benzyloxy*-6-*methoxy*-3 : 4-*dihydro*isoquinoline (24%), m.p. 183° (and 7-*hydroxy*-6-*methoxy*-3 : 4-*dihydro*isoquinoline, m.p. 182°), which affords the *methiodide*, m.p. 194°, and thence the hygroscopic methochloride, which, best, with H_2–PtO_2 in H_2O gives (I), m.p. 167°. 5-*Bromo*-ω-*nitro*-3 : 4-*dimethoxystyrene*, m.p. 159°, is obtained from 3 : 4 : 5 : 1-$(OMe)_2C_6H_2Br$·CHO [prep. from 4 : 3 : 5 : 1-OH·C_6H_2Br(OMe)·CHO by Me_2SO_4–NaOH], $MeNO_2$, and KOH–aq. EtOH, and by the methods given above yields β-5-bromo-3 : 4-dimethoxyphenylethylamine (*formate*, hygroscopic; N-*CHO* derivative, an oil), 8-*bromo*-6 : 7-*dimethoxy*-3 : 4-*dihydro*isoquinoline, m.p. 102° [*hydrochloride*, decomp. 196°; *methiodide*, m.p. 179° (decomp.); *methochloride*, hygroscopic], and (II), an oil [*platinichloride*, m.p. 213° (decomp.); *hydrochloride*, hygroscopic, m.p. 210°]. The structure of (II) is proved by its prep. from (I) by Br–AcOH (gives the 8-*Br*-derivative, m.p. 185°), followed by CH_2N_2.

R. S. C.

Amyostatic poisons. Synthesis of polyaminohydrocarbostyrils. U. Ueda (Proc. Imp. Acad. Tokyo, 1939, **15**, 148—155).—The structure of the derivatives described below is proved by the oxidations noted. Nitro- and particularly polynitrohydrocarbostyrils suffer ring-fission by 0·5N-NaOH and the resulting acids can be isolated. Aminohydrocarbostyrils are usually too unstable to be isolated except as salts. Colour reactions with Br–H_2O distinguish 3-NH_2- and 3 : 6-$(NH_2)_2$- from 3 : 8-$(NH_2)_2$- and 3 : 6 : 8-$(NH_2)_3$-derivatives. Hydrocarbostyril (I) with H_2SO_4–NHO_3 (*d* 1·52) at 0° gives the 6-NO_2-derivative (II), m.p. 203—204° [oxidised by $KMnO_4$ to 5 : 2 : 1-NO_2·$C_6H_3(NH_2)$·CO_2H], converted by further nitration into the 6 : 8-$(NO_2)_2$-derivative (III), m.p. 177°, also obtained directly from (I) (cf. Menon *et al.*, A., 1930, 795). Zn–HCl at 100° reduces (II) to 6-*aminohydrocarbostyril*, m.p. 178° (*hydrochloride*, decomp. ~315°; *Bz*, m.p. 241°, and *Ac* derivative, m.p. 263—264°). With 0·05N-KOH at 100°, (III) gives β-3 : 5-*dinitro*-2-*aminophenylpropionic acid*, but with hot N-NaOH gives 2 : 3 : 5 : 1-OH·$C_6H_2(NO_2)_2$·$[CH_2]_2$·CO_2H, m.p. 159—160°. Zn–HCl and (III) give 6 : 8-diaminohydrocarbostyril (*Bz*$_2$ derivative, m.p. 264—265°). H_2SO_4–HNO_3 (*d* 1·52) at 100° oxidises as well as nitrates (I), giving 3 : 6 : 8-trinitrocarbostyril (IV), m.p. 182° (cf. Kaufmann, A., 1917, i, 354). 6 : 8-*Dinitro*-3-*acetamidohydrocarbostyril* (V) (prep. from the 3-NHAc-compound), m.p. 235°, and $K_2Cr_2O_7$ in hot 30% H_2SO_4 give 2 : 3 : 5 : 1-NH_2·$C_6H_2(NO_2)_2$·CO_2H and thence by NaOH 2 : 3 : 5 : 1-OH·$C_6H_2(NO_2)_2$·CO_2H. Hot 0·05N-NaOH converts (V) into α-*acetamido*-β-3 : 5-*dinitro*-2-*aminophenylpropionic acid*, m.p. 225° (decomp.), and Zn–HCl yields 3 : 6 : 8-triaminohydrocarbostyril [*hydrochloride*; *Bz*$_3$ derivative, m.p. 250°, obtained also from (IV) by red P and HI (*d* 1·7) and subsequent benzoylation, whence the structure of (IV) follows].

R. S. C.

Sharp-tasting acylamines. T. Széki (Math. nat. Anz. ung. Akad. Wiss., 1936, **54**, 807—818; Chem. Zentr., 1937, i, 1690; cf. A., 1930, 597).—*Piperoylpyrrolidine*, m.p. 144°, which is analogous in constitution to piperine, has a sharp taste. The aminophenol group in the spicy acylamines may be replaced by an NH_2-alcohol; thus NH_2·$[CH_2]_3$·OH gives spicy derivatives (*piperoyl*-, m.p. 148·5°, producing a strong burning action on the mucous membrane; *undecenoyl*-, m.p. 53°, similar in odour to capsaicine). *Piperoyl*-β-*aminoethanol*, m.p. 162°, has no spicy character, but the *undecenoyl* derivative, m.p. 70·5°, has a sharp, aromatic taste. Substitution of C_6H_3·O_2CH_2 or $C_6H_3(OMe)_2$ in the C-chain of the NH_2·$[CH_2]_3$·OH grouping (β-*undecenamido*-α-*hydroxydihydroisosafrole*, m.p. 95°, and *-dihydroisoeugenol Me ether*, m.p. 91°) destroys the spicy taste. Compounds of unsaturated acids with piperidine and pyrrolidine (*undecenoyl*-, b.p. 170°/3 mm. and 168°/3 mm., re-

spectively) are spicy. *Undecenoyl-4-aminoquinoline*, m.p. 71·5° (*hydrochloride*, m.p. 169°), *-tetrahydroquinoline*, b.p. 234—235°/4 mm., *piperoyl-4-aminoquinoline*, m.p. 233°, *-tetrahydroquinoline*, m.p. 145°, and *diundecenoylpiperazine*, m.p. 63°, are tasteless. The prep. of the above compounds from the base and piperoyl or undecenoyl chloride is described.

A. J. E. W.

Constitution of the quinaldinic acids. V. M. MITCHOVITCH (Bull. Soc. chim., 1939, [v], **6**, 1156—1162).—Me_2 quinaldine-3 : 4-dicarboxylate (A., 1938, II, 293) and excess of PhCHO at 160—165° afford the *CHPh:* derivative, m.p. 124°, hydrolysed by KOH–EtOH to 2-*styrylquinoline*-3 : 4-*dicarboxylic acid* (I), $+H_2O$, m.p. 213° [= m.p. of (II)]. It loses $2H_2O$ at 100—110°/0·2 mm. to give the *anhydride* (II), m.p. 213°, convertible into (I). (I) and $KMnO_4$–aq. KOH at 100° (bath) give *quinoline* 2 : 3 : 4-*tricarboxylic acid*, $+H_2O$, m.p. 254° (decomp.) (*Me_3* ester, m.p. 102·5°). Isatic acid and $CO_2H{\cdot}[CH_2]_2{\cdot}CO{\cdot}CO_2H$ afford *quinoline*-3-*acetic acid*-2 : 4-*dicarboxylic acid*, m.p. 245° (decomp.) [*Et_2* ester, m.p. 195° (decomp.)].

A. T. P.

Quinoline series. IV. New synthesis of quinic acid. E. THIELEPAPE and A. FULDE (Ber., 1939, **72**, [*B*], 1432—1443).—Acet-*N*-methyl-*p*-methoxyacetanilide is converted by $Et_2C_2O_4$ and NaOEt in Et_2O into *ethoxalylacet*-N-*methyl*-p-*methoxyacetanilide*, m.p. 80·0—80·5° (corr.) [*Cu* salt, m.p. 194—195° (corr.)], converted by conc. H_2SO_4 at $< -5°$ into *Et* 2-*keto*-6-*methoxy*-1-*methyl*-1 : 2-*dihydroquinoline*-4-*carboxylate* (I), m.p. 105° (corr.), which is hydrolysed by aq. NaOH to the *acid*, m.p. 316—317° (corr.) [*Me* ester, m.p. 113° (corr.)]. Addition of (I) to a boiling solution of PCl_5 in $POCl_3$ affords *Et* 2-*chloro*-6-*methxoyquinoline*-4-*carboxylate* (II), m.p. 100° (corr.), hydrolysed by boiling very dil. NaOH to 2-*chloro*-6-*methoxyquinoline*-4-*carboxylic acid* (III), m.p. 230° (corr.; decomp.). Boiling 30% NaOH transforms (II) into 2-hydroxy-6-methoxyquinoline-4-carboxylic acid, m.p. 335—336° (corr.) [*Me*, m.p. 233—234° (corr.), and Et, m.p. 195° (corr.), ester]. Red P, KI, and HI (*d* 1·5 or 1·7) transform (II) at 100° and subsequently at 150° into 2-*iodo*-6-*methoxyquinoline*-4-*carboxylic acid* (IV), m.p. 190° (corr.; decomp.) after becoming brown at 186° (corr.). (II) is transformed by $SnCl_2$ and HCl (*d* 1·19) at 100° into 6-methoxyquinoline-4-carboxylic (quinic acid), m.p. 285° (corr.; decomp.) [hydrazide, m.p. 154° (corr.); *aurichloride*, m.p. 223° (corr.); *stannichloride*, $(C_{11}H_9O_3N,HCl)_2SnCl_4$, m.p. 274—275° (corr.; decomp.); *picrate*, m.p. 244° (corr.); Et, m.p. 69° (corr.), and Me, m.p. 87° (corr.), ester]. Dechlorination of (II) or (III) could not be effected in presence of Pt-sponge, whereas Pd–$BaSO_4$ is almost quantitatively efficient at room temp. Dehalogenation of (IV) occurs slowly in presence of Pt-sponge. H. W.

Course of the quinoline synthesis with tetrahydronaphthylamines. 7 : 8-Tetramethylenequinoline. J. LINDNER and B. ZAUNBAUER (Monatsh., 1939, **72**, 213—215).—1-Aminotetrahydronaphthylamine, glycerol, H_2SO_4, and $PhNO_2$ afford 7 : 8-*tetramethylenequinoline*, m.p. 26° [*hydrochloride*, m.p. ~215° (decomp.); *picrate*, m.p. 186°]. H. W.

Hydrindene derivatives. III. 7 : 8-Trimethylene-quinoline and -quinaldine. J. LINDNER, J. SELLNER, and A. BERGER. **IV. 5 : 6- and 6 : 7-Trimethylenequinoline.** J. LINDNER, J. SELLNER, E. HOFMANN, and J. HAGER. **V. 5 : 6- and 6 : 7-Trimethylenequinaldine.** J. LINDNER, A. BERGER, and W. MIGNON. **VI. Action of formaldehyde on, and proof of the constitution of, 6 : 7-trimethylenequinaldine.** J. LINDNER and J. HAGER (Monatsh., 1939, **72**, 330—334, 335—349, 354—360, 361—367).—III. 4-Aminohydrindene with glycerol, conc. H_2SO_4, and $PhNO_2$ gives 7 : 8-*trimethylenequinoline*, m.p. 51—53° [*hydrochloride*, decomp. ~210°; *hydrobromide*, decomp. ~210°; *hydriodide*, decomp. >210°; *picrate*, m.p. 211—212° (decomp. from ~207°)], and with MeCHO, HCl, and H_2SO_4 at 100° gives 2-*methyl*-7 : 8-*trimethylenequinoline*, m.p. 89° (*hydrochloride*, decomp. 250°; *hydrobromide*, decomp. ~230°; *hydriodide*, decomp. ~240—250°; *picrate*, m.p. 190—191°).

IV. 5-Aminohydrindene (I) gives >90% of 6 : 7- (II), m.p. 79—80·5° [*hydrochloride*; *hydrobromide*; *hydriodide*; *picrate*, m.p. 269—271° (decomp.)], and <10% of 5 : 6-*trimethylenequinoline* (III), m.p. 43–44·5° (*hydrochloride*; *hydrobromide*; *hydriodide*; *picrate*, m.p. 190—191°). $KMnO_4$ converts (II) into *quinoline*-6 : 7-*dicarboxylic acid*, m.p. 240—250° (decomp. from 230°) (*Me_2* ester, m.p. 104·5°). (III) gives the known quinoline-5 : 6-dicarboxylic acid, m.p. 228° (lit., 238—241°) (*Me_2* ester, sinters at 119°, m.p. 120—121°).

V. By the Döbner–Miller quinaldine synthesis, (II) gives 2-*methyl*-6 : 7- (IV), m.p. 93—95° (*hydrochloride*; *hydrobromide*, decomp. ~185°; *hydriodide*, decomp. ~190—195°; *picrate*, m.p. 202—203°), with a very small amount of -5 : 6-*trimethylenequinoline* (V), m.p. 53—54° (*picrate*, m.p. 193—194°).

VI. The constitution of (IV) and thus by exclusion of (V) is proved as follows. 70% of (IV) is recovered after heating with 40% aq. CH_2O (0·85 mol.) at 100°, but the remainder yields 6 : 7-*trimethylene*-2-β-*hydroxyethyl*- (VI), m.p. 92—93°, -2-ββ′-*dihydroxyisopropyl*-, m.p. 121—122°, and -2-ββ′β″-*trihydroxy*-tert.-*butylquinoline*, m.p. 165°. With HI (*d* 1·96) and red P at 100°, (VI) gives 6 : 7-*trimethylene*-2-β-*iodoethylquinoline*, an oil [*hydriodide*, m.p. 124° (sinters at 120°; decomp. from 100°)], converted by conc. NaOH–H_2O–$COMe_2$ into 6 : 7-*trimethylene*-2-*vinylquinoline*, m.p. 65°, which with $KMnO_4$–H_2SO_4 at 0° gives 6 : 7-*trimethylenequinoline*-2-*carboxylic acid*, decomp. ~208—210°. This, when heated with $Ba(OH)_2$ in N_2 at 220—230°/vac., gives (II).

The above reactions show that the ethylenic linkings of hydrindene exist mostly, but not entirely, as in $\left.\begin{matrix}CH{\cdot}CH{:}C{\cdot}CH_2\\CH{\cdot}CH{:}C{\cdot}CH_2\end{matrix}\right\rangle CH_2$.

R. S. C.

Heterocyclic derivatives of *p*-aminobenzenesulphonamide and 4 : 4′-diaminodiphenylsulphone. W. H. GRAY (J.C.S., 1939, 1202).—*p*-Aminobenzenesulphonamide with 2-chloropyridine (I) gives p-(2-*pyridylamino*)-, m.p. 235°, and with 2-chloroquinoline (II) affords p-(2-*quinolylamino*)-*benzenesulphonamide*, m.p. 263° (*hydrochloride*, m.p. 279°). *pp′*-Diaminodiphenylsulphone with (I) yields pp′-*bis*-(2-*pyridylamino*)-, m.p. 241°, and with (II) gives

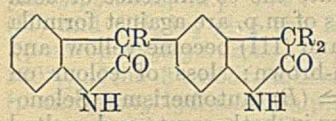
-(2-*quinolylamino*)-*diphenylsulphone*, m.p. 306°. These compounds have low toxicity but are inactive in streptococcal and pneumococcal infections of mice.

F. R. S.

10-Substituted acridoneanils and acridoneazines. K. GLEU and R. SCHAARSCHMIDT (Ber., 1939, **72**, [*B*], 1404—1407).—The additive compound (I) of 10-methylacridine and $POCl_3$ is almost instantaneously converted by NH_2Ph in cold H_2O into 10-methylacridoneanil, m.p. 162°. 10-*Ethyl*-, m.p. 147°, and 10-*phenyl*-, m.p. 142°, -*acridoneanil* are obtained similarly. Under analogous conditions (I) and N_2H_4,H_2O afford 10-*methylacridoneazine*, m.p. 290°; the hydrazone is not obtained even with a very large excess of N_2H_4,H_2O. 10-*Ethyl*-, m.p. 204°, and 10-*phenyl*-, m.p. 286°, -*acridoneazine* are described.

H. W.

Diphenylisatin and its derivatives. III. By-products of dianisylisatin and their oxidation products. IV. Monobromo-compounds of dianisylisatin and their oxidation products. V. Oxidation product of diacetoxyphenylisatin. VI. Ditolylisatin and its oxidation products. VII. Synthetic preparation of phenyldioxindoles and their oxidation products. S. INAGAKI (J. Pharm. Soc. Japan, 1939, **59**, 1—4, 4—5, 5—6, 7, 7—10).—III. The by-product, m.p. 325—327°, of the condensation of isatin with anisole is identified as *anisylisatyldianisylisatin* (I). It is oxidised by CrO_3 in AcOH followed by $KMnO_4$ after treatment of the product with conc. H_2SO_4 to $CO(C_6H_4{\cdot}OMe\text{-}p)_2$ and *p*-$OMe{\cdot}C_6H_4{\cdot}CO_2H$. With MeI it yields a Me_2 compound and is acetylated to a diacetate. Bromination of dianisylisatin (II) gives a 5-bromodianisylisatin. Oxidation with CrO_3 in AcOH causes union of 1 O with each isatin nucleus and acetylation of 1 NH, giving a *compound*, decomp. 178—180°; this when treated successively with conc. H_2SO_4, H_2O, and NaOH gives o-*amino*-p'-*methoxybenzhydrylanhydro*-2-*acetamido*-4' : 4''-*dimethoxytriphenylcarbinol* or *anhydro*-o-*acetamido*-p'-*methoxybenzhydryl*-2-*amino*-4' : 4''-*dimethoxytriphenylcarbinol*, m.p. 203—204°. Isatin is converted by Mg *o*-methoxyphenyl iodide into o-*methoxyphenylisatylcarbinol*, m.p. 240°; this with anisole and conc. H_2SO_4 yields 3-2' : 4''-*dimethoxydiphenylisatin*, m.p. 232° (*Ac* derivative, m.p. 172°), which is not identical with (I); it is oxidised and then converted by H_2SO_4, H_2O, and NaOH into 2'-*amino*-2'' : 4'''-*dimethoxytriphenylcarbinol*.



(I.) R = ·C_6H_4·OMe-*p*

IV. 4-, 5-, 6-, and 7-Bromoisatin have been prepared and the position of Br therein has been determined by oxidation by H_2O_2 to the corresponding bromoanthranilic acids. They condense with anisole in AcOH containing conc. H_2SO_4 to 4-, m.p. 211°, 5-, m.p. 220°, 6-, m.p. 193—194°, and 7-, m.p. 222—224°, -*bromodianisylisatin*, of which the 5-derivative is identical with the product of the bromination of (II) in AcOH. These are oxidised by CrO_3 in AcOH to 4-, m.p. 213—214°, 5-, m.p. 220°, 6-, m.p. 201—202°, and 7-, m.p. 198—199°, -*bromodianisylisatoic anhydride*, respectively. The anhydrides lose CO_2 when treated with conc. H_2SO_4 and the products are transformed by H_2O and NaOH into 3-, non-cryst., 4-, m.p. 125—128°, 5-, m.p. 143—145°, and 6-, m.p. 235—236°, -*bromo*-2-*amino*-4' : 4''-*dimethoxytriphenylcarbinol*. 3-*Bromo*-2-*acetamido*-4' : 4''-*dimethoxytriphenylcarbinol* has m.p. 149—152°.

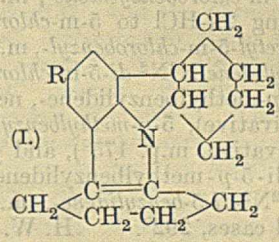
V. Oxidation of 3-4' : 4''-diacetoxyphenylisatin with CrO_3 in AcOH gives a small yield of *diacetoxyphenylisatoic anhydride*, which is transformed by conc. H_2SO_4 into 2-*amino*-4' : 4''-*dihydroxytriphenylmethane* (III), m.p. 218° (*Ac*$_3$ derivative, m.p. 139°), and 2-*hydroxy*-5-4'-*hydroxyphenylacridine* (IV), m.p. >350° (*diacetate*, m.p. 167°). 2-Amino-4' : 4''-dimethoxytriphenylcarbinol is transformed by Zn and AcOH into 2-acetamido-4':4''-dimethoxytriphenylmethane, which is converted by HBr–AcOH into (III). NH_2Ph and *m*-$C_6H_4(OH)_2$ afford 3-hydroxytriphenylamine, which is condensed with *p*-$OH{\cdot}C_6H_4{\cdot}CO_2H$ in presence of $ZnCl_2$ to (IV).

VI. Condensation of isatin with PhMe by conc. H_2SO_4 gives 3-p'p''-*ditolylisatin*, m.p. 204—205°, oxidised by CrO_3 in AcOH to ditolylisatoic anhydride, which with conc. H_2SO_4 loses CO_2 and gives 2-amino-4' : 4''-dimethyltriphenylcarbinol.

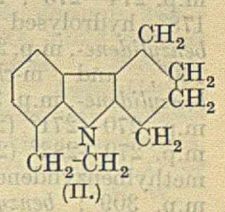
VII. The action of the requisite Grignard reagent on powdered isatin gives *p*-, m.p. 205°, m-, m.p. 200°, and o-, m.p. 215—216°, -*tolyldioxindole* and p-, m.p. 194°, m-, m.p. 179·5°, and o-, m.p. 240°, -*anisyloxindole*. All are colourless. Conc. H_2SO_4 gives red colours with the *p*- and *m*- but blue colours with the *o*-compounds. They are converted by Ac_2O at 145° or by boiling Ac_2O containing NaOAc into the Ac_2 derivatives, m.p. 158°, 136°, 142—144°, 143°, 133—134°, and 160°, respectively. Phenyldioxindole yields a *diacetate*, m.p. 143°. Oxidation of the oxindoles by H_2O_2 in alkaline solution affords respectively *p*-$C_6H_4Me{\cdot}CO_2H$ and *o*-$NH_2{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_4Me\text{-}p$; m-$C_6H_4Me{\cdot}CO_2H$ and 2-*amino*-3'-*methylbenzophenone*, m.p. 60°; *o*-$C_6H_4Me{\cdot}CO_2H$ and 2-*amino*-2'-*methylbenzophenone*, m.p. 81—82°; *p*-$OMe{\cdot}C_6H_4{\cdot}CO_2H$ and *o*-$NH_2{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_4{\cdot}OMe\text{-}m$; *m*-$OMe{\cdot}C_6H_4{\cdot}CO_2H$ and 2-*amino*-3'-*methoxybenzophenone*; *o*-$OMe{\cdot}C_6H_4{\cdot}CO_2H$ and 2-*amino*-2'-*methoxybenzophenone*, m.p. 110°.

H. W.

Stereochemistry of tervalent nitrogen. F. LIONS and E. RITCHIE (J. Amer. Chem. Soc., 1939, **61**, 1927—1928).—Manjunath's "8 : 9-(1' : 2'-*cyclo*hexyl)tetrahydrocarbazole" (A., 1927, 978) was really (I) (R = H). 9-Nitroso-6-methyl-1 : 2 : 3 : 4 : 1*a* : 4*a*-hexahydrocarbazole, *cyclo*hexanone, and Zn dust in AcOH give similarly the *substance* (I)



(I.)



(II.)

(R = Me), but no analogue could be obtained from the 8-methylcarbazole derivative owing to steric hindrance. A similar reaction with 1-nitrosoindoline gives the *substance* (II), m.p. 154°.

R. S. C.

Formation and constitution of skatole-red from urine. M. RANGIER and P. DE TRAVERSE (Compt. rend., 1938, **207**, 1257—1259; cf. A., 1939, III, 393).—Urochrome, freed from indoxyl sulphate and glycuronates, with 2% H_2SO_4 at 100° affords indoxyl, removed by Et_2O. Evaporation of the mother-liquor yields a substance, m.p. 85°, which polymerises easily, gives a red colour [skatole-red (I)] with warm HCl in air, and with $FeCl_3$ an intense blue. (I) is probably indirubin. J. L. D.

Amino-acids. XI. Condensation of creatinine with aromatic aldehydes. P. CATTANEO, V. DEULOFEU, and T. H. GUERRERO (Ber., 1939, **72**, [*B*], 1461—1470).—5-p-Hydroxybenzylidenecreatinine, m.p. 284—285 or, +Ac_2O, m.p. 225—227°, obtained from creatinine and *p*-OH·C_6H_4·CHO at 150—155° or in boiling piperidine (Ac derivative, m.p. 225°), is reduced by Na–Hg in H_2O to 5-*p*-hydroxybenzylcreatinine, m.p. (dry) 255—256°. The following *-creatinines* are obtained analogously: 5-3′-*hydroxy*-4′-*methoxy-benzylidene-*, m.p. 280°, and *-benzyl-*, m.p. 253°; 5-2′:4′-*dimethoxy-benzylidene-*, m.p. 244—245° (2-*Ac* derivative, m.p. 205°), and *-benzyl-* (*Ac* derivative, m.p. 129°); 5-3′:4′-*dimethoxybenzylidene-*, m.p. 244—245° (*Ac* derivative, m.p. 213—214°); 5-3′:4′:5′-*trimethoxy-benzylidene-*, m.p. 257—258° (2-*Ac* derivative, m.p. 215°), and *-benzyl-* (2-*Ac* derivative, m.p. 125°); 5-furfurylidene-, m.p. 273—275° (2-Ac derivative, m.p. 252°), and 5-furfuryl- (2-*Ac* derivative, m.p. 189°); 5-*cinnamylidene-*, m.p. 280° (2-*Ac* derivative, m.p. 248°); 2-*acetyl*-5-2′-*acetoxy*-3′-*methoxybenzylidene-*, m.p. 218°; 5-*o*-methoxybenzylidene-, m.p. 243—244° (2-*Ac* derivative, m.p. 194°), and *o*-methoxybenzylidene-N^2N^2-di-5-*o*-methoxybenzylidene-, new m.p. 306—308°; 5-m-*methoxybenzylidene-*, m.p. 231°, 5-m-*methoxybenzyl-*, m.p. 268° (non-cryst. 2-*Ac* derivative), and m-*methoxybenzylidene*-N^2N^2-*di*-5-m-*methoxybenzylidene-*, m.p. 270°; 5-*p*-methoxybenzylidene-, m.p. 259°, and p-*methoxybenzylidene*-N^2N^2-*di*-5-p-*methoxybenzylidene*-, prisms or needles, m.p. >300°; 3:4-*dimethoxybenzylidene*-N^2N^2-*di*-5-3:4-*dimethoxybenzylidene-*, m.p. 260°; 5-4′-*hydroxy*-3′:5′-*dimethoxybenzylidene-*, m.p. 250° or, + AcOH, m.p. 148° (Ac_2 derivative, m.p. 205°), and 4-*hydroxy*-3:5-*dimethoxybenzylidene*-N^2N^2-*di*-5-4-*hydroxy*-3:5-*dimethoxybenzylidene-*, m.p. >300° (Ac_3 derivative, m.p. >300°); *o*-chlorobenzylidene-, new m.p. 250—251° (2-*Ac* derivative, m.p. 198°), 2-*acetyl*-5-*o*-*chlorobenzyl-*, m.p. 148°, and *o*-chlorobenzylidene-N^2N^2-di-5-*o*-chlorobenzylidene-, m.p. 274—275°; 2-*acetyl*-5-m-*chlorobenzylidene-*, m.p. 178°, hydrolysed by boiling 2N-HCl to 5-m-*chlorobenzylidene-*, m.p. 265°, 2-*acetyl*-5-m-*chlorobenzyl-*, m.p. 160°, and m-*chlorobenzylidene*-N^2N^2-*di*-5-m-*chlorobenzylidene-*, m.p. 300°; 5-*p*-methylbenzylidene-, new m.p. 270—271° (2-*Ac* derivative), 5-p-*methylbenzyl-*, m.p. 270—282° (2-*Ac* derivative, m.p. 175°), and *p*-methylbenzylidene-N^2N^2-di-5-*p*-methylbenzylidene-, m.p. 309°; *benzylidene*-N^2N^2-*di*-5-*benzylidene-*, m.p. 281—282° or, in individual cases, 292°. H. W.

Reaction between organic sulphur compounds and hydrogen peroxide. XII. Constitution of antipyrine and related compounds. I. R. KITAMURA (J. Pharm. Soc. Japan, 1938, **58**, 86—101; cf. A., 1938, II, 206).—Thiopyrine (I) with aq. KOH and H_2O_2 slowly gives antipyrine (II). 3-Thiopyrine (III) also slowly gives 3-antipyrine (IV), and antithiopyrine and bisthiopyrine (V) give bisantipyrine (VI). MeCS·NPhMe and 1-phenyl-3:4:4-trimethyl-5-thiopyrazole (VII) react more rapidly, as do HCS·NHPh, PhCS·NH_2, PhCS·NHPh, and MeCS·NHPh. The slow reaction of (I) may be due to tautomerism between a preponderant but little reactive betaine form (*A*) and a more reactive form (*B*) (Knorr's formula). Neutral H_2O_2 converts (I) into thioantipyrine trioxide, decomp. 301—302° (new temp)., but does not react with (VII). The stability of (II), (IV), pyramidone (VIII), and 4-aminoantipyrine (IX) to Pt–Pd–H_2 is against formula (*B*). Coloured compounds with $FeCl_3$ are described, as follows. From (I), (II), (IV), and (IX), *compounds* of type 3M,2$FeCl_3$, decomp. 115—120°, 220—300°, 180—187°, and 243—245°, respectively; from (V), (VI) and methylenebisantipyrine, *compounds* of type 3M,4$FeCl_3$, decomp. 169—172°, 250—260°, and 174—179°, respectively; and from (VIII) a *compound*, M,$FeCl_3$, decomp. 132—134°. All these compounds support formula (*A*); relations between colour and constitution of antipyrines etc. are discussed. Absorption spectra indicate the co-existence of both structures; abnormalities of m.p. are against formula (*B*). When melted, (I) and (III) become yellow, and 3-selenopyrine yellowish-brown; loss of colour on cooling suggests a (*A*) ⇌ (*B*) tautomerism. Selenopyrine is, however, yellow in both cryst. and melted states. While (II) distils unchanged at 147°/0·05 mm., supporting formula (*B*), (I) at ~140°/0·05 mm. in part distils unchanged, and in part gives *ψ*-thiopyrine. It is concluded that the structure of (I) is best represented by forms (*B*) and CH(CS⁻)=CMe:N⁺Me>NPh in equilibrium, and of (II) by similar forms in which O replaces S. E. W. W.

Reaction between organic sulphur compounds and hydrogen peroxide. XIII. Constitution of antipyrine and related compounds. II. Proof of the betaine form. R. KITAMURA (J. Pharm. Soc. Japan, 1938, **58**, 161—164).—Thiopyrine trioxide (I), CMe=CH(C·SO_3^-)>N⁺Me·NPh (from thiopyrine and neutral H_2O_2), is unaffected by cold aq. KOH but with H_2O_2 and KOH in 60% EtOH at room temp. for 36 hr. gives antipyrine (II), thus establishing the betaine structure of (II). Conversion of (I) into (II) is also effected with 0·5N-KOH at 100° (bath) and, less readily, N-K_2CO_3; hot N-HCl is without action. H. B.

Reaction between organic sulphur compounds and hydrogen peroxide. XIX. Mechanisms of reaction. XX. Constitution of antipyrine and related compounds: tautomerism and mesomerism. R. KITAMURA (J. Pharm. Soc. Japan, 1939, **59**, 61—72, 73—78).—Theoretical considerations. A. T. P.

Pyrazole synthesis. IV. Action of α-halogenohydrazones on sodium derivatives of β-

ketonic esters. V. Action of α-halogenohydrazones on sodium salts of *sym.*-β-diketones. VI. Action of α-halogenohydrazones on sodium salts of *as.*-β-diketones. R. Fusco (Gazzetta, 1939, **69**, 344—352, 353—364, 364—378; cf. A., 1938, II, 206).—IV. In EtOH, COMe·CHNa·CO_2Et or COPh·CHNa·CO_2Et with CPhCl:N·NHPh (I) gives Et 1 : 3-diphenyl-5-methyl- or 1 : 3 : 5-triphenyl-pyrazol-one-4-carboxylate, respectively. With *p*-NO_2·C_6H_4·NH·N:CBr·CO_2Et (II), the products are the *Et*$_2$ esters, m.p. 98—99° and 90°, respectively, of 1-*p*-*nitrophenyl*-5-*methyl*- (III), m.p. 265° (decomp.), and 5-*phenyl*-1-*p*-*nitrophenyl*-*pyrazole*-3 : 4-*dicarboxylic acid* (IV), m.p. 215° (decomp.). Above the m.p., (III) and (IV) lose CO_2, giving the corresponding 4-*carboxylic acids*, m.p. 227—231° and 248°. $KMnO_4$–KOH oxidation of (III) gives 1-*p*-*nitrophenyltriazole*-3 : 4 : 5-*tricarboxylic acid*, m.p. 70—72° (+ 3H_2O), 204—205° (anhyd.), of which the *Et*$_3$ ester, m.p. 76°, is obtained from (I) and CO_2Et·CO·CHNa·CO_2Et.

V. (I) and CH_2Ac_2 with NaOEt in EtOH give 4-*acetyl*-1 : 3-*diphenyl*-5-*methylpyrazole*, m.p. 88° (*phenylhydrazone*, m.p. 182°), or, in EtOH–Et_2O, a *product*, $C_{18}H_{18}O_2N_2$ (? 3 : 5-*diphenyl*-2-*methyl*-2-*acetonyl*-2 : 3-*dihydro*-1 : 3 : 4-*oxadiazole*), m.p. 156°, easily decomposed into NHPh·NHBz and (I). With $CHNaBz_2$ in EtOH, (I) gives 4-*benzoyl*-1 : 3 : 5-*triphenylpyrazole*, m.p. 174°. With NaOEt in EtOH, (II) and CH_2Ac_2 give the *Et* ester, m.p. 173—174° [(*p*-*nitrophenylhydrazone*, m.p. 310° (decomp. from 300°)], of the -3-*carboxylic acid* (V), m.p. 205° (decomp.) (*p*-*nitrophenylhydrazone*, m.p. 260—262°), of 4-*acetyl*-1-*p*-*nitrophenylpyrazole* (VI), m.p. 156° (obtained by decarboxylation at 200—210°). In 80% HNO_3, (V) and (VI) are oxidised to 1-*p*-*nitrophenyl*-5-*methylpyrazole*-3 : 4-*dicarboxylic acid*, m.p. 265° (decomp.), and -4-*carboxylic acid*, m.p. 230°, respectively. With $CHNaBz_2$, (II) gives the *Et* ester, m.p. 174°, of the -3-*carboxylic acid*, m.p. 233° (decomp.), of 4-*benzoyl*-5-*phenyl*-1-*p*-*nitrophenylpyrazole*, m.p. 163—164° (obtained by decarboxylation); the last three compounds do not react with *p*-NO_2·C_6H_4·NH·NH_2.

VI. With COPh·CHNa·CHO in EtOH, EtOH–C_6H_6, or EtOH–Et_2O, (II) gives the *Et* ester, m.p. 165° (*p*-*nitrophenylhydrazone*, m.p. 283°), of the 3-*carboxylic acid* (VII), m.p. 263° (decomp.) (*NH*$_4$ salt, decomp. 255—268°; *p*-*nitrophenylhydrazone*, m.p. 300°), of 4-*benzoyl*-1-*p*-*nitrophenylpyrazole*, m.p. 195—197° [*p*-*nitrophenylhydrazone*, m.p. 251° (sinters ~220°)]. With COPh·CH_2·COMe and NaOEt in EtOH, (II) gives the *Et* ester, m.p. 170°, of the -3-*carboxylic acid* (VIII), m.p. 200° (decomp.) (no *p*-nitrophenylhydrazone obtained from ester or acid), of 4-*benzoyl*-1-*p*-*nitrophenyl*-5-*methylpyrazole*, m.p. 155—156°. With aq. $KMnO_4$–KOH, (VIII) yields (VII). With COPh·CH_2·CO·CO_2Me and NaOMe in MeOH, (II) gives 5-*carbomethoxy*-3-*carbethoxy*-4-*benzoyl*-1-*p*-*nitrophenylpyrazole*, m.p. 136—138°, hydrolysed to 4-*benzoyl*-1-*p*-*nitrophenylpyrazole*-3 : 5-*dicarboxylic acid* (+H_2O lost at ~140°), m.p. 185—190° (decomp.) (no *p*-nitrophenylhydrazone obtained from ester or acid), decarboxylated to (VII). With COMe·CHNa·CO·CO_2Me [from $COMe_2$, $Et_2C_2O_4$, and NaOMe in MeOH] in C_6H_6, EtOH, or (slowly) in Et_2O, (II) gives 5-*carbomethoxy*-3-*carbethoxy*-4-*acetyl*-1-*p*-*nitrophenylpyrazole*, m.p. 158—159° (no *p*-nitrophenylhydrazone), hydrolysed to 4-*acetyl*-1-*p*-*nitrophenylpyrazole*-3 : 5-*dicarboxylic acid* (+H_2O, lost at 140°), m.p. 176° (decomp.) [*p*-*nitrophenylhydrazone*, m.p. 258—261° (softens 238°)], oxidised (HNO_3) to the 3 : 4 : 5-tricarboxylic acid. The following order of reactivity for the formation of pyrazole and *iso*oxazole rings is proposed: CHO > CO·CO_2R > Ac > Bz > CN > CO_2Et > CO·NH_2. E. W. W.

Action of hydriodic acid on *cyclo*glycylglycine [diketopiperazine] and biological significance of product obtained. V. S. Isupov (Compt. rend. Acad. Sci. U.R.S.S., 1939, **23**, 158—162).—Diketopiperazine with aq. 25% HI at 100° for 6 hr. yields a *substance* (I), $C_9H_{21}O_7N_5I_2$, m.p. 224°, which when boiled with EtOH gives a *substance*, $C_4H_{10}O_4N_2$. The formation and structure of these compounds are discussed. NH_2-acids and polypeptides do not form I-compounds under the above conditions. (I) causes a decrease in blood pressure when injected intravenously into cats [(II) has no effect], and when introduced into the cavities of axolotls transforms them into amblystomes in 38 days. J. N. A.

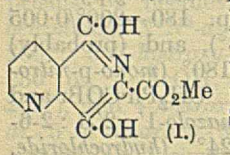
Polarisation in heterocyclic rings with aromatic character. III. Polarisation of the pyrimidine ring. E. Ochiai and M. Yanai (J. Pharm. Soc. Japan, 1939, **59**, 97—104).—$NaNH_2$ and 6-methylpyrimidine in decahydronaphthalene at ~130° briskly evolve H_2 and give 2-*amino*-6-*methylpyrimidine* (I), m.p. 158—159°, 2 : 4-*diamino*-6-*methylpyrimidine*, m.p. 183—185° (*hydrochloride*, m.p. 253—255°), a *dimethyldipyrimidyl*, $C_{10}H_{10}N_4$, b.p. 110—120°/0·002 mm. (*picrate*, decomp. 212—214°; *hydrobromide*, decomp. 209—210°; *mercurichloride*, decomp. 250—251°), and a viscous liquid, b.p. 180—200°/0·002 mm., which does not afford cryst. salts. Hence $C_{(2)}$, $C_{(4)}$, and $C_{(6)}$ of pyrimidine show electrophilic activity and $C_{(2)}$ is highly active. 2 : 4 : 6-Trimethylpyrimidine and CH_2Ph·COBr in abs. EtOH yield 2 : 4 : 6-*trimethylpyrimidine hydrobromide*, 4′ : 6′-*dimethylpyrimidino*-1′ : 2′-1 : 5-3-*phenylpyrrole*, b.p. 180—200°/0·005 mm. (*picrate*, decomp. 220—223°), and (probably) *phenylacetonylpyrrole*, m.p. 178—180° (*mono*-*p*-*nitrophenylhydrazone*, m.p. 233—235°). CH_2Ph·COBr and (I) in hot EtOH give 4′-*phenyliminazolo*-1′ : 2′-1 : 2-6-*methylpyrimidine*, m.p. 223—224° (*hydrochloride*, decomp. 240—243°; *hydrobromide*, decomp. 260—261°; *picrate*, decomp. 239—240·5°; *mercurichloride*, decomp. 259—260°). 4-Amino-6-methylpyrimidine and CH_2Ph·COBr give some *hydrobromide*, decomp. 226—227°, and the *phenacylobromide*, decomp. 263—264°, converted by warm aq. $NaHCO_3$ into 4′-*phenyliminazolo*-1′ : 2′-3 : 4-6-*methylpyrimidine*, decomp. 244° (*picrate*, decomp. 212—214°; *hydrochloride*, decomp. 247—250°). The base is relatively unstable and passes when recrystallised into a black, tarry mass. It is unchanged by $NaHCO_3$, $KHCO_3$ KOH–H_2O, or KOH–EtOH. H. W.

Action of Grignard's reagent on the carbethoxy side-chain of halogenated [ethyl] pyrimidine[acetates]. E. Ochiai and Z. Itikawa (J. Pharm. Soc. Japan, 1938, **58**, 168—171).—*Et* 4-*chloro*-2-*methylpyrimidine*-5-*acetate*, m.p. 39—40° (from the 4-OH derivative and $POCl_3$), and MgMeI

give 4-*chloro*-2-*methyl*-5-β-*hydroxy*-β-*methylpropylpyrimidine* (I), b.p. 160—240°/0·01 mm. (*hydrochloride*, decomp. 267—268°), and a little 4-*chloro*-5-*acetonyl*-2-*methylpyrimidine*, decomp. 254° (*semicarbazone*, decomp. 174—175°). 4-*Amino*-2-*methyl*-5-β-*hydroxy*-β-*methylpropylpyrimidine*, m.p. 160—162° [from (I) and EtOH–NH_3 at 100°], and AcOH–HBr at 100° afford 4-*amino*-2-*methyl*-5-β-*bromo*-β-*methylpropylpyrimidine hydrobromide*, decomp. 187—188°, which does not give a quaternary salt with 4-methyl-5-β-hydroxyethylthiazole but loses HBr to yield 4-amino-2-methyl-5-Δ^{α}-*iso*butenylpyrimidine (*picrate*, decomp. 202°). H. B.

Condensation of 2 : 4 : 6-trimethylpyrimidine and benzaldehyde. II. E. Ochiai and M. Yanai (J. Pharm. Soc. Japan, 1938, **58**, 76—79).—This condensation gives 4 : 6-*dimethyl*-2-*styryl*- (I), new m.p. 57—58°, 6-*methyl*-2 : 4-*distyryl*- (II), m.p. 177—178·5°, and 2 : 4 : 6-*tristyryl*-*pyrimidine*. With O_2–O_3 in $CHCl_3$, (II) gives PhCHO and 6-*methylpyrimidine*-2 : 4-*dialdehyde* (*bis*-p-*nitrophenylhydrazone*, decomp. 290—292°), oxidised by $KMnO_4$ to the -2 : 4-*dicarboxylic acid* (+$2H_2O$), decomp. 195—197°. With O_2–O_3 (I) similarly gives 4 : 6-*dimethylpyrimidine*-2-*aldehyde* (p-*nitrophenylhydrazone*, m.p. 215—216°), oxidised to the -2-carboxylic acid. The following data are also given: 2 : 4 : 6-trimethylpyrimidine, m.p. 199—200° (picrate, decomp. 222—224°); *pyrimidine*-2 : 4 : 6-*trialdehyde* (2-p-*nitrophenylhydrazone*, decomp. >320°), and -2 : 4 : 6-*tricarboxylic acid*, decomp. >320°; *picrate*, decomp. 187—189° (?), of (I). E. W. W.

2 : 5-Naphthyridine derivatives. II. E. Ochiai and H. Miyaki (J. Pharm. Soc. Japan, 1938, **58**, 207—211; cf. A., 1937, II, 467).—Hydrolysis of Me 1 : 4-dihydroxy-2 : 5-naphthyridine-3-carboxylate (I) (Ac derivative, m.p. 225°) by strong acids gives 1 : 4-*dihydroxy*-2 : 5-*naphthyridine* (II), m.p. >310° [*picrate*, m.p. 230° (decomp.); *Ac* derivative, m.p. 216—217° (decomp.)]. Both (I) and (II) are phenolic, giving greenish-blue $FeCl_3$ colours, being indifferent to CO: reagents, and not allowing replacement of the lactim O by S. $POCl_3$ converts (II) into 1-*chloro*-4-*hydroxy*-2 : 5-*naphthyridine* (III), m.p. 215°, the Cl of which resists replacement by H. The 3-CO_2Me-derivative (IV) of (III) with NH_3–EtOH gives only 1-*chloro*-4-*hydroxy*-2 : 5-*naphthyridine*-3-*carboxylamide*, m.p. 288—289° (decomp.). The Ac derivative of (IV) resists replacement of Cl by SH. H_2–PtO_2 in AcOH reduces only the C_5H_5N ring, giving 1-*chloro*-4-*hydroxy*-5 : 6 : 7 : 8-*tetrahydro*-3 : 5-*naphthyridine*, m.p. 149°, and its 3-CO_2Me-derivative, m.p. 206°.



(I.)

R. S. C.

Reaction between *m*-phenylenediamine and ethyl acetoacetate. G. Jacini (Gazzetta, 1939, **69**, 405—408).—This reaction, in AcOH at 50°, gives Et_2 *m*-phenylenebisaminocrotonate, new m.p. 31° (cf. Backeberg, A., 1936, 64). At 200—250°, this gives 4 : 8-*dihydroxy*-2 : 6-*dimethyl*-1 : 5-*phenanthroline*, decomp. 330°, stable to CrO_3 in AcOH or H_2SO_4, which is oxidised by alkaline $KMnO_4$, with $POCl_3$ gives 4 : 8-*dichloro*-2 : 6-*dimethyl*-1 : 5-*phenanthroline*, m.p. 168°, and when distilled over Zn gives 2 : 6-dimethylphenanthroline. E. W. W.

1-Aminoindolizine derivatives. E. Ochiai, M. Wada, M. Suzuki, and T. Nishizawa (J. Pharm. Soc. Japan, 1938, **58**, 172—174).—Attempts to synthesise compounds containing the annexed ring system from derivatives of 1-aminoindolizine were unsuccessful. The Schiff *base*, m.p. 120°, from $AcCO_2Me$ and 1-amino-3-acetyl-2-methylindolizine (I) (*CHPh*:, m.p. 129—130°, and *N*-Ac, m.p. 219°, derivative) with H_2SO_4, AcOH, $AlBr_3$, $ZnCl_2$, or NaOEt undergoes no condensation. The N-*chloroacetyl* derivative, m.p. 223° (decomp.), of (I) is either unaffected or resinified by $AlCl_3$ in CS_2, $PhNO_2$, or $C_2H_2Cl_4$. H. B.

Synthesis of 3 : 4 : 8 : 9-dibenzo-5 : 10-diazapyrene. G. R. Clemo and E. C. Dawson (J.C.S., 1939, 1114—1118).—1 : 5-*Dianilinonaphthalene*, m.p. 214°, prepared from the OH-compound and NH_2Ph, is oxidised (O_2–$AlCl_3$) to 3 : 4 : 8 : 9-*dibenzo*-5 : 10-*diazapyrene*, m.p. 362°. PbO_2 and β-$C_{10}H_7$·NH_2 give 1 : 2 : 6 : 7-dibenzophenazine and a substance, $C_{20}H_{14}N_2$, m.p. 195° (? 5 : 10-dihydro-1 : 2 : 6 : 7-dibenzophenazine). N_2H_4 and β-$C_{10}H_7$·OH, followed by HCl, yield 2 : 2′-diamino-1 : 1′-dinaphthyl (45% yield), which could not be cyclised. F. R. S.

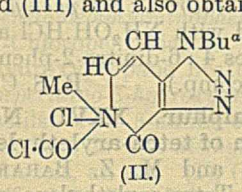
Sulphoxytriazine [5-keto-3-thion-2 : 3 : 4 : 5-tetrahydro-1 : 2 : 4-triazine] ethers. E. Cattelain (Compt. rend., 1939, **208**, 1912—1914; cf. A., 1928, 308).—Alkylation of the appropriate *S*-monoethers of 6-benzylsulphoxytriazine (cf. A., 1939, II, 390) in a neutral medium leads to 3-*benzylthiol*-2 : 6-*dibenzyl*- (I), m.p. 106°, 3-*methylthiol*-6-*benzyl*-2-*methyl*-, m.p. 116·5°, and 3-*ethylthiol*-6-*benzyl*-2-*ethylsulphoxytriazine*, a liquid, all of which are hydrolysed (EtOH–HCl) to the 2-mono-ether and a mercaptan, thereby proving the structure of the di-ethers. 3-*Benzylthiol*-6-*benzylsulphoxytriazine* (II) has m.p. 167°. (I) and (II) when reduced give 3-*benzylthiol*-2 : 6-*dibenzyl*-, a liquid, and 3-*benzylthiol*-6-*benzyl*-, m.p. 125°, -1 : 6-*dihydrosulphoxytriazine* respectively, which do not behave as mono-acids and are oxidised by I–NaOH to (I) and (II), respectively. J. L. D.

Condensation of formaldehyde with thioarylhydrazines. H. Wuyts and (Mlle.) A. L. Lacourt (Bull. Soc. chim. Belg., 1939, **48**, 165—175; cf. A., 1934, 537; A., 1937, II, 434).—Equimols. of the appropriate thioaryl-α-phenylhydrazine and CH_2O in EtOH–HCl afford 1 : 5-*di*-(*thioacetyl*)-, m.p. 186°, -(*thiophenylacetyl*)- (II), m.p. 172°, -(*thiobenzoyl*)- (III), m.p. 187°, -(*thio*-p-*toluoyl*)- (IV), m.p. 190°, and -(*thio*-α-*naphthoyl*)-2 : 4-*diphenylhexahydrotetrazine*, m.p. 200°, of type R·CS·N$<^{CH_2\cdot N(CSR)}_{NPh\text{——}CH_2}>$NPh. In contrast with the lower-melting thiodiazolines (*loc. cit.*) (made with less HCl), the above are almost insol. in Et_2O or EtOH, and are crystallised from C_5H_5N–H_2O. 3-Phenyl-5-benzyl- or -*p*-tolyl-2 : 3-dihydro-1 : 3 : 4-thiodiazole and HCO_2H (*d* 1·22) at 90° or 110° afford (II) or (IV), respectively. (III) and I–$CHCl_3$ give a I_{10}-derivative, m.p. 195°, transformed by dis-

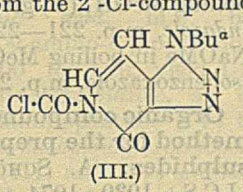
solution in $COMe_2$ and pptn. with Et_2O into a I_6-derivative, m.p. 225° (decomp.). A. T. P.

Attempted hydrogenation of 3-methylxanthine. T. B. JOHNSON and J. C. AMBELANG (Science, 1939, **90**, 68—69).—Xanthine (I) and 3-methylxanthine (II) resist structural changes when hydrogenated in presence of certain catalysts. They are unaltered by exposure in AcOH to H_2 for 8 hr. in presence of Adams' Pt (1·5—2·0 atm.). Shaking with H_2 for 10 hr. at 200°/160—200 atm. in abs. EtOH in presence of Raney Ni partly destroys (I) and (II), but 60% of (II) was recovered unchanged. Catalytic hydrogenation of (I) at different pressures and temp. in presence of Cu–Cr oxide catalyst resulted in extensive decomp. Glyoxaline, 2 : 4 : 5-trimethylglyoxaline, histidine, lysidine, and benziminazole are not reduced in presence of Pt-black. Benziminazole-benzimide could not be hydrogenated using Adams' Pt, Raney Ni, or Cu–Cr oxide. L. S. T.

Pyridino-3 : 4-triazole series. III. O. BREMER (Annalen, 1939, **539**, 276—296; cf. A., 1937, II, 308). —Numerous derivatives of pyridino-3′ : 4′-4 : 5-triazole are prepared; all structures, if not obvious, are proved by the ring-closures described. They differ from *iso*quinoline derivatives in many respects. Halogen in position 2 of the C_5H_5N ring is very reactive, but in position 5 is extremely inert. Cl is introduced into 2′-keto-1′-methyl-1-*n*-butyl-1′ : 2′-dihydropyridino-3′ : 4′-4 : 5-triazole by PCl_5 at 100°, but $COCl_2$ in PhOH gives a substance, converted by H_2O or EtOH into 2′-*hydroxy*-1-n-*butylpyridino*-3′ : 4′-4 : 5-*triazole* (I), m.p. 223°, probably by way of (II) and (III) and also obtained from the 2′-Cl-compound

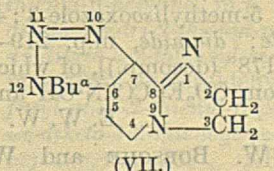


(II.)

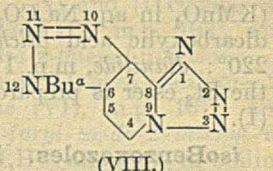


(III.)

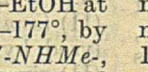
by 15% KOH–MeOH–H_2O at 100°. Br–KOAc in AcOH converts (I) into 5′-*bromo*-2′-*hydroxy*-1-n-*butylpyridino*-3′ : 4′-4 : 5-*triazole*, m.p. 163°, and fuming HNO_3 in conc. H_2SO_4 at 5—10° gives the 5′-NO_2-derivative, m.p. 198°. 3-Nitro-4-butylaminopyridine is reduced and chlorinated by $SnCl_2$ in hot fuming HCl, giving 2-*chloro*-3-*amino*-4-n-*butylaminopyridine*, m.p. 107—108° (*hydrochloride*, m.p. 223—224°), converted by diazotisation into 2′-*chloro*-1-n-*butylpyridino*-3′ : 4′-4 : 5-*triazole*, m.p. 10°, b.p. 171—172°/3 mm. This is converted by NaOEt–EtOH at 100° into the 2′-*OEt*-, m.p. 50—51°, by 32% KSH–MeOH at 100° into the 2′-*SH*, m.p. 203—204°, by 10% NH_3–EtOH at 150—160° into the 2′-NH_2- (IV), m.p. 176—177°, by 33% NH_2Me–EtOH at 150—160° into the 2′-*NHMe*-, m.p. 93—94°, by 25% $NHMe_2$–EtOH at 150—160° into the 2′-NMe_2-, m.p. 119—120°, b.p. 160—161°/3 mm., by $NH_2{\cdot}[CH_2]_2{\cdot}NEt_2$ at 150—160° into the 2′-β-*diethylaminoethylamino*-, b.p. 209—210°/3 mm., by N_2H_4,H_2O in EtOH at room temp. into the 2′-$NH_2{\cdot}NH$- (V), m.p. 80°, by *cyclo*hexylamine and a little EtOH at 150—160° into the 2′-cyclo*hexylamino*-, m.p. 74°, and by $OH{\cdot}[CH_2]_2{\cdot}NH_2$ and a little EtOH at 150—160° into the 2′-β-*hydroxyethylamino*-derivative, m.p. 78—79° {*hydrochloride*, m.p. 193—194°; converted by $SOCl_2$ at 100° into the 2′-β-*chloroethylamino*-derivative (VI), cryst. [*hydrochloride*, m.p. 190° (decomp.)]}. Diazotisation of 2 : 5-*dichloro*-3-*amino*-4-*butylaminopyridine* (prep. from 5-chloro-3-nitro-4-butylaminopyridine by $SnCl_2$–HCl), b.p. 163—164°/3 mm., m.p. <0°, gives 2′ : 5′-*dichloro*-1-n-*butylpyridino*-3′ : 4′-4 : 5-*triazine*, m.p. 48°, b.p. 198°/3 mm., which with *p*-$OMe{\cdot}C_6H_4{\cdot}NH_2$ at 130—140° gives 5′-*chloro*-2′-p-*anisidino*-1-n-*butylpyridino*-3′ : 4′-4 : 5-*triazine*, m.p. 103—104°. 2-*Chloro*-5-*bromo*-3-*amino*-4-n-*butylaminopyridine* (similarly prepared), m.p. 45° [*hydrochloride*, m.p. 167° (decomp.)], gives similarly 2′-*chloro*-5′-*bromo*-1-n-*butylpyridino*-3′ : 4′-4 : 5-*triazine*, m.p. 66—67°, and thence (by 10% NH_3–EtOH at 120—130°) 2′-*chloro*-5′-*amino*-, m.p. 222° [also obtained from (IV) by Br–AcOH at 100°], and (by N_2H_4,H_2O in EtOH at room temp.) 2′-*chloro*-5′-*hydrazino*-1-n-*butylpyridino*-3′ : 4′-4 : 5-*triazole*, m.p. 124°. With fuming HNO_3 in conc. H_2SO_4, (IV) yields in a short time 2′-*nitroamino*-1-n-*butylpyridino*-3′ : 4′-4 : 5-*triazine*, m.p. 165—166° (decomp.), or after being kept overnight 5′-*nitro*-2′-*amino*-1-n-*butylpyridino*-3′ : 4′-4 : 5-*triazine*, m.p. 259°, reduced by $SnCl_2$ in fuming HCl at 100° to the 2′ : 5′-$(NH_2)_2$-derivative, m.p. 202—203° [Ac_2 derivative, m.p. 205—206°; *monohydrochloride*, m.p. 266—267° (decomp.)], which consumes 1 HNO_2 and then with a further mol. of diamine gives the *diazoamino*-compound, cryst., also obtained directly by diazotisation in presence of insufficient HCl. 5-*Bromo*-1-n-*butylpyridino*-3′ : 4′-4 : 5-*triazine*, m.p. 43—44° (*picrate*, m.p. 122—123°), is obtained from 4-chloro-5-bromo-3-nitropyridine by way of 5-*bromo*-3-*nitro*-, an oil, and 5-*bromo*-3-*amino*-4-n-*butylaminopyridine*, m.p. 46°, b.p. 163°/3 mm.; with NH_3–EtOH at 170—180° it affords the 5-NH_2-derivative, m.p. 148°, converted by HNO_2 into the 5-*OH*-derivative, m.p. 109—110°. When heated at 170—180°, (VI) gives impure 1″-n-*butyltriazino*-4″ : 5″-3′ : 4′-*pyridino*-1′ : 2′-1 : 2-4 : 5-*dihydroglyoxaline* (VII), cryst. (*ethiodide*, m.p. 176°; author's numbering as shown). Diazotisation of (V) gives



(VII.)



(VIII.)

1″-n-*butyltriazino*-4″ : 5″-3′ : 4′-*pyridino*-1′ : 2′-1 : 5-1 : 2 : 3 : 4-*tetrazole* (VIII) (author's numbering as shown), m.p. 157—158°, and the 5′-*Br*-derivative, m.p. 114°, is similarly prepared. Diazotisation of 5-nitro-2-hydrazinopyridine gives 5′-*nitropyridino*-1′ : 2′-1 : 5-1 : 2 : 3 : 4-*tetrazole*, m.p. 142—143° (decomp.). The K salt of 5′-bromopyridino-3′ : 4′-4 : 5-triazine with Bu^aI in MeOH at 150—160° gives the *base*,  (" 5′-*bromo*-1-n-*butylpyridino*-3′ : 4′-4 : 5-*triazole* "), m.p. 106°, b.p. 167—168°/3 mm. (*picrate*, m.p. 134—144°). In the formation of (IX) and the tricyclic compounds, the C_5H_5N derivatives react in tautomeric forms. R. S. C.

Anomalous decomposition of the tetrazo-derivative of 2 : 2′-diamino-1 : 1′-dinaphthyl. VI. Dehydrogenating action of thionyl chloride on an ethylenic double linkage. A. CORBELLINI, C. GHIOLDI, and F. CHEVALLARD (Gazzetta, 1939, **69**, 291—301).—The acid $C_{20}H_{12}O_2N_2$ obtained by oxidation of *cis-o*-(4 : 5 : 1′ : 2′-naphthopyrazolyl)-cinnamic acid (I) by $SOCl_2$ (A., 1939, II, 391) is shown to be the corresponding *-propiolic acid* (II). The Et ester (III) of (II) is oxidised by $KMnO_4$ in C_5H_5N to the corresponding -benzoic acid (IV) (A., 1936, 979), also obtained by similar oxidation of the Et ester of (I). With *iso*-C_5H_{11}·OH–N_2H_4,H_2O, (III) gives 3-*o*-(4′ : 5′ : 1″ : 2″-*naphthopyrazolyl*-3′)-*phenylpyrazol*-5-*one*, m.p. 295° [*hydrochloride*, m.p. 191°; *NO*-derivative, m.p. 186° (decomp.); *PhN*$_2$-compound, m.p. 273·5°; *Ac* derivative, m.p. 85—92°]. The acid chloride of (I) with N_2H_4,H_2O in $CHCl_3$ gives the *hydrazide*, m.p. 261—262° (decomp. from 250°), of (I). With KOH–*iso*-C_5H_{11}·OH, (I) gives (IV), AcOH, and a substance, m.p. 228°. E. W. W.

Water-soluble *c*-hæmin from blood.—See A., 1939, III, 552.

Action of nitric acid on phenacylacetone. II. S. CUSMANO (Gazzetta, 1939, **69**, 214—221).—Angeli's product, "$C_{22}H_{18}O_{11}N_4$," m.p. 210° (A., 1893, i, 197), from COPh·[CH_2]$_2$·COMe and HNO_3 (*d* 1·45) is identified as 5-p-*nitrophenyl*isooxazole-3-*carboxylic acid* (I) [*Et* ester (II), m.p. 183°; *NHPh·NH*$_2$ salt, m.p. 168—170° (decomp.)], oxidised by alkaline $KMnO_4$ to *p*-NO_2·C_6H_4·CO_2H. With HNO_3 (*d* 1·45), COPh·CH_2·CH(COMe)·CO_2Et gives (II), and 5-phenyl*iso*oxazole-3-carboxylic acid gives, at >60°, (II), or, at the b.p., (I). E. W. W.

New syntheses of *iso*oxazolepolycarboxylic acids. I. L. PANIZZI (Gazzetta, 1939, **69**, 322—329).—CHPh:CH·CCl:N·OH and COMe·CHNa·CO_2Et (I) give *Et* 5-*methyl*-3-*styrylisooxazole*-4-*carboxylate*, m.p. 60—60·5°, easily hydrolysed (KOH–MeOH) to the 4-*carboxylic acid*, m.p. 240—241° (decomp.) (acid *chloride*, m.p. 98—99°; *amide*, m.p. 226·5—227·5°; *anilide*, m.p. 178—178·5°), which is oxidised ($KMnO_4$ in aq. Na_2CO_3) to 5-methyl*iso*oxazole-3 : 4-dicarboxylic acid [*dichloride*; *diamide*, m.p. 219—220°; *dianilide*, m.p. 177—178° (decomp.)], of which the Et$_2$ ester is prepared from CO_2Et·CCl:N·OH and (I). E. W. W.

***iso*Benzoxazoles. II.** W. BORSCHE and W. SCRIBA (Annalen, 1939, **540**, 83—98; cf. A., 1921, i, 652).—Formation of *iso*benzoxazoles from *o*-halogenophenyl ketoximes often depends on the alkali used. Addition of PCl_5, followed by $AlCl_3$, to *o*-$C_6H_4Br·CO_2H$ in C_6H_6 gives ~80% of *o*-$C_6H_4Br·COPh$ (I), b.p. 190°/14 mm., the oxime, m.p. 132°, of which in hot KOH–MeOH (1 : 4) gives 2-phenyl*iso*benzoxazole (II), m.p. 83°, obtained also from *o*-$C_6H_4F·CPh:N·OH$. *o*-$C_6H_4Br·COCl$ (0·1), Ph_2 (0·3), and $AlCl_3$ (0·2 mol.) at 100° give 4-*o*-*bromobenzoyldiphenyl*, m.p. 90°, b.p. 230—235°/1 mm., the *oxime*, m.p. 187—188°, of which with 2N-aq. KOH–MeOH (1 : 1) at 140° gives 4-2′-*isobenzoxazolyldiphenyl*, m.p. 119—120°, but the crude ketone with NH_2OH,HCl and KOH in boiling MeOH gives also some (?) 2-2′-*isobenzoxazolyldiphenyl*, m.p. 100—101°. An excess of *o*-$C_6H_4Br·COCl$ yields 4 : 4′-*di*-*o*-*bromobenzoyldiphenyl*, m.p. 155—156°, the *dioxime*, m.p. 229—230°, and thence 4 : 4′-*di*-2-*isobenzoxazolyldiphenyl*, m.p. 235—236°. With Br–AcOH at room temp., (II) gives the 4-*Br*-, m.p. 88—89°, and with KNO_3–H_2SO_4 gives the mixed $(NO_2)_2$-derivatives (mainly m.p. 164—165°; a part has m.p. up to 190°; cf. lit.). Na–EtOH reduces (II) to 2-hydroxybenzhydrylamine, m.p. 104—105° (*Ac*$_2$, m.p. 141—141·5°, and *ON*-Bz$_2$ derivative, new m.p. 175°, hydrolysed by KOH–MeOH to the *N*-Bz derivative, new m.p. 213—214°; CH_2N_2–$COMe_2$ gives *o-methoxybenzhydryl*isopropylideneamine, m.p. 93—94°). N_2H_4,H_2O at 200° converts (II) into PhOH, *o-hydroxybenzophenoneazine*, m.p. 273°, *o-hydroxydiphenylmethane*, b.p. 159—162°/12 mm., and a *substance*, m.p. 199—200°. N_2H_4,H_2O and (I) at 200° give 3-*phenylindazole* (III), m.p. 115—116°, b.p. 220—225°/14 mm., and *o*-*bromodiphenylmethane*, m.p. 30—31°, b.p. 159—160°/14 mm. [$(NO_2)_2$-derivative, m.p. 127—128°]. 5 : 2 : 1-NO_2·$C_6H_3Br·COPh$ (IV) and N_2H_4,H_2O in MeOH at 140° give 5-*nitro*-3-*phenylindazole*, m.p. 187—188°, hydrogenated to the 5-*NH*$_2$-compound (*Bz* derivative, m.p. 252—253°), which with *iso*-$C_5H_{11}O$·NO–HCl–MeOH and later HPO_2 yields (III). 3 : 5 : 2 : 1-$(NO_2)_2C_6H_2$(OMe)·COPh (V) and N_2H_4,H_2O in boiling MeOH afford 5 : 7-*dinitro*-3-*phenylindazole*, m.p. 278—279°. NHPh·NH_2,HCl and (IV) in MeOH at 140—150° give 5-nitro-1 : 3-diphenyl-*iso*indazole, reduced by H_2–Pd–C in EtOAc to the 5-NH_2-compound (Bz derivative, m.p. 200—202°), which by a diazo-reaction gives 1 : 3-*diphenyl*iso-*indazole*, m.p. 100—101°. With NHPh·NH_2 in boiling MeOH, (V) gives 5 : 7-*dinitro*-1 : 3-*diphenyl*iso-*indazole*, m.p. 221—222°, and with NH_2OH,HCl and NaOMe in boiling MeOH gives 4 : 6-dinitro-2-phenyl-*iso*benzoxazole, m.p. 243° (decomp.). R. S. C.

Organic compounds of sulphur. XXVI. New method for the preparation of tetra-arylethylene sulphides. A. SCHÖNBERG and M. Z. BARAKAT (J.C.S., 1939, 1074—1075).—Tetra-arylethylene sulphides can be prepared from H_2S and boiling EtOH solutions of 2 : 2 : 5 : 5-tetra-aryl-2 : 5-dihydro-1 : 3 : 4-oxadiazoles. Tetra-phenyl-, -p-*tolyl*-, m.p. 194—195°, and -anisyl-ethylene sulphide are prepared respectively from 2 : 2 : 5 : 5-tetra-phenyl-, -p-*tolyl*-, m.p. 177—178° (efferv.), and *-anisyl*-2 : 5-*dihydro*-1 : 3 : 4-*oxadiazole*, m.p. 174° (decomp.). F. R. S.

3-Acyl*iso*oxazole. III. T. AJELLO and S. CUSMANO (Gazzetta, 1939, **69**, 391—398).—3-Acetyl-5-methyl*iso*oxazole (or its oxime) with free NH_2OH in EtOH gives the *oxime* (I), m.p. 88° (*Bz* derivative, m.p. 112°) of 3-*methyl*-4-*acetonyl*-1 : 2 : 5-*oxadiazole* (II) (*semicarbazone*, m.p. 190°), to which (I) is hydrolysed by boiling dil. HCl. With $NaNO_2$ in AcOH, (II) gives its *oximino*-derivative, m.p. 153° (*Bz* derivative, m.p. 84°), which with free NH_2OH in EtOH forms 4-*pyruvyl*-3-*methyl*-1 : 2 : 5-*oxadiazole dioxime*, m.p. 172° (*Bz* derivative, m.p. 163°; *Ni* salt). Pyruvylacetone trioxime and boiling aq. KOH give (I). E. W. W.

Polarisation in heterocyclic rings of aromatic nature. II. Thiazole ring. E. OCHIAI and F.

NAGASAWA (J. Pharm. Soc. Japan, 1939, **59**, 43—49). —4-Methylthiazole (I) is not nitrated by HNO_3–H_2SO_4 at 0—100° (decomp. at 200°). With 20% oleum at 200° (no reaction at 100°) (I) gives 4-*methylthiazole*-5-*sulphonic acid*, m.p. 287—288° (*Ba* salt). 2-Thiol-4-methylthiazole and H_2O_2–KOH give 4-*methylthiazole*-2-*sulphonic acid*, m.p. 207—211° (*K* salt, m.p. 273—277°). 2-Hydroxy-4-methylthiazole (II) and 20% oleum at 100° (bath) give 2-*hydroxy*-4-*methylthiazole*-5-*sulphonic acid*, m.p. 129—130° (+ $1H_2O$), then solidifies and decomposes at ~212° (anhyd. form, decomp. ~225°) (*Zn* salt). (II) and HNO_3–H_2SO_4 at 0° give 5-*nitro*-2-*hydroxy*-4-*methylthiazole*, m.p. 158—159°. (I) and $NaNH_2$ in decahydronaphthalene at 150° afford 2-amino-4-methylthiazole (III), converted by 20% oleum at 0° or 100° (bath) respectively, into 4-*methylthiazole*-2-*sulphonamic acid* (IV), decomp. 256° (*Ba* salt), or 2-*amino*-4-*methylthiazole*-5-*sulphonic acid* (V), decomp. >340° (*Ba* salt), respectively; (IV) and H_2SO_4 at 100° (bath) give (V). (III) and HNO_3–H_2SO_4 give 5-*nitro*-2-*nitroamino*-4-*methylthiazole*, decomp. 185°. Theoretical aspects of the results are discussed. A. T. P.

Benzthiazole derivatives. III. 1-Aminobenzthiazole derivatives. N. S. DROZDOV and V. I. STAVROVSKAJA (J. Gen. Chem. Russ., 1939, **9**, 409—414).—1-Chloro-5-nitrobenzthiazole (I) is reduced (Fe in AcOH) to 1-*chloro*-5-*aminobenzthiazole*, m.p. 164°, from which 1-chloro-5-iodo- (II) or 1 : 5-dichlorobenzthiazole is prepared (Sandmeyer). When heated with a no. of NH_2Ph derivatives, (I) yields 5-nitro-1-anilino-, -1-o-*toluidino*-, m.p. 204—205°, and -1-p-*dimethylaminoanilino*-*benzthiazole*, m.p. 234°, whilst with arsanilic acid the product is 4-*di*-(5′-*nitro*-1′-*benzthiazolyl*)*aminophenylarsinic acid*, m.p. 63°. 1-Chlorobenzthiazole and γ-amino-α-piperidino-β-hydroxypropane heated at 100° for 1 hr. yield 1-(γ-*piperidino*-β-*hydroxypropyl*)*aminobenzthiazole*, an oil, whilst with β-amino-ε-diethylaminopentane (IV) the product is 1-(δ-*diethylamino*-α-*methylbutyl*)*aminobenzthiazole*, an oil. (I), (II), or (III) and (IV) similarly afford 5-*nitro*-, 5-*iodo*-, or 5-*chloro*-1-(δ-*diethylamino*-α-*methylpropyl*)*aminobenzthiazole* (oils). None of the products described possessed any antimalarial activity. R. T.

Substitution of thiazole. E. OCHIAI and F. NAGASAWA (Ber., 1939, **72**, [*B*], 1470—1476).—The $C_{(2)}$ position of thiazole is active towards electron-donating reagents and the activity of the $C_{(2)}$ and $C_{(5)}$ positions towards electron acceptors is slight. The activity of the $C_{(5)}$ position towards electron acceptors is greatly enhanced by the presence of NH_2 or OH at $C_{(2)}$. 4-Methylthiazole is not attacked by Br in 20% H_2SO_4 or in $CHCl_3$. Under similar conditions 5-*bromo*-2-*amino*-4-*methylthiazole*, decomp. 105—108·5°, is obtained from 2-amino-4-methylthiazole (II). 2-Hydroxy-4-methylthiazole (II) is converted by Br in $CHCl_3$ into 5-*bromo*-2-*hydroxy*-4-*methylthiazole*, decomp. 147·5°, and by the successive actions of $Hg(OAc)_2$ in dil. AcOH, NaCl, and Br in $CHCl_3$ into *dibromo*-4-*methylthiazole*, decomp. 151°. AcCl, $AlCl_3$, and (III) in $PhNO_2$ or $C_2H_2Cl_4$ afford 2-*hydroxy*-5-*acetyl*-4-*methylthiazole* (*semicarbazone*, decomp. 244°). Under similar conditions (II) yields 2-acetamido-4-methylthiazole (IV), m.p. 134°, whereas (I), (IV), and 2-thiol-4-methylthiazole are largely unchanged. (III) is transformed by HCN and HCl in $C_2H_2Cl_4$, followed by H_2O, into 2-*hydroxy*-4-*methylthiazole*-5-*aldehyde*, decomp. 248° (p-*nitrophenylhydrazone*, decomp. 297—300°), also obtained by the action of KOH and $CHCl_3$. In these circumstances (I) is unattacked. H. W.

Syntheses of 2-thio-4-arylthiazolines. F. B. DAINS and O. A. KROBER (J. Amer. Chem. Soc., 1939, **61**, 1830—1831).—$ArCO{\cdot}CH_2{\cdot}SCN$ (prep. from $ArCO{\cdot}CH_2Cl$ by KCNS in hot EtOH) adds $PhCS_2H$ to give $NHBz{\cdot}CS{\cdot}S{\cdot}CH_2Ar$, which with hot, dil. HCl yields BzOH and the 2-thio-4-arylthiazoline. $MeCS_2H$ is also added, but the thiazoline is formed directly. The following are thus obtained: p-*bromo*-, m.p. 147°, p-*chloro*-, m.p. 135°, p-*iodo*-, m.p. 152°, p-*methoxy*-, m.p. 121°, and 4-*nitro*-, m.p. 119°, -*phenacyl thiocyanate*; *phenacyl* N-*benzoyldithiocarbamate*, m.p. 95°; p-*chloro*-, m.p. 148°, p-*bromo*-, m.p. 158°, and m-*nitro*-, m.p. 157°, -*benzoyldithiocarbamate*; 2-*thio*-4-p-*chloro*-, m.p. 148°, -4-p-*bromo*-, m.p. 214°, -4-p-*iodo*-, m.p. 220°, and -4-m-*nitro*-, m.p. 209°, -*phenylthiazoline*; 2-thio-4-phenyl-, m.p. 168°, and 2-*thio*-4-p-*anisyl*-*thiazoline*, m.p. 194°. $COPh{\cdot}CHPh{\cdot}CNS$ and $MeCS_2H$ give 2-*thio*-4 : 5-*diphenylthiazoline*, m.p. 214° (2-CH_2Ph *thioether*, m.p. 106°), also obtained by $PhCS_2H$ by way of an intermediate compound, m.p. 132—133° (cf. a compound, m.p. 137°, of Wheeler *et al.*, A., 1901, i, 705). $CH(CO_2Et)_2{\cdot}CNS$ and $PhCS_2H$ in C_6H_6 give rhodanine. R. S. C.

Thiophen series. XLVIII. Thiophen analogues of 2 : 4 : 6-triphenylpyridine. W. STEINKOPF and W. POPP (Annalen, 1939, **540**, 24—30).—Thiophen-2-aldehyde (I), COPhMe, and 40% NaOH in boiling EtOH give αε-*diketo*-αε-*diphenyl*-γ-2-*thienyl*-n-*pentane* (II), m.p. 104°, and some αη-*diketo*-δ-*benzoyl*-αη-*diphenyl*-γε-*di*-2-*thienyl*-n-*heptane*, m.p. 251°. PhCHO and 2-acetylthiophen (III) give similarly αε-*diketo*-αε-*di*-2-*thienyl*-γ-*phenyl*-n-*pentane* (IV), m.p. 103°, and αη-*diketo*-δ-2-*thienoyl*-γε-*diphenyl*-αη-*di*-2-*thienyl*-n-*heptane*, m.p. 266°. (I) and (III) give αε-*diketo*-αγε-*tri*-2-*thienyl*-n-*pentane* (V), m.p. 103°, and αη-*diketo*-δ-2-*thienoyl*-αγεη-*tetra*-2-*thienyl*-n-*heptane*, m.p. 268°; furfuraldehyde and (III) give αε-*diketo*-γ-2-*furyl*-αε-*di*-2-*thienyl*-n-*pentane* (VI), m.p. 107°, and αη-*diketo*-δ-2-*thienoyl*-γε-*di*-2-*furyl*-αη-*di*-2-*thienyl*-n-*heptane*, m.p. 239°. NH_2OH,HCl and P_2O_5 in boiling abs. EtOH convert (II), (IV), and (V) into 2 : 6-*diphenyl*-4-2′-*thienylpyridine*, m.p. 157° (stable *picrate*, m.p. 212°; 3′ : 5′-Br_2-derivative, m.p. 163°), 4-*phenyl*-2 : 6-*di*-2′-*thienylpyridine*, m.p. 126° (unstable *picrate*, m.p. 166°; 3′ : 5′ : 3″ : 5″-Br_4-derivative, m.p. 252°), and 2 : 4 : 6-*tri*-2′-*thienylpyridine*, m.p. 132° (unstable *picrate*, m.p. 148°; 3′ : 5′ : 3″ : 5″ : 3‴ : 5‴-Br_6-derivative, m.p. 316°); however, (VI) is resinified by this treatment. The picrates illustrate the decrease in basicity caused by C_4H_3S. The similar m.p. of the analogous ketones are lowered by admixture. R. S. C.

Reaction of organic sulphur compounds with hydrogen peroxide. XIV. Constitution of antipyrine and related compounds. III. Mechan-

ism of desulphurisation of thiopyrine to antipyrine. XV. Compounds containing C:C·S. XVI. Synthesis of compounds of a new type. Thioperimino-acids. R. Kitamura (J. Pharm. Soc. Japan, 1938, **58**, 238—242, 243—246, 246—250). —XIV. Thiopyrine is converted into antipyrine by H_2O_2 more completely in presence of KOH than of K_2CO_3 in H_2O or 67% EtOH. The reaction is partly this conversion and partly formation of the trioxide, which yields antipyrine much more slowly.

XV. CHPh:C(SH)·CO_2H, SH·CPh:CH·CO_2H, and CHPh:CH·CH:C(SH)·CO_2H are indifferent to alkaline H_2O_2, which renders their structure doubtful. 10 cyclic compounds containing C:C·S react, although incompletely.

XVI. RCS·NH_2 and H_2O_2 (1 mol.) give thioperimino-acids, NH:CR·S·OH. Thus are prepared *benzoic* (I), m.p. 128—129°, *phenylacetic* (II), m.p. 135—136°, *benzamidoacetic*, m.p. 137—138°, and *anilinophenylacetic*, m.p. 124—125°, *perimino-acid*, all unstable in air or light. When heated, (I) gives PhCN and 3 : 5-diphenyl-1 : 2 : 4-thiodiazole (III) with a little SO_2 and NH_2Bz. (I) is sol. in 0·1N-KOH, but fairly rapidly decomposes therein. It is a weak acid, neutralising ≪1 KOH (phenolphthalein). With Me_2SO_4–KOH, (I) gives PhCN. The perimino-acids give an indigo $FeCl_3$ reaction, give platinichlorides and picrates, reduce $AuCl_3$ and $AgNO_3$, and liberate a little I from acidified KI. They react with 3 H_2O_2, giving H_2SO_4 quantitatively. With NH_2OH, (I) gives S and NH:CPh·NH·OH nearly quantitatively; with fuming HNO_3 and H_2SO_4 it gives S and *m*-NO_2·C_6H_4·CN; with boiling H_2O it gives PhCN, much (III), and a little NH_2Bz. Tautomeric forms, NH:CPh·S(H)→O, $^+NH_2$:CPh·SO^-, and NH_2·CPh:S→O, are probably present. With PhCN, NH_2Bz, or, best, PhCS·NH_2 at 115—120°, (I) gives (III). At 115—120° PhCS·NH_2 and (II) give 3-*phenyl*-5-*benzyl*-1 : 2 : 4-*thiodiazole*, m.p. 76—76·5°. (I) is an intermediate in the prep. of (III) from PhCS·NH_2 by $(NH_4)_2S_2O_8$ or I.

R. S. C.

Isosteric and structurally similar compounds. XII. Preparation and properties of 4 : 4′-dithiazolyl. H. Erlenmeyer and H. Ueberwasser (Helv. Chim. Acta, 1939, **22**, 938—939).—HCS·NH_2 and (CO·CH_2Br)$_2$ in Et_2O–EtOH and then in EtOH at 70° yield 4 : 4′-*dithiazolyl* (I), m.p. 170—171°. It is almost insol. in H_2O; a colour is not developed in presence of $FeSO_4$ but (I) dissolves to a clear solution in the hot liquid and does not separate when the solution is cooled, thus indicating the possible formation of a colourless complex. There is no indication of the production of mixed crystals in the systems, (I)–2 : 2′-dithiazolyl or –2 : 2′-dipyridyl. H. W.

Synthetic experiments concerning eserine. VI. Constitution of methyleserethole. II. T. Kobayashi (Annalen, 1939, **539**, 213—218).—The structure of methyleserethole (I) (A., 1938, II, 511) is confirmed by synthesis. 1 : 2-Dimethylindole with MgEtI in Et_2O, followed by (CO·CH_2Br)$_2$, gives 2 : 3-*dimethyl*-2-β-*bromoethylindolenine*, an oil, converted by NH_3–EtOH at 100—105° into dinordeoxy-9-methyleseroline. Skatole similarly gives dinordeoxyeseroline. *p*-OEt·C_6H_4·N_2Cl and CH_2Ac·CO_2Et in aq. $NaHCO_3$ yield *Et* 5-*ethoxyskatole*-2-*carboxylate*, m.p. 171—172°, hydrolysed by alkali to the derived *acid*, m.p. 184—185° (decomp.) (*Me* ester, m.p. 178—179°), which at 200° gives 5-*ethoxyskatole*, m.p. 65—66°. With MgEtI in Et_2O, followed by (CO·CH_2Br)$_2$, this gives dinoreserethole or, if the indolenine is heated with NH_2Me or $NHMe_2$ in EtOH at 100—105°, *iso*noreserethole or (I), respectively. R. S. C.

Alkaloids of *Arthrophytum leptocladum*, M. Pop. N. K. Juraschevski (J. Gen. Chem. Russ., 1939, **9**, 595—597).—The dry leaves contained 0·7% of alkaloids, of which *leptocladine*, $C_{13}H_{16}N_2$, m.p. 109—110° [*hydrochloride*, m.p. 234—235° (decomp.); *platinochloride*, decomp. at 197—198°; *picrate*, sinters at 94—95°, m.p. 112—114°; *Bz* derivative, m.p. 132—133°], was isolated. R. T.

Lupine. XIII. Octalupine, an alkaloid from *Lupinus sericeus*, var. *flexuosus*, C. P. Smith. J. F. Couch (J. Amer. Chem. Soc., 1939, **61**, 1523—1524; cf. A., 1937, II, 434).—This plant yields *octalupine*, $C_{15}H_{22}O_2N_2$, m.p. 167·5—169·5°, b.p. 270—280°/6 mm., hygroscopic, $[\alpha]_D^{25}$ +52·3° in EtOH [*dihydrochloride*, +1·5H_2O (0·5H_2O lost at 110°), m.p. 298—299°, $[\alpha]_D^{25}$ +36·3° in H_2O, and +H_2O, m.p. 288—289°; *methiodide*, m.p. 259°; *aurichloride*, m.p. 208—209°], which is stable to acid $KMnO_4$, is reduced electrolytically to *d*-lupanine and sparteine, and is thus probably 2 : 16-diketosparteine. M.p. are corr. R. S. C.

Lupin alkaloids. XVIII. Synthesis of *allo*lupinine. K. Winterfeld and F. W. Holschneider (Arch. Pharm., 1939, **277**, 221—237; cf. A., 1939, II, 395).—δ-Ethoxy-γ-valerolactone [prep. from $CH_2(CO_2Et)_2$ and epichlorohydrin described] with Et picolinate and Na in C_6H_6 yields 2-*pyridyl* α-(δ-*ethoxy*-γ-*valerolactonyl*) *ketone*, b.p. 173—175°/0·4 mm. [$HgCl_2$ *compound*, m.p. 98—99°, clearing at 117°; p-*sulphophenylhydrazone*, m.p. 234—236° (decomp.); *reineckate*, m.p. 128—130°, decomp. 161—162°], which gives a red colour with $FeCl_3$. With conc. HCl this yields 2-*pyridyl* γ-*hydroxy*-δ-*ethoxy*-n-*butyl ketone*, b.p. 110—120°/0·3 mm. [$HgCl_2$ *compound*, m.p. 75°, clearing at 103°; p-*sulphophenylhydrazone*, m.p. 235°, decomp. 248—252°; *reineckate*, m.p. 117°, decomp. 175—178°; 2 : 4-*dinitrophenylhydrazone*, m.p. 164—165°; phenylhydrazone and aurichloride (oils)], reduced (H_2, PtO_2 in AcOH) to αδ-*dihydroxy*-ε-*ethoxy*-α-2-*piperidyl*-n-*propane* [$HgCl_2$ *compound*, m.p. 129°; *reineckate*, m.p. 129—130°; *Bz* and PhCNO derivatives (oils)], which gives a deep red colour with Na nitroprusside and MeCHO. Cyclisation (PBr_3 followed by NaOEt) of this yields a mixture of 1-bromo-4-ethoxymethyl-octahydro- and 4-ethoxymethyl-Δ^{10}-hexahydroquinolizine which with H_2–Pd–$CaCO_3$ in EtOH–KOH yields 4-*ethoxymethyl*-, b.p. 142—144° (*aurichloride*, m.p. 85—87°; $HgCl_2$ *compound*, m.p. 125—126°; *reineckate*, m.p. 143—145°), hydrolysed (HI) to 4-*hydroxymethyl*-*octahydroquinolizine* (*allo*lupinine), m.p. 123—125° [$HgCl_2$ *compound*, m.p. 201° (decomp.); *reineckate*, m.p. 152—153°; aurichloride and picrate (oils)]. A. Li.

Microcrystalline narcotine oxalate and phthalate. Y. VOLMAR, P. DUQUÉNOIS, and M. ELLERT (Compt. rend., 1939, **208**, 2000—2001).—Equimol. amounts of *l*-narcotine (I) and $H_2C_2O_4,2H_2O$ crystallise from $COMe_2$ as *narcotine oxalate*, m.p. 174°, $[\alpha]_D^{20}$ +39·5° in H_2O. Equimol. amounts of (I) and *o*-$C_6H_4(CO_2H)_2$ crystallise from EtOH as *narcotine phthalate*, m.p. 160°, $[\alpha]_D^{22}$ +115° in $CHCl_3$. J. L. D.

Synthesis of hydrohydrastinine derivatives. M. TOMITA and M. SATOMI (J. Pharm. Soc. Japan, 1938, **58**, 165—168).—Phenylacethomopiperonylamide, m.p. 97—98° (from $COPh{\cdot}CHN_2$, homopiperonylamine, and Ag_2O), is converted ($POCl_3$ in PhMe) into 6 : 7-methylenedioxy-1-benzyl-3 : 4-dihydro*iso*quinoline (I) [*methiodide*, m.p. 258° (decomp.)], the methochloride of which is reduced (H_2–PtO_2 or Sn–HCl) to 6 : 7-methylenedioxy-1-benzyl-2-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline (1-benzylhydrohydrastinine) [hydrochloride (+$2H_2O$), m.p. 110—120°; platinichloride, decomp. 205°; *methiodide*, (+H_2O), m.p. 240° (decomp.)]. Reduction (H_2, PtO_2) of (I) gives the 1 : 2 : 3 : 4-H_4-derivative (1-benzylnorhydrohydrastinine) [hydrochloride (+H_2O), m.p. 105—110°]. Similarly, p-*anisylacethomopiperonylamide*, m.p. 90°, is converted into 6 : 7-methylenedioxy-1-*p*-methoxybenzyl-3 : 4-dihydro- and -1 : 2 : 3 : 4-tetrahydro-*iso*quinoline [*hydrochloride* (+H_2O), m.p. 105°] and 6 : 7-methylenedioxy-1-*p*-methoxybenzyl-2-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline (1-*p*-methoxybenzylhydrohydrastinine) [*platinichloride*, decomp. 184°; *methiodide*, m.p. 184° (decomp.)]. H. B.

Conversion of quinine into quinotoxin. A. MACHADO (Rev. Soc. Brasil. Quím., 1939, **8**, 59—61).—Quinine in olive, cotton seed, or manobi oil at 140° for 1 hr. yields quinotoxin. F. R. G.

Syntheses in the series of *Cinchona* alkaloids. V. PRELOG, R. SEIWERTH, V. HAHN, and E. CERKOVNIKOV (Ber., 1939, **72**, [*B*], 1325—1333).—Condensation of Et β-4-tetrahydropyranylpropionate with Et cinchoninate by NaOEt in C_6H_6 at 80—90° gives 4′-*quinolyl* β-4-*tetrahydropyranylethyl ketone* (I), b.p. 187°/0·02 mm., m.p. 46° (*hydrochloride*, m.p. 166—166·5°; *picrate*, m.p. 154·5—155°; *semicarbazone*, m.p. 182°; *oximino*-derivative, m.p. 158·5—159·5°). Under similar conditions Et quinate affords 6′-*methoxy*-4′-*quinolyl* β-4-*tetrahydropyranylethyl ketone* (II), b.p. 195—205°/0·2 mm., m.p. 54·5—55·5° [*hydrochloride*, m.p. (indef.) 204—205°; *picrate*, m.p. 173—173·5°; *oximino*-derivative, m.p. 167·5—168°]. Reduction (PtO_2 in MeOH) of (I) yields α-4′-*quinolyl*-γ-4-*tetrahydropyranylpropanol* (III), m.p. 126·5—127° (*hydrochloride*, m.p. 177—178°; *picrate*, m.p. 180—181°). Analogously (II) affords α-6′-*methoxy*-4′-*quinolyl*-γ-4-*tetrahydropyranylpropanol* (IV), non-cryst. (*hydrochloride*, m.p. 185—186°; *picrate*, m.p. 178—178·5°). The appropriate oximino-derivative is reduced (PtO_2 in EtOH) to β-*amino*-α-4′-*quinolyl*- (V), m.p. 171·5—172° (corr.), and -α-6′-*methoxy*-4′-*quinolyl*- (VI), m.p. (indef.). 180—181°, -γ-4-*tetrahydropyranylpropanol dihydrochloride*. α-4-*Tetrahydropyranyl*-γ-4-*quinolylpropane*, b.p. 160—170°/0·02 mm. (*picrate*, m.p. 198·5°), obtained from the appropriate semicarbazone and NaOEt–EtOH at 180°, is transformed by 73% HBr at 180° into α-*bromo*-δ-4′-*quinolyl*-γ-β′-*bromoethylhexane hydrobromide*, m.p. 114°, which is transformed by MeOH–NH_3 into α-4-*piperidyl*-γ-4′-*quinolylpropane* [*rubatoxan*], b.p. 185°/0·02 mm. (*dihydrochloride*, m.p. 197°; *platinichloride*, m.p. >360°; *dipicrate*, m.p. 203—205°), and by K_2S in boiling EtOH into α-4-*tetrahydrothiopyranyl*-γ-4′-*quinolylpropane*, m.p. 61°. 67% HBr at 100° converts (I) into α-*bromo*-ζ-4′-*quinolyl*-γ-β′-*bromoethylheptan*-ζ-*one hydrobromide*, m.p. 142—143°, which with Br–HBr at 100° gives αε-*dibromo*-ζ-4′-*quinolyl*-γ-β′-*bromoethylheptan*-ζ-*one hydrobromide*, m.p. 136—137°, and with KOH–EtOH yields ζ-4-*quinolyl*-γ-*vinyl*-Δ^{α}-*hexen*-ζ-*one*, m.p. 59° (*hydrobromide*, m.p. 207°; *picrate*, m.p. 204—208°). Et 2-ethoxycinchoninate is converted by condensation followed by hydrolysis with 10% HCl into 2′-*hydroxy*-4′-*quinolyl* β-4-*tetrahydropyranylethyl ketone* (VII), m.p. 179—180° (H_4-derivative, m.p. 203—204°; *oximino*-derivative, m.p. 213°). (I), (II), (III), (IV), (V), and (VI) have no antimalarial action. H. W.

Cinchona alkaloids in pneumonia. VII. Amyl and hydroxyalkyl *apo*cupreine ethers. M. H. GREEN, A. G. RENFREW, and C. L. BUTLER (J. Amer. Chem. Soc., 1939, **61**, 1783—1784; cf. A., 1938, II, 341).—The following are prepared by standard methods: β-, b.p. 128—132°/6 mm., and δ-*benzyloxy*-n-*butan*-α-*ol*, b.p. 146—149°/6 mm.; γ-*benzyloxy*-n-*butan*-β-*ol*, b.p. 122—125°/6 mm.; $CHEt_2$, m.p. 37°, β-*hydroxy*-n-*propyl*, m.p. 46°, and β-*benzyloxy*-sec.-*butyl*, m.p. 47°, p-*toluenesulphonate*; *apocupreine* δ-*benzyloxy*-n-*butyl*, m.p. 104°, [α] −152° in EtOH, β-*hydroxy*-n-*propyl*, m.p. 170°, [α] −180° in EtOH (*dihydrochloride*, [α] −216° in H_2O), β-*hydroxy*iso-*butyl*, m.p. 102°, [α] −169° in EtOH (*dihydrochloride*, [α] −218° in H_2O), δ-*hydroxy*-n-*butyl*, m.p. 178°, [α] −179° in EtOH (*dihydrochloride*, [α] −213° in H_2O), α-*hydroxymethyl*-n-*propyl*, amorphous, [α] −165° (*dihydrochloride*, [α] −202° in H_2O), β-*hydroxy*-sec.-*butyl*, amorphous, [α] −163° (*dihydrochloride*, [α] −212° in H_2O), *n*-amyl, m.p. 146°, [α] −178° in EtOH (*dihydrochloride*, +1·5H_2O, [α] −230° in H_2O), iso-*amyl*, m.p. 175°, [α] −181° in EtOH (*dihydrochloride*, +2H_2O, [α] −206° in H_2O), β-*methyl*-n-*butyl*, m.p. 169°, [α] −172° in EtOH (*dihydrochloride*, +H_2O, [α] −225° in H_2O), sec.-*amyl*, amorphous, [α] −163° in EtOH (*dihydrochloride*, +2H_2O, [α] −212° in H_2O), and α-*ethyl*-n-*propyl*, amorphous, [α] −150° in EtOH (*dihydrochloride*, +1·5H_2O, [α] −213° in H_2O), *ether*. The *in vitro* bacteriostatic activity and toxicity of the *apo*cupreine alkyl and hydroxyalkyl ethers are recorded. OH reduces both effects. R. S. C.

Methiodides of quinidine and hydroquinidine. F. VON KONEK (Math. nat. Anz. ung. Akad. Wiss., 1936, **54**, 821—829; Chem. Zentr., 1937, i, 1694).—Quinidine (I) [*methiodide*, m.p. 235—236° (decomp.)] and KI in HCl give the *hydriodide*, which forms a *MeI* compound (II) with excess of MeI and MeOH (>100°; 2—4 hr.). *Hydroquinidine methiodide*, m.p. 242—243° (decomp.), *hydriodide* (*MeI* compound), and *MeI* compound (impure) are similarly prepared. A. J. E. W.

Reduction studies in the morphine series. IX. Hydroxycodeinone. R. E. LUTZ and L. SMALL (J.

Org. Chem., 1939, 4, 220—233).—Thebaine in glacial AcOH is oxidised by 30% H_2O_2 to hydroxycodeinone (I), m.p. 275—276° (vac.), $[\alpha]_D^{25}$ −111° in 10% AcOH [*hydrochloride dihydrate*, m.p. 272—274° (vac.), $[\alpha]_D^{24}$ −80° in H_2O; *hydriodide* (+1H_2O), m.p. 255—260° (vac.), $[\alpha]_D^{22}$ −74° in H_2O; *perchlorate* (+2H_2O), m.p. 241—242° (decomp.), $[\alpha]_D^{23}$ −80° in H_2O; Ac derivative, m.p. 185°, $[\alpha]_D^{25}$ +21° in 10% AcOH, and its hydrochloride, m.p. 260—261° (vac.), $[\alpha]_D^{25}$ +15·7° in H_2O]. Reduction (Pd–$BaSO_4$ in 10% AcOH) of (I) affords dihydrohydroxycodeinone (II), m.p. 218°, $[\alpha]_D^{25}$ −97° in 10% AcOH [*hydrochloride* (+2·5H_2O), m.p. 270—272° (decomp.), $[\alpha]_D^{25}$ −123° in H_2O], which is not affected by Zn and AcOH at 80—90° and is transformed by Zn–Hg and conc. HCl into dihydrohydroxythebainone, m.p. 143°. Boiling Ac_2O containing NaOAc transforms (II) into *acetoxydihydrocodeinone enol acetate*, m.p. 207·5°, $[\alpha]_D^{25}$ −167° in EtOH. Zn dust and glacial AcOH at 50—55° convert (I) into hydroxythebainol and hydroxycodeine (+1H_2O), m.p. 304—305° (vac.), $[\alpha]_D^{25}$ −143° in 10% AcOH [*hydrochloride*, m.p. 269—275° (*decomp.*)]; the base is reduced (PtO_2 in 10% AcOH) to *dihydrohydroxycodeine*-A, m.p. 301—302° (vac.), $[\alpha]_D^{20}$ −64° in 10% AcOH, which has no phenolic properties and does not give a cryst. Ac_1 or Ac_2 derivative. Hydrogenation (PtO_2 in 10% AcOH) of (II) slowly yields *dihydrohydroxycodeine*-B (III), m.p. 145—145·5°, $[\alpha]_D^{26}$ −136° in 10% AcOH, and -C (IV), m.p. 166—167°, $[\alpha]_D^{23}$ −152° in 10% AcOH. (III) is transformed by Ac_2O and C_5H_5N at 100° into its *Ac*$_2$ derivative, m.p. 181—182°, $[\alpha]_D^{22}$ −127° in 10% AcOH [*H tartrate monohydrate*, m.p. 181—182°, $[\alpha]_D^{20}$ −78° in H_2O (*c* = 0·72)]. Excess of MeI at 100° transforms (III) into the *methiodide*, m.p. 223—224° (decomp.), $[\alpha]_D^{21}$ −87° in H_2O, transformed by boiling aq. NaOH into *dihydrohydroxycodeine*-B-*methine*, m.p. 103°, $[\alpha]_D^{21}$ −70° in 10% AcOH [*H tartrate* (+4H_2O), m.p. 190—191° (decomp.), $[\alpha]_D^{21}$ −25° in H_2O]; this is hydrogenated (PtO_2 in 75% AcOH) to *dihydrohydroxycodeine*-B-*dihydromethine*, m.p. 168°, $[\alpha]_D^{22}$ −44° in 10% AcOH [*acetate* (+1·5H_2O)]. PCl_5 and (III) in $CHCl_3$ at room temp. yield *dihydrohydroxychlorocodide* (V), m.p. 213·5—214°, $[\alpha]_D^{23}$ −151° in 10% AcOH, which is not reduced by Pt–H_2 in 5% AcOH, or by Clemmensen's method; it is transformed by NaOEt at 140° into liquid phenolic products free from halogen whilst it is indifferent to gentler treatment. $SOCl_2$ at room temp. converts (III) into *chlorodihydrohydroxycodeine*-B (*hydrochloride*, m.p. 238—239°, $[\alpha]_D^{21}$ −106° in H_2O), which is unaffected by boiling 10% AcOH or by Clemmensen reduction and is converted by Na and abs. EtOH under N_2 into (III). $SOCl_2$ and (V) give *chlorodihydrohydroxychlorocodide*, m.p. 163·5°, $[\alpha]_D^{22}$ −141° in 10% AcOH, also obtained by use of PCl_5. Reduction of (V) with Na and boiling EtOH affords *dihydrodeoxyhydroxycodeine*, m.p. 137—138°, $[\alpha]_D^{22}$ −19° in 10% AcOH, hydrogenated (PtO_2 in 3% AcOH) to *tetrahydrodeoxyhydroxycodeine* (*perchlorate*, m.p. 242—244°, $[\alpha]_D^{21}$ −28° in H_2O). PCl_5 and (IV) in $CHCl_3$ give a compound, m.p. 136—139°, which contains P. With $SOCl_2$ (IV) affords a substance which can be distilled in a high vac. but does not give cryst. derivatives. *Deacetyldihydrohydroxycodeine*-C, m.p. 203°, $[\alpha]_D^{23}$ −107° in 10% AcOH [*H tartrate monohydrate*, m.p. 209—210°, $[\alpha]_D^{29}$ −67° in H_2O (*c* = 0·80)], does not appear to be isomerised by prolonged treatment with boiling Ac_2O–C_5H_5N.

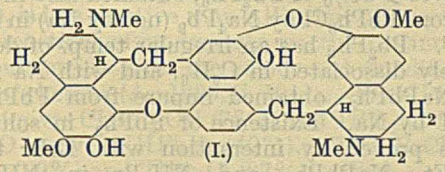
H. W.

***Strychnos* alkaloids. XXI. Synthesis of isomeric pyrroloquinolines and an isomeride of vomipyrine.** L. Horner (Annalen, 1939, **540**, 73—83; cf. A., 1938, II, 514).—6-*Amino*-8-*ethylquinoline*, m.p. 89° (yellow hydrochloride), is prepared from *o*-$C_6H_4Et{\cdot}NHAc$ by way of 4 : 2 : 1-$NO_2{\cdot}C_6H_3Et{\cdot}NH_2$, m.p. 58°, and 6-nitro-8-ethylquinoline, m.p. 68° [hydrochloride, m.p. 150° (decomp.)], and gives a hydrazone, which with $Pr^aCO{\cdot}CO_2H$ gives the *hydrazone*, $C_{16}H_{19}O_2N_3$, m.p. 135°, converted by $ZnCl_2$ into 8 : 4′-*diethylpyrrolo*-2′ : 3′-6 : 5-*quinoline*, m.p. 142° [*hydrochloride*, m.p. 244° (decomp.); not vomipyrine (I)]. Decarboxylation of the 10-carboxylic acids by molten $ZnCl_2$ (heating with Cu powder is without effect) yields *pyrrolo*-2′ : 3′-5 : 6-, m.p. 236—238°, and -1′ : 2′-8 : 7-*quinoline*, m.p. 94—96°. Absorption spectra are detailed for these and other tricyclic bases containing two nitrogenous rings, and it is concluded therefrom that (I) is a pyrroloquinoline, the position of the substituents remaining, however, uncertain. CHPhMeEt and HNO_3–H_2SO_4 give mixed *o*- and *p*-NO_2-derivatives, reduced to the mixed amines, b.p. 115°/12 mm., which yield an *Ac* derivative, m.p. 122—124°; with fuming HNO_3 in AcOH this gives *p*-$NO_2{\cdot}C_6H_4{\cdot}NHAc$ and *p*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$, and with HNO_3–H_2SO_4 gives *p*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$.

R. S. C.

Curare alkaloids. IV. Bebeerine and tubocurarine. Orientation of phenolic groups. H. King (J.C.S., 1939, 1157—1164).—Ethylation (EtI) of the Na salt of bebeerine (I) gives *O*-ethylbebeerine, the methochloride of which on Hofmann degradation in two stages affords O-*ethylbebeerilene* (II), m.p. 168—169°; this is oxidised ($KMnO_4$) to a mixture of two acids, $C_{18}H_{16}O_9$,H_2O, m.p. 197° (efferv.), and $C_{18}H_{16}O_9$, 0·5H_2O, m.p. 255°. Diazotised NH_2Ph and *o*-4-xylenol give a mixture of 2-hydroxy-4 : 5-(III) and 6-hydroxy-2 : 3-dimethylazobenzene; reduction ($Na_2S_2O_3$) of the Me derivative of (III) yields NH_2Ph, 5 : 1 : 2 : 4-$OMe{\cdot}C_6H_2Me_2{\cdot}NH_2$, and 4′-*amino*-3 : 4-*dimethyldiphenylamine*, m.p. 114—115° (*monohydrochloride*, m.p. 205°). Nitration, followed by esterification, of 4 : 1 : 2-$OMe{\cdot}C_6H_3(CO_2H)_2$ (IV) gives some 2-*Me* 1-*H* 3-*nitro*-4-*methoxyphthalate*, m.p. 186—187°, and 5 : 4 : 1 : 2-$NO_2{\cdot}C_6H_2(OMe)(CO_2Me)_2$, reduced (Pd–C–$H_2$) to *Me* 5-*amino*- (V), m.p. 149°, and 5-*azoxy*-4-*methoxyphthalate*, m.p. 175—180°. (V) is converted into the corresponding -*I*-derivative (VI), m.p. 111—112°, which condenses (Cu) with Me *iso*vanillate to give veratric acid, 4-methoxyphthalic acid, and 4 : 5 : 5′-tricarboxy-2 : 2′-dimethoxydiphenyl ether, identical with the compound obtained by degradation and oxidation of *O*-methylbebeerine. Demethylation (HBr) of *O*-ethylvanillic acid affords some protocatechuic acid and 3-*hydroxy*-4-*ethoxybenzoic acid*, m.p. 218—219°, the *Me* ester, m.p. 127—128°, of which condenses with (VI) to give 4 : 5 : 5′-tricarboxy-2-methoxy-2′-ethoxydiphenyl ether, m.p. 258—259° [identical with one of the acid oxidation products from (II)], 3 : 4-

$OMe{\cdot}C_6H_3(OEt){\cdot}CO_2H$, (IV), and *m*-hemipinic acid. NaOH with Cu (trace) and (VI) yields *O*-methylnor-*m*-hemipinic acid, which is brominated to 3-bromo-4-hydroxy-5-methoxyphthalic acid, the Me_2 ester, m.p. 153—154°, of which is ethylated ($C_2H_4N_2$) to *Me 3-bromo-5-methoxy-4-ethoxyphthalate*, m.p. 83—84° [*acid*, m.p. 206° (efferv.); 1-Et 2-H ester, m.p. 131°]. This ester condenses with *p*-$OH{\cdot}C_6H_4{\cdot}CO_2Me$ to give anisic acid, 5-methoxy-4-



(I.)

ethoxyphthalic acid [*monohydrate*, m.p. 192° (efferv.)], and 5 : 6 : 4′-tricarboxy-3-methoxy-2-ethoxydiphenyl ether ($+H_2O$), m.p. 195° (efferv.), identical with the second oxidation product from (II). These syntheses fix the structure of (I) as shown.

F. R. S.

Constitution of cassaine and partial synthesis of the alkaloid. F. Faltis and L. Holzinger (Ber., 1939, **72**, [*B*], 1443—1450).—Cassaine (I), m.p. 140°, $[\alpha]_D^{20}$ −104·2° in 96% EtOH, −114·6° in 0·1N-HCl, from *Erythrophleum guineense*, Don., is hydrolysed to cassaic acid (II), $[\alpha]_D^{20}$ −111·6° in $COMe_2$, *allo*cassaic acid (III), $[\alpha]_D^{20}$ −109·7° in $COMe_2$, and $NMe_2{\cdot}[CH_2]_2{\cdot}Cl$. Its partial syntheses from Na cassaate (III) and the base in boiling xylene is described. Analogously (III) and $NEt_2{\cdot}[CH_2]_2{\cdot}Br$ afford *homocassaine* [*diethylaminoethyl cassaate*], m.p. 107—109° after softening at 106°. *Diethylaminoethyl bromide hydrobromide*, m.p. 203° (decomp.), is obtained from $NEt_2{\cdot}[CH_2]_2{\cdot}OH$ and HBr (saturated at 0°) at 100°. CH_2N_2 and (II) yield *Me cassaate*, m.p. 188—189° after softening at 183°, which does not depress the m.p. of the compound obtained similarly from (III). (II) contains one double linking since it is hydrogenated (Pd-sponge in AcOH) to *dihydrocassaic acid* (IV), m.p. 229—235° after softening at 224°, also obtained from (III) [*Me* ester, m.p. 108°, and its *semicarbazone*, m.p. 185—187° (decomp.) after softening at 177°]. CrO_3 in AcOH oxidises (IV) to *dehydrodihydrocassaic acid* $C_{20}H_{30}O_4$, m.p. 228—229° (decomp.) after softening at 215° (*Me* ester, m.p. 98·5—99°, and its *disemicarbazone*, m.p. 249—250°).

H. W.

Veratrine alkaloids. V. Selenium dehydrogenation of cevine. L. C. Craig and W. A. Jacobs (J. Biol. Chem., 1939, **129**, 79—87).—Se dehydrogenation of cevine in H_2 yields various volatile products including β-picoline, 5-methyl-2-ethylpyridine, and a base, C_8H_9ON (*picrate*, m.p. 150—151°). The non-volatile products, on chromatographic adsorption in C_6H_6, yield the following: cevanthridine ($C_{23}H_{25}N$, m.p. 211—212°); unidentified bases possibly homologous with cevanthridine; a *base*, $C_{25}H_{25}N$, m.p. 229—230°; a *base*, $C_{24}H_{25}N$ or $C_{23}H_{23}N$, m.p. 186°; a *hydrocarbon*, $C_{17}H_{16}$, m.p. 138—150°, possibly derived from cevanthrol; a *hydrocarbon*, $C_{18}H_{18}$, m.p. 116—118°; and cevanthrol, $C_{17}H_{16}O$, m.p. 195—196°.

P. G. M.

Alkaloids of *Sinomenium* and *Cocculus*. XLIX. Alkaloids of *Stephania cepharantha*, Hayata. VI. Systematic method of separation of the alkaloids. H. Kondo, M. Tomita, M. Satomi, and T. Ikeda (J. Pharm. Soc. Japan, 1938, **58**, 276—279).—*iso*Tetrandrine (I) (3 g.) is obtained by crystallisation of the total alkaloids (12 g.) from $COMe_2$. The residue from the $COMe_2$ mother-liquors is extracted with aq. HCl and the sol. material separated by KOH and Et_2O into phenolic (*A*) and non-phenolic (*B*) (5 g.) fractions. Fractional crystallisation of (*B*) from $COMe_2$ and then $COMe_2$–C_6H_6 gives methyl*iso*chondodendrine (0·25 g.), then 3 g. of cepharanthine, m.p. 155° (non-cryst.) as the cryst. adduct, decomp. 103°, with $1C_6H_6$ (also + 1PhMe, decomp. 98°), and finally amorphous base. Fractional crystallisation of (*A*) from C_6H_6 affords a little berbamine (II), m.p. 170° [as *adduct*, m.p. 127° (decomp.), with $1{\cdot}5C_6H_6$; also $+4H_2O$, m.p. 156° (decomp.)], $[\alpha]_D^{25}$ +106·3° in $CHCl_3$ [diperchlorate, m.p. 278° (decomp.); dihydrochloride, m.p. 270° (decomp.); hydrobromide, m.p. 283° (decomp.); hydriodide, m.p. 260—264° (decomp.); methiodide, m.p. 261° (decomp.)], and amorphous base. Methylation (CH_2N_2) of (II) gives (I).

H. B.

Sinomenine. XLVI. Constitution of tudaranine. K. Goto and H. Shishido (Annalen, 1939, **539**, 262—265; cf. A., 1937, II, 435).—The structure of tudaranine is proved by synthesis of its *dl*-*N*-Et derivative Et ether ethiodide (I) and the degradation thereof already announced (A., 1939, II, 189), and now detailed. 2 : 4 : 1-$NO_2{\cdot}C_6H_3(OEt){\cdot}CH_2{\cdot}COCl$ and 2 : 4 : 1-$(OMe)_2C_6H_3{\cdot}[CH_2]_2{\cdot}NH_2$ give *2′-nitro-4′-ethoxyphenylacet*-β-2 : 4-*dimethoxyphenylethylamide*, m.p. 127—128·5°, converted by P_2O_5 in hot PhMe into 1-*2′-nitro-4′-ethoxybenzyl*-6 : 7-*dimethoxy*-3 : 4-*dihydro*isoquinoline, m.p. 145—147°, the *ethiodide*, m.p. 160—162°, of which is reduced by Zn dust in HCl to 1-*2′-amino*-4-*ethoxybenzyl*-6 : 7-*dimethoxy*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline, m.p. 116—118°. Diazotisation and treatment with Cu-bronze gives 5 : 6-dimethoxy-3-ethoxy-*N*-ethylnoraporphin [*hydrobromide*, m.p. 246—248°; *hydrochloride*, m.p. 234—236°; ethiodide = (I)].

R. S. C.

***Kurchi* alkaloids. II. Extraction of conessine and accompanying bases.** A. Bertho (Arch. Pharm., 1939, **277**, 237—237; cf. A., 1933, 728).—The extraction of the following bases is described: conessidine (I), $[\alpha]_D^{21}$ −63·5° in $CHCl_3$ [*dimethiodide*, m.p. 269° (decomp., slow heating)], conkurchine (II), $[\alpha]_D^{25}$ −43·8° in 96% EtOH [*dinitrate* ($+1{\cdot}5H_2O$), darkens at 180° and then explodes; *diperchlorate*, decomp. 272° (rapid heating); Ac_3 derivative, m.p. 263° (the derivative reported in A., 1933, 728 was not completely acetylated)], kurchine (A., 1932, 406), a di*tert.* base, $[\alpha]_D^{23}$ +10·6° in EtOH [*diperchlorate*, m.p. 250° (decomp.); *dimethiodide*, m.p. 286·5°], and *conkurchinine* (III), $C_{25}H_{36}N_2$, a di*tert.* base containing no NMe, m.p. 161°, $[\alpha]_D^{23}$ −47·0° in EtOH [*diperchlorate* ($+2H_2O$), darkens at 260° but does not melt at <330°; *dimethiodide*, m.p. 255—256° (decomp.)]. Since (III) is decomposed by dil. HNO_3, giving the nitrate of (II), and gives a red colour with fuchsin–SO_2, it probably contains the grouping

·N:CH·[CH_2]$_3$·N:. Many of these bases, in presence of alkali, or when recrystallised or kept, form mol. associates (also formed from mixed bases); some of these occur in the crude alkaloids, and they yield the unimol. forms when treated with conc. HCl and then aq. NH_3. (I) gives an amorphous form, m.p. 288—289° or >300°, and (II) gives an associate m.p. 323°, and another, m.p. 335—336°, identical with "kurchenine" (A., 1933, 728). The "norconessine" of Haworth (A., 1932, 406) is probably impure kurchine. The properties of the *Kurchi* alkaloids are summarised. A. Li.

Constitution of matrine. XXI. Curtius degradation of methyl methylmatrate. E. Ochiai and K. Noda (J. Pharm. Soc. Japan, 1938, **58**, 174—176).—*Methylmatrhydrazide*, m.p. 94° (*CMe*$_2$: derivative, m.p. 128·5°), from the Me ester and N_2H_4,H_2O at 100° (bath), is converted by HCl and amyl nitrite in EtOH into a *compound*, $C_{16}H_{28}O_2N_2$, b.p. 145°/0·02 mm. (*platinichloride*, decomp. 231°), and by $NaNO_2$–aq. HCl into a little *decarbonylmethylmatrinamine*, m.p. 120°, also obtainable in better yield by the Hofmann degradation. *iso*Propylidenebenzhydrazide has m.p. 144·5°. H. B.

Alkaloid (hydrobromide, m.p. 287°) from Twan Chan Tsao.—See A., 1939, III, 639.

Organoboron–nitrogen compounds. I. Reaction of boron chloride with aniline. R. G. Jones and C. R. Kinney (J. Amer. Chem. Soc., 1939, **61**, 1378—1381).—BCl_3 reacts violently with NH_2Ph, but only very slowly with NH_2Ph,HCl. With NH_2Ph (0·8 mol.) in C_6H_6 it gives the additive *compound* (I), BCl_3,NH_2Ph (not obtained quite pure), m.p. ~100°, decomp. ~120°, which decomposes in moist air and dissociates in boiling C_6H_6. With NH_2Ph in C_6H_6, (I) gives a very poor yield of the *compound*, BCl_2·NHPh,NH_2Ph, decomposed by H_2O to NH_2Ph, HCl, and H_3BO_3. When NH_2Ph is added to BCl_3 in C_6H_6 at −15° and the mixture first kept at room temp. and then boiled, *trichlorotriphenyltriboron nitride*, $BCl<^{NPh\cdot BCl}_{NPh\cdot BCl}>NPh$ (II), sinters at 255—260°, decomp. 265—270°, is obtained (cf. Rideal, A., 1889, 769). With cold H_2O (II) gives *trihydroxytriphenyltriboron nitride* [as (II) with OH replacing Cl], m.p. indefinite, 95—130°, sol. in aq. NaOH and readily hydrolysed to H_3BO_3 and NH_2Ph. With 5 mols. of NH_2Ph in boiling C_6H_6, (I) gives *boric trianilide* (III), $B(NHPh)_3$, m.p. 166—169° (decomp.; softens at 155°, if heated slowly), which gives no additive compound with NH_2Ph, is readily hydrolysed by H_2O, and with dry HCl in C_6H_6 gives (II). BCl_2·NHPh is a probable intermediate in formation of (II) by both methods. The "*tert.* B triethylimine," $B(NHEt)_3$, of Kraus *et al.* (A., 1931, 77) is renamed (ortho)boric triethylamide, this name and that of (III) showing the relation to H_3BO_3. BCl_3 and $NPhMe_2$ in C_6H_6 give the 1 : 1 additive *compound*, sinters at 125—130°, molten at 146°, after resolidification remelts at 144—145°, which is stable in C_6H_6 or over P_2O_5, loses HCl in moist air, reacts with H_2O in C_6H_6 but in H_2O alone forms an unreactive, insol. coating, reacts with MeOH to give $NPhMe_2$, Me_3BO_3, and HCl, and is decomposed by NH_2Ph. Analysis of the products is discussed. Et_3BO_3 and NH_2Ph do not react, even if boiled (cf. carboxylic esters). R. S. C.

Preparation and reactions of lead triphenyl derivatives. L. S. Foster, W. M. Dix, and I. J. Gruntfest (J. Amer. Chem. Soc., 1939, **61**, 1685—1687).—$PbPh_4$ (prep. in ≯81% yield from $PbCl_2$ and MgPhBr in boiling xylene) and I in $CHCl_3$ give $PbPh_3I$, m.p. 142° (uncorr.), which with Na in liquid NH_3 gives >90% of Pb_2Ph_6, obtained also in similar yield from $PbPh_3Cl$ by Na_4Pb_9 (not by Na) in NH_3 at −33·4°. Pb_2Ph_6 has an irregular temp. of decomp., is largely dissociated in C_6H_6, and with Na in NH_3 gives $NaPbPh_3$, obtained impure from $PbPh_3Cl$ or $PbPh_3I$ by Na. Existence of $PbPh_3^-$ in solution in NH_3 is proved by interaction with EtBr to give $PbPh_3Et$. $NaPbPh_3$ and NH_4Br in NH_3 give NH_4PbPh_3 (not isolated owing to its solubility), which is ionised in solution (proof: formation of $PbPh_3Et$) and destroyed only by a large excess of NH_4^+. Reaction of $NaPbPh_3$ with CH_2Cl_2 is complex. R. S. C.

Lead tetraphenyl and lead diphenyl dihalides. W. C. Setzer, R. W. Leeper, and H. Gilman (J. Amer. Chem. Soc., 1939, **61**, 1609—1610).—Adding $PbCl_2$ slowly to MgPhBr in Et_2O–PhMe and then heating gives 82—83% of $PbPh_4$, m.p. 225—226°, with sometimes, 6% of $PbPh_3Br$. $PbPh_3$ and $MgBr_2$ give $PbPh_3Br$, but $PbPh_4$ is unaffected by $MgBr_2$ or Mg + $MgBr_2$. $PbPh_3$ is thus an intermediate in the prep. of $PbPh_4$. Adding $PbPh_4$ to boiling, conc. HNO_3 gives $PbPh_2(NO_3)_2$, which with NaBr or NaI in very dil. HNO_3 gives 96% of $PbPh_2Br_2$ or 98% of $PbPh_2I_2$, respectively. $PbPh_2(NO_3)_2$ and conc. HCl give 93% of $PbPh_2Cl_2$. $PbPh_2I_2$ and KF in aq. EtOH give 92% of *PbPh*$_2F_2$, m.p. >300°, which with MgPhBr gives $PbPh_4$. R. S. C.

Ammino-compounds of lead triphenyl chloride. L. S. Foster, I. J. Gruntfest, and L. A. Fluck (J. Amer. Chem. Soc., 1939, **61**, 1687—1690).—By measuring the vol. of NH_3 absorbed and by isolating the compounds, it is shown that at −33·4° $PbCl_2$ with NH_3 vapour gives compounds containing 9·65, 2·7, 1·8, or 1·3 mols. of NH_3. Only the first-mentioned compound was examined in detail. R. S. C.

Synthesis in the selenophen series. IV. Introduction of side-chains into the selenophen nucleus. S. Umezawa (Bull. Chem. Soc. Japan, 1939, **14**, 155—161; cf. A., 1937, II, 172).—C_4H_4Se and AcCl with $SnCl_4$ in C_6H_6 or CS_2 yield *α-acetoselenenone* (I), b.p. 107°/14·5 mm. (*phenylhydrazone*, m.p. 114—116°), oxidised (dil. NaOH–$KMnO_4$) to *α-selenenylglyoxylic acid*, m.p. 92—94° [*monohydrate*, m.p. 44—46·5°; *semicarbazone*, m.p. 192—193°; *Ba* salt (+H_2O)], which with H_2O_2 yields *α-selenenoic acid* (II), m.p. 122—124° (*Ag* salt). *α-Chloromercuriselenophen*, m.p. 201—202° (from C_4H_4Se, NaOAc, and $HgCl_2$ in aq. EtOH), with EtCOCl at 100° yields *α-propioselenenone*, b.p. 115°/14 mm. [also prepared as (I)] (*semicarbazone*, m.p. 175—176°), oxidised (dil. NaOH–$KMnO_4$) to (II). C_4H_4Se and BzCl with P_2O_5, or with $SnCl_4$ in CS_2, give *Ph α-selenenyl ketone* (poor yield), m.p. 57—58° (*phenylhydrazone*, m.p. 175—176·5°). (I) with PhCHO and HCl gas at −10° yields

styryl α-selenenyl ketone, m.p. 81—82·5° (*dibromide*, m.p. 155·5—156°). These ketones are much more stable than C_4H_4Se. (I) and (II) give the indophenin reaction. A. Li.

Relative reactivities of organometallic compounds. XXVII. Thallium triphenyl. H. Gilman and R. G. Jones (J. Amer. Chem. Soc., 1939, **61**, 1513—1515; cf. A., 1939, II, 350).—$TlPh_3$ (prep. from LiPh and $TlPh_2Br$ in 70% yield), m.p. 169—170° (in N_2), is less reactive than AlR_3, but undergoes some of the reactions of moderately reactive organometallic compounds. It gives the colour test (modified) with Michler's ketone (A., 1925, ii, 1011). With PhCHO in C_6H_6 it gives $CHPh_2$·OH (76%) and $TlPh_2$·OH. With PhNCO it gives NHPhBz (40%). With BzCl it gives $COPh_2$ (89%) and $TlPh_2Cl$ (97%). With COPh·CH:CHPh in C_6H_6 it gives COPh·CH_2·$CHPh_2$ (41%) and COPh·CH($CHPh_2$)·CHPh·CO·COPh (30%). With Hg in hot C_6H_6 it gives $HgPh_2$ (45%) (obtained in 90% yield from $TlPh_2Br$ and Hg in hot, dry C_5H_5N). With O_2 in C_6H_6 it gives 11% of PhOH and some Ph_2. With CO_2 in boiling xylene it gives BzOH (70%) and Ph_2 (73%). It gives oils with $COPh_2$ or CO_2 in C_6H_6. R. S. C.

Structure of proteins. L. Pauling and C. Niemann (J. Amer. Chem. Soc., 1939, **61**, 1860—1867).—*X*-Ray data are shown in a crit. review to be incompatible with the cyclol structure of proteins instead of supporting it as assumed by Wrinch. Bond energy vals. and heats of combustion each show that the cyclol structure would be less stable than the polypeptide chain by about 28 kg.-cal. per mol. of NH_2-acid, so that at most 3% of the NH_2-acid residues possess the former structure. Other evidence against the cyclol theory is assembled and accepted, and Wrinch's more important arguments are refuted in detail. Moreover, the necessary overlapping of side-chains at corners and edges, contrasted with the rather uniform distribution of matter revealed by crystal structure analysis, is held to refute all cage structures and not merely Wrinch's particular choice. Proteins are considered to consist of polypeptide chains or rings built up from several hundred NH_2-acids; small nos. of residues held together by H bonds etc. would be at once disrupted in acid or alkali, which is not the case. The chains are given definite shapes by NH_2–CO_2H, S–S, and ester linkings, but mainly by H bonds, which latter, although individually weak, are very effective in aggregate. If the structure thus assumed is the most stable possible, denaturation is reversible (trypsin, hæmoglobin); if not, denaturation is irreversible, as with antibodies, the initial structure of which is enforced by the antigen during synthesis. The nature of the end-groups is important only for enzymic attack and biological action, but not for structure. Whilst the periodicity proved by Bergmann indicates 288 residues in the mol. of many proteins, this no. will be modified by side-groups or occasional variations in assembly of the residues and will often be only approx. The significance of this no. is not clear. Favoured mol. wts. probably have a biological rather than a chemical cause, viz., retention of this protein property throughout evolution of the species. R. S. C.

***X*-Rays and the cyclol hypothesis.** J. D. Bernal, I. Fankuchen, and D. Riley (Nature, 1939, **143**, 897).—A reply to Wrinch (A., 1939, II, 397). L. S. T.

Casein. III. Fractionation of casein and paracasein by ammonium chloride. IV. Hammarsten's proteose is not a degradation product of casein. E. Cherbuliez and J. Jeannerat (Helv. Chim. Acta, 1939, **22**, 952—959, 959—961).—III. Casein is dissolved in aq. NH_4Cl with the aid of NaOH and fractionally pptd. by HCl and $COMe_2$; the process leads essentially to two fractions, casein-α_1 and -γ with a little δ. Each contains a little Ca but the presence of this ion does not influence the result since no difference is observed if NaOH is replaced by $Ca(OH)_2$. Rennet is practically without action on casein-δ and has its max. action on the mixture of -α_1 and -γ, whereas each of the latter separately is only incompletely coagulated. Paracasein is obtained by the action of rennet on a solution of Ca caseinate, whereby it is pptd. as its Ca salt free from casein; elimination of Ca from the ppt. necessitates repeated dissolution and pptn. Alternatively a solution of casein is treated with rennet in the absence of alkaline-earth ions, whereby the product is as free as the original material from Ca but is liable to be contaminated with unchanged casein. Fractionation of paracasein gives essentially α_1 and γ with less δ than is the case with casein.

IV. Hammarsten's proteose is identical with casein-δ in content of P, S, and methionine, in the coloration with CH_2O and HCl in presence of H_2SO_4, and in physical properties. Proteose is therefore not a degradation product of casein formed under the proteolytic influence of rennet, but a preformed constituent in the mixture, casein. H. W.

Pantothenic acid. IV. Formation of β-alanine by cleavage. H. H. Weinstock, jun., H. K. Mitchell, E. F. Pratt, and R. J. Williams (J. Amer. Chem. Soc., 1939, **61**, 1421—1425; cf. A., 1939, II, 172).—Pantothenic acid is synthesised by yeast only if the medium contains β-alanine, which is shown by quant. chemical, physical, and biological tests to be formed by acid or alkaline degradation of the acid and is isolated from the products as β-*naphthalenesulphonyl* derivative, m.p. 135·5—136·5°. The acid is probably a protein, ~80% pure, yielding 1 equiv. of β-alanine. R. S. C.

Eisinin, $C_{13}H_{20}O_6N_4$, m.p. 225—226° (decomp.), $[\alpha]_D^{14}$ —54·3° in H_2O, from *Eisenia bicyclis*.—See A., 1939, III, 733.

Precipitation of proteins with complex salts.—See A., 1939, III, 885.

Organic chemical operations with small amounts of material. J. Erdös and B. László (Mikrochem., 1939, **27**, 211—215).—A review.

Organic micro-analysis. VII. Improvements to Pregl's micro-analytical apparatus. S. Sakamoto (J. Pharm. Soc. Japan, 1938, **58**, 304—306).—An improved CO_2 generator and pressure regulator are described. S. H. H.

Refractive index measurements in qualitative organic micro-analysis. P. L. Kirk and C. S.

Gibson (Ind. Eng. Chem. [Anal.], 1939, **11**, 403).—A method of measuring n of small quantities of org. liquids is described. For solids immersion methods can be applied when the val. of n is known. Determination of n is a valuable adjunct to the identification of org. compounds. L. S. T.

Handling of hygroscopic substances in the micro-determination of carbon and hydrogen. C. J. Rodden (Ind. Eng. Chem. [Anal.], 1939, **11**, 405).—The apparatus described and illustrated consists of a jacketed drying tube arranged so that it may be kept at a const. temp., and a weighing bottle of special design. The sample is dried, weighed, and introduced into the C and H combustion tube without contact with moisture. L. S. T.

Quantitative organic elementary micro-analysis without a micro-balance. J. B. Niederl, V. Niederl, R. H. Nagel, and A. A. Benedetti-Pichler (Ind. Eng. Chem. [Anal.], 1939, **11**, 412—414; cf. A., 1939, I, 341).—Micro-procedures with minor changes, such as in the time factors in the C and H determination and in the Dumas N method, can be employed when an assay balance or an ordinary analytical balance of suitable precision is available. Changes in equipment and micro-apparatus are unnecessary. Typical results thus obtained in the determination of metals, neutralisation equiv., N by the Kjeldahl and micro-Dumas methods, C and H, and mol. wt. are recorded. L. S. T.

Detection of nitrogen in the organic laboratory. A. G. Epprecht and B. Hornung (Helv. Chim. Acta, 1939, **22**, 925—927).—A few mg. of the substance are mixed with CaO in a glass tube $\not>5$ mm. in diameter; if NO_2- or azo-compounds are present a little Cu powder is added. A drop of HCl (1 : 1) on a Pt or glass loop or placed in filter-paper is brought into the tube, which is moderately heated. The loop of paper is placed in a drop of Riegler's solution to which an excess of CaO is added. If N is present a distinct red colour due to NH_4 is developed in the solution after a short time. A micro-analytical modification of the test is described. H. W.

Semimicro-determination of halogens in organic substances. A. Giacalone (Annali Chim. Appl., 1939, **29**, 271—277).—The substance (~50 mg.) is heated with $K_2Cr_2O_7$–H_2SO_4 (for Br or I) or Ag_2SO_4–H_2SO_4 (for Cl); Br or Cl liberated is absorbed in aq. H_2O_2 and the HBr or HCl formed is determined gravimetrically as Ag salt. With I, HIO_3 in the (diluted) digestion liquor and the residual CrO_4'' are reduced by SO_2 and I is determined gravimetrically as AgI. F. O. H.

"Deflagration" with sodium peroxide as simple analytical process for determination of halogen, sulphur, and other constituents in organic substances. R. Kraus (Z. anal. Chem., 1939, **117**, 243—252).—Deflagration of solid org. substances and certain liquids by quick and short heating with a large excess of Na_2O_2 in a covered Ni crucible by the method detailed gives a quick and complete combustion with relatively little attack on the crucible, and permits subsequent determinations of halogens, S, and P to be made accurately. Viscous liquids are first mixed with MgO, and liquids of high b.p. are absorbed in filter-paper in the crucible before mixing with the Na_2O_2. The method is limited for low % of Cl, S, etc. only by the "blank" of the Na_2O_2. It is applicable to substances, such as chlorotoluidine, which are not readily decomposed by the Carius method. The method is especially suitable for routine analyses. L. S. T.

Organic micro-analysis. IV. Simple volumetric micro-determination of ionisable organic halogen derivatives with adsorption indicators. S. Uyeo and S. Sakamoto (J. Pharm. Soc. Japan, 1938, **58**, 212—218).—Ionisable halogen in org. compounds is determined by dissolving 3—5 mg. of the substance in H_2O or aq. EtOH, adding (for Cl) bromophenol-blue and 10% AcOH or (for Br or I) eosin, and titrating with 0·01—0·002N-$AgNO_3$. In 102 examples the error exceeds 0·4% in 9 cases (±0·2—0·3% claimed). R. S. C.

Reaction of organic sulphur compounds with hydrogen peroxide. XVII. Gravimetric micro-analysis of organic sulphur compounds. III. R. Kitamura and F. Masuda (J. Pharm. Soc. Japan, 1938, **58**, 251—254).—S in compounds containing N:C·SH, O:C·SH, S:C·SH, N·C:S, O·C:S, $S(C:N)_2$, or C·CS·C is determined by treating 3—5 mg. with H_2O_2–KOH at 40°, followed by $BaCl_2$, and weighing the $BaSO_4$ produced. R. S. C.

Micro-determination of dipentadeuterethyl ether.—See A., 1939, III, 804.

Differentiating action of solvents on the strength of acids. I. Potentiometric titration of salts by the displacement method, in differentiating solvents. N. A. Izmailov and M. A. Belgova (J. Gen. Chem. Russ., 1939, **9**, 453—459).—Na salts of carboxylic acids are dissolved in aq. $COMe_2$, and the solutions are electro-titrated with HCl. The org. acids thus liberated dissociate to a very small extent only, as compared with aq. solutions, whilst dissociation of HCl is not affected. The $[COMe_2]$ should be $\not<85\%$. The method is applicable to all carboxylic acids, including $CCl_3{\cdot}CO_2H$. R. T.

Accuracy of iodometry for the determination of ascorbic acid; method for standardisation of preparations. K. Shinohara (J. Pharm. Soc. Japan, 1938, **58**, 279—292).—Ascorbic acid (I) can be determined accurately by titration with 0·01N-I in solutions of p_H 0·7—5 containing KCNS. At p_H >6 and <9 results are too low [owing to atm. oxidation of (I)] unless titration is carried out in N_2. Direct titration of (I) in $\not<0{\cdot}5$M-HCl also gives low results owing to slow reaction; excess of I and back titration with $Na_2S_2O_3$ give moderately accurate vals. Oxidation of dehydroascorbic acid (II) by I is negligible at p_H <6 but occurs at 6—8 and is a max. at 7·4—7·6. Aq. solutions of (I) are more stable [to atm. oxidation to (II)] than those in dil. HCl or H_2SO_4; KCNS (25×10^{-4}M.) has a pronounced inhibitory effect and is more effective than HPO_3. The procedure recommended is: (I) (0·1761±0·0001 g.) is dissolved in 25×10^{-4}M-KCNS to 200 c.c. and 5 or

10 c.c. are then titrated with 0·01N-I (in 4% KI) using starch solution as indicator; the error is $<\pm 0{\cdot}3\%$. H. B.

Determination of formaldehyde. I. Hydrogen peroxide method. A. Foschini and M. Talenti (Z. anal. Chem., 1939, **117**, 94—99).—Sources of error in the official method of the Italian Pharmacopœia (5th edition) for the determination of CH_2O by H_2O_2 are discussed and methods for their elimination suggested. The CH_2O should be measured by a micro-burette, and the alkaline mixture constantly agitated to facilitate the removal of gases. Contamination by CO_2 from gas-heated water-baths should be avoided by electrical heating. Results thus obtained are more const. and are lower than those obtained by the official method. L. S. T.

Determination of metaldehyde. Schonberg (Ann. Falsif., 1939, **32**, 178—181).—Metaldehyde is depolymerised by heating at 65—75° for 1—2 hr. with aq. H_3PO_4, the MeCHO formed being absorbed in aq. $NaHSO_3$ and determined iodometrically. E. C. S.

Identification of ethers. P. P. T. Sah (Rec. trav. chim., 1939, **58**, 758—760).—A small sample of the ether is passed through a quartz tube at 500° and the issuing gas passed through a solution of a reagent (*o*- or *p*-tolylsemicarbazide; *m*-nitro- or *p*-chloro-benzhydrazide) by which the aldehyde or ketone is identified and the ether may be deduced. Et_2O gives C_2H_6 and MeCHO; $Pr^{\alpha}{}_2O$ gives C_3H_8 and EtCHO; $Pr^{\beta}{}_2O$ gives C_3H_8 and $COMe_2$; $Bu^{\alpha}{}_2O$ gives C_4H_{10} and $Pr^{\alpha}CHO$; $Bu^{\beta}{}_2O$ gives C_4H_{10} and $Pr^{\beta}CHO$; (*sec.*-Bu)$_2O$ gives C_4H_{10} and COMeEt; $CH_2Ph{\cdot}OEt$ gives PhMe, C_2H_6, MeCHO, and PhCHO; $CH_2Ph{\cdot}OPr$ gives PhMe, C_3H_8, EtCHO, and PhCHO; $CH_2Ph{\cdot}OPr^{\beta}$ gives PhMe, C_3H_8, $COMe_2$, and PhCHO; $CH_2Ph{\cdot}OBu^{\alpha}$ gives PhMe, C_4H_{10}, $Pr^{\alpha}CHO$, and PhCHO; $CH_2Ph{\cdot}OBu^{\beta}$ gives PhMe, C_4H_{10}, $Pr^{\beta}CHO$, and PhCHO; $(CH_2Ph)_2O$ gives PhMe and PhCHO. J. D. R.

Saccharolactone as reagent for precipitating certain amines. A. C. Kurtz and D. W. Wilson (J. Biol. Chem., 1939, **129**, 693—699).—Saccharolactone (I) (deteriorates slowly in EtOH) and the free amine in EtOH at room temp. give NN′-*dimethyl*-, m.p. 188°, *-ethyl*-, m.p. 174°, -n-, m.p. 179—181°, and -iso-*propyl*-, m.p. 176—178°, -n-, m.p. 178°, and -iso-*butyl*-, m.p. 159°, -n-, m.p. 173—174°, and -iso-*amyl*-, m.p. 138°, -n-*heptyl*-, m.p. 174—176°, -β-*hydroxyethyl*-, m.p. 129—130°, *-benzyl*-, m.p. 174—176°, and -β-*phenylethyl-saccharimide*, m.p. 185—186°. Similar *derivatives* from tyramine and piperidine had m.p. 204° and 191° (darkens >140°), respectively. The derivatives of m.p. <174° show browning and frothing at the m.p. Some solubilities are recorded. Pptn. of the less sol. saccharimides is more rapid with the more symmetrical amines. NH_2Bu gives almost immediate pptn., NH_2Bu^{β} after 30 min., and NH_2Bu-*sec.* no ppt. $(CH_2{\cdot}NH_2)_2$, putrescine, and cadaverine give an immediate gummy ppt. (I) and $NMe_4{\cdot}OH$, NMe_3, or NEt_3 give no ppt. Sp. pptn. of saccharimides may be used to determine certain amines in mixtures. Aromatic amines give (slowly) cryst. ppts., *e.g.*, from NH_2Ph, m.p. 204—205° (decomp.); *o*-, m.p. 190—191° (decomp.), and *p*-$C_6H_4Me{\cdot}NH_2$, m.p. 202—203° (decomp.); xylidine, m.p. 190—191° (decomp.); and benzidine, m.p. 275—280° (decomp.). A. T. P.

Semimicro-determination of amino-acids. H. R. Ing and M. Bergmann (J. Biol. Chem., 1939, **129**, 603—607).—Apparatus for semimicro-determination of NH_2-acids in proteins by the solubility method (cf. A., 1939, II, 236) is described. The reaction product is filtered by centrifugal means. Experiments are recorded giving results of the determination of glycine by means of Na dioxypyridate and of proline in gelatin by NH_4 rhodanilate. A. T. P.

Naphthalene-2-sulphonic acid as a reagent for amino-acids. M. Bergmann and W. H. Stein (J. Biol. Chem., 1939, **129**, 609—618; cf. A., 1939, II, 236).—2-$C_{10}H_7{\cdot}SO_3H$ (I) and *l*-leucine or *l*-phenylalanine (II) in dil. HCl form sparingly sol. *salts* ("nasylates"), $+H_2O$ (III), m.p. 187·5—189° (decomp.) and 232—233° (decomp.), respectively. *l*-Arginine and *l*-histidine afford *salts*, *B*,2(I), m.p. 209—211° (decomp.), and 265° (decomp.), respectively, converted by C_5H_5N–MeOH into the corresponding *mono-salts*, *B*,(I), m.p. 243° (decomp.) and 206—207° (decomp.), respectively, which give the di-salts with strong acids. Commercial leucine is freed from methionine by pptn. as (I) salt and treatment with C_5H_5N–EtOH at room temp.; it had $[\alpha]_D^{24}$ +15·33° in 21% HCl. Determination of NH_2-acids by the solubility method [of their (I) salts] (*loc. cit.*) is illustrated. Acetyl-*l*-phenylalanyl-*l*-glutamic acid and boiling HCl give a solution, which on evaporation to dryness and treatment with (I) gives (III), converted by C_5H_5N–EtOH at 20° for 2 days into (II), $[\alpha]_D^{26}$ −34·6° in H_2O. The sparingly sol. (I) salt, m.p. 211—212° (decomp.), of glycyl-*l*-leucine can be used for its determination. Tryptophan, methionine, and cysteine give salts with (I). Flavianic acid forms sparingly sol. salts with leucine, phenylalanine, tyrosine, cystine, and tryptophan. NH_2-acid salts can also be obtained from β-naphtholazobenzene-*p*-sulphonic acid, 4-nitro-4′-methyldiphenylamine-3-sulphonic acid, and anthraquinone-2-sulphonic acid. A. T. P.

Determination of glutamic acid. A. A. Arhimo and T. Laine (Suomen Kem., 1939, **12**, **B**, 18).—The acid is oxidised (HNO_2) to α-hydroxyglutaric acid and finally (acid $KMnO_4$) to succinic acid, which is extracted with Et_2O and determined by titration of the Ag salt with 0·1N- or 0·005N-NH_4CNS (cf. Cohen, A., 1939, III, 639). F. O. H

Volumetric determination of thiocarbamide. C. Mahr (Z. anal. Chem. 1939, **117**, 91—94).—The solution of $CS(NH_2)_2$ is titrated at 35° with 0·1N-BrO_3'+Br in presence of acid (H_2SO_4, HCl, or $HClO_4$), KI, and starch. The formation of a stable blue colour shows when oxidation to the corresponding ·S·S· compound is complete. Cu and Hg salts, but not small [NO_3'], interfere. H_3PO_4 must be added when Fe^{III} salts are present. L. S. T.

Effects of methionine, djenkolic acid, and benzylcysteine on the determination of cystine by the dropping mercury electrode. E. R. Smith and C. J. Rodden (J. Res. Nat. Bur. Stand., 1939, **22**,

669—672).—The polarographic determination of cystine in a buffered solution containing $Co^{\cdot\cdot}$ is unaffected by the presence of methionine or benzylcysteine at concns. up to ~ twice the concn. of cystine. Djenkolic acid, however, reduces the height of the reduction max. of cystine. W. R. A.

Determination of arginine in the presence of other amino-acids by means of the Sakaguchi reaction. L. E. Thomas, J. K. Ingalls, and J. M. Luck (J. Biol. Chem., 1939, **129**, 263—271).—The Sakaguchi method of determining arginine is further modified so as to be applicable in presence of NH_4 salts and other NH_2-acids. The colour is always fugitive (cf. lit.). The following arginine contents are determined: casein 3·37—4·12, edestin 16·01—17·01, total protein of liver, plasma, and serum of the dog 5·86, 5·59, and 4·51, respectively, globulin II (dog) 5·93—6·76, insulin 3·31, and protamine 68·3%. R. S. C.

Titrimetric modification of the glyoxalase method for the determination of reduced glutathione. E. F. Schroeder and G. E. Woodward (J. Biol. Chem., 1939, **129**, 283—294).—Reduced glutathione is determined by its accelerating effect on the conversion of AcCHO into lactic acid by glyoxalase. The amount of unchanged AcCHO is determined by a modification of the H sulphite method of Clift and Cook (cf. A., 1933, 491). E. M. W.

Drop detection of diazotisable amines. S. I. Burmistrov (Prom. Org. Chim., 1939, **6**, 328).—A no. of aromatic amines are identified from the colour developing after diazotisation and coupling with $NHPh{\cdot}C_{10}H_7$-α. R. T.

Micro-determination of phenols by the "volume-colorimetric" method. A. Ionesco-Matiu, C. Popesco, and A. Popesco (J. Pharm. Chim., 1939, [viii], **30**, 49—58).—The method, involving titration of the sol. blue compounds formed from phenols and phosphotungstic acid with $K_3Fe(CN)_6$, has been successfully applied to *o*- and *p*-$C_6H_4(OH)_2$, pyrogallol, gallic acid, and the tannins. H. G. R.

Colour reaction for the detection and determination of small quantities of β-naphthol. J. A. Gautier (J. Pharm. Chim., 1939, [viii], **30**, 70—76).—The method described utilises the colour reaction with $NaNO_2$ and HCl and will detect 10 μg. of β-$C_{10}H_7{\cdot}OH$ per c.c. H. G. R.

Colour reaction for polyhydric phenols. J. B. Aschkinazi (J. Appl. Chem. Russ., 1939, **12**, 309—312).—NaOEt in EtOH is added to the substance, and the solution is shaken with air. Under these conditions polyhydric phenols give the following colorations: *o*-$C_6H_4(OH)_2$ grass-green, changing to dull green, 1 : 3 : 4-$C_6H_3Me(OH)_2$ blue, changing to red, 1 : 2 : 3-$C_6H_3(OH)_3$ red, changing through brown to violet, 1 : 2 : 3-$C_6H_3(OH)_2{\cdot}OMe$ green, changing through blue to violet, gallic acid a white, changing to ultramarine, ppt., *m*-$C_6H_4(OH)_2$ olive-green, orcinol rose-red, changing to cerise, phloroglucinol bluish-violet, quinol orange. Guaiacol, veratrole, safrole, *iso*safrole, piperonaldehyde, mono- and di-ethers of *o*-, *m*-, and *p*-$C_6H_4(OH)_2$, vanillin, 1 : 2 : 3-$C_6H_3(OMe)_3$, 1 : 2 : 6-$OH{\cdot}C_6H_3(OMe)_2$, and monohydric phenols give no colorations under the above conditions. R. T.

Colour reactions of lignin and tannins. W. G. Campbell and J. C. McGowan (Nature, 1939, **143**, 1022).—The Mitchell colour reaction of gallotannins (A., 1923, ii, 188) and the Cl_2–Na_2SO_3 reaction of hardwood lignin (B., 1937, 1057) are essentially similar. With lignin, reactions showing the importance of removing excess Cl_2 while the system is still acid and then rendering the solution weakly alkaline for the colour development are described. L. S. T.

Reactions between thiophen and calcium hypochlorite solutions.—See A., 1939, I, 476.

Colorimetric determination of pyrrole with isatin and the application of the method to biological materials. G. H. Guest and W. D. McFarlane (Canad. J. Res., 1939, **17**, B, 133—138).—Fromm's method (A., 1935, 998) is modified and applied to the determination of pyrrole (I) produced by the dry distillation of proteinaceous substances. The (I) (yield increased by addition of Na_2O_2) obtained from gelatin (II) is derived entirely from proline (III) and hydroxyproline. $CuSO_4$ catalyses the oxidation of (III) to (I) by Na_2O_2. (I) is absent from the hydrolysates of (II), gliadin, and glutenin. S. H. H.

Bromometric determination of antipyrine. V. Madis (Österr. Chem.-Ztg., 1939, **42**, 290—293).—Antipyrine is determined in 0·4N-HCl containing KBr and 0·1% $AuCl_3$ (1 c.c.; indicator) by titrating with $KBrO_3$ (2 Br added). Aminopyrine, quinine salts, and codeine salts interfere, but *o*-$OH{\cdot}C_6H_4{\cdot}CO_2H$, NHAcPh, caffeine, or phenacetin do not. The method is adapted for micro-quant. work. R. S. C.

Alkaloids and their reagents. C. C. Fulton (Amer. J. Pharm., 1939, **3**, 184—192).—A new systematic classification of some 100 reagents in use for identification of alkaloids is proposed, and a table is given showing them in the order of their pptg. power. Phosphomolybdic acid forms a convenient standard for dil. solutions. P. G. M.

Micro-electrophotometric determination of morphine. R. Cahen and H. Feuer (Compt. rend., 1939, **208**, 1907—1910; cf. A., 1911, ii, 79; 1915, ii, 76).—The solution containing morphine (0·02—0·20 mg.) is evaporated to dryness and the residue treated with pure H_2SO_4 (2·4 c.c.) in a boiling water-bath for 2 min. After cooling, saturated aq. NaOAc (5 c.c.) and 4% $HgCl_2$ (2 drops) are added; the mixture is boiled, cooled, made up to 10 c.c., and the emerald-green colour determined electrophotometrically (red, neutral, or green filter). The red and grey filters give a 1—5%, and the green a 5—10%, error. J. L. D.

Detection of ergotamine and ergotaminine in gynergen. A. Kofler (Angew. Chem., 1939, **52**, 251—253; cf. A., 1937, II, 393; 1938, II, 164; L. Kofler, A., 1939, II, 43).—The microscopical detection method is extended; Et_2O and then $CHCl_3$ (from $NaHCO_3$ mixture) extracts (also by intermediate Al_2O_3 adsorption) afford crystals of ergotaminine and ergotamine (hydrated), respectively. A. T. P.