BRITISH CHEMICAL ABSTRACTS

A., II.—Organic Chemistry

MAY, 1937.

New synthetic methods in organic chemistry. J. VAN ALPHEN (Chem. Weekblad, 1937, 34, 262—273).—A review. S. C.

Ebulliometric and tonometric researches on chemically pure liquids.—See A., I., 174.

Catalytic reactions among complex molecules.—See A., I, 252.

Catalytic isomerisation of *n*-octane. J. K. JURIEV and P. J. PAVLOV (J. Gen. Chem. Russ., 1937, 7, 97—99).—5—15% of *iso*-hydrocarbons are obtained by passing *n*-octane over various catalysts (Pt–C, Ni–Al_2O_3, Ni–ZnO, Al_2O_3, C) at 310°. R. T.

***cis–trans* Rearrangement of ethylene compounds catalysed by molecular oxygen.**—See A., I, 251.

Absorption of propylene and *cyclo*propane by solutions of sulphuric acid. F. F. RATMAN (J. Gen. Chem. Russ., 1937, 7, 14—17).—The rate of absorption by H_2SO_4 (*d* 1·59—1·83) of *cyclo*propane is > of propylene. The reactions take place in the surface film, between gas and H_2SO_4 mols., and involve rupture of the trimethylene ring. R. T.

Separating butenes from butanes. Distillation of azeotropic mixtures with sulphur dioxide. M. P. MATUSZAK and F. E. FREY (Ind. Eng. Chem. [Anal.], 1937, 9, 111—115).—Separation of a mixture of C_4-hydrocarbons into a butane and a butene fraction is best accomplished by distilling the min.-boiling azeotropic mixtures formed with SO_2. V.p. and equilibrium concns. of liquid and vapour phases at different temp. are determined for samples of refinery gas fractions. The relationships between the SO_2 content of the liquid phase and the distribution of butenes and butanes between the vapour and liquid are linear. As the temp. of distillation increases, the molar concn. of SO_2 in the vapour phase increases linearly, the azeotropes decrease in hydrocarbon content, and the separation of the hydrocarbons is more difficult. J. L. D.

Stereochemical studies. II. *cis*-Δ^{β}-Butene from $\Delta^{\alpha\gamma}$-butadiene. K. ZIEGLER, F. HÄFFNER, and H. GRIMM (Annalen, 1937, 528, 101—113; cf. A., 1934, 865).—Examination of the physical properties of the butene obtained by the successive action of alkali metal and amines on $\Delta^{\alpha\gamma}$-butadiene shows it to be homogeneous and its behaviour when brominated and then treated with KOH–MeOH proves it identical with the Δ^{β}-butene of higher b.p. obtained by Wislicenus from angelic acid. Reasons are advanced for regarding it as the *cis*-compound. Since *trans*-Δ^{β}-butene is not isomerised by contact with Li or Na or with their alkylanilides, the sterically homogeneous course of butadiene reduction is a peculiarity of the addition reaction in itself and is probably inherent to the initial stage of addition of metal. H. W.

Possible detection of conjugated carbon double linkings. K. MEINEL (Ber., 1937, 70, [*B*], 429—434).—The compounds obtained by treatment of a substance containing two conjugated ethylenic linkings or one ethylenic linking in conjugation with the C_6H_6 nucleus with 1 mol. of Br in EtOH give a red colour when mixed with a suspension of AgCNS in EtOH containing $Fe^{\cdots}$; products from substances which do not contain a conjugated system do not yield this colour or do so slowly and the final intensity is < that given by the former class. With $CHPh{:}CH_2$ the production of colour is not immediate and whilst that with $CHPh{:}CH{\cdot}CH_2OH$ or $CHPh{:}CH{\cdot}CHO$ is instantaneous, the max. intensity is observed only after several days. Substances with conjugated ethylenic linking (dihydrobenzene; dimethylbutadiene) give an immediate, pronounced colour. Substituents in the C_6H_6 nucleus may cause an immediate, marked colour (*iso*safrole) or immediate max. intensity (anethole). The behaviour of crotonaldehyde depends on its age. PhBr does not react. The change is accelerated by AgBr, which causes the development of colour in cases in which it is not otherwise observed. The behaviour of raw and boiled linseed oil shows the presence of a conjugated system in the latter. The products of the reactions have not yet been isolated. H. W.

Peroxide effect in the addition of reagents to unsaturated compounds. XIII. Addition of hydrogen bromide to butadiene. M. S. KHARASCH, E. T. MARGOLIS, and F. R. MAYO (J. Org. Chem., 1936, 1, 393—404).—In presence of antioxidants HBr and butadiene react rapidly (vac.; −78°) giving mainly α-bromo-Δ^{α}-butene (I) and some α-bromo-Δ^{β}-butene (II), the proportion of (I) formed decreasing with increasing temp. In presence of air or peroxides the main product is (II). At −12° (I) is converted into an equilibrium mixture [15% (I) and 85% (II)] by HBr in presence of a peroxide (ascaridole), but not by either of these reagents alone, except at higher temp. (30—45°), when HBr effects equilibration probably owing to the enhanced activity of minute quantities of peroxides at higher temp. Addition of HBr to (II) (which does not contain a terminal double linking) in presence either of antioxidants or of peroxides gives 80% of αγ- and 20% of βγ-dibromobutane (III). A mixture of the same proportions is obtained from (I) and HBr in presence

of peroxides, but in presence of an antioxidant 60% of (III) is formed. These results are correlated with the effect of HBr and peroxides on the isomerisation of the bromobutenes. H. G. M.

Isomerisation of allene hydrocarbons by silicates. III. Isomerisation of tetramethylallene. IV. Tautomerism in the system allene–propylene. J. M. Slobodin (J. Gen. Chem. Russ., 1936, 6, 1806—1814, 1892—1896; cf. A., 1935, 957).—III. $CMe_2Bu^{\beta}\cdot OH$ is heated at 130—135° with $H_2C_2O_4$, to yield $CMe_2{:}CHPr^{\beta}$, which with Br in Et_2O at −10° yields a mixture of CMe_2BuBr (I), $CMe_2Br\cdot CHPr^{\beta}Br$ (II), and $CHBr(CMe_2Br)_2$ (III). (I) reacts further with Br at 60°, to yield (II), (III), $CBr_2(CMe_2Br)_2$ (IV), and $CMe_2Br\cdot CHBr\cdot CMeBr\cdot CH_2Br$, and further yields of (III) may similarly be obtained from (II). (III) distilled from KOH at 135—140°/10 mm. yields *βγ-dibromo-βδ-dimethyl-Δ$^{\gamma}$-pentene*, b.p. 96—97°/14 mm., from which $CMe_2{:}C{:}CMe_2$ (V) is obtained by heating with Zn in 85% EtOH. (V) is also obtained from (IV) in the same way. Varying amounts of polymerides, and an equilibrium mixture of (V) (85%) and $CMe_2{:}CH\cdot CMe{:}CH_2$ (VI) (15%), are obtained by passing (V), (VI), or (V) + (VI) vapour over floridin at 120—200°.

IV. A product containing polymerides and an equilibrium mixture of allene 38·5 and propylene 61·5% is obtained by passing allene vapour over floridin at 325°. R. T.

Hydrolysis of alkyl halides.—See A., I, 249.

Exchange reactions of iodine compounds.—See A., I, 259.

Iodofluoromethane. A. E. van Arkel and E. Janetzky (Rec. trav. chim., 1937, **56**, 167—168).—By the action of Hg_2F_2 on CH_2I_2 at about 120° *iodofluoromethane*, b.p. 53·4°, has been obtained. R. C.

Synthesis of polychloro-compounds with aluminium chloride. III. Condensation of chloroethanes with chloroethylenes. H. J. Prins (Rec. trav. chim., 1936, **56**, 119—125).—$CHCl{:}CHCl$ (I) readily adds HCl in presence of $AlCl_3$ giving $CHCl_2\cdot CH_2Cl$ (II), which reacts further with (I) giving two isomeric ααβγδ-pentachlorobutanes, a solid (III), m.p. 48° (cf. A., 1932, 717), and a *liquid* (IV), b.p. 95·3—95·5°/11 mm. Both forms give *α-chlorobutadiene*, b.p. 68°, when treated with warm Zn–EtOH, and can be titrated in boiling EtOH with 0·1*N*-KOH, 1·44—1·59 mols. of HCl being evolved. (II), C_2HCl_3, and $AlCl_3$ (40°; 7 days) give *ααδδ-pentachloro-Δ$^{\beta}$-butene*, b.p. 78·5—80°/11 mm., which is stable to boiling 0·1% $KMnO_4$, reduces $AgNO_3$–NH_3–H_2O in presence of a trace of alkali, and is also obtained from $CCl_3\cdot CH_2Cl$ and (I) in presence of $AlCl_3$ (40°, 10 days). (I), C_2HCl_5, and $AlCl_3$ yield (III), (IV), and *ααββγδ-heptachlorobutane*, b.p. 97·5°/2 mm., reduced by Zn–EtOH to trichlorobutadiene. $CHCl_2\cdot CHCl_2$, (I), and $AlCl_3$ give a mixture from which only (III) could be isolated (cf. A., 1931, 597). C_2HCl_5, C_2HCl_3, and $AlCl_3$ give traces of a *compound*, m.p. 179—181°. H. G. M.

Photochemistry of some aliphatic nitroso-compounds. See A., I, 255.

Zinc oxides as catalysts in the methyl alcohol decomposition.—See A., I, 253.

Catalytic reduction of ethylene chlorohydrin. M. I. Uschakov and B. M. Michailov (J. Gen. Chem. Russ., 1937, **7**, 249—252).—Hydrogenation of $CH_2Cl\cdot CH_2\cdot OH$ (I) in aq. NaOH in presence of Ni, Ni–SiO_2, or Pd–$CaCO_3$ results in the production of EtOH (80—90%) and $(CH_2\cdot OH)_2$ (II) (10—20%). The probable reactions are: (I) + NaOH → $(CH_2)_2O$ (III) + H_2O + NaCl; (III) + H_2 → 2EtOH; (III) + H_2O → (II). R. T.

Cobalt ethoxide and its hydrolysis. B. Kandelaki and I. Setaschvili (Kolloid. Shurn., 1936, **2**, 807—809; cf. A., 1935, 1349).—Co ethoxide, from $CoCl_2$ and NaOEt, affords with H_2O greenish-yellow sols of $Co(OH)_2$, with EtOH + H_2O thixotropic gels. J. J. B.

Simultaneous dehydrogenation and dehydration of [amyl] alcohol by catalysts.—See A., I, 252.

Preparation of diacetylene glycols. J. S. Salkind and M. A. Aizikovitsch (J. Gen. Chem. Russ., 1937, **7**, 227—233).—The reaction $2OH\cdot CRR'\cdot C{:}CH \rightarrow (OH\cdot CRR'\cdot C{:}C)_2 + H_2$ takes place at room temp. in presence of CuCl, NH_4Cl, and O_2, in the cases R = R′ = Me, and OH·CRR′· = 1-hydroxy*cyclo*hexyl. R. T.

Synthesis of glycerol. G. Darzens (Compt. rend., 1937, **204**, 506—507).—Diethoxyacetone (cf. A., 1934, 394) with H_2–Ni (Raney) at room temp. affords β-hydroxy-αγ-diethoxypropane, which with conc. HCl under pressure at 120—125° gives glycerol in excellent yield. J. L. D.

Molecular compounds of dioxan. IV. Dioxanates of the halides of the alkali metals and of ammonium. H. Rheinboldt, A. Luyken, and H. Schmittmann (J. pr. Chem., 1937, [ii], **148**, 81—87; cf. A., 1933, 719).—The stable *compounds*, $LiCl,C_4H_8O_2$, $LiBr,C_4H_8O_2$, and $LiI,2C_4H_8O_2$, are obtained from their components directly or in EtOH. No compounds could be obtained from NaCl, NaBr, KCl, KBr, NH_4Cl, or NH_4Br, so that Li appears to resemble the elements of the second group of the periodic scheme in its behaviour. The *compound* $NaI,3C_4H_8O_2$ (I) is moderately stable whereas the *substance* $KI,C_4H_8O_2$ speedily loses $C_4H_8O_2$ at room temp. The *compound* $NH_4I,2C_4H_8O_2$ resembles (I) in stability. H. W.

Polymembered ring systems. VII. Tendency of formation of rings containing oxygen. K. Ziegler and H. Holl (Annalen, 1937, **528**, 143—154).—A 10-membered ring containing 9 C and 1 O is much more readily obtained than one with 10 C and the formation of a 13-membered ring with 11 C and 2 O is less difficult than that of a ring with 13 C. $(CH_2Br\cdot CH_2)_2O$, from $(OH\cdot CH_2\cdot CH_2)_2O$ and PBr_3 in C_5H_5N or from technical $(CH_2Cl\cdot CH_2)_2O$, is transformed by $CHNa(CO_2Et)_2$ into the *ester*, $O[CH_2\cdot CH_2\cdot CH(CO_2Et)_2]_2$, b.p. 175°/0·375 mm., hydrolysed to the *tetracarboxylic acid*, which passes into γ-hydroxybutyrolactone at 170°/vac. but is converted by piperidine at 100° into *γγ′-dicarboxydipropyl*

ether, b.p. 188°/0·45 mm. The corresponding Me_2 ester, b.p. 140—142°/14 mm., is reduced (Bouveault–Blanc) to *δδ′-dihydroxydibutyl ether*, b.p. 138°/0·6 mm., whence *δδ′-dibromodibutyl ether*, b.p. 142—147°/10 mm., and *δδ′-dicyanodibutyl ether*, b.p. 157°/0·4 mm. The nitrile is cyclised by NPhMeNa in Et_2O to *6-imido-5-cyanononamethylene oxide*, m.p. 115—116°, in about 5% yield. *Glycol di-β-bromoethyl ether*, b.p. 140°/12 mm., and $CHNa(CO_2Et)_2$ afford the *ester* $(CH_2)_2[O{\cdot}CH_2{\cdot}CH_2{\cdot}CH(CO_2Et)_2]_2$, b.p. 194—195°/0·375 mm., whence successively the corresponding *tetracarboxylic acid*, m.p. 131°, *dicarboxylic acid*, b.p. 222°/1·5 mm., m.p. 43—45°, and its Me_2 ester, b.p. 182°/10 mm. The latter substance is reduced to *glycol di-δ-hydroxybutyl ether*, b.p. 165—172°/0·5 mm., whence *glycol di-δ-bromobutyl ether*, b.p. 132—135°/0·5 mm., and *glycol di-δ-cyanobutyl ether*, b.p. 162°/0·01 mm. Cyclisation of the last compound followed by hydrolysis with acid leads to the *keto-nitrile*, $[CH_2]_2\langle^{O{\cdot}[CH_2]_3{\cdot}CH{\cdot}CN}_{O{\cdot}[CH_2]_4{\cdot}CO}$, b.p. 133°/0·01 mm., in 70% yield. H. W.

New synthesis of glycerides. V. P. Golendeev (J. Gen. Chem. Russ., 1936, 6, 1841—1846).—Allyl esters with I in aq. EtOH yield β-iodomonoglycerides, which when heated with K salts of fatty acids at 100° give αβ-diglycerides; these yield triglycerides when heated at 100—120° in a H_2 atm. with a mixture of chloride and K salt of a fatty acid. R. T.

Electrolysis of salts in anhydrous glycerol.—See A., I, 254.

Reaction of dichromate with formate in light.—See A., I, 255.

Compounds of magnesium chloride with magnesium acetate and ethyl acetate.—See A., I, 256.

Reaction of magnesium *tert.*-butyl chloride with ethyl acetate and propionate. K. I. Karasev (J. Gen. Chem. Russ., 1937, 7, 179—184).—$MgBu^{\gamma}Cl$ and EtOAc in Et_2O at 80—85° yield $COMe_2$, $COMeBu^{\gamma}$, $CHMeBu^{\gamma}{\cdot}OAc$, mesityl oxide, *βδ-diketo-εε-dimethylhexane*, b.p. 160—170° (*Cu* salt, m.p. 191·5°), and other unidentified products. $EtCO_2Et$ under similar conditions yields chiefly *ethyl-*tert.*-butylcarbinyl propionate*, b.p. 170—171°, together with *γ-keto-δ-methyl-ε-ethyl-*Δ^{δ}*-heptene*, b.p. 91—91·5°/18 mm. (*phenylhydrazone*, m.p. 128°). $MgPr^{\alpha}Cl$ and $PrCO_2Et$ at 0° afford $CPr^{\alpha}_3{\cdot}OH$ and $COPr^{\alpha}_2$. R. T.

Allylic transposition. VI. Allylidene diacetate. A. Kirrmann (Bull. soc. chim., 1937, [v], 4, 502—509; cf. A., 1936, 962).—$CH_2{:}CH{\cdot}CH(OAc)_2$ (I), b.p. 76°/13 mm., and HCl give *γ-acetoxyallyl chloride* (II), b.p. 65°/12 mm., probably by direct replacement of OAc to give $CH_2{:}CH{\cdot}CHCl{\cdot}OAc$, followed by allylic rearrangement. The structure of (I) is proved by hydrogenation (Ni) to $CHEt(OAc)_2$; that of (II) is proved by the lability of the Cl (quant. hydrolysis by cold 0·1*N*-NaOH in <1 hr.), and reaction with (*a*) Br at −10° to give *β-chloro-α-bromopropaldehyde*, b.p. 62—63°/13 mm. (*$NaHSO_3$-compound*), and the *diacetate*, b.p. 119—122°/10 mm., (*b*) Br, followed by CrO_3, to give $CH_2Cl{\cdot}CHBr{\cdot}CO_2H$, m.p. 52°, and (*c*) HBr to give *γ-chloro-α-bromopropyl acetate*, b.p. 95—96°/13 mm., oxidised to $CH_2Cl{\cdot}CH_2{\cdot}CO_2H$ [and a little $CH_2Br{\cdot}CH_2{\cdot}CO_2H$, formed by reaction of (II) and HBr to give the acetoxybromide]. (II) and NaOAc in AcOH (not MeOH) re-form (I) (impure) by allylic rearrangement. Distillation of (II) at 760 mm. gives $CH_2{:}CH{\cdot}CHO$ and AcCl. EtCHO and AcCl give *α-chloropropyl acetate*, b.p. 36—37°/12 mm. (I) and HBr give similarly *γ-acetoxyallyl bromide*, b.p. 76—78°/12 mm. (*dibromide*, b.p. 105—107°/12 mm.). R. S. C.

Photochemical addition of hydrogen peroxide to the double linking. N. A. Milas, P. F. Kurz, and W. P. Anslow, jun. (J. Amer. Chem. Soc., 1937, 59, 543—544).—Ethylenic compounds and 10% H_2O_2 in ultra-violet light give the corresponding glycols; free OH radicals are assumed to be first formed. Thus, crotonic acid gives dihydroxybutyric acid; maleic acid affords *meso*tartaric acid; Et maleate yields Et *meso*tartrate; allyl alcohol furnishes glycerol. H. B.

Spontaneous separation of stereoisomerides. C. Neuberg (Biochimia, 1937, 2, 383—386; cf. A., 1906, i, 923).—The hexoic acid fraction (K salts) of a mixture of fatty acids obtained by bacterial putrefaction spontaneously separated, on keeping for 30 years, into the *d*- and *l*-forms. W. McC.

Electrolysis of Δ^{γ}- and Δ^{β}-hexenoic acid. F. Fichter and T. Holbro (Helv. Chim. Acta, 1937, 20, 333—345).—Present experience and that of other workers shows that the interposition of $\not<2$ CH_2 between CO_2H and the double linking is generally necessary for the success of Kolbe's hydrocarbon synthesis from unsaturated acids. Apart from other considerations, its failure with aromatic acids containing CO_2H directly united to the C_6H_6 nucleus is therefore readily followed. The reason is not obvious since BzOH and various unsaturated acids give peroxides which readily decompose thermally in the sense of Kolbe's synthesis. Electrolysis of a solution of Δ^{γ}-hexenoic acid and K Δ^{γ}-hexenoate at Pt electrodes gives $\Delta^{\alpha\gamma}$-pentadiene and a neutral oil containing Δ^{γ}-penten-α-ol (identified as the *phenylcarbamate*, $C_{12}H_{15}O_2N$, b.p. 136—142°/0·15 mm.), small amounts of $\Delta^{\beta\theta}$*-decadiene*, b.p. 168—170°/735 mm. (oxidised to adipic acid and transformed by Br in CS_2 into *βγθι-tetrabromodecane*, b.p. 140—150°/0·1 mm.), and Δ^{γ}*-pentenyl* Δ^{γ}*-hexenoate*. Δ^{β}-Hexenoic acid affords $\Delta^{\alpha\beta}$-pentadiene and Δ^{β}*-pentenyl* Δ^{β}*-hexenoate* but not $\Delta^{\gamma\gamma}$-decadiene. H. W.

Autoxidation of linoleic and linolenic acid in buffered solution in presence of porphyrins. K. Hinsberg and R. Ammon (Z. physiol. Chem., 1937, 246, 139—148).—The process is restricted by addition of hæmin and still more by that of hæmato-, copro-, or *iso*uro-porphyrin. No restriction is produced by non-fluorescent esters of porphyrins or by porphyrins in which fluorescent power has been destroyed by irradiation with ultra-violet light. W. McC.

Electrochemical oxidation of copper lactate. W. E. Bradt and H. O. Fallscheer (Trans. Electrochem. Soc., 1937, 71, Preprint 15, 157—169).—Cu lactate (I) is oxidised at >60° by aq. $Cu(NO_3)_2$

without the passage of a current, the products being CuC_2O_4, basic Cu nitrate, CO, CO_2, and AcOH. Cu pyruvate is not formed (cf. Smull and Subkow, A., 1923, i, 298). Electrochemical oxidation of (I) at <60° with a high $[Cu(NO_3)_2]$ yields CO_2, AcOH, and MeCHO. Above 60° the ordinary thermal oxidation is superposed, CO_2 and CuC_2O_4 being the chief products. The insol. ppt. is CuC_2O_4 containing basic Cu nitrate. 67% of the (I) oxidised by $Cu(NO_3)_2$ forms equimol. amounts of $H_2C_2O_4$ and CO_2.

H. J. E.

Isomerism of chloralides. I. N. M. Shah and R. L. Alimchandani (J. Univ. Bombay, 1936, **5**, Part II, 132—136).—*cis-trans*-Isomerism of chloralides is regarded as demonstrated by isolation of two *forms* of the chloralides of the following acids: lactic, (I) b.p. 210—212°, (II) m.p. 56—57° [(I) gives (II) when kept or distilled]; *r*-tartaric, m.p. 161° and 213—215°; mucic, m.p. 198° and 174°, the latter being obtained by crystallisation from EtOH. Each pair of forms gives the same reduction product with Zn–AcOH. R. S. C.

Acetone compounds of dihydroxy-acids. I. Acetonation of 9:10-dihydrostearic acid. V. I. Esafov (J. Gen. Chem. Russ., 1936, **6**, 1818—1822).—*cis*-9:10-Dihydroxystearic acid (m.p. 95°), $COMe_2$, and HCl (at room temp.; 6 days) give 9:10-*isopropylidenedioxystearic acid* (I), an oil, in 85% yield. Under analogous conditions the *trans*-acid, m.p. 132°, gives 12—16% yields of (I), pointing to partial conversion of the *trans*- to the *cis*-form under the conditions of the experiment. R. T.

Production of oxidoethylene-αβ-dicarboxylic acid by a mould.—See A., III, 182.

Detection of malic acid by means of brucine. C. J. van Nieuwenburg and L. M. Brobbel (Mikrochem., Molisch Festschr., 1936, 338—341).—*l*-Malic acid (I) forms with excess of brucine a salt of characteristic cryst. habit. Less characteristic salts are formed by other org. acids. Mineral acids interfere, but (I), in 0·3% concn., may be detected in presence of a large excess of lactic acid or sugars. J. S. A.

Condensation of diacetyltartaric anhydride with aromatic amines. R. Małachowski (Rocz. Chem., 1937, **17**, 33—35).—The compound described by Wróbel (A., 1934, 309) as *N*-phenyl-2 : 3-dihydrooxazine-2 : 3-dicarboxylphenylimide is actually the dianilide of tartaric acid, and those described as 3 : 3′-diketo-5 : 5′-dimethyldihydro-2 : 2′-di-indolyl and 3 : 3′-diketo-1 : 1′ : 2 : 2′ : 3 : 3′ : 4 : 4′-tetrahydro-2 : 2′-diquinolyl (this vol., 77) are in reality the di-*p*-toluidide of tartaric acid and *o*-toluidino-*N*-*o*-tolylmalcimide, respectively. The structure of the Br- and NO_2-derivatives of the above compounds should be revised accordingly. R. T.

Physiological degradation of citric acid.—See A., III, 174.

Nature and properties of the dienolic group of vitamin-*C*. N. A. Bezssonoff (Biochimia, 1937, **2**, 230—241).—The colours produced by the interaction of vitamin-*C*, quinol (I), and pyrogallol and phosphomolybdic acid (II) and the fact that no colour is produced when (II) is mixed with pyrocatechol show that the dienolic groups of -*C* and (I) are polar.

W. McC.

Synthesis of ascorbic acid. B. Helferich and O. Peters (Ber., 1937, **70**, [*B*], 465—468).—Condensation of glucose with $OH{\cdot}CH_2{\cdot}CO_2Et$ (I) in presence of NaCN in absence of air affords *glucoheptoascorbic acid* which crystallises with difficulty. The synthesis can be extended to all aldoses and to their acetates which become hydrolysed during the change. Acetylated cyanohydrins are particularly suitable. Thus *d*-threose cyanohydrin tetra-acetate and (I) give *d*-xyloascorbic acid in very good yield. H. W.

Synthesis of vitamin-*C* from sucrose. P. P. T. Sah (Ber., 1937, **70**, [*B*], 498—499).—Sucrose (I) is hydrolysed by acid to *d*-glucose (II) and *d*-fructose (III), which are reduced by Na–Hg to *l*-sorbitol and *d*-mannitol. Oxidation with Br–H_2O yields a mixture of (II), (III), *l*-gulose, and *l*-sorbose the last two of which remain after fermentation with yeast. They afford *l*-gulosazone, converted by PhCHO into *l*-gulosone, which is oxidised to *l*-ketogulonic acid (IV). Esterification of (IV) by $CH(OMe)_3$ in presence of HCl–MeOH followed by enolisation of the Me ester by NaOMe and neutralisation of the product with HCl–EtOH gives *l*-ascorbic acid. (I) can be replaced advantageously by (II) or carbohydrates which yield (II). Galactose can also be used. H. W.

Ferrous gluconate, $[\alpha]_D$ +3·5° in H_2O.—See A., III, 171.

Stereoisomeric forms of methylenedi-α-thiopropionic acid. A. Fredga (Arkiv Kemi, Min., Geol., 1937, **12**, A, No. 15, 12 pp.).—Saturation of $SH{\cdot}CHMe{\cdot}CO_2H$ in 40% CH_2O with HCl ppts. a mixture of the cryst. dl-*form* (I), m.p. 155—156°, and an oil from which the meso-*form*, m.p. 81·5—82·5° (*quinine* salt $+2H_2O$), of methylenedi-α-thiopropionic acid is isolated. Fractional crystallisation of the quinine salt of (I) from 45% $COMe_2$ affords (−)-, m.p. 82·5—83·5°, $[\alpha]_D^{25}$ −376·3° in 0·5*N*-HCl (*quinine* salt $+4H_2O$), and (from the mother-liquor) (+)-*methylenedi-α-thiopropionic acid*, m.p. 82·5—83·5°, $[\alpha]_D^{25}$ +375·2° in 0·5*N*-HCl (*quinine* salt + H_2O). A mixed m.p. diagram shows the existence of a 1 : 1 mol. *compound*, m.p. 80·7°, of the (−) and *meso*-forms. The primary *K* for both *meso*- and *dl*-forms (by conductivity measurements) is $4{\cdot}2 \times 10^{-4}$.

J. W. B.

Catalysis of formaldehyde condensation by hexoses. IV. Vitamin-*C* as catalyst for synthesis of carbon chains. A. M. Kuzin (Biochimia, 1937, **2**, 127—134; cf. A., 1936, 703).—In presence of $Ca(OH)_2$ at 37° CH_2O yields no sugar in <5 hr. but is completely converted into sugar in 2 hr. when ascorbic acid is added. *iso*Ascorbic acid (I) is less effective because of dissociation, with production of catalytically inactive ions, of the Ca enolate but the Me ether of (I) is a powerful catalyst, the methylation causing a 40—50% increase in the activity. In neutral and acid media CH_2O combines with (I).

W. McC.

Decomposition of acetaldehyde catalysed by bromine. W. Brenschede and H. J. Schumacher (Ber., 1937, **70**, [*B*], 452—456).—The decomp. of

MeCHO at 300—400° in presence of Br is not due to catalytic action of the latter. The substances react very rapidly with production mainly of HBr and MeBr, which with a less-volatile, unidentified Br-compound accelerate the reaction to the expected extent. Br is not regenerated in the change. H. W.

Aldol condensation of *n*-butaldehyde. V. S. Batalin and S. E. Slavina (J. Gen. Chem. Russ., 1937, 7, 202—206).—$Pr^{\alpha}CHO$ in Et_2O and 10% NaOH at 25—40° yield *n-butyraldol* (δ-hydroxy-γ-aldehydoheptane), b.p. 92—94°/5 mm. (*oxime*, b.p. 148—149°/613 mm.). At 40—50° the sole product of the reaction is γ-aldehydo-Δ^{δ}-heptene (*oxime*, b.p. 99—101°/8 mm.). R. T.

Production of dihydroxyacetone by the action of *Acetobacter suboxydans* on glycerol.—See A., III, 182.

Artemisia ketone. Y. Asahina and S. Takagi (Helv. Chim. Acta, 1937, 20, 220—221).—Oxidation of artemisia ketone (I) by $KMnO_4$ gives $CMe_2(CO_2H)_2$ whilst its H_4-derivative and CrO_3 give $CMe_2Et{\cdot}CO_2H$, thereby establishing the structure of one part of the mol. Hydroxylamino*iso*artemisia ketone, $CH_2{:}CH{\cdot}CMe_2{\cdot}CO{\cdot}CH_2{\cdot}CMe_2{\cdot}NH{\cdot}OH$, is converted by HgO into the corresponding *NO*-derivative, which is colourless when solid but blue when molten or dissolved; hence NO replaces a *tert.* H. Artemisia oil contains (I) and *iso*artemisia ketone (II) since it gives a mixture of products when treated with $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$ in cold solution. Prolonged action of acids isomerises (I) to (II). Semicarbazino*iso*artemisia ketone (III) is transformed by HNO_2 into the corresponding, sparingly sol. *azide*, m.p. 156°, which can be used for the determination of (III). *Hydroxylamino*iso*artemisia ketone*, m.p. 170°, is oxidised by HgO in boiling $CHCl_3$ to *nitrosodihydroartemisia ketone*, m.p. 64°. The constitutions, $CH_2{:}CH{\cdot}CMe_2{\cdot}CO{\cdot}CH_2{\cdot}CMe{:}CH_2$ and $CH_2{:}CH{\cdot}CMe_2{\cdot}CO{\cdot}CH{:}CMe_2$, are ascribed to (I) and (II), respectively. H. W.

[**Artemisia ketone.**] L. Ruzicka (Helv. Chim. Acta, 1937, 20, 221).—In reply to Asahina (preceding abstract), it is pointed out that the colour reactions of a NO-derivative can scarcely be regarded as conclusive evidence of the C skeleton of a compound particularly as it has not been found possible to oxidise the terminal CMe_2 to $COMe_2$. H. W.

Gravimetric micro-determination of acetoin and diacetyl. R. Kunze (Mikrochem., Molisch Festschr., 1936, 279—289).—Acetoin is oxidised to Ac_2 by warming with $FeCl_3$ at 50—60°. The total Ac_2 is finally distilled at 90° into a solution of $NH_2OH{,}HCl + NaOAc + NiCl_2$, kept at 50°. The pptd. Ni dimethylglyoxime is collected and weighed, preferably by the Donau technique. J. S. A.

Hydrogenation of *iso*butyroin under the conditions of alcoholic fermentation. A. E. Favorski and (Mlle.) F. J. Rudneva (Bull. Soc. chim., 1937, [v], 4, 435—438).—Addition of $COPr^{\beta}{\cdot}CHPr^{\beta}{\cdot}OH$ (I) to yeast and aq. sucrose gives a little $Pr^{\beta}CO_2H$, βε-*dimethylhexane-γδ-diol* (II), m.p. 72—74°, b.p. 93—97°/12 mm., and $Pr^{\beta}CHO$. Probably (I) gives 2 mols. of $Pr^{\beta}CHO$, the (II) and acid being formed by reduction of (I) by $Pr^{\beta}CHO$. R. S. C.

Keto-ethers. II. Alkyl α-α′γ′-dichloro*iso*propoxyethyl ketones. B. B. Allen [with H. R. Henze] (J. Amer. Chem. Soc., 1937, 59, 540—542; cf. A., 1934, 871).—*α-Chloroethyl αγ-dichloroisopropyl ether*, b.p. 89—90°/18 mm. (from αγ-dichlorohydrin, paracetaldehyde, and dry HCl), and CuCN in C_6H_6 give *α-α′γ′-dichloroisopropoxypropionitrile* (I), b.p. 99°/4 mm., which with the requisite Grignard reagent affords *Me*, b.p. 105—106°/5 mm. (using MgMeBr) (*semicarbazone*, m.p. 110·5°), *Et*, b.p. 117°/7—7·5 mm. (*semicarbazone*, m.p. 131·5—132°), Pr^{α}, b.p. 127·5°/5 mm. (*semicarbazone*, m.p. 114·5°), Pr^{β}, b.p. 124—125·5°/12 mm., Bu^{α}, b.p. 136—136·5°/6 mm. (*semicarbazone*, m.p. 94·8°), Bu^{β}, b.p. 127—128°/5—6 mm., sec.-*Bu*, b.p. 129—130°/5 mm., n-*amyl*, b.p. 148·5—149°/5—5·5 mm. (*semicarbazone*, m.p. 108·6°), and iso*amyl*, b.p. 143—144°/5 mm. (*semicarbazone*, m.p. 111·5°), *α-α′γ′-dichloroisopropoxyethyl ketones.* (I) and MgMeI give some Me α-α′-chloro-γ′-iodo*iso*propoxyethyl ketone [*semicarbazone*, m.p. 123—124° (decomp.)]. Howells and Little's modification (A., 1932, 854) of the Hoesch test is valueless as a micro-method for the identification of chloroalkoxy-nitriles; (I) and *s*-$C_6H_3(OH)_3$ thus afford a little of a *trihydroxyphenyl α-α′γ′-dichloroisopropoxyethyl ketone*, m.p. 175·5°. All b.p. and m.p. are corr. H. B.

Reaction of sugars with boric acid.—See A., I, 249.

First identifiable products of the anaërobic catalytic decomposition of sugars. A. N. Bach, E. P. Alexeeva, and V. P. Dreving (Biochimia, 1936, 1, 75—93).—Glucose in 0·1—0·5*N*-NaOH, in absence of O_2, and presence of Pt-black gives equal amounts of gluconic acid (I), sorbitol (II), and H_2. Similarly, galactose yields galactonic acid and dulcitol, arabinose gives arabonic acid (III) and arabitol, and mannose affords mannonic acid and mannitol. Fructose affords HCO_2H, MeOH, (I), (II), and (III); the production of (I) and (II) is ascribed to conversion of fructose into glucose in the alkaline medium. R. T.

Active form of simple sugars. II. Comparative study of oxidation of glucose 6-phosphate and glucose. A. Kuzin and A. Kotschkin (Biochimia, 1936, 1, 676—684).—The velocity of oxidation by Br of glucose-6-phosphoric acid in acid solution >, and in neutral solution <, that of glucose. R. T.

Bromine oxidation and mutarotation measurements of the α- and β-aldoses. H. S. Isbell and W. W. Pigman (J. Res. Nat. Bur. Stand., 1937, 18, 141—194).—Vals. of the rate of oxidation by $Br–H_2O$, [α], and the rates and heats of activation of mutarotation are recorded for α-*d*- and β-*d*-glucose, α-*d*- and β-*d*-galactose, α-*d*-talose, α-*d*- and β-*d*-mannose, mannose–$CaCl_2{,}4H_2O$, α-*d*-gulose–$CaCl_2{,}H_2O$, α-*d*-xylose, α-d- and β-*d*-lyxose, α-*l*-arabinose, β-*l*-arabinose–$CaCl_2{,}4H_2O$, *d*- and *l*-ribose, α-*l*-rhamnose, α- and β-lactose, and β-maltose. The results are discussed in relation to the structure of the sugars, particularly

their classification into α- and β-isomerides, and to the composition of the equilibrium sugar solutions. A. J. E. W.

Catalytic oxidation of carbohydrates and related compounds by oxygen in the presence of iron pyrophosphates. IV. Methyl alcohol, formaldehyde, formic acid, sodium formate, ethyl alcohol, acetaldehyde, acetic acid, sodium acetate, glycol, glycollic acid, sodium glycollate, oxalic acid, and sodium oxalate. E. F. Degering (Proc. Indiana Acad. Sci., 1934, **44**, 129—131).—With the exception of MeCHO the above do not give CO_2 on oxidation and could thus be detected as end products in sugar oxidation. Ch. Abs. (*r*)

Sulphuric esters of sugars. I. Rough estimate of proportion of glucose polysulphates in their mixture. T. Soda and W. Nagai (J. Chem. Soc. Japan, 1935, **56**, 1258—1262).—Such an estimate may be made from the hydrolysis velocity coeff. Ch. Abs. (*r*)

Action of sulphuric acid on glucose and sucrose. K. A. N. Rao and P. L. N. Rao (J. Annamalai Univ., 1937, **6**, 155).—Glucose undergoes no charring with conc. H_2SO_4 below 25° or with dil. (1 : 1) acid at 50—80°. Sucrose darkens rapidly in both cases. F. L. U.

Preparation and properties of 2 : 3 : 4 : 6-tetraethyl-α-methyl-*d*-glucoside and of 2 : 3 : 4 : 6-tetraethyl-*d*-glucose. A. R. Padgett and E. F. Degering (J. Org. Chem., 1936, **1**, 336—339).—Details for the prep. of 2 : 3 : 4 : 6-*tetraethyl-α-methyl*-d-*glucoside* (I), b.p. 94—96°/0·15 mm. and 97—100°/0·2 mm., $[\alpha]_D^{20}$ +76·5° in EtOH, from α-methyl-*d*-glucoside (II) by modifications of the known methods for methylation are recorded. (I) was purified by fractionation with a Podbielniak column, and is hydrolysed to 2 : 3 : 4 : 6-*tetraethyl*-d-*glucose*, m.p. 80—82°. It is assumed that the pyranoid ring structure of (II) is stable to ethylation. H. G. M.

Structure of agar-agar. E. G. V. Percival, J. Munro, and J. C. Somerville (Nature, 1937, **139**, 512—513).—Simultaneous deacetylation and methylation of acetylated agar gives an apparently homogeneous, fully methylated agar (OMe 31%), $[\alpha]_D^{15}$ −78° in $CHCl_3$, hydrolysed to an acid, and a mixture of methylated sugars (approx. 75%) which on conversion into the glycosides gave cryst. *trimethyl-α-methyl-galactoside*. The trimethylgalactose is probably the 2 : 4 : 6 compound. The main carbohydrate portion of agar-agar probably consists of β-galactopyranose units linked at positions 1 and 3. L. S. T.

***d*-β-Galaheptose and its derivatives.** R. M. Hann and C. S. Hudson (J. Amer. Chem. Soc., 1937, **59**, 548—551).—Details are given for the isolation of *d*-β-galaheptonic acid (I) (as phenylhydrazide, m.p. 189—190°) from the reaction product from *d*-galactose and HCN (A., 1936, 193). The lactone of (I) with liquid NH_3 affords d-β-*galaheptonamide*, m.p. 170—171°, $[\alpha]_D^{20}$ −20° in H_2O; reduction (Na–Hg, H_2O) gives α-*d*-β-galaheptose (II), m.p. 196—197° (decomp.), $[\alpha]_D^{20}$ (in H_2O) about −19° → −53·95°, which closely resembles the configuratively related *l*-glucose in chemical and physical properties. Acetylation (Ac_2O, NaOAc) of (II) affords α-d-β-*galaheptose hexa-acetate* (III), m.p. 151—152°, $[\alpha]_D^{20}$ +30·2° in $CHCl_3$, rearranged by cold Ac_2O–AcOH–conc. H_2SO_4 into β-d-β-*galaheptose hexa-acetate*, m.p. 100—101°, $[\alpha]_D^{20}$ −55·8° in $CHCl_3$. The syrup from (III) and AcOH–HBr with MeOH + Ag_2CO_3 gives α-*methyl*-d-β-*galaheptoside penta-acetate*, m.p. 122—123°, $[\alpha]_D^{20}$ +51·8° in $CHCl_3$, converted by MeOH–NH_3 into α-*methyl*-d-β-*galaheptoside*, m.p. 182—183°, $[\alpha]_D^{20}$ +36° in H_2O. (II) and $CH_2Ph{\cdot}SH$ in conc. HCl afford d-β-*galaheptose dibenzyl mercaptal*, m.p. 146—147°, $[\alpha]_D^{20}$ +73·8° in C_5H_5N (*hexa-acetate*, m.p. 82—83°, $[\alpha]_D^{20}$ +9·2° in $CHCl_3$). All m.p. are corr. H. B.

New reagents for recognising ketoses. E. Votoček and R. Muller (Coll. Czech. Chem. Comm., 1937, **9**, 120—125).—The sugar is treated, at 100°, with Ac_2O saturated with HCl (or with Ac_2O–AcCl), and with αα′-dinaphthylamine, or with 1 : 2 : 7 : 8-dibenzocarbazole (I), which give stable, intense violet colorations with ketoses but not with aldoses. 3 : 4 : 5 : 6-Dibenzocarbazole similarly gives (less intense) green colorations with ketoses. With hydroxymethylfurfuraldehyde (II), (I) gives a violet colour, changing to blue; the colour produced by ketoses is thus not necessarily due to (II), but possibly to chloromethylfurfuraldehyde. The colour reactions of the last, and of furfuraldehyde, are examined. E. W. W.

Rotatory power of alkaline solutions of sucrose.—See A., I, 236.

Polysaccharides synthesised by micro-organisms. III. Molecular structure of galactocarolose produced from glucose by *Penicillium Charlesii* (G. Smith). W. N. Haworth, H. Raistrick, and M. Stacey (Biochem J., 1937, **31**, 640—644).—Galactocarolose (I) is hydrolysed by 0·01*N*-HCl at 100°, giving a 90% yield of *d*-galactose. Methylgalactocarolose is hydrolysed by boiling 3% MeOH–HCl, yielding 2 : 3 : 5 : 6-*tetramethyl-methylgalactofuranoside*, $[\alpha]_{5780}^{20}$ −67·0°, and 2 : 3 : 6-*trimethyl-methylgalactoside*, which can be characterised by oxidation to the respective lactones. (I) has a min. chain length of 9—10 units of β-galactofuranose linked through the 1 : 5 positions. P. G. M.

Hydrogenation of glucosides in presence of active nickel. M. M. Janot and T. Tomesco (Compt. rend., 1937, **204**, 504—506).—Salicin, arbutin, æsculin, and phloridzin are not reduced with H_2–Ni (Raney) at 9—12° in aq. EtOH–NaOH (cf. A., 1934, 992); other glucosides are reduced, whilst vanillin, aucubin, and amygdalin are hydrolysed after reduction. J. L. D.

Gluconointol, m.p. 196—198°, $[\alpha]_D^{20}$ +1·5° in H_2O (Ac derivative, m.p. 179—180°). Glucosides, (?) $C_{20}H_{24}O_{11}$, m.p. 154—155°, $[\alpha]_D^{20}$ −92·6° in EtOH, and (?) $C_{13}H_{20}O_9$, m.p. 172—174°, $[\alpha]_D^{20}$ −163·6° in H_2O.—See A., III, 190.

Emulsin. XXVIII. *p*-Toluenesulphonic esters of vanillin-β-d-glucoside and their fission by emulsin of sweet almonds. B. Helferich and S. Grünler (J. pr. Chem., 1937, [ii], **148**, 107—116).—Hydrolysis of the susceptible vanillin-β-*d*-glucoside by emulsin is inhibited by the entry of a single

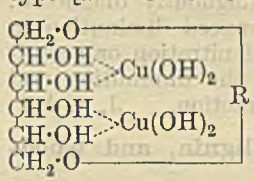
p-$C_6H_4Me{\cdot}SO_2$ in any part of the mol. β-*d*-Glucose 1 : 2 : 3 : 4-tetra-acetate 6-*p*-toluenesulphonate is converted by HBr–AcOH into 1-*bromo*-d-*glucose* 2 : 3 : 4-*triacetate* 6-p-*toluenesulphonate*, m.p. 89—90°, $[\alpha]_D^{20}$ +165° in $CHCl_3$, converted by vanillin and KOH in H_2O–$COMe_2$ at room temp. into *vanillin*-β-d-*glucoside* 2 : 3 : 4-*triacetate* 6-p-*toluenesulphonate*, m.p. 161—162°, $[\alpha]_D^{19}$ −60·5° in $CHCl_3$, deacetylated by NaOMe in boiling MeOH to *vanillin*-β-d-*glucoside* 6-p-*toluenesulphonate*, m.p. (indef.) 125—130° after softening at about 85° or (+3H_2O) m.p. about 80°, (anhyd.) $[\alpha]_D^{21}$ −92° in $CHCl_3$. Similarly, 1-bromo-*d*-glucose 2 : 3 : 6-triacetate 4-*p*-toluenesulphonate is converted into *vanillin*-β-d-*glucoside* 2 : 3 : 6-*triacetate* 4-p-*toluenesulphonate*, m.p. 168—170° (decomp.) in bath preheated to 150°, $[\alpha]_D^{19}$ −49° in $CHCl_3$, hydrolysed by NaOMe in MeOH–$CHCl_3$ at −20° to *vanillin*-β-d-*glucoside* 4-p-*toluenesulphonate*, (+2H_2O), m.p. 162—165° after softening at about 150° (+0·5H_2O), and (anhyd.), m.p. 165—170° $[\alpha]_D^{20}$ −53° in C_5H_5N. 1-Bromo-*d*-glucose 2 : 4 : 6-triacetate 3-*p*-toluenesulphonate affords *vanillin*-β-d-*glucoside* 2 : 4 : 6-*triacetate* 3-p-*toluenesulphonate*, m.p. 170—171°, $[\alpha]_D^{19}$ −16° in $CHCl_3$, whence *vanillin*-β-d-*glucoside* 3-p-*toluenesulphonate* (+3H_2O) and (anhyd.), m.p. 126—128° after softening at 90°, $[\alpha]_D^{21}$ −25° in $CHCl_3$. 1-Chloro- is converted by HBr in AcOH containing a little Ac_2O at room temp. into 1-*bromo*-d-*glucose* 3 : 4 : 6-*triacetate* 2-p-*toluenesulphonate*, m.p. 113—115°, $[\alpha]_D^{18}$ +176° in $CHCl_3$, which, under strictly defined conditions, is converted into *vanillin*-β-d-*glucoside* 3 : 4 : 6-*triacetate* 2-p-*toluenesulphonate*, m.p. 132—133°, $[\alpha]_D^{18}$ −50·5° in $CHCl_3$, and thence into *vanillin*-β-d-*glucoside* 2-p-*toluenesulphonate* (+1H_2O), m.p. (anhyd.) 165—168° after slight softening, $[\alpha]_D^{20}$ −127° in C_5H_5N. H. W.

Glucoside of the flavone of the white flower. IV. Constituents of *Cosmos bipinnatus*, Cav. T. Nakaoki (J. Pharm. Soc. Japan, 1935, **55**, 967—978).—EtOH extraction of the flowers yields *cosmosiin* (I), $C_{21}H_{22}O_{11}$, m.p. 178° (*Ac*$_6$ derivative, m.p. 207—208°), hydrolysed (10% H_2SO_4) to glucose and *apigenin*, $C_{15}H_{10}O_5$, m.p. 347° (*triacetate*, m.p. 181—182°; no depression with apiin acetate; *benzoate*, m.p. 210—212°). (I) with MeI yields a *substance*, m.p. 205—206°, hydrolysed to another *substance*, m.p. 258—259°, not depressed on admixture with acacetin. With CH_2N_2, (I) yields a *glucoside*, $C_{23}H_{24}O_{10}$, m.p. 255°, hydrolysed to *apigenin Me*$_2$ *ether*, m.p. 267°. Quercetin and inositol were isolated from the mother-liquors from (I).

Ch. Abs. (*r*)

Action of alkalis on araban. T. K. Gaponenkov (J. Gen. Chem. Russ., 1937, **7**, 236—240).—The sp. conductivity of KOH, $Ca(OH)_2$, or $Ba(OH)_2$ falls with increasing araban concn., to an extent >, in the case of NaOAc <, and in that of KCl equal to that which would follow from the increase in η; the p_H of the solutions inversely ∝ araban concn. The results are ascribed to formation of non-ionised araban salts. R. T.

Carbohydrates. VIII. Cellulose and its solutions. T. Lieser [with R. Ebert] (Annalen, 1937, **528**, 276—295; cf. A., 1936, 592, 595).—The simplest tetra-alkylammonium bases do not dissolve cellulose (I) but with those of higher mol. wt. the least concn. required for dissolution appears to be a linear function of the mol. wt. Dissolution is observed only within a very narrow limit of concn. above which only swelling occurs. Similar results are recorded with tetra-alkyl-phosphonium and -arsonium bases and with trialkyl-sulphonium and -selenonium bases; as with CsOH the mol. vol. appears to be the controlling factor. Dissolution is regarded as dependent on the formation of mol. compounds. When dialysed against aq. NaOH until the org. bases have been removed (I) remains in solution if >0·6*N*-NaOH is used. (I) is therefore regarded as fundamentally sol. in dil. NaOH, but a pre-condition for its dissolution is the diminution of micellary arrangement by solvation of all the main valency chains of the micelle. The solubility of (I) in ice-cold, superconc. HCl is thus explained. Addition of MeOH to solutions of (I) in $Cu(OH)_2$–NH_3 in absence of excess of $Cu(OH)_2$ gives materials with about 18·5% Cu, whilst if excess of $Cu(OH)_2$ is present the ppts. contain 22—23% of Cu and 62—64% of (I). There is thus no stoicheiometric relationship. Application of the method to hexitols and β-glucosan gives compounds of the annexed type [R = Cu or $Cu(NH_3)_4$]. The behaviour of (I) is explained by the hypothesis that more glucose anhydride chains are present on the surface than in the interior of the micelle. This conception of the Cu reaction as a micro-heterogeneous, micellary surface change brings it into line with the pseudo-stoicheiometric xanthate reaction. Treatment of (I) with $Cu(OH)_2$–$(CH_2{\cdot}NH_2)_2$ yields products containing > the calc. amount of Cu per $2C_6H_{10}O_5$. Reasons are advanced for assigning the constitution $(C_6H_{10}O_5)\,C_6H_7O_2(OH)(OH{\cdots}Cu(OH)_2)(OH{\cdots}R)$ to the initial product from (I) and $Cu(OH)_2$–NH_3 where R = $Cu(NH_3)_4(OH)_2/2$ and $(C_6H_{10}O_5)$ is the glucose anhydride chain in the interior of the micelle; this passes when heated with MeOH into the substance R = $Cu(OH)_2/2$. Treatment of regenerated (I) with NaOH and CS_2 gives products with more S than those obtained from (I) and finally leads to a permutoid monoxanthate. Viscose therefore, like (I), has a micellary structure, but the degree of arrangement or density of the micellary packing is < in (I). Absorption of Cu by regenerated (I) is ≫ of (I) and does not increase considerably with time. Action of the Cu-ammine bases on hydrocelluloses therefore appears to be much milder than that of conc. NaOH. H. W.



Preparation of homogeneous forms of soda-cellulose and their importance for the mechanism of mercerisation. III. Soda-cellulose IV. K. Hess and J. Gundermann (Ber., 1937, **70**, [*B*], 527—537).—Treatment of soda-cellulose I (I) with NaOH of diminishing concn. yields products with the interferences of soda-cellulose IV (II) when the NaOH content of the fibres sinks in an unusually marked degree. It is therefore possible that the

cryst. component giving the diagram assigned to (II) is free from alkali and hence not an alkali-cellulose. The characteristic lines of (II) harmonise exactly with those of cellulose III (III) (from cellulose and anhyd. NH_3), but the identity of (II) and (III) is not regarded as established completely. At 100° (I) passes into (II) when 10% NaOH is used whereas at 20° the transformation requires >6% NaOH. At 100° (II) is converted by 2% NaOH into hydrocellulose (IV) but at 20° it can be preserved for months in presence of 0·5% NaOH. The observation that the introduction of mixed micelles of (II) and (IV) into NaOH of suitable concn. causes a weakening of the intensities of the reflexes of (IV) is regarded as a proof that (II) can be formed synthetically. H. W.

Optical differentiation of different types of cellulose. A. Frey-Wissling (Mikrochem., Molisch Festschr., 1936, 106—117).—Natural cellulose (I) fibres may be differentiated microscopically from hydrocellulose (II) by their greater refractivity: n_e (= index for extraordinary ray) for (I) > n for NH_2Ph > n_e for (II). Attack by oxidising agents may be detected by its elevation of n_e above 1·600; in conjunction with the Cu no., the presence of either (I) or (II) may thus be unambiguously diagnosed. Esterification leads to a pronounced diminution in both n_e and n_o. The degree of nitration or acetylation may be correlated with the diminution and reversal of sign of the double refraction. J. S. A.

***X*-Ray studies of wood, lignin, and wood-cellulose.**—See A., I, 226.

Optically active amino-acids. [Resolution of *dl*-benzenesulphonyl-α-methylasparagine.] S. Berlingozzi and S. De Cecco (Atti V Congr. Naz. Chim., 1936, **1**, 307—310).—dl-*Benzenesulphonyl-α-methylasparagine*, m.p. 174°, is resolved into the d-*form*, $[\alpha]_D^{20}$ +10·38° [*brucine* salt, m.p. 158° (decomp.)], and l-*form*, $[\alpha]_D^{20}$ −9·72° [*brucine* salt, m.p. 160° (decomp.)]; rotations are of *Na* salts in H_2O. E. W. W.

Scorbamic acid. F. Micheel and R. Mittag (Naturwiss., 1937, **25**, 158—159).—α-Deoxy-*l*-ascorbic acid (A., 1936, 706) with PhN_2Cl affords the *phenylhydrazone* of dehydroascorbic acid (I) [not obtained directly from (I) with $NHPh{\cdot}NH_2$], reduced (H_2–Pd) in neutral or acid solution to *scorbamic acid*, which adds 2 I, reduces cold $AgNO_3$, and protects guinea-pigs against scurvy in daily doses of 0·5—1·0 mg. J. L. D.

Cystine content of insulin.—See A., III, 186.

Behaviour of peptides in aqueous solutions.—See A., I, 240.

Colour reaction between nitroprusside and cysteine. G. Scagliarini (Atti V Congr. Naz. Chim., 1936, **2**, 546—547; cf. A., 1929, 160; this vol., 139).—By the action of cysteine hydrochloride on Na nitroprusside and KOH in aq. MeOH a red-violet *ppt.*, $K_4[Fe(CN)_5NO{\cdot}S{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2],4H_2O$, is obtained. The reaction is sensitive for cysteine to a dilution of 1 : 60,000. Cystine and glutathione give the same reaction after reduction. O. J. W.

Action of mercuric sulphate and chloride on cysteine, cystine, cysteinesulphinic acid ($R{\cdot}SO_2H$), and cysteic acid with reference to the dismutation of cystine. T. F. Lavine (J. Biol. Chem., 1937, **117**, 309—323; cf. A., 1936, 596).—Cysteine (I), cysteic acid (II), and cysteinesulphinic acid (III) are pptd. from $2N$-H_2SO_4 by $HgSO_4$, the ppt. from the last two compounds being sol. in solutions of chlorides. Analytical methods indicate the presence of (I) and (III) (although the latter has not been isolated) in the ppt. obtained from cystine (IV)–$HgSO_4$–$2N$-H_2SO_4, the dismutive decomp. of (IV) being represented by $2(\cdot SR)_2 + 2H_2O = 3RSH + R{\cdot}SO_2H$ (cf. *loc. cit.*). Re-formation of (IV) occurs when the Hg has been removed. The optical rotation of solutions of (II), (III), and (IV) in HCl is unaffected by $HgCl_2$, but that of (I) is dependent on the amount of $HgCl_2$ present. According to method of prep. (III) is obtained as a mono-, m.p. 143° (decomp.) or di-, m.p. 146°, -hydrate. H. G. M.

Pyruvic and oxaloacetic cyanohydrins. D. E. Green and S. Williamson (Biochem. J., 1937, **31**, 617—618).—On mixing aq. solutions of KCN with $AcCO_2H$ pyruvic acid cyanohydrin (*K* salt, m.p. 87°) is obtained. Oxaloacetic acid cyanohydrin gives a very hygroscopic *K* salt, m.p. 135° (decomp.). P. W. C.

Compounds of carbamide with magnesium nitrate and sulphate.—See A., I, 256.

Hydrazides of higher unsaturated acids. II. Hydrazide of dehydroundecenoic acid, and its derivatives. A. F. Oskerko (Mem. Inst. Chem. Ukrain. Acad. Sci., 1936, **3**, 577—586).—*Et dehydroundecenoate*, b.p. 115—120°/3 mm., and boiling N_2H_4,H_2O yield *dehydroundecenohydrazide*, m.p. 84—85° (*hydrochloride*, m.p. 134·5°; *compound* with $COMe_2$, m.p. 75—77°; *Ac* derivative, m.p. 113—114°), converted by I in aq. EtOH into s-*didehydroundecenoylhydrazine*, m.p. 131—132°. R. T.

Esters of hydroferrocyanic and hydroferricyanic acids. J. Meyer, H. Domann, and W. Müller (Z. anorg. Chem., 1937, **230**, 336—356).—When CH_2N_2 and $H_4Fe(CN)_6$ react in Et_2O, the products are $[(CNMe)_4Fe(CN)_2]$, $[(CNMe)_4(H_2O)Fe(CN)_2]CN$, and an unidentified mixture of substances. The action of CH_2N_2 on $H_3Fe(CN)_6$ gives $H_2[Fe(CN)_5(CNMe)]$, which forms *salts* in which H_2 is replaced by Cu, Ni, Zn, or Ag_2. The *compound* $Ag_3Fe_2(CN)_9(CNMe)_2$ is also described. The corresponding reaction with $CHMeN_2$ yields $H_2[Fe(CN)_5(CNEt)]$, which forms *salts* in which H_2 is replaced by Ag_2, Cu, or Ni. E. S. H.

Two-shell ferrocyanide complex compounds.—See A., I, 241.

Constitution of some additive compounds of tertiary amines and phosphines. K. A. Jensen (J. pr. Chem., 1937, [ii], **148**, 101—106).—The most probable structure of additive compounds of *tert.* phosphines and CS_2 is $S{:}C{<}^{S}_{PR_3}$ (Hantzsch and Hibbert, A., 1907, i, 496), now modified to $PR_3{\cdot}CSS$. NMe_3 and CS_2 yield a compound similarly formulated

as the betaine of HCS_2H. In analogy with the structure assigned by Biilmann *et al.* (A., 1935, 331) to the additive products of MeI and betaines, the compound from PEt_3, CS_2, and MeI is $[PEt_2{\cdot}CS_2Me]I$, which is in harmony with its great electrolytic conductivity and the direct titratability of I. The corresponding chloride could not be obtained from PEt_2 and $ClCS_2Et$. The very unstable *compounds*, $CO_2Et{\cdot}PEt_3Cl$, $COSEt{\cdot}PEt_3Cl$, $CO_2Et{\cdot}NMe_3Cl$, $COSEt{\cdot}NMe_3Cl$, and $CS_2Et{\cdot}NMe_3Cl$ (I), are obtained from their components in well-cooled anhyd. Et_2O. (I) is yellow and at slightly above 0° forms reddish-yellow smeary products with partial reproduction of HCS_2Et and NMe_3. The remainder are colourless and can be preserved for a short time in complete absence of H_2O, with which they react, *e.g.*, $CO_2Et{\cdot}NMe_3Cl + H_2O \rightarrow CO_2 + EtOH + NMe_3,HCl$. The instability is explicable when $ClCO_2Et$ and $ClCS_2Et$ are regarded as acid chlorides which with *tert.* amines yield cryst. compounds immediately decomposed by H_2O in the same sense. The condensation of these compounds to cyclic materials in the absence of H_2O does not find its counterpart with the substances now described; $CO_2Et{\cdot}NMe_3Cl$ in Et_2O at 35° slowly gives CO_2, $NMe_2{\cdot}CO_2Et$, and, probably, a mixture of NMe_3,HCl, NMe_4Cl, and NMe_3EtCl. H. W.

Organic magnesium compounds. V. Reaction between alkyl esters of *p*-toluenesulphonic acid and OR·MgX. K. Mine (J. Chem. Soc. Japan, 1935, **56**, 1112—1117).—The reaction is $2C_6H_4Me{\cdot}SO_3R' + 2OR{\cdot}MgX = (C_6H_4Me{\cdot}SO_3)_2Mg + 2R'X + Mg(OR)_2$. Ch. Abs. (*r*)

Tri-diamino-salts of cobalt, rhodium, and chromium.—See A., I, 258.

Polarographic study of titano-tartaric complexes.—See A., I, 245.

Dehydrogenation of *cyclo*hexane by sulphide and oxide catalysts. B. Moldavski, G. Kamuscher, and S. Livschitz (J. Gen. Chem. Russ., 1937, **7**, 131—137).—Of a no. of catalysts, Cr_2O_3 had the highest activity and stability at 410—440° (77% yield of C_6H_6 at 434°). The activity of MoS_2 is enhanced by pptn. on SiO_2 gel. R. T.

Desulphuration of organic compounds by catalysis with platinum. N. D. Zelinski and E. M. Schachnazarova (Bull. Acad. Sci. U.R.S.S., 1936, 563—569).—Pt–C at 350° catalyses both desulphuration and dehydrogenation of mixtures of *cyclo*hexane and mercaptans and org. sulphides, which yield practically pure C_6H_6 after two passages over the catalyst. R. T.

(A) Phenyl*cyclo*pentylethane and *cyclo*pentyl-*cyclo*hexylethane, (B) Phenyl*cyclo*pentylpropane and *cyclo*pentyl*cyclo*hexylpropane, and their relation to hydrogenation-dehydrogenation catalysis. J. I. Denisenko (Bull. Acad. Sci. U.R.S.S., 1936, 577—582, 583—589).—(A) $CH_2Ph{\cdot}CH_2Cl$ and *cyclo*pentanone in presence of Mg in Et_2O yield β-1′-*hydroxy*cyclo*pentylethylbenzene*, b.p. 140—141°/5 mm., converted by dehydration ($H_2C_2O_4$) into β-Δ^1-cyclo*pentenylethylbenzene*, b.p. 124—125°/10 mm., which gives β-cyclo*pentylethylbenzene* (I), b.p. 255—256°, with H_2 in presence of Pt-black. (I) and H_2 (Pt–C catalyst at 230°) yield β-cyclo*pentylethyl*-cyclo*hexane* (II), b.p. 251—252°; the reverse reaction takes place when (II) is passed over Pt–C at 290°.

(B) The following substances, prepared as above, react analogously: γ-1′-*hydroxy*cyclo*pentylpropylbenzene*, b.p. 136—138°/2·5 mm.; γ-Δ^1-cyclo*pent-ylpropylbenzene*, b.p. 117—118°/3 mm.; γ-cyclo-*pentylpropylbenzene*, (III), b.p. 270—272°; γ-cyclo-*pentylpropyl*cyclo*hexane* (IV), b.p. 268—270°. (I), (II), (III), and (IV) are probably present in petroleum. R. T.

Decomposition of ethyl*cyclo*pentane under conditions of dehydrogenation catalysis. N. D. Zelinski and E. M. Schachnazarova (Bull. Acad. Sci. U.R.S.S., 1936, 571—576).—Ethyl*cyclo*pentane (I) is converted into heptane by H eliminated from *cyclo*hexane (II) when (I)–(II) mixtures are passed over Pt catalyst at 305—310°. R. T.

Catalytic cyclisation of aliphatic compounds. I. Cyclisation of aliphatic hydrocarbons in presence of chromic oxide. B. L. Moldavski, G. D. Kamuscher, and M. V. Kobilskaja (J. Gen. Chem. Russ., 1937, **7**, 169—178).—The following aromatic hydrocarbons were obtained by passing paraffins over Cr_2O_3 at 460°: *o*- 85, *m*- 2·5, and *p*-xylene 3, and PhEt 10%, from *n*-octane; PhMe, from *n*-heptane; C_6H_6, from *n*-hexane; *p*-xylene, from $Bu^{\beta}{}_2$; *m*-$C_6H_4MePr^{\beta}$, from $(CH_2Bu^{\beta})_2$; *o*-xylene, from Δ^{α}- + Δ^{β}-octene, and $C_{10}H_8$ from PhBu. R. T.

Substitution reactions of substituted benzenes.—See A., I, 224.

Organic reactions with boron fluoride. XIII. Alkylation of benzene with alcohols. J. F. McKenna and F. J. Sowa (J. Amer. Chem. Soc., 1937, **59**, 470—471).—Mono-, *p*-di- (with traces of *o*-), and poly-alkylbenzenes are formed from C_6H_6 (1 g.-mol.), AlkOH (1 g.-mol.), and BF_3 (20—65 g.); the ease of reaction is dependent on the ease of dehydration of the AlkOH. The following AlkOH are used: $Pr^{\alpha}OH$ and $Pr^{\beta}OH$, both yielding Pr^{β} derivatives; $Bu^{\alpha}OH$ and *sec.*-BuOH, both give *sec.*-Bu derivatives; $Bu^{\beta}OH$ and $Bu^{\gamma}OH$, both afford Bu^{γ} derivatives; *cyclo*hexanol; $CH_2Ph{\cdot}OH$; allyl alcohol. The alkylating agent is probably the intermediate olefine. H. B.

Chlorination of chlorobenzene in the gaseous phase at 500—600°; *meta*-directing influence of the chlorine atom. J. P. Wibaut, L. M. F. van de Lande, and G. Wallagh (Rec. trav. chim., 1937, **56**, 65—70).—The relative proportions of *o*-, *m*-, and *p*-$C_6H_4Cl_2$ in the mixture (I) of $C_6H_4Cl_2$ formed together with a considerable quantity of more highly chlorinated benzenes and some C when excess of PhCl interacts with Cl_2 in presence of pumice at 500°, 550°, and 600° are recorded. (I) contains 50—60% of *m*-$C_6H_4Cl_2$, which exists in only one form, m.p. −24·1° (cf. Kalff, Diss., Amsterdam, 1924). Attempts to repeat the results of Wheeler *et al.* (B., 1933, 421) failed. H. G. M.

Action of nitrogen peroxide on benzene, toluene, and chlorobenzene. I. Nitration in pres-

ence of sulphuric and phosphoric acids. A. I. Titov and A. N. Barischnikova. II. A. I. Titov (J. Gen. Chem. Russ., 1936, **6**, 1801—1805, 1855—1862).—I. $PhNO_2$ is obtained in 98·4% yield, and of high purity, by adding a solution of 35 g. of N_2O_4 in 100 g. of 94% H_2SO_4 to C_6H_6 at 40—50°. The reaction proceeds with explosive velocity in presence of Hg. PhMe is nitrated similarly, at 0—15°, whilst PhCl is nitrated with saturated $NO{\cdot}HSO_4$, adding oleum during the reaction.

II. The products of reaction of PhMe with gaseous N_2O_4 in diffused daylight, sunlight, or ultra-violet light were $CH_2Ph{\cdot}NO_2$, $CHPh(NO_2)_2$, PhCHO, BzOH, and $C_6H_4Me{\cdot}NO_2$. R. T.

Preparation of nitrobenzene with maximum specific resistance. L. Zepalova-Michailova (Trans. Inst. Pure Chem. Reagents, U.S.S.R., 1935, No. 14, 49—57).—The problem is discussed in detail. Ch. Abs. (*r*)

Preparation of *m*-dinitrobenzene. S. V. Shah and D. G. Pishawikar (J. Chem. Educ., 1937, **14**, 33).—By increasing the proportion of conc. H_2SO_4, conc. HNO_3 can be used instead of fuming HNO_3 for the nitration of $PhNO_2$. 10 g. of $PhNO_2$, 15 g. of HNO_3 (*d* 1·41), and 40 g. of conc. H_2SO_4 (*d* 1·82) give an 88% yield of *m*-$C_6H_4(NO_2)_2$. L. S. T.

Colour reactions of the dinitrobenzenes in alkaline solution. R. Truhaut (J. Pharm. Chim., 1937, [viii], **25**, 216—222; cf. A., 1933, 1314).—Reducing sugars, uric acid, allantoin, and phenyl-β-alanine give colour reactions with only *o*-$C_6H_4(NO_2)_2$. Most NH_2-acids and the sexual hormones react only with *m*-$C_6H_4(NO_2)_2$ and the simple aldehydes and ketones react with both derivatives. Ninhydrin reacts with both isomerides, each giving characteristic reactions. E. H. S.

Mechanism of reduction of unsaturated compounds with alkali metals and water. C. B. Wooster and K. L. Godfrey (J. Amer. Chem. Soc., 1937, **59**, 596—597).—PhMe does not react with Na or K in liquid NH_3; addition of H_2O causes immediate reaction (? reduction), this being ascribed to the production of nascent H. Use of H_2O to determine excess of Na in reaction media containing liquid NH_3 + PhMe will give misleading results; NH_4Cl (or ammonolysis catalyst) should be used. H. B.

Preparation and optical rotation of α-phenyl-α-deuteromethylethane. R. L. Burwell, jun., F. Hummel, and E. S. Wallis (J. Org. Chem., 1936, **1**, 332—335).—*d*-$CH_2Br{\cdot}CHPhMe$ (cf. J.C.S., 1915, **107**, 899) when converted into the Grignard reagent and then treated with D_2O (99·5%) yields d-α-*phenyl-α-deuteromethylethane*, b.p. 151—152°, $[\alpha]_D^{25}$ +0·019°. The smallness of the rotation is in accord with the considerations of Boys (A., 1934, 832), the observed val. being regarded as the upper limit. H. G. M.

Displacement of bromine from mono- and di-bromoethylbenzenes. W. Taylor (J.C.S., 1937, 343—351).—α- and β-Bromo- and αα- (from dry HBr and cooled CPh:CH) and αβ-dibromo-ethylbenzenes undergo substitution of Br by OEt when heated in dry or aq. (80%) EtOH at 55° for 12—24 hr. Measurements of increase in acidity show that the reaction is kinetically unimol., and is accelerated by H_2O. This and the high vals. of *P* indicate a composite reaction, with ψ-unimol. formation, and unimol. decomp., of an intermediate oxonium salt. With KOH or NaOEt (0·2*N*) in dry EtOH, α- yields 20%, β- 91%, αβ- 87% (all independent of temp.), and αα- none, of the corresponding olefine (determined by Br addition in the dark), the reaction being bimol., and accompanied by both uni- and bi-mol. substitution reactions. A. Li.

Relative stability of penta-arylethanes. III. Reversible dissociation of penta-arylethanes. W. E. Bachmann and F. Y. Wiselogle (J. Org. Chem., 1936, **1**, 354—382; cf. A., 1933, 943).—*Diphenyl*-p-*diphenylyl*- (I), m.p. 127·5—128°, *phenyldi*-p-*diphenylyl*-, m.p. 145—146·5° and m.p. 70—72° from C_6H_6–light petroleum, and *tri*-p-*diphenylyl*-, m.p. 207·5—208°, *-bromomethane* are obtained from the appropriate carbinol (modified or improved prep. described) and $AcBr$–C_6H_6. Only the first two give a Grignard reagent, but in presence of $HgBr_2$ and Mg–Et_2O–C_6H_6, the last gives a double salt $2(C_6H_4Ph)_3CBr,3MgBr_2$, decomposed by KOH–MeOH to $(C_6H_4Ph)_3C{\cdot}OMe$. Interaction of the Grignard reagent from (I) and the appropriate diarylbromomethane (cf. A., 1933, 703) gives α-p-*diphenylyl*-ααββ-*tetraphenyl*- (II), m.p. 190—192°, and αβ-*di*-p-*diphenyl*-ααβ-*triphenyl*-, m.p. 180—185°, *-ethane*, but the following are obtained from the appropriate triarylmethyl-sodium compound and diarylbromomethane: αββ-*tri*-p-*diphenylyl*-αα-*diphenyl*-, m.p. 227—230°, αα-*di*-p-*diphenylyl*-αββ-*triphenyl*-, m.p. 198—199°, ααβ-*tri*-p-*diphenylyl*-αβ-*diphenyl*-, m.p. 206—209°, ααββ-*tetra*-p-*diphenylyl*-α-*phenyl*-, m.p. 222—228°, ααα-*tri*-p-*diphenylyl*-ββ-*diphenyl*-, m.p. 164—167°, αααβ-*tetra*-p-*diphenylyl*-β-*phenyl*-, m.p. 215—220°, αααββ-*penta*-p-*diphenylyl*- (III), m.p. 172—185° from $CHCl_3$–EtOH and m.p. 226—234° from C_6H_6, *-ethane*. All the foregoing penta-arylethanes as well as pentaphenyl- (IV), β-*p*-diphenylyl-αααβ-tetraphenyl-, and ββ-di-*p*-diphenylyl-ααα-triphenyl-ethane (*loc. cit.*) are cleaved by AcOH–HI at 120° giving the corresponding di- and tri-arylmethanes, and by 40% Na–Hg giving the corresponding di- and tri-arylmethylsodium compounds. No cleavage occurs with 1% Na–Hg. The temp. at which the penta-arylethanes in EtOBz first become coloured due to dissociation into radicals are recorded, and indicate that successive substitution of C_6H_4Ph for Ph progressively weakens the C·C linking. The dissociation is reversible, (IV) being obtained when CPh_3Cl, $CHPh_2Br$, and Hg are shaken in C_6H_6, and when $CHPh_2Br$ is shaken in presence of Hg with CPh_3 radicals previously formed from CPh_3Cl–Hg–C_6H_6, but the position of the equilibrium is almost entirely in favour of the undissociated penta-arylethane. When (II) is refluxed (213°) in EtOBz in N_2 some $(CHPh_2)_2$ is formed by the irreversible combination of the resulting $CHPh_2$ radicals. The corresponding $CPh_2{\cdot}C_6H_4Ph$ radicals depress the equilibrium concn. of $CHPh_2$ and hence the rate of disproportionation to $(CHPh_2)_2$. Similar results were obtained with (IV) and (III), also with other solvents.

The kinetics of the oxidation of (IV) in *o*-$C_6H_4Cl_2$ by O_2 show that the reaction consists of a relatively slow dissociation into free radicals, which then rapidly combine with O_2 to give the unsymmetrical peroxide as the chief product. In the presence of > 2 mols. of pyrogallol the reaction is strictly of the first order, side reactions are suppressed, and each radical combines with 1 mol. of O, the peroxide radicals being stabilised by the pyrogallol. The heat of activation of dissociation is 27·6±0·5 kg.-cal. The following *peroxides* were prepared by shaking the appropriate penta-arylethane in *o*-$C_6H_4Cl_2$ in O_2: *triphenylmethyl benzhydryl*, m.p. 93—94°, which reacts with MgMeI–Bu^a_2O at 100° to give C_2H_6 and on subsequent hydrolysis CPh_3·OH and $CHPh_2$·OH; *triphenylmethyl phenyl*-p-*diphenylylmethyl*, m.p. 129·5—130°; *triphenylmethyl di*-p-*diphenylylmethyl*, m.p. 148—149°, decomposed when heated (180°; 1 hr.; N_2 atm.) into (p-$C_6H_4Ph)_2CO$; *diphenyl*-p-*diphenylylmethyl di*-p-*diphenylylmethyl*, m.p. 161° (decomp.); *phenyldi*-p-*diphenylylmethyl benzhydryl*, m.p. 151—152°; *tri*-p-*diphenylylmethyl phenyl*-p-*diphenylylmethyl*, m.p. 168°. The structures of these peroxides were confirmed by cleavage with 2% Na–Hg, hydrolysis of the resulting products giving the di- and tri-arylcarbinols corresponding with the di- and tri-arylmethyl radicals. With H_2SO_4 the peroxides give colours characteristic of the sulphates of these carbinols. H. G. M.

Exchange of sulphonyl groups. D. T. Gibson and J. D. Loudon (J.C.S., 1937, 487—489).—The equilibrium point in the reaction $C_{10}H_{15}O·SO_2·SMe + R·SO_2Na \rightleftharpoons R·SO_2·SMe + C_{10}H_{15}O·SO_2Na$ was approx. determined for a series of 14 sulphinates by mixing the reactants in aq. EtOH or aq. EtOH–dioxan solution and observing the rotation. The weaker sulphonyl anion retains the greater hold on the thioaryl group. Change of solvent changes the end-point, but substitution of Me by 2 : 5-$C_6H_3Cl_2$ has little effect. The exchange equilibrium (ester type) p-$C_6H_4Me·SO_2·SMe + C_{10}H_{15}O·SO_2·S·C_6H_3Cl_2 \rightleftharpoons$ can be displaced by excess of reactant or product. Reaction of $R·SO_2·CH(SAlk)·COMe$ or 1 : 2 : 4-$R·SO_2·C_6H_3(NO_2)_2$ with sulphinate ions is obscured by side-reactions. With 2 : 5-$C_6H_3Cl_2·SO_2·S·C_6H_3Cl_2$ in EtOH, Na camphorsulphinate (I) gives the *camphorthiolsulphinate*, m.p. 121—122°, p-$C_6H_4Cl·SO_2Na$ the *4-chlorobenzenethiolsulphinate*, m.p. 121—122°, and 1 : 3 : 4-$SO_2Na·C_6H_3Me·OMe$ the *4-methoxy*-m-*toluenethiolsulphinate*, m.p. 96°, of 2 : 5-dichlorophenyl. 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$ and (I) in hot EtOH yield 2 : 4-*dinitrophenyl* 10-*camphoryl sulphone*, m.p. 168°, $[\alpha]^{18}_{5461}$ —165° in dioxan. A. Li.

Volatile plant substances. V. Preparation of the fundamental substance of the azulene series. P. A. Plattner and A. S. Pfau (Helv. Chim. Acta, 1937, **20**, 224—232; cf. A., 1936, 993).—*cyclo*-Pentenocycloheptanone is hydrogenated (Ni in EtOH) to *cyclo*pentanocycloheptanone, which is reduced by Na and EtOH to cyclo*pentano*cyclo*heptanol*, b.p. 126—128°/10 mm., dehydrogenated by Pd–C at 300—350° to *azulene* (dicyclo-[0·3·5]-$\Delta^{1:3:5:7:9}$-*decapentaene*) (I), m.p. 98·5—99°. Isolation of (I) is effected by fractional sublimation of its additive *product* (II), m.p. 166·5—167·5°, with $C_6H_3(NO_2)_3$, or, preferably, by treatment of (II) with Al_2O_3 in presence of C_6H_6–*cyclo*hexane. The analogous *compound*, m.p. 99·5—100°, with 2 : 4 : 6-$C_6H_2Me(NO_2)_3$ is described. (I) dissolves readily in conc. mineral acids and is repptd. by immediate addition of H_2O but is relatively unstable in solution. (I) has a marked odour of $C_{10}H_8$ which appears to be proper to it since mixtures of (II) and the corresponding compound of $C_{10}H_8$ are readily separable. Small amounts of (I) appear to be formed during the dry distillation of Ca adipate, apparently owing to the presence of a dehydrogenating reagent. The utility of the chromatographic method is illustrated further by the isolation of *S*-guaiazulene from its picrate or compound with $C_6H_3(NO_2)_3$ and of vetivazulene from its picrate. H. W.

Mechanism of reaction of destructive hydrogenation of tetrahydronaphthalene. S. B. Anisimov and V. F. Polozov (J. Gen. Chem. Russ., 1936, **6**, 1847—1854).—The products of hydrogenation in presence of SiO_2,WO_3 catalyst at 420—480° are successively, $PhBu^a$, $PhPr^a$, PhEt, and PhMe. The same process takes place with catalysts containing halogen (VCl_4, $AlCl_3$, I, $HgCl_2$, $BiCl_3$), except that part of the $PhBu^a$ formed isomerises to $C_6H_3Me_4$. R. T.

Polymerisation of tetrahydronaphthalene. H. I. Waterman, J. J. Leendertse, and J. B. Nieman (Rec. trav. chim., 1937, **56**, 59—64).—Polymerisation of tetrahydronaphthalene at 50° in presence of $AlCl_3$ gives products the physical consts. of which indicate that opening and closing of rings has occurred to a slight extent. A substance, m.p. 72°, probably an anthracene or phenanthrene derivative, has been isolated (cf. Schroeter, A., 1925, i, 125). H. G. M.

Derivatives of 4-iodonaphthalene-1-sulphonic acid. H. Goldstein, T. Blezinger, and H. Fischer (Helv. Chim. Acta, 1937, **20**, 218—220).—Diazotisation of 1 : 4-$NH_2·C_{10}H_6·SO_3H$ and treatment of the product with NaI gives *Na* 4-*iodonaphthalene*-1-*sulphonate* (+1H_2O) [corresponding *Ba*, *Ag* (I), and *anilinium*, m.p. 308° (corr.), salts]. (I) is transformed by EtI in boiling anhyd. C_6H_6 into *Et* 4-*iodonaphthalene*-1-*sulphonate*, m.p. 102° (corr.); the *Me* ester has m.p. 113°. The m.p. of the chloride, amide, and anilide are 124·5° (corr.), 206·5° (corr.), and 136·5° (corr.), respectively. H. W.

Dinaphthyldisulphonic acids. W. M. Cumming and G. D. Muir (J. Roy. Tech. Coll., 1937, **4**, 61—71).—The Na or K salts of 1 : 4-chloro-, 1 : 2- and 2 : 1-bromo-, 1 : 2- (*sulphonamide*, m.p. 247°), 1 : 4-, 1 : 5-, 1 : 8-, 2 : 1-, and 2 : 6-iodo-naphthalenesulphonic acids were boiled with Cu powder and a little $CuSO_4$. The 2 : 1-Br- and -I-compounds yielded salts of 2 : 2′-*dinaphthyl*-1 : 1′-*disulphonic acid* [$(NH_4)_2$ salt m.p. 303°—304°; *disulphonyl chloride*, m.p. 245—246° (decomp.)]; 1 : 8-iodo- gave (probably) Na_2 1 : 1′-*dinaphthyl*-8 : 8′-*disulphonate*, which was decomposed by PCl_5, but with NH_2Ph,HCl gave 1 : 1′-*dinaphthyl*-8 : 8′-*sultone*, m.p. 252° (decomp.); 1 : 2- and 1 : 4-$C_{10}H_6I·SO_3H$ merely lost their halogen, while the remainder did not react. In another

series, 1 : 2-, 1 : 4-, 1 : 8-, 2 : 6-, and 2 : 1-diazonaphthalenesulphonic acids were treated with NH_3–Cu_2O (reduced by NH_2OH); the last-named afforded the dinaphthyldisulphonate, the remainder giving *azonaphthalenedisulphonic acids* of the Ciba Orange type. A. Li.

Nitration of polycyclic aromatic hydrocarbons by means of nitrous fumes. (Signa.) L. Monti (Atti V Congr. Naz. Chim., 1936, **1**, 407—410).—Nitrous fumes convert acenaphthene in Et_2O into the 5-NO_2- and in C_6H_6 or AcOH at room temp. into the 5 : 6-$(NO_2)_2$-derivative. Fluorene at room temp. gives only the 2-NO_2, but at 80—90° a mixture of the 2 : 7- and 2 : 5-$(NO_2)_2$-derivatives. Ph_2 does not react at room temp., but at 90° yields the 4-NO_2- and, slowly, the 4 : 2′-$(NO_2)_2$-derivative. E. W. W.

Destructive hydrogenation of octahydroanthracene and -phenanthrene. E. I. Prokopetz (J. Appl. Chem. Russ., 1937, **10**, 126—130).—The products of hydrogenation (485—490°/100 atm.) of octahydro-anthracene (I) or -phenanthrene (II) or 7-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene (III) are *m*- and *p*-xylene. The reaction is believed to consist of (I) or (II) → (III) → *m*- and *p*-xylene. R. T.

Reaction of alkali metals with polycyclic hydrocarbons : 1 : 2-benzanthrene, 1 : 2 : 5 : 6-dibenzanthrene, and methylcholanthrene. W. E. Bachmann (J. Org. Chem., 1936, **1**, 347—353).—1 : 2-Benzanthracene (I) (obtained in 54% yield by heating 1-$C_{10}H_7$·CO·C_6H_4Me-*o* with Zn at 410°) when treated with Na–Hg–C_6H_6–Et_2O gives a blue solution which turns rose-red : subsequent addition of MeOH gives 9 : 10-*dihydro*-1 : 2-*benzanthracene*, m.p. 112—112·5° (*dipicrate*, m.p. 139—139·5°), dehydrogenated by S to (I) and oxidised by CrO_3–AcOH to 1 : 2-benz-9 : 10-anthraquinone. Similarly 1 : 2 : 5 : 6-dibenzanthracene (II) gives a solution which changes from green to blue and with MeOH gives 9 : 10-dihydro-1 : 2 : 5 : 6-dibenzanthracene, m.p. 218·5—219·5° [*dipicrate*, m.p. 221—222° (decomp.) according to method of heating] (cf. A., 1934, 180), dehydrogenated by S to (II) and oxidised to the corresponding 9 : 10-anthraquinone. 20-Methylcholanthrene (III) (for numbering see A., 1935, 1117), m.p. 180·3—180·6° [prepared by pyrolysis of 4-(1-naphthoyl)-7-methylindane, m.p. 82·7—83·5° (cf. A., 1935, 853)], with Na–C_6H_6–Et_2O gives a purple solution which with MeOH gives 11 : 14-*dihydro*-20-*methylcholanthrene*, m.p. 136—137°, dehydrogenated by S to (III) and oxidised to 6-methyl-1 : 2-benzanthraquinonyl-5-acetic acid (A., 1934, 656). Similar reactions occur with Li–C_6H_6–Et_2O; in each case, however, the colour of the resulting solution was blue. H. G. M.

Polycyclic aromatic hydrocarbons. XV. New homologues of 1 : 2-benzanthracene. J. W. Cook, A. M. Robinson, and F. Goulden (J.C.S., 1937, 393—396).—5-Ketododecahydro-1 : 2-benzanthracene with MgEtBr, followed by dehydration ($KHSO_4$) and dehydrogenation (Pt-black) of the carbinol, yields 5-*ethyl*-1 : 2-*benzanthracene*, m.p. 120° (*picrate*, m.p. 150—151°), oxidised ($Na_2Cr_2O_7$) to 5-*ethyl*-1 : 2-*benzanthraquinone*, m.p. 97—98°. *o*-1-Naphthoylbenzoic acid and MgMeI yield (1-*naphthyl*)*methylphthalide*, m.p. 152—153°, reduced (after hydrolysis) by Zn dust to o-α-(1-*naphthyl*)*ethylbenzoic acid*, m.p. 167—168°; cyclisation (anhyd. $ZnCl_2$) gives an anthrone, which is reduced (Zn + NaOH) to 9-*methyl*-1 : 2-*benzanthracene*, m.p. 138—139° (*picrate*, m.p. 115—116°). β-o-*Tolylethylchloride*, b.p. 100°/15—20 mm. (from the alcohol by $SOCl_2$ and $NPhMe_2$), reacts in the form of a Grignard reagent with *trans*-2-ketodecahydronaphthalene to give 2-(β-o-*tolylethyl*)-*trans*-2-*decahydronaphthol*, b.p. 170—180°/0·6 mm. (crystallises slowly at 0°), which is dehydrated ($KHSO_4$) to 2-(β-o-*tolylethyl*)-$\Delta^{2:3}$-*octahydronaphthalene*, b.p. 160—162°/0·7 mm.; this is cyclised by $AlCl_3$ in CS_2 to 4′*methyldodecahydro*-1 : 2-*benzanthracene*, m.p. 92·5—93·5°, which with Se at 300° yields 4′-*methyl*-1 : 2-*benzanthracene*, m.p. 194—195° (*picrate*, m.p. 139—140°), oxidised to 4′-*methyl*-1 : 2-*benzanthraquinone*, m.p. 219—220°. 10-Methyl-1 : 2-benzanthracene was synthesised from 1 : 2-benz-10-anthrone and MgMeI, the carbinol being treated with picric acid, followed by Na_2CO_3. A. Li.

Preparation of dibenzpyrene. G. B. Zilberman (J. Gen. Chem. Russ., 1937, **7**, 234—235).—1 : 2 : 6 : 7-Dibenzpyrene-3 : 8-quinone is reduced by HI and red P at 190—200° (14 hr.) to 1 : 2 : 6 : 7-*dibenzpyrene*, m.p. 320—320·5°. R. T.

Oxidation of rubrene in light.—See A., I, 255.

Carcinogenic hydrocarbons. I. 15 : 20-Dimethylcholanthrene. W. F. Bruce [with L. F. Fieser] (J. Amer. Chem. Soc., 1937, **59**, 479—480).—A mixture (prep. as Bachmann *et al.*, A., 1936, 326) of 4-*bromo*-2 : 7-*dimethyl*-, b.p. 115—117°/0·15 mm., and 7-*bromo*-2 : 4-*dimethyl*-*hydrindone*, m.p. 81°, is reduced (Clemmensen) to 4-*bromo*-2 : 7-*dimethylhydrindene*, b.p. 104—106°/2·5 mm., the Grignard reagent from which with α-$C_{10}H_7$·COCl gives 4-α-*naphthoyl*-2 : 7-*dimethylhydrindene* (I), b.p. 200°/1 mm., m.p. 80—81°, and some 2 : 4-*dimethylhydrindene*, b.p. 105—106°/25 mm. (I) heated at 405—410°/30 min. affords poor yields of 15 : 20-*dimethylcholanthrene*, m.p. 134—136°, and (mainly) 20-methylcholanthrene (for numbering see A., 1935, 1117). H. B.

Synthesis of 5 : 6-(3′-methyl*cyclo*penteno)retene, a compound structurally related to Diels' hydrocarbon. D. E. Adelson and M. T. Bogert (Proc. Nat. Acad. Sci., 1937, **23**, 117—119).—The synthesis of 5 : 6-(3′-*methyl*cyclo*penteno*)-1-*methyl*-7-iso*propylphenanthrene* (I), m.p. 74·5—75·5° (corr.), is outlined through the following stages; 6-acetylretene R·COMe (R = $C_{18}H_{17}$) + Zn + $CH_2Br·CO_2Et$ → OH·CRMe·CH_2·CO_2H + Ac_2O + NaOAc → CRMe:CH·CO_2H + Na–Hg → CHRMe·CH_2·CO_2H → CHRMe·CH_2·CO·Cl + $AlCl_3$ → $C_{18}H_{16}<^{CHMe}_{CO}>CH_2$ + Zn–Hg–HCl → (I). No details are given. J. W. B.

Decomposition of aryldithiocarbamates. N. S. Drozdov (J. Gen. Chem. Russ., 1937, **7**, 185—187).—The reactions NHR·CS_2M (I) → $CS(NHR)_2$ + H_2S; 2(I) → NHR·CS·NH_2 (II) + M_2CS_3; (I) → R·NCS → (II) (R = Ph, *o*-tolyl; M = NH_4, Cu) take place

when (I) is heated in aq. solution in presence of $(NH_4)_2CO_3$, whilst in presence of excess of Cu" the chief product is R·NCS. R. T.

Condensations of aromatic amines with formaldehyde in media containing acid. IV. Conversion of diarylaminomethanes into substituted dihydro- and tetrahydro-quinazolines in non-aqueous media. J. K. Simons (J. Amer. Chem. Soc., 1937, 59, 518—523).—Di-*p*-toluidinomethane (I), *p*-$C_6H_4Me·NH_2$ (II), and *p*-$C_6H_4Me·NH_2$,HCl at 60—90° in absence of solvent give (according to proportions of reagents used) varying amounts of *o*-amino-*m*-xylyl-*p*-toluidine [*p*-tolyl-(2-amino-5-methylbenzyl)amine] (III), 3-*p*-tolyl-6-methyl-1 : 2 : 3 : 4-tetrahydro- (IV) and -3 : 4-dihydro- (V) -quinazoline, and *p*-$C_6H_4Me·NHMe$ (VI). The production of (IV) and (V) probably occurs thus: (III) + (I) → (IV) + (II) (2 mols.); (IV) + (I) → (V) + (II) + (VI). Thus, (I) and (III) in EtOH give (IV) (86·3%) and (II) (60·5%). (IV) and *p*-$C_6H_4Me·NH_2$,HCl in EtOH afford (V), (VI), and 2 : 2′-diamino-5 : 5′-dimethyldiphenylmethane (*dibenzylidene* derivative, m.p. 186°), whilst (I), (IV), and *p*-$C_6H_4Me·NH_2$,HCl in EtOH yield (V) and (VI). (V) is also obtained by oxidation ($KMnO_4$, $COMe_2$) of (IV). (IV) is cleaved by BzCl in C_5H_5N to give the Bz_2 derivative, m.p. 190·2—190·5°, of (III). Di-*p*-phenetidinomethane and *p*-OEt·$C_6H_4·NH_2$,HCl at 100° (bath) afford 6-ethoxy-3-*p*-phenetyl-3 : 4-dihydroquinazoline, m.p. 141—142° [reduced (Na, EtOH) to the 1 : 2 : 3 : 4-H_4-derivative, m.p. 143—143·5°], and *p*-OEt·$C_6H_4·NHMe$. H. B.

Rearrangement of alkylanilines. VII. Behaviour of alkylanilines with *tert.* alkyl groups. W. J. Hickinbottom (J.C.S., 1937, 404—406; cf. A., 1935, 76).—NHPhBu$^\gamma$, or its hydrochloride, when heated with $CoCl_2$ at 212° under conditions allowing escape of volatile products, gives much *iso*-C_4H_8 and only 1% of *p*-$C_6H_4Bu^\gamma·NH_2$. *tert.*-Hexylaniline gives similarly much CHMe:CMeEt and only 2—4% of *sec.* amine. Formation of *p*-$C_6H_4X·NH_2$ (X = alkyl) from NH_2Ph and olefine in presence of promoters is thus a direct union and not a secondary reaction due to rearrangement of the *sec.* amine. R. S. C.

Catalytic condensation of actylene with toluidines. N. S. Kozlov and J. D. Mogilanski (J. Gen. Chem. Russ., 1936, 6, 1897—1901).—*o*-Toluidine in PhMe and C_2H_2 in presence of CuCl yield *trans*-diethylidene-*o*-toluidine, 2 : 8-dimethylquinoline, *o*-$C_6H_4Me·NHEt$, and dimethyltetrahydroquinoline. With *p*-toluidine, the products are trans-*diethylidene-p-toluidine* (βγ-*di*-p-*tolylamino*-Δ$^\beta$-*butene*), m.p. 140°, and 2 : 6-dimethylquinoline; *m*-toluidine gives 2 : 7-dimethylquinoline. It is supposed that diethylidenetoluidines are in all cases intermediate products in the production of methylquinolines. R. T.

Action of amines on semicarbazones. A. B. Crawford and J. Primrose (J. Roy. Tech. Coll., 1937, 4, 28—31).—The reaction of semicarbazones with NH_2R is restricted if R is electronegative. Acetonesemicarbazone (I), heated with *o*-anisidine, gives *acetone-δ-o-anisylsemicarbazone*, m.p. 143—144°, hydrolysed to δ-o-*anisylsemicarbazide hydrochloride*, m.p. (decomp.) 179—180°. The free *base* melts at 144—145° (*benzylidene* derivative, m.p. 178°). With *p*-$NH_2·C_6H_4·NO_2$ or NH_2Bz (I) undergoes thermal decomp. without condensing, and with Et oxamate it gives dimethylketazine, urazole, oxamide, and EtOH. A. Li.

Some substituted anilines. A. Mangini (Atti V Congr. Naz. Chim., 1936, 1, 395—402).—1 : 3 : 4-$C_6H_3Cl(NO_2)_2$ (cf. A., 1935, 855) and the appropriate amines yield *5-chloro-2-nitroallylaniline*, m.p. 52—53°; *5-chloro-2-nitro-3′-methyldiphenylamine*, m.p. 192—193° (decomp.); the corresponding 4′-*Me* derivative (I); *5-chloro-4′-bromo-2-nitrodiphenylamine* (II), m.p. 161—162°; 4-(5″-*chloro-2″-nitroanilino*)-*diphenyl* (III), m.p. 138—139°; *5-chloro-2-nitro-3′-*, m.p. 143—144° (decomp.), and *-4′-hydroxydiphenylamine*, m.p. 142—143°; *5-chloro-2-nitrodiphenylamine-3′-*, m.p. 240—241°, and *-4′-carboxylic acid*, m.p. 270—272° (decomp.); and 2-(*5′-chloro-2′-nitroanilino*)-*pyridine*, m.p. 153—154°. *o*-$C_6H_4Me·NH_2$, *o*-$NH_2·C_6H_4·CO_2H$, and *o*-$NH_2·C_6H_4·OH$ gave no positive reaction, nor did *o*-, *m*-, or *p*-$NO_2·C_6H_4·NH_2$; *p*-$NO_2·C_6H_4·NH·NH_2$, however, gives *5-chloro-2 : 4′-dinitrohydrazobenzene*, m.p. 190·5—192°, converted by Ac_2O into *5-chloro-2-p-nitrophenyl-2 : 1 : 3-benztriazole 1-oxide*, m.p. 143—144°. (I), (II), and (III) are converted by HNO_2 into *6-chloro-1-p-tolyl-*, m.p. 239—241°, *-1-p-bromophenyl-*, m.p. 209—210°, and *-1-p-diphenylyl-1 : 2 : 3-benztriazole*, m.p. 175—176°, respectively. (I) and (II), and especially *NN′*-bis-(5″-chloro-2″-nitrophenyl)benzidine (*loc. cit.*), are sensitive reagents for HNO_2 and HNO_3; other colour reactions are tabulated. E. W. W.

Diphenyl and its derivatives. XV. Passage from the diphenyl to the fluorene system. L. Mascarelli (Gazzetta, 1936, 66, 843—850).—A review of previous work. Diazotised 2-amino-2′-methyldiphenyls, when decomposed by H_2O, generally give fluorenes, except when further substituted in both the 6 and 6′ positions; when one of these positions is substituted, the yield of the fluorene is low. E. W. W.

Manufacture of quaternary ammonium compounds.—See B., 1937, 215.

Compounds of cyclic diamines with metallic salts. Zinc salts. R. Cernatesco and (Mlle.) M. Poni (Ann. Sci. Univ. Jassy, 1935, 21, 393—406).—The prep. of $ZnCl_2$,Tm, $ZnCl_2$,Tp, $ZnBr_2$,Tm (Tm, Tp = *m*- and *p*-tolylenediamines), $ZnCl_2$,2*N*, ZnI_2,2*N*, $ZnBr_2$,2*N*, $ZnCl_2$,*N* [*N* = $C_{10}H_6(NH_2)_2$] is described. By Hieber's method (A., 1929, 691) of displacement of the base by NH_3, it is established that in $ZnCl_2$,2N, $ZnBr_2$,2*N*, $Cd(NO_3)_2$,2*N*, $Cu(NO_3)_2$,2*N*, $ZnBr_2$,Tm, and $ZnCl_2$,Tp, both NH_2 in each mol. of base are bound to the salt mols. by one co-ordinate linking, whereas in $ZnCl_2$,Tm only one is so bound. R. C. M.

Complex salts of the racemic and optically active diamino*cyclo*hexane with tervalent cobalt and rhodium.—See A., I, 259.

Peculiar type of crystal growth of certain 3-benzamido-4-methoxy-*o*-toluidine derivatives. V. A. Izmailski and V. I. Stavrovskaja (J. Gen. Chem. Russ., 1937, 7, 80—83).—The following

substances crystallise from org. solvents in curved, spirally propagating needles: 2-p-*nitrobenzamido*-, m.p. 286°, -p-*nitrobenzylidineamino*-, m.p. 193°, -β-*hydroxynaphthaleneazo*-, m.p. 231—232° (decomp.), and -p-*dimethylaminobenzeneazo*-3-*benzamido*-4-*methoxytoluene*, m.p. 172—172·5°. R. T.

Thioformylation of amines. A. R. Todd, F. Bergel, Karimullah, and R. Keller (J.C.S., 1937, 361—364).—HCS_2H (I) and $MeCS_2H$ with PhNCO or PhNCS yield thio-form- and -acet-anilide, respectively. From (I) or HCS_2K, and the appropriate amine, *thioformyl* derivatives of the following are obtained; 6-aminoquinoline, m.p. 236°, tryptamine, m.p. 82°, mescaline, m.p. 92°, *o*-$C_6H_4(NH_2)_2$, m.p. 77° (unstable; slowly transformed into benziminazole), *o*-$NH_2{\cdot}C_6H_4{\cdot}NHAc$, m.p. 173°, $NH_2{\cdot}CH_2Ph$, m.p. 64°, $NH_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2$-*o*, m.p. 94°. With HCS_2K, *o*-$NH_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}NH_2$ affords dihydroquinazoline, and $(CH_2{\cdot}NH_2)_2$ gives *ethylenebisthioformamide*, m.p. 146—147°. *iso*Amylamine and (I) give N-iso*amylthioformamide*, b.p. 143—146°/10 mm., which, treated successively with CH_2BzBr and picric acid, affords 4-*phenyl*-3-iso*amylthiazolium picrate*, m.p. 101°. An improved prep. of thioformamide from HCS_2K and aq. NH_3 is described. J. D. R.

Auxo-enoid systems. IV. The colour of nitrobenzoyl derivatives of aromatic amines. V. A. Ismailski and B. M. Bogoslovski (Compt. rend. Acad. Sci. U.R.S.S., 1937, **14**, 17—22).—The absorption curves of N-(4-*nitrobenzoyl*)-N-*benzyl*-p-*aminophenol* (I), pale yellow, m.p. 180—181°, -p-*phenetidine* (II), yellow, m.p. 101—102°, and N′-(4-*nitrobenzoyl*)-N′-*benzyl*-NN-*dimethyl*-p-*phenylenediamine*, red, m.p. 118—119°, have been measured in order to provide further support for the theory that their colour is not due to tautomerism between ·CO·NH· and ·C(OH):N· (A., 1936, 1396), which is prevented by CH_2Ph, but is due to the direct action of the nitro-enoid system on the auxo-enoid system in the same mol. Compared with *p*-$NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}NHPh$ (I) and (II) show bathochromic displacement of the absorption band, as does also (II) compared with $NHBz{\cdot}C_6H_4{\cdot}NMe_2$. The absorption maxima at 270 A. approx. coincide with that for NHBzPh, thus demonstrating that in the latter substance it cannot be due to ·C(OH):N·. K. H. S.

Heterocyclic compounds containing nitrogen. XXVI. Preparation of *o*-aminated *p*-phenylenediethylamines (*p*-di-β-aminoethylbenzenes). P. Ruggli and W. Müller (Helv. Chim. Acta, 1937, **20**, 189—198).—p-*Phenylenediethylamine sulphate* (I), m.p. (indef.) 210°, in conc. H_2SO_4 is converted by HNO_3 (*d* 1·52) and conc. H_2SO_4 into 2-*nitrophenylene*-1 : 4-*diethylamine sulphate*, transformed by BzCl and NaOH into the 2-*nitro*-1 : 4-*di*-β-*benzamidoethylbenzene*, m.p. 184—185°. This is reduced (Ni in H_2O–EtOH–EtOAc) to 2-*amino*-1 : 4-*di*-β-*benzamidoethylbenzene*, m.p. 201°, which does not afford a cryst. Bz derivative but is transformed by Ac_2O into 2-*acetamido*-1 : 4-*di*-β-*benzamidoethylbenzene* (II), m.p. 176°. (II) with HNO_3 (*d* 1·52) at −15° to −5° affords 5-*nitro*-2-*acetamido*-1 : 4-*di*-β-*benzamidoethylbenzene*, decomp. about 150°, reduced to 5-*amino*-2-*acetamido*-1 : 4-*di*-β-*benzamidoethylbenzene*, whence 2 : 5-*diacetamido*-1 : 4-*di*-β-*benzamidoethylbenzene* (III), m.p. 285°. Mild hydrolysis of (III) with EtOH–HCl affords 2 : 5-*diacetamido*-1 : 4-*di*-β-*aminoethylbenzene dihydrochloride*, decomp. 245—250°, whereas with HCl (*d* 1·19) at 120° it gives 2 : 5-*diamino*-1 : 4-*di*-β-*aminoethylbenzene tetrahydrochloride*, decomp. about 300—305°. Attempts to effect ring-closure to a pyrrolidine derivative were unsuccessful. Gradual addition of (I) to HNO_3 (*d* 1·52) and conc. H_2SO_4 at 80—100° gives 2 : 6-*dinitrophenylene*-1 : 4-*diethylamine disulphate*, darkens at 250°, whence 2 : 6-*dinitro*-1 : 4-*di*-β-*benzamidoethylbenzene*, m.p. 216—218°, 2 : 6-*diamino*-, m.p. 214°, and 2 : 6-*diacetamido*-, m.p. 268—270°, -1 : 4-*di*-β-*benzamidoethylbenzene*. The last-named substance is hydrolysed to 2 : 6-*diaminophenylene*-1 : 4-*diethylamine tetrahydrochloride*, m.p. 275° (decomp.), with which ring-closure could not be effected. *p*-$C_6H_4(CH_2{\cdot}CN)_2$, *p*-$NO{\cdot}C_6H_4{\cdot}NMe_2$, and NaOH in EtOH give the *anil* *p*-$C_6H_4[C(CN):N{\cdot}C_6H_4{\cdot}NMe_2$-*p*$]_2$, m.p. 240°, hydrolysed to *p*-$C_6H_4(CO_2H)_2$ and HCN. Oxidation of the "polymeric nitrile" [obtained by the action of KCN on *p*-$C_6H_4(CH_2Br)_2$] by $KMnO_4$ in alkaline solution yields *p*-$C_6H_4(CO_2H)_2$. H. W.

Diphenyl series. VII. New derivatives. VIII. Bromination of 2-nitro-4′-amino- and 4-nitro-2′-amino-diphenyl. V. Bellavita (Atti V Congr. Naz. Chim., 1936, **1**, 290—295, 296—306).—VII. 4-Nitro- is reduced to 4-*amino*-2 : 4′-*diacetamidodiphenyl*, m.p. 233—234° (2 : 4 : 4′-*triacetamidodiphenyl*, m.p. 309—311°), from which the Ac_2 derivative, m.p. 225°, of 4-*bromo*-2 : 4′-*diaminodiphenyl*, m.p. 102° (*hydrochloride*, m.p. 285°), is obtained. 3′-Nitro- is reduced to 3′-*amino*-2 : 4′-*diacetamidodiphenyl*, m.p. 296—302° (2 : 3′ : 4′-*triacetamidodiphenyl*, m.p. 288—290°), which on diazotisation and treatment with CuBr gives 2 : 4′-*diacetamido*-3′-*hydroxydiphenyl*, m.p. 258°. 2 : 4′-Diaminodiphenyl is brominated in AcOH to 3 : 5 : 3′ : 5′-*tetrabromo*-2 : 4′-*diaminodiphenyl*, m.p. 186° (Ac_2 derivative, m.p. 155°), converted by diazotisation and H_3PO_2 into 3 : 5 : 3′ : 5′-tetrabromodiphenyl. 4 : 3′-Dinitro-2 : 4′-diaminodiphenyl diazotised and treated with $Hg(NO_3)_2$ and KCl or KBr gives 2 : 4′-*dichloro*-, m.p. 142°, and 2 : 4′-*dibromo*-4 : 3′-*dinitrodiphenyl*, m.p. 141°. The corresponding 5 : 3′-$(NO_2)_2$-compound is similarly converted into 2 : 4′-*dibromo*-5 : 3′-*dinitrodiphenyl*, m.p. 170°.

VIII. 2-Nitro-4′-aminodiphenyl is brominated in AcOH to 4 : 5-*dibromo*-2-*nitro*-4′-*aminodiphenyl* (I), m.p. 141° (*Ac* derivative, m.p. 182—183°), reduced to 4 : 5-*dibromo*-2 : 4′-*diaminodiphenyl*, m.p. 108—109° (Ac_2 derivative, m.p. 245°, also obtained from 4′-bromo-2 : 4′-diacetamidodiphenyl). The last diazotised gives with H_3PO_2 3 : 4-dibromodiphenyl, new m.p. 42°; (I) similarly gives 4 : 5-*dibromo*-2-*nitrodiphenyl*, m.p. 108°, reduced to 4 : 5-*dibromo*-2-*aminodiphenyl*, m.p. 86° [*hydrochloride*, m.p. 215° (decomp.); *Ac* derivative, m.p. 151—152°]. This is converted (HNO_2 and CuBr) into 2 : 4 : 5-*tribromodiphenyl*, m.p. 68°. (I) similarly gives 4 : 5 : 4′-*tribromo*-2-*nitrodiphenyl*, m.p. 144°, reduced to 4 : 5 : 4′-*tribromo*-2-*aminodiphenyl* (II), m.p. 113° (*Ac* derivative, m.p. 189—190°), from which, or from 4 : 5-dibromo-2 : 4′-diaminodiphenyl, 2 : 4 : 5 : 4′-*tetrabromodiphenyl*,

m.p. 135°, is obtained. (II) is diazotised and reduced (H_3PO_2) to 4 : 5 : 4′-*tribromodiphenyl*, m.p. 102°. 4′-Nitro-2-aminodiphenyl is similarly brominated to 3 : 4-*dibromo*-4′-*nitro*-2-*aminodiphenyl* (III), m.p. 189° (*Ac* derivative, m.p. 158°), converted into 3 : 4-*dibromo*-2 : 4′-*diaminodiphenyl*, m.p. 105° (Ac_2 derivative, m.p. 108°) (again converted into 3 : 4-dibromodiphenyl), into 3 : 4-*dibromo*-4′-*nitrodiphenyl*, m.p. 160°, 3 : 4-*dibromo*-4′-*aminodiphenyl*, m.p. 114° (*Ac* derivative, m.p. 217—218°) (again converted into 4 : 5-dibromo- and into 4 : 5 : 4′-tribromo-diphenyl), and into 2 : 3 : 4-*tribromo*-4′-*nitrodiphenyl*, m.p. 148°, reduced to 2 : 3 : 4-*tribromo*-4′-*aminodiphenyl*, m.p. 116° (*Ac* derivative, m.p. 220°), which gives 2 : 3 : 4-*tribromodiphenyl*, m.p. 225—227°, and 2 : 3 : 4 : 4′-*tetrabromodiphenyl*, m.p. 127°, also obtained from 3 : 4-dibromo-2 : 4′-diaminodiphenyl. The structures of (I) and (III) and their derivatives are confirmed by the above reactions, and by the fact that (I) does not react with piperidine (thus excluding the 3 : 4-dibromo-2-nitro-4′-aminodiphenyl structure). E. W. W.

Diphenyl series. B. Longo (Atti V Congr. Naz. Chim., 1936, **1**, 386—388).—3-Nitro-*o*-toluidine diazotised and decomposed gives, not the nitrocresol, but 7-nitroindazole. 6 : 6′-Diamino-2 : 2′-dimethyldiphenyl similarly treated yields a small amount of 2 : 2′-dimethyldiphenylene 6 : 6′-oxide. Prep. of 5 : 2′-dinitro-2-methyldiphenyl [from 2-iodo-4-nitrotoluene and *o*-$C_6H_4I{\cdot}NO_2$ (Cu), from which only 2 : 2′-dinitrodiphenyl is isolated] and of 2′-nitro-2 : 5-dimethyldiphenyl is attempted. E. W. W.

Action of concentrated hydrochloric acid on arylazocarboxylamides [arylazoformamides]. R. Justoni (Atti V Congr. Naz. Chim., 1936, **1**, 370—382).—This reaction gives semicarbazides chlorinated in the nucleus. Benzeneazocarboxylamide with conc. HCl at −15° forms *p*-chlorophenylsemicarbazide. This is converted by HNO_2 into *p*-chlorobenzeneazocarboxylamide, which when heated with conc. HCl gives 1-2′ : 4′-*dichlorophenylsemicarbazide* (I), m.p. 192·5° (cf. *loc. cit.*) (synthesised from 2 : 4-dichlorophenylhydrazine and KCNO). This again gives 1-2′ : 4′-*dichlorobenzeneazocarboxylamide* (II), m.p. 166—167° (decomp.) (from which it is re-formed by $SnCl_2$ reduction). 1-*o*-Chlorophenylsemicarbazide is oxidised ($KMnO_4$) to *o*-chlorobenzeneazocarboxylamide, which with HCl also gives (I). (II), also obtained from 2 : 4-dichlorobenzeneazocyanide, is converted by HCl into 1-2′ : 4′ : 6′-*trichlorophenylsemicarbazide*, m.p. 243—244°, which with HCl yields 2 : 4 : 6-*trichlorobenzeneazocarboxylamide*, m.p. 155° (decomp.). *p*-Tolueneazocarboxylamide forms 1-(3′-*chloro*-p-*tolyl*)*semicarbazide* (cf. *loc. cit.*), converted into 3-*chloro*-p-*toluneazocarboxylamide* (III). Either of these with Br–KOH gives 3-*chloro*-p-*tolylazoimide*, which condenses with $CH_2Ac{\cdot}CO_2Et$ to form 1-(3′-*chloro*-p-*tolyl*)-5-*methyl*-1 : 2 : 3-*triazole*-4-*carboxylic acid*, m.p. 120°. With HCl, (III) gives 1-(3′ : 5′-*dichloro*-p-*tolyl*)*semicarbazide*, m.p. 219—220°, reduced by $SnCl_2$ to 3 : 5-dichloro-*p*-toluidine, and oxidised by HNO_2 to 3 : 5-dichloro-*p*-toluneazocarboxylamide. *p*-Nitrobenzeneazocarboxylamide and HCl yield 1-(2′-*chloro*-4′-*nitrophenyl*)*semicarbazide*, m.p. 219—220°, converted by HNO_2 into 2-*chloro*-4-*nitrobenzeneazocarboxylamide*, m.p. 181·5° (decomp.).

E. W. W.

Action of halogen acids on arylazoformamidoximes [arylazocarboxylamidoximes]. A. Quilico (Atti V Congr. Naz. Chim., 1936, **1**, 514—522).—Benzeneazoformamidoxime and conc. HCl give the *hydrochloride*, m.p. 188° (decomp.), of p-*chlorobenzeneazoformamidoxime*, m.p. 209° (decomp.), which is again converted by conc. HCl into the *hydrochloride*, decomp. 190—194°, of 2 : 4-*dichlorobenzeneazoformamidoxime*, m.p. 172° (decomp.), from which the 2 : 4 : 6-Cl_3-compound is obtained. Using HBr, the *hydrobromide*, m.p. 180° (decomp.), of *p*-bromobenzeneazoformamidoxime, m.p. 210° (decomp.), and the *hydrobromide*, m.p. 197—198° (decomp.), of 4-*chloro*-2-*bromobenzeneazoformamidoxime*, m.p. 185°, are obtained, together with 4-*chloro*-2 : 6-*dibromo*-, m.p. 206° (decomp.), and 2 : 4 : 6-*tribromo*-*benzeneazoformamidoxime*. E. W. W.

Reaction of selenium dioxide with certain hydrazines. I. J. Postovski, B. P. Lugovkin, and G. F. Mandrik (J. Gen. Chem. Russ., 1937, **7**, 37—42).—Certain substituted hydrazines and SeO_2 react in aq. solution as follows: $NHR{\cdot}NH_2,HCl + SeO_2 \rightarrow R{\cdot}N_2Cl + Se + 2H_2O$ (R = Ph, *p*-C_6H_4Br, α- and β-$C_{10}H_7$, *m*-$C_6H_4{\cdot}NO_2$). When R = *p*-$C_6H_4{\cdot}NO_2$, the reaction proceeds further; $R{\cdot}N_2Cl$ (I) → $R{\cdot}N_2{\cdot}OH \rightarrow p\text{-}NH_2{\cdot}C_6H_4{\cdot}NO_2$ (II) + HNO_2; (I) + (II) → $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NO_2$; $NHR{\cdot}NH_2 + HNO_2 \rightarrow NO_2{\cdot}C_6H_4{\cdot}N_3 + H_2O$. $NPh_2{\cdot}NH_2$ is oxidised as follows: $NPh_2{\cdot}NH_2 \rightarrow (NPh_2{\cdot}NH{\cdot})_2 \rightarrow NHPh_2 + N_2$. Semicarbazide yields hydrazodicarbonamide. R. T.

Chloro- and bromo-nitrophenyl-hydrazines and -methylhydrazines and their derivatives. L. Maaskant (Rec. trav. chim., 1937, **56**, 211—232).—$NHMe{\cdot}NH_2$ and the appropriate halogenonitrobenzene in EtOH afford α-(4-nitrophenyl)-, -(2-*nitrophenyl*)-, m.p. 63° (*Ac* derivative, m.p. 176°), -(4-*chloro*-2-*nitrophenyl*)-, m.p. 91° (*Ac* derivative, m.p. 165°), -(4-*bromo*-2-*nitrophenyl*)-, m.p. 93° (*Ac* derivative, m.p. 169°), -α-*methylhydrazine*, which give the corresponding *hydrazones* of the following aldehydes (temp. are m.p.; — indicates no compound prepared): PhCHO, 137°, 85°, 150°, 149°; 2-, 198°, —, 132°, 133°, 3-, 154°, —, 153°, 131°, and 4-chloro-, 220°, 130°, 109°, 132°, 2-, —, —, 134°, 131°, 3-, —, 156°, 186°, 197°, and 4-nitro-, —, —, 182°, 171°, 4-methoxy-, 160°, 107°, 102°, 118°, 4-hydroxy-3-methoxy-, 189°, 147°, 120°, 150°, 2-hydroxy-, —, —, 140°, 128°, 3 : 4-methylenedioxy-, —, 136°, 129°, 144°, -benzaldehyde; furfuraldehyde, —, 130°, 134°, 143°, 5-methyl-, 120°, 61°, 105°, 93°, and hydroxymethyl-, 196°, 90°, 55—62°, 90°, -furfuraldehyde; COPhMe, 76°, —, —, —; $CH_2Ac{\cdot}CO_2Et$, 82°, —, —, —; *n*-$C_6H_{13}{\cdot}CHO$, 61°, —, —, —. N_2H_4 and 1 : 3 : 4-$C_6H_3Cl(NO_2)_2$ or -$C_6H_3Br(NO_2)_2$ in EtOH afford 3-*chloro*-, 161° (*Ac* derivative, 190°), and 3-*bromo*-, 165° (*Ac* derivative, 211°), -6-*nitrophenylhydrazine*, which give the corresponding *hydrazones* of PhCHO, 175°, 190°, 2-, 186°, 211°, 3-, 235°, 235°, and 4-chloro-, 232°, 216°, 2-, 208°, 196°, 3-, 253°, 254°, and 4-nitro-, 275°, 263°, 2-, 230°, —, and 4-hydroxy-, 228°, 210—215°, 4-methoxy-, 187°, 210°, 3 : 4-methylenedioxy-, 218°, 210°, 4-hydroxy-3-

methoxy-, 210°, 207°, -benzaldehyde; cuminaldehyde, 168°, 167°; $CH_2Ph{\cdot}CHO$, 131°, 145°; CH_2O, 125°, 144°; MeCHO, 155°, 184°; *n*-$C_6H_{13}{\cdot}CHO$, 93°, 89°; $COMe_2$, 130°, 138°; $COEt_2$, —, 58°; $COPh_2$, 160°, 152°; $CH_2Ac{\cdot}CO_2Et$, 121°, 129°; furfuraldehyde, 198°, 204°; 5-methyl-, 194°, 164—172°, and hydroxymethyl-, 192°, 195°, -furfuraldehyde. J. D. R.

Mechanism of diazotisation. H. Schmid [with G. Muhr] (Ber., 1937, **70**, [*B*], 421—424).—The process of diazotisation in H_2SO_4 can be divided into a preliminary equilibration, $NH_3Ph' + NO_2' \rightleftharpoons NH_3Ph{\cdot}NO_2$ (I), and a time-decisive change, (I) + $HNO_2 \rightarrow N_2Ph' + NO_2' + 2H_2O$. Similar conditions are observed in HCl of low concn. but with increasing concn. of the latter the accelerating influence of Cl′ becomes increasingly pronounced and ultimately is the controlling factor of the change. The component reactions are: $NH_3Ph' + Cl' \rightleftharpoons NH_3PhCl$ (II) and (II) + $HNO_2 \rightarrow N_2Ph' + Cl' + 2H_2O$. H. W.

Rapid determination of diazo-compounds. O. M. Golesenko (Zavod. Lab., 1936, **5**, 598—600).—The entire diazo-N is rapidly eliminated as N_2 by shaking a solution of diazonium salt with *p*-$C_6H_4(NH_2)_2$. The reaction is applied to the nitrometric determination of diazo-compounds. R. T.

Interaction of arylated unsaturated substances with diazonium salts. A. D. Ainley and R. Robinson (J.C.S., 1937, 369—371).—*p*-Methoxystyrene and 2 : 4-dinitrobenzenediazonium sulphate (I), in EtOH afford anisaldehyde-2 : 4-dinitrophenylhydrazone, but similar treatment of styrene yields an unidentified substance, m.p. 76° (decomp.). With *p*-nitrobenzenediazonium chloride in EtOH, *p*-$OMe{\cdot}C_6H_4{\cdot}C{:}CH$ (II) yields p-*methoxyphenylglyoxal*-p-*nitrophenylhydrazone*, m.p. 261°, and $CPh{:}CH$, *phenylglyoxyl*-p-*nitrophenylhydrazone*, m.p. 252°. (I) and (II) in EtOH afford *p-methoxyphenylglyoxal*-2 : 4-*dinitrophenylhydrazone* (III), m.p. 235°, converted by 2 : 4-$C_6H_4(NO_2)_2{\cdot}NH{\cdot}NH_2$ (IV) into p-*methoxyphenylglyoxalbis*-2 : 4-*dinitrophenylhydrazone* (V), m.p. 292°. (III) and (V) are also obtained from *p*-methoxyphenylglyoxal and (IV). J. D. R.

Manufacture of diazoamino-compounds.—See B., 1937, 216.

Condensation of methylene chloride with phenols. II. P. P. Sohorigin, I. P. Losev, and V. V. Korschak (J. Appl. Chem. Russ., 1937, **10**, 138—140).—Condensation of PhOH with CH_2Cl_2 takes place at 130° in presence of NH_3, NH_2Me, $NHMe_2$, or NMe_3. R. T.

Reaction of metal chlorides with phenol and β-naphthol. H. Funk and W. Baumann (Z. anorg. Chem., 1937, **231**, 264—268; cf. A., 1928, 408).—The *compound* $WCl_2(OPh)_4$, m.p. 136°, was prepared by refluxing WCl_6 with PhOH and CCl_4. β-$C_{10}H_7{\cdot}OH$ gave the corresponding *compound* $WCl_2(O{\cdot}C_{10}H_7)_4$, m.p. 210°. Fusion of PhOH with WCl_6 gave the *compound*, $W(OPh)_6$, m.p. 98°. The analogous *compound*, $W(O{\cdot}C_{10}H_7)_6$, m.p. 154°, is described. The *compounds*, $Nb(OPh)_5$, m.p. 208°, and $Ta(OPh)_5$, m.p. 224°, were prepared by adding the corresponding pentahalides to molten PhOH. The *compounds*, $Nb(O{\cdot}C_{10}H_7)_5$, m.p. 185°, and $Ta(O{\cdot}C_{10}H_7)_5$, m.p. 188° (decomp.), were prepared from the pentahalides and β-$C_{10}H_7{\cdot}OH$ in presence of a solvent. H. J. E.

Derivatives of *o*-[4-]*tert.*-butyl-*m*-cresol. Preparation of musc ambrette. A. E. Tschitschibabin [with A. Bestougev] (Bull. Soc. chim., 1937, [v], **4**, 439—448).—2 : 6-Dinitro-4-*tert.*-butyl-*m*-cresol (I), m.p. 97—98°, is best obtained by nitration in AcOH or Et_2O, but some mononitration, replacement and hydrolysis of the Bu, and formation of the quinone occurs even in these solvents; 2-, an oil, and 6-nitro-*tert.*-butyl-, m.p. 163—165°, and 2 : 4 : 6-trinitro-*m*-cresol are thus obtained as by-products. (I) and Me_2SO_4–KOH give musc ambrette (II). 4-tert.-*Butyl*-m-*tolyl acetate*, b.p. 133—135°/16 mm., is unchanged by 90% HNO_3 in AcOH, but in Ac_2O gives a mixture of oily and solid (m.p. 165°) NO_2-derivatives. The Me ether of (I) and $Cu(NO_3)_2$ in Ac_2O give mainly the 6-NO_2-derivative, m.p. 59°, with 5—10% of the oily 2-NO_2-compound and some 4-nitro-*m*-cresol, m.p. 55°. R. S. C.

Acyl derivatives of *o*-aminophenol. C. E. Sparks and R. E. Nelson (Proc. Indiana Acad. Sci., 1934, **44**, 132—134).—Condensation of *o*-hydrocinnamoylaminophenol with $ClCO_2Me$ and of Me *o*-hydroxycarbanilate (I) with hydrocinnamoyl chloride affords the same *diacyl compound*, m.p. 60·8—61·5°. Similarly, *o-iso*valerylaminophenol and $ClCO_2Me$, and (I) and *iso*valeryl chloride, afford the same *diacyl compound*, m.p. 68—69°. Ch. Abs. (*r*)

Behaviour of *p*-anisidine in binary systems containing phenols. K. Hrynakowski, H. Staszewski, and B. Szulc (Rocz. Chem., 1937, **17**, 20—29).—1 : 1 *Compounds* are formed in the systems *p*-anisidine (I)–PhOH (m.p. 58·4°), –α- (m.p. 58·5°) and –β-$C_{10}H_7{\cdot}OH$ (m.p. 94°), and –*m*-$NH_2{\cdot}C_6H_4{\cdot}OH$ (transition point 52·6°), whilst compound formation does not take place in the systems (I)–*o*- and –*p*-$NH_2{\cdot}C_6H_4{\cdot}OH$ and –*p*-toluidine (II). The systems closely resemble the analogous ones with (II) in place of (I). The activity of the NH_2-group is greater with OMe in the C_6H_6 ring than with Me. R. T.

Nitroamines. VII. Phenetylnitroamines. E. Macciotta and (Signa.) V. Deffenu (Atti V Congr. Naz. Chim., 1936, **1**, 389—394).—*p*-$OEt{\cdot}C_6H_4{\cdot}NH_2$ in KOEt–EtOH–Et_2O is readily converted by $EtNO_3$ into the *K* salt of p-*phenetylnitroamine* (I), m.p. 54—55° (decomp.), which with Me_2SO_4 gives p-*phenetylmethylnitroamine*, m.p. 42—43°. The last rearranges in boiling aq. NaOH or in cold conc. H_2SO_4 to form 3-nitro-*p*-phenetidine, m.p. 109—110° (*Ac* derivative, m.p. 102—103°). As a by-product with (I), *pp*′-diethoxyazobenzene, m.p. 157—158°, is obtained. The *K* salt of *o-phenetylnitroamine* (decomp. in air at room temp.) and o-*phenetylmethylnitroamine*, m.p. 50—51°, are obtained similarly, but less readily. Treatment of the nitroamine, in AcOH, with H_2SO_4 gives 5-nitro-*o*-phenetidine. The *K* salt of m-*phenetylnitroamine* is formed only extremely slowly and in poor yield. E. W. W.

Variations in taste of [acetyl derivatives of] dulcin. C. Alberti (Atti V Congr. Naz. Chim., 1936, **1**, 271—279).—Dulcin yields, through its

MgBr and $(MgBr)_2$ derivatives, *Ac* and Ac_2 derivatives, viz., N'-*acetyl*-, m.p. 220°, and NN'-*diacetyl*-N-p-*phenetylcarbamide*, m.p. 120°. These are both tasteless; their hydrolysis is studied. E. W. W.

Hydroxy-derivatives of 3 : 4-benzpyrene and 1 : 2-benzanthracene. L. F. Fieser, E. B. Hershberg, L. Long, jun., and M. S. Newman (J. Amer. Chem. Soc., 1937, **59**, 475—478).—4'-Hydroxy-3 : 4-benzpyrene (I) [previously described (A., 1935, 1233) as 4'-hydroxy-1 : 2-benzpyrene] (*acetate*, m.p. 194—195°; *benzoate*, m.p. 191—192°; *Me ether*, m.p. 183—184°; CO_2Me derivative, m.p. 243—244°; p-*nitrobenzoate*, m.p. 252—253°; p-*aminobenzoate*, m.p. 268—269°) is best obtained from 4'-keto-1' : 2' : 3' : 4'-tetrahydrobenzpyrene (modified prep.; cf. *ibid.*, 741) and S at 210—215°. 3-Methoxy-1 : 2-benzanthracene (II) is best prepared by reduction of the 10-anthrone with activated Zn dust and *N*-NaOH + PhMe. 3-Hydroxy-1 : 2-benzanthracene (III) (*benzoate*, m.p. 174—174·5°; *stearate*, m.p. 87—89°; CO_2Me derivative, m.p. 216—217°) coupled with diazotised (using $Pr^{\beta}O{\cdot}NO$ and AcOH–conc. H_2SO_4) *p*-$NHAc{\cdot}C_6H_4{\cdot}NH_2$ gives the 4-p-*acetamidobenzeneazo*-, m.p. 278—279° (uncorr.), hydrolysed (EtOH–KOH) to the 4-p-*aminobenzeneazo*-derivative, amorphous, m.p. 211—213° (uncorr.). (III), $NaHSO_3$, and dioxan–aq. NH_3 at 180—190° afford 3-*amino*-1 : 2-*benzanthracene*, m.p. 211·5—212·5°; 3-*methylamino*-1 : 2-*benzanthracene*, m.p. 115·5—116·5°, is similarly prepared using NH_2Me. All m.p. are corr. unless stated otherwise. (II) and (III) have weak carcinogenic properties; (I) appears to be inactive. H. B.

Condensation products of phenols with Δ'-octadecenyl alcohol.—See B., 1937, 218.

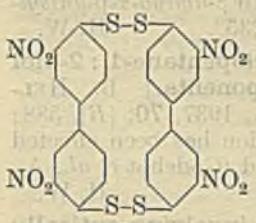
Hydroxyarylaminoanthracene derivatives.—See B., 1937, 217.

Preparation of 3 : 4-methylenedioxytoluene from 3 : 4-dihydroxytoluene. J. V. Aschkinazi and M. S. Rabinovitsch (J. Appl. Chem. Russ., 1937, **10**, 131—137).—3 : 4-Methylenedioxytoluene is obtained in 71% yield from 1 : 3 : 4-$C_6H_3Me(OH)_2$, CH_2Cl_2, and KOH in 30% aq. EtOH or MeOH (18 hr. at 100°), in presence of bronze catalyst. R. T.

Contact changes of safrole. Y. Fujita (J. Chem. Soc. Japan, 1935, **56**, 1205—1209).—On passing safrole and H_2O through a Cu tube containing active C at 450—500°, *iso*safrole, pyrocatechol, 4-propylpyrocatechol, cresol, ethylpyrocatechol methylene ether, and *p*-ethylphenol are formed. Ch. Abs. (*r*)

Rearrangement of *o*-aminodiphenyl ethers. V. K. C. Roberts and J. A. Rhys (J.C.S., 1937, 39—41; cf. A., 1935, 1491).—The rates of rearrangement of some 5-substituted 2' : 4'-dinitro-2-aminodiphenyl ethers, $NHX{\cdot}C_6H_3R{\cdot}O{\cdot}C_6H_3(NO_2)_2$ (R = OMe, Me, H, I, Cl; X = H, and in some cases also Ac and *o*-$NO_2{\cdot}C_6H_4{\cdot}CO$), to the isomeric 4-substituted diphenylamines are recorded and are analogous to those of the corresponding 4-substituted ethers (cf. A., 1935, 484). Rearrangement of the 5-substituted ethers, unlike that of the 4-substituted ethers, is not catalysed by the simple alcohols. The 5-Me ether, but not any of the others, is rapidly rearranged by $C_5H_{11}N$, and the 5-OMe- and 5-Cl-ethers are stable towards all reagents tried. The following are described: 2' : 4'-*dinitro*-2-*hydroxy*-4-*methoxydiphenylamine*, m.p. 178°, exhibits chromoisomerism. 2' : 4'-*Dinitro*-2-*hydroxy*-5-*methoxy*-, m.p. 162°, -2-*amino*-5-*methyl*-, m.p. 134° (*Ac*, m.p. 146°, and o-*nitrobenzoyl*, m.p. 206°, derivative), and -2-amino-, m.p. 133° (cf. lit.), -*diphenyl ether*; 5-*iodo*-, m.p. 175° (o-*nitrobenzoyl* derivative, m.p. 194°), and 5-*chloro*-, m.p. 176° (o-*nitrobenzoyl* derivative, m.p. 202°), -2' : 4'-*dinitro*-2-*aminodiphenyl ether*; 2' : 4'-*dinitro*-2-*hydroxy*-4-*methyl*-, m.p. 166—167° (*acetate*, m.p. 145°; o-*nitrobenzoate*, m.p. 185°), -2-hydroxy-, m.p. 205° (cf. lit.), -*diphenylamine*; 4-*iodo*-, m.p. 180° (o-*nitrobenzoate*, m.p. 206°), and 4-*chloro*-, m.p. 208° (two chromoisomeric forms; o-*nitrobenzoate*, m.p. 196°), -2' : 4'-*dinitro*-2-*hydroxydiphenylamine*. H. G. M.

Diphenyl series. IV. Preparation and properties of substituted diaminodiphenyls. H. H. Hodgson and P. F. Holt (J.C.S., 1937, 37—38).—4 : 4'-Dichloro-3 : 3'-dinitrodiphenyl when refluxed with Na_2S_2 in EtOH–H_2O yields a *polysulphide*, m.p. >340° (decomposes suddenly if rapidly heated to this temp.), probably (I). This when reduced by Na–EtOH and then methylated (Me_2SO_4) yields



(I.)

3 : 3'-*dinitro*-4 : 4'-*dimethylthioldiphenyl*, m.p. 262°, reduced by Sn–HCl and by Fe–AcOH–H_2O to 3 : 3'-*diamino*-4 : 4'-*dimethylthioldiphenyl* (II), m.p. 71° (*dihydrochloride*, m.p. 228°; *stannichloride*, m.p. 242°), which when tetrazotised and then coupled with β-$C_{10}H_7{\cdot}OH$–NaOH gives 4 : 4'-*dimethylthioldiphenylene*-3 : 3'-*bisazo*-β-*naphthol*, m.p. 318°. Similarly, reduction of 3 : 3'-*dinitro*-4 : 4'-*dimethoxydiphenyl*, m.p. 214° (obtained from the phenol and Me_2SO_4–K_2CO_3–H_2O), yields 3 : 3'-*diamino*-4 : 4'-*dimethoxydiphenyl* (III), m.p. 262° (*dihydrochloride*, m.p. 262°; Ac_2 derivative, m.p. 330°), from which 4 : 4'-*dimethoxydiphenylene*-3 : 3'-*bisazo*-β-*naphthol*, m.p. 334°, was obtained. 4 : 4'-*Dichloro*-3 : 3'-, m.p. 133·5°, -2 : 3'-, m.p. 83° (Ac_2 derivative, m.p. 90°), and -2 : 2'-, m.p. 87°, -*diaminodiphenyl* were similarly prepared. (II) and (III) with Schäffer, H-, and J-acids give rise to a series of bisazo-dyes of much lower substantivity for cotton than that of the isomeric 3 : 3'-disubstituted 4 : 4'-bisazo-compounds. H. G. M.

Preparation of pure benzyl acetate. E. Shapiro (Maslob. Shir. Delo, 1935, **11**, 321—322).—The prep. from $CH_2Ph{\cdot}OH$, Ac_2O, and H_3PO_4 is described. Ch. Abs. (*r*)

Acyl migrations. III. Use of ψ-nitrosites of phenolic ethers containing the propenyl group in the synthesis of α-arylated β-hydroxylamino- and β-amino-propanols. A. Krämli and V. Bruckner (J. pr. Chem., 1937, [ii], **148**, 117—125; cf. A., 1935, 972).—Anethole-ψ-nitrosite, m.p. 126° (decomp.), obtained by the action of conc. $NaNO_2$ and 20% H_2SO_4 on anethole in Et_2O, is smoothly converted by Ac_2O containing a little H_3PO_4 (*d* 1·75) into β-*nitro*-α-p-*anisyl*-n-*propyl acetate*, b.p. 195°/3 mm. (slight decomp.), the constitution of which is established by

its transformation by 20% KOH–EtOH into β-nitroanethole, m.p. 47°. Electrolytic reduction of (I) in HCl at a technical Pb cathode at 35—40° gives β-*N*-*acetylhydroxylamino*-α-*anisylpropan*-α-*ol* (II). *p*-OMe·C_6H_4·CH(OH)·CHMe·NAc·OH, m.p. 144°, which strongly reduces hot Fehling's solution, is immediately sol. in dil. alkali, and gives an intense violet colour with $FeCl_3$. Cold *N*-HCl–MeOH causes acyl migration in (II) with production of β-hydroxylamino-α-*p*-anisyl-*n*-propyl acetate, *p*-OMe·C_6H_4·CH(OAc)·CHMe·NH·OH, stable as the *hydrochloride* (III), m.p. 145° (decomp.), which is re-converted into (II) by 10% Na_2CO_3. Migration is not instantaneous since the *compound*, *p*-OMe·C_6H_4·CH(OH)·CHMe·N$<^{CHPh}_{O}$, m.p. 148° (also derived from β-hydroxylamino-α-*p*-anisylpropan-α-ol), is obtained when (III) is emulsified with PhCHO–H_2O and Na_2CO_3 is gradually added. Under conditions described previously (*loc. cit.*) (I) is electrolytically reduced to β-*acetamido*-α-p-*anisylpropan*-α-*ol* (IV), m.p. 141°, transformed by *N*-HCl in $COMe_2$ into β-*amino*-α-p-*anisyl*-n-*propyl acetate hydrochloride* (V), m.p. 188°. Migration in the reverse direction occurs when (V) is treated with *N*-Na_2CO_3. (IV) is hydrolysed by 2*N*-HCl at 100° to β-*amino*-α-p-*anisylpropan*-α-*ol hydrochloride*, m.p. 235°. H. W.

[Resolution of *trans-cyclo*pentane-1 : 2-diol into optically active components.] B. Helferich and R. Hiltmann (Ber., 1937, 70, [*B*], 588; cf. this vol., 146).—The resolution has been effected previously by a different method (Godchot *et al.*, A., 1935, 851). H. W.

Molecular rearrangements involving optically active radicals. VI. Displacement of hydroxyl by chlorine in optically active β-phenyl-β-methyl-*n*-butyl alcohol. E. S. Wallis and P. I. Bowman (J. Org. Chem., 1936, **1**, 383—392).—Resolution by means of quinine of α-phenyl-α-methylbutyric acid, prepared from β-*methoxy*-β-*phenylbutane*, b.p. 63—65°/2—3 mm. (obtained from the alcohol), gives the l-*acid*, $[\alpha]_D^{20}$ − 23·28°, the l-*amide*, m.p. 64—64·6°, $[\alpha]_{5893}^{20}$ −14·90°, of which is reduced to l-β-*phenyl*-β-*methyl*-n-*butyl alcohol* (I), b.p. 123—125°/12—13 mm., α_{6563} −4·20°, α_{5893} −4·90°, α_{5463} −5·78°, α_{4861} −7·35°, α_{4358} −9·6° (pure liquid in 1-dm. tube at 19°) (*Bz* derivative, m.p. 46—46·2°). This with $SOCl_2$ gives 59·10% of CMeEt:CHPh (*NOCl* derivative, m.p. 105·7—106°), 31·3% of β-chloro-α-phenyl-β-methylbutane (II), and some of the corresponding carbinol formed by hydrolysis of the preceding chloride during purification of the reaction product. (II) had $[\alpha]_{5893}^{15}$ +0·63° and the carbinol formed on hydrolysis had $[\alpha]_{5893}^{19}$ +0·88° (pure liquid in 1-dm. tube). The intramol. rearrangement occurring in the formation of (II) from (I) and $SOCl_2$ takes place with partial racemisation and inversion in sign; an interpretation in terms of modern electronic theories is given. In the study of configurative relationships of compounds, the formation of optically active products is not trustworthy evidence for the absence of a complete structural change. H. G. M.

Condensation of methyl hexyl ketone with phenylacetylene. N. M. Malenok and I. V. Sologub (J. Gen. Chem. Russ., 1936, **6**, 1904—1909).—CPh:CH and Me *n*-hexyl ketone (I) yield β-*hydroxy*-β-*phenylacetylenyloctane* (II), b.p. 158°/5 mm., by the Grignard reaction. (II) regenerates CPh:CH and (I) with boiling 15% KOH, and gives β-*phenylacetylenyl*-Δ^{β}-*octene* (III), b.p. 141—142°/5 mm., with Ac_2O (at the b.p.; 8 hr.). (III) and AcO_2H at 0° yield β*γ*-*dihydroxy*-β-*phenylacetylenyloctane*, m.p. 76°, and its β-O-*Ac* derivative, b.p. 187°/6 mm. R. T.

Formation of benzhydrol from benzophenone in Grignard's reaction. S. P. Lagerev (J. Gen. Chem. Russ., 1936, **6**, 1766—1768).—$MgPr^{\beta}Cl$ and $COPh_2$ in Et_2O yield $CHPh_2$·OH and *diphenyliso*-*propylcarbinol*, b.p. 148°/7 mm. R. T.

Dehydration of αα-diphenyl-β-*o*-tolylethylene glycol. R. Roger and F. C. Harper (Rec. trav. chim., 1937, **56**, 202—207).—*o*-C_6H_4Me·CO·CN is hydrolysed by HCl in EtOH to Et *o*-tolylglyoxylate, b.p. 135°/13 mm., reduced by Al–Hg in Et_2O to *Et o-tolylglycollate*, b.p. 140°/13 mm., which with MgPhBr affords αα-*diphenyl*-β-o-*tolylethylene glycol*, m.p. 125—126°, dehydrated by conc. H_2SO_4 or AcOH to *o*-C_6H_4Me·CO·$CHPh_2$ and by 25% H_2SO_4 or fused $H_2C_2O_4$ to *o*-C_6H_4Me·CPh_2·CHO. J. D. R.

Oxidation of 3-*epi*dihydrocholesterol acetate with chromic oxide. 3-*epi*Hydroxy*allo*cholanic acid. S. Kuwata and T. Toyama (J. Pharm. Soc. Japan, 1935, **55**, 978—984).—The oxidation affords 3-epi*acetoxy*allo*cholanic acid* (I), m.p. 199·5° (*Me* ester, m.p. 148°). The Na salt of (I), with EtOH–KOH, yields 3-epi*hydroxy*allo*cholanic acid*, m.p. 244° (*Me ether*, m.p. 164·5°). (I) is oxidised to 3-*keto*allo-*cholanic acid*, m.p. 187°, with CrO_3. Ch. Abs. (*r*)

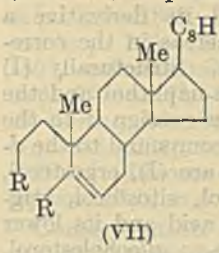
Sterol group. XXIX. Constitution of the isomeric ethers of cholesterol. J. H. Beynon, I. M. Heilbron, and F. S. Spring. XXX. Oxidation of ergosterol, ergosteryl and lumisteryl acetate with chromic anhydride. A. Burawoy. **XXXI. Structure of lumisterol.** I. M. Heilbron, G. L. Moffet, and F. S. Spring (J.C.S., 1937, 406—409, 409—411, 411—414; cf. A., 1936, 1105).—XXIX. The isomeric cholesterol ethers have *cis–trans* relationship and are correctly named *cis*- and *trans*-3-alkoxy-Δ^5-cholestenes. "*cis*"-Cholesterol Me ether (I) with H_2–PtO_2 in AcOH at 65—70° gives cholestane and with conc. HNO_3 in AcOH at 0° gives 6-nitrocholesteryl nitrate, and the "*trans*"-Me ether (II) affords 6-*nitro*-3-*methoxy*-Δ^5-*cholestene*, m.p. 114°, which is reduced by Zn dust in hot AcOH to 3-*methoxycholestan*-6-*one*, m.p. 92°, $[\alpha]_D^{19}$ −11·2° in $CHCl_3$ (*oxime*, m.p. 210°), and is also obtained from 6-ketocholestanol, MeI, and Ag_2O in C_6H_6. With $Zn(OAc)_2$ or KOAc in AcOH (I) gives quantitatively cholesteryl acetate, and with AcCl–C_5H_5N cholesteryl chloride, whereas (II) is unchanged. Br–KOAc converts (I) into tribromocholestane, wherefore this change is not due to HBr. *cis*-Cholestanol, "mol." K (no reaction with Ag_2O), and MeI in C_6H_6 give by epimerisation *trans*-cholestanyl Me ether, m.p. 83°, $[\alpha]^{20}$ +19·8° in $CHCl_3$, which is unaffected by Br or HHal at room temp. The *cis*-ether could not be obtained.

XXX. Ergosterol (III) and lumisterol (IV) are

shown to have the conjugated ethylenic linkings at $C_{(5-6)}$ and $C_{(7-8)}$. CrO_3 and ergosteryl acetate in AcOH at 50° give 20% of ergostadiene-3 : 6-dion-5-ol, hydrolysed to a mixture of acidic and neutral products. Ergosteryl acetate and CrO_3 at 80° give *3-acetoxy-ergostadien-6-on-5-ol* (V) (25%), m.p. 264° (decomp.), $[\alpha]_D^{21}$ −4·7° in $CHCl_3$ (absorption max. at 2515 A., subsidiary at 3330; 1 active H; unchanged by Ac_2O), reduced by $Al(OPr^{\beta})_3$ to ergostadiene-3 : 5 : 6-triol-II. Lumisteryl acetate and CrO_3 at 45° give *3-acetoxylumistadien-6-on-5-ol*, m.p. 177—178°, $[\alpha]_D^{19}$ + 11·7° in $CHCl_3$ [absorption very similar to that of (V)], also obtained from lumistadiene-3 : 5 : 6-triol monoacetate and CrO_3 at room temp.

XXXI. Lumisteryl acetate gives a maleic anhydride *adduct*, m.p. 176—177°, $[\alpha]_D^{22}$ +28·2° in $CHCl_3$, unchanged by distillation at 180°/3 × 10^{-4} mm., but quantitatively dissociated at 240°/15 mm. This acetate and H_2–PtO_2 in AcOH at 70—80° give *lumistenyl acetate*, m.p. 178—179°, $[\alpha]_D^{20}$ −33·1° in $CHCl_3$ (1 ethylenic linking proved by BzO_2H; hydrolysed to *lumistenol*, m.p. 114—116°, $[\alpha]_D^{20}$ −0·5° in $CHCl_3$), and *lumistanol* (VI), m.p. 126—127°. CrO_3 and (VI) give *lumistanone*, m.p. 121—122°, $[\alpha]_D^{22}$ −17·5° in $CHCl_3$ (*oxime*, m.p. 165—166°), and *lumistanedicarboxylic acid*, m.p. 208—210°, $[\alpha]_D^{22}$ +24·6° in $CHCl_3$ (*Me*$_2$ ester, m.p. 48—49°). *p*-$C_6H_4Me{\cdot}SO_2Cl$ converts (IV) into lumistatetraene, m.p. 88°, obtained also by $POCl_3$ (cf. ergosterol). Lumistadiene-3 : 5 : 6-triol-I and -II differ only in the orientation at $C_{(6)}$, since with CrO_3 both give *lumistadiene-3 : 6-dion-5-ol*, m.p. 182—183°. When distilled with Cu-bronze at 5—6 mm., (IV) gives a *ketone*, $C_{28}H_{42-44}O$, m.p. 156—157°, $[\alpha]_D^{21}$ +5·5° in $CHCl_3$ (2 : 4-*dinitrophenylhydrazone*, m.p. 204—205°; *oxime*, m.p. 168—169°), but dihydrolumisterol gives a *lumistadienone*, m.p. 175—176°, $[\alpha]_D^{24}$ +31·6° in $CHCl_3$ [*oxime*, m.p. 210—212° (decomp.)]. The above reactions and absorption spectra show that (III) and (IV) differ only stereochemically, in the orientation at $C_{(10)}$ and/or $C_{(14)}$ and possibly at $C_{(3)}$ and $C_{(9)}$. R. S. C.

Action of selenium dioxide on sterols and bile acids. III. Cholesterol. O. Rosenheim and W. W. Starling (J.C.S., 1937, 377—384).—Cholesterol with SeO_2 in aq. AcOH affords cis-*Δ*$^{5:6}$*-cholestene-3 : 4-diol* (I), b.p. 255—260°/0·2 mm., m.p. 176—177°, $[\alpha]_D^{18}$ −60·0° in $CHCl_3$, of which the following derivatives are described: *diacetate* (II), m.p. 169—170°, $[\alpha]_D^{23}$ −96·1° in $CHCl_3$; *3-benzoate*, m.p. 209—210°, $[\alpha]_D^{20}$ −30·7° in $CHCl_3$ [from cholesteryl benzoate and SeO_2 in AcOH, or from (I) and BzCl in C_5H_5N]; *3-benzoate 4-acetate*, m.p. 166—167°, $[\alpha]_D^{20}$ −55·9° in $CHCl_3$; *dibenzoate*, m.p. 150—151°, $[\alpha]_D^{23}$ −53·9° in $CHCl_3$; *bis-3 : 5-dinitrobenzoate*, m.p. 220—221°, $[\alpha]_D^{22}$ −39·6° in $CHCl_3$. (I) is oxidised (BzO_2H) to cis-*cholestane-3 : 4-diol oxide*, m.p. 173—174°, $[\alpha]_D^{19}$ +3·9° in $CHCl_3$ (*diacetate*, m.p. 178—179°, $[\alpha]_D^{19}$ −22·1° in $CHCl_3$), and with Br in $CHCl_3$ affords cis-*cholestene-3 : 4-diol dibromide*, m.p. 110—112° (decomp.), which, when warmed in $COMe_2$, is converted into iso*propylidenecholestene-3 : 4-diol*, m.p. 133—134°, $[\alpha]_D$ −38·2° in $CHCl_3$, also obtained from (I) in $COMe_2$–HCl. (I) is reduced (PtO_2–H_2) in AcOH to cis-*cholestane-3 : 4-diol* (III), m.p. 202—203°, $[\alpha]_D^{24}$ +18·8° in $CHCl_3$ (*diacetate*, m.p. 136—137°, $[\alpha]_D^{22}$ −7·1° in $CHCl_3$), cholestane (IV), and cholestan-3-ol (V). With Pd–C, (I) is reduced in EtOH to (IV), (V), and coprostane (VI), whilst (II) in AcOH or neutral solution affords (IV) and (V). (I) is oxidised by $Pb(OAc)_4$ in AcOH to the *dialdehyde* (VII; R = CHO) (*di-o-tolylsemicarbazone*, m.p. 192—193°; *disemicarbazone*, m.p. 218—219°), which is oxidised (H_2O_2–AcOH) to Diels' acid (VII; R = CO_2H), also obtained by oxidation of (I) with KOBr. Oxidation [$Pb(OAc)_4$] of (III) affords dihydro-Diels' acid. With HCl in EtOH, or with H_2O at 200°, (I) affords coprostenone (cholestenone) (VIII) (*o-tolylsemicarbazone*, m.p. 243—244°; 2 : 4-*dinitrophenylhydrazone*, m.p. 233—234°). Cholesteryl acetate, oxidised [$Pb(OAc)_4$] followed by acetylation and hydrolysis of the product, yields trans-*Δ*$^{5:6}$*-cholestene-3 : 4-diol* (IX), m.p. 257—258°, b.p. 255—260°/0·2 mm., $[\alpha]_D^{20}$ +6·0° in C_5H_5N, of which the following derivatives are described: *diacetate* (X), m.p. 135—136°, $[\alpha]_D^{18}$ −13·3 in $CHCl_3$; *dibenzoate*, m.p. 181—182°, $[\alpha]_D^{20}$ −74·4° in $CHCl_3$; *3-benzoate 4-acetate*, m.p. 128—129°, $[\alpha]_D^{20}$ −21·2° in $CHCl_3$; *dibromide*, m.p. 196—197°. (IX) is oxidised by BzO_2H to trans-*cholestane-3 : 4-diol oxide*, m.p. 164—165°, $[\alpha]_D^{20}$ −7·5° (*diacetate*, m.p. 154—155°, $[\alpha]_D^{20}$ −58·5°). (X) is reduced (PtO_2–H_2 in Et_2O–AcOH) to (IV), (V), and trans-*cholestane-3 : 4-diol*, m.p. 194—195°, $[\alpha]_D^{20}$ +10·2° (*diacetate*, m.p. 140—141°); reduction with Pd catalysts yields (IV), (V), and (VI). (IX) with HCl–EtOH affords (VIII) and a *substance*, $C_{27}H_{46}O_2$, m.p. 139—140°. (IX) is also obtained by debromination of cholesterol dibromide with NaOAc. The ease of dehydration of (I) and (IX) to (VIII) is discussed in relation to the biochemical problem of the conversion of cholesterol into coprosterol in the animal organism. J. D. R.



(VII)

Transformation of ergosterol with nickel. F. Laucht (Z. physiol. Chem., 1937, 246, 171—176; cf. Windaus, A., 1929, 1065).—Ergosterol heated with Ni at 225° for 3·5 hr. in absence of air and reduced with Na in EtOH gives a *compound* (I), m.p. 195°, $[\alpha]_D^{20}$ + 13·9° in $CHCl_3$, of dihydroergosterol (II) and *u*-ergostadienol (III), m.p. 170°, $[\alpha]_D^{20}$ +50·6° in $CHCl_3$. When (I) in the min. amount of hot $CHCl_3$–C_5H_5N is treated with BzCl the benzoate of (II) separates. The more sol. benzoate of (III) is hydrolysed with KOH in EtOH and traces of (II) are removed with digitonin. The acetate of *u*-ergostanol (IV) with CrO_3 gives an oil, probably a hydroxyketone analogous to pregnanolone, which yields a *semicarbazone*, m.p. 232°. (IV) with CrO_3 in AcOH gives the corresponding ketone, m.p. 94°, which, in AcOH, with Zn + HCl gives *u-ergostane*, m.p. 55°, $[\alpha]_D^{15}$ +20°. (IV) combines with ergostanol and is probably homologous with *epi*-coprosterol. W. McC.

Stereochemistry of the sterols and related, natural substances. H. Lettré (Ber., 1937, 70, [*B*], 450—452).—Examination of the optical activity of neoergosterol (I) and its derivatives shows the $[\alpha]_D$ is composed of a portion *B* determined by the asym-

metric centre $C_{(3)}$ and a part *A* dependent on the other asymmetric centres. In (I) and its derivative a negative val. is assigned to *B* whereas in the corresponding *epi*-series it is positive. Structurally (I) appears related to *ac*-tetrahydro-β-naphthol and the observed displacements of rotation consign it to the *l*-isomeride (II) and hence the *epi*-compound to the *d*-substance (III). Related to (II) are (I), ergosterol, cholesterol, ergostanol, cholestanol, sitosterol, stigmasterol, β-3-hydroxy*allo*cholanic acid and its lower homologues, *trans*-androsterone, *allo*cholesterol, coprosterol, β-3-hydroxycholanic acid and its lower homologues, tigogenin, and uzarigenin with OH at $C_{(3)}$ *cis* to Me at $C_{(10)}$. (III) is related to *epi*neoergosterol, *epi*cholesterol, *epi*ergostanol, *epi*cholestanol, β-3-hydroxy*allo*cholanic acid and its lower homologues, androsterone, *epiallo*cholesterol, *epi*coprosterol, lithocholic acid and its lower homologues, and digitoxigenin with OH at $C_{(3)}$ *trans* to Me at $C_{(10)}$. H. W.

Provitamin-*D* activity and structure. Addition of Grignard reagents to 7-ketocholesteryl acetate. S. Weinhouse and M. S. Kharasch (J. Org. Chem., 1936, **1**, 490—495).—7-Ketocholesteryl acetate (I) and MgMeI in C_6H_6 give *7-hydroxy-7-methylcholesterol*, m.p. 164—165° (*Bz* derivative, m.p. 172—173°), and *7-methylenecholesterol*, m.p. 81—82° (*Bz* derivative, m.p. 139—140°); MgEtBr yields only *7-ethylidenecholesterol*, m.p. 66—68° (*Bz* derivative, m.p. 109—110°). $MgBu^{\beta}Br$ gives 7-iso*butylidenecholesterol*, m.p. 120—121° (from the *Bz* derivative, m.p. 164—165°); the crude product heated at 200°. or slowly distilled at low pressure, and irradiated, is antirachitic. Only side-chain dehydration (as indicated by absorption spectra) of 7-OH-compounds is observed; *7-hydroxy-7-phenylcholesterol*, m.p. 151—152° (*Bz* derivative, m.p. 201—202°), from MgPhBr, could not be dehydrated. *7-Ethylidenecholesteryl acetate*, m.p. 110—111°, is oxidised (CrO_3–AcOH) to (I). E. W. W.

Condensation of ethyl dichloroacetate with ketones and aldehydes by magnesium amalgam. G. Darzens and A. Levy (Compt. rend., 1937, **204**, 272—274).—*cyclo*Hexanone condenses with $CHCl_2{\cdot}CO_2Et$ in the presence of Mg amalgam (30°) to yield *Et* 1-*hydroxy*cyclo*hexylchloroacetate*, b.p. 130—140°/4 mm., dehydrated (P_2O_5) to *Et* cyclo*hexylidenechloroacetate*, b.p. 138—139°/16 mm., which with NaOH–aq. EtOH affords α-keto*cyclo*hexylacetic acid which in turn gives *cyclo*hexylaldehyde. Similarly *cyclo*pentanone affords *Et* 1-*hydroxy*cyclo*pentylchloroacetate*, b.p. 128°/15 mm., whilst PhCHO yields *Et* α-*chloro*-β-*hydroxyphenylpropionate*, b.p. 165°/4 mm., which is dehydrated to $BzCO_2H$ and with NaOEt gives *Et* αβ-*epoxyphenylpropionate*. With the appropriate aliphatic aldehydes *Et* α-*chloro*-β-*hydroxybutyrate*, b.p. 100—105°/15 mm., *-nonoate*, b.p. 144—148°/5 mm., and *-γ-methyl*-n-*valerate*, b.p. 112—115°/18 mm., are produced. F. N. W.

Diaryl-*p*-nitrobenzamidines. R. C. Shah (J. Univ. Bombay, 1936, **5**, Part II, 62—68).—*p*-Nitrobenzanilide (from $p\text{-}NO_2{\cdot}C_6H_4{\cdot}COCl$ and NH_2Ph in $NPhEt_2$), new m.p. 216°, gives the imidochloride (I), which with NH_2Ph in $NPhEt_2$ gives *diphenyl*-p-*nitrobenzamidine*, $+0{\cdot}5C_6H_6$, CCl_4, EtOH, $CHCl_3$, or C_5H_5N, m.p. 155° [*hydrochloride*, m.p. 280—290° (decomp.); *sulphate*, m.p. 210—215° (decomp.); *Ac*, m.p. 155—156°, and *Bz* derivative, m.p. 152—153°], reduced by Zn–AcOH or NH_4HS to the aminobenzamidine. *p*-Nitrobenz-*p*-toluidide, new m.p. 207—208°, with PCl_5 gives the *imidochloride* (II), m.p. 120° (cf. Gattermann *et al.*, A., 1892, 839), converted by NH_2Ph in $NPhEt_2$ into *phenyl*-p-*tolyl*-p-*nitrobenzamidine*, m.p. 138° [*hydrochloride*, m.p. 290—300° (decomp.); *sulphate*, m.p. 270—275° (decomp.); *Bz* derivative, m.p. 157—158°], also obtained from (I) and $p\text{-}C_6H_4Me{\cdot}NH_2$ in $NPhEt_2$. (II) and $p\text{-}C_6H_4Me{\cdot}NH_2$ afford *di*-p-*tolyl*-p-*nitrobenzamidine*, m.p. 160° (*hydrochloride*, m.p. >300°; *sulphate*, m.p. 198—201°; *Bz* derivative, m.p. 163—164°). R. S. C.

Condensation of aminomethyl*iso*propylcarbinol (α-amino-γ-methyl*iso*butyl alcohol) with benzaldehyde, *cyclo*hexanone, and hydrocyanic acid, by Strecker's method. V. F. Liubomudrov and S. V. Tzukerman (Ukrain. Chem. J., 1937, **12**, 21—25).—$OH{\cdot}CHPr^{\beta}{\cdot}CH_2{\cdot}NH_2$,HCl, KCN, and PhCHO in aq. EtOH (24 hr. at room temp.) yield *phenyl*-β-*hydroxy*iso*amylaminoacetonitrile*, m.p. 63—64° (*hydrochloride*, m.p. 120—124°), hydrolysed by boiling with HCl to *phenyl*-β-*hydroxy*iso*amylaminoacetic acid*, m.p. 208—209° (*hydrochloride*, m.p. 164—165°). 1-β-*Hydroxy*iso*amylaminohexahydro-benzonitrile*, m.p. 59—60° (*hydrochloride*, m.p. 112—117°), and *-benzoic acid* [*hydrochloride*, m.p. 234—238° (decomp.)] are obtained analogously, using *cyclo*hexanone in place of PhCHO. R. T.

Synthesis of *cyclo*hexane*spirocyclo*pentane. R. D. Desai and M. A. Wali (J. Univ. Bombay, 1936, **5**, Part II, 69—72).—Et sodio-1-cyano*cyclo*hexane-1-cyanoacetate and $CH_2I{\cdot}CH_2{\cdot}CO_2Et$ give *Et*$_2$ *α-cyano*-α-1-*cyano*-1-cyclo*hexylglutarate*, b.p. 227—228°/15 mm., converted by H_2SO_4 followed by EtOH–H_2SO_4 into *Et*$_2$ α-1-*carbethoxy*-1-cyclo*hexylglutarate*, b.p. 174—175°/15 mm., which with alkali gives α-1-*carboxy*-1-cyclo*hexylglutaric acid*, m.p. 165—168° (decomp.). The Na_3 salt thereof with Ac_2O at 130—140°, followed by H_2SO_4–EtOH, gives *Et* cyclo*hexane*spirocyclo*pentan*-2-*one*-5-*carboxylate*, b.p. 141—142°/15 mm., and thence the corresponding *acid*, m.p. 104—105°; Clemmensen reduction affords the crude *cyclo*pentane acid, the Ca salt of which with soda-lime affords *cyclo*hexane*spirocyclo*pentane, b.p. 70—75°/15 mm. (tetrabromide, m.p. 131—132°). R. S. C.

Configurative relationships of the aliphatic and aromatic amino-acids. P. A. Levene and S. Mardashew (J. Biol. Chem., 1937, **117**, 179—182).—Oxidation (CrO_3–AcOH; water-bath; 3 hr.) of *N*-benzoyl-*l*-tyrosine Et ester, obtained from *l*-tyrosine, followed by hydrolysis with HCl, gives *l*-aspartic acid. H. G. M.

Configurative relationship of mandelic acid to lactic acid. M. Kuna and P. A. Levene (J. Biol. Chem., 1937, **118**, 315—320).—The configurative relation of *l*-mandelic acid to *l*-lactic acid is established chemically (cf. A., 1936, 466). *l*-Acetylmandelic acid is hydrogenated (Adams; 3 atm.) to (+)-*acetyl*-cyclo*hexylglycollic acid* (*acetylhexahydromandelic acid*), b.p. 115—120°/0·1 mm., $[\alpha]_D^{25}$ +17·7°, which is also obtained, b.p. 135—140°/0·3 mm., $[\alpha]_D^{25}$ +11·1°, by

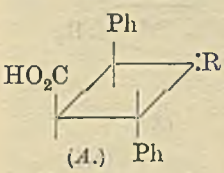
$KMnO_4$–$COMe_2$ oxidation of (+)-α-cyclo*hexylcrotyl acetate*, b.p. 87°/1 mm., $[\alpha]_D^{25}$ +6·51°, the acetylation (C_5H_5N) product of (−)-*propenyl*cyclo*hexylcarbinol*, b.p. 108—109°/15 mm., $[\alpha]_D^{25}$ −10·4°. The last is obtained by resolving the product from Mg *cyclo*hexyl bromide and CHMe:CH·CHO through the *brucine* salt of the *H phthalate*, and is correlated, by hydrogenation (Adams), to *l-cyclo*hexyl-*n*-propylcarbinol (A., 1932, 1027), which has already been related to *l*-lactic acid, through (−)-phenyl-*n*-propylcarbinol, (+)-*n*-propyl-*n*-hexylcarbinol, and (−)-α-hydroxyoctoic acid. E. W. W.

Isomeric menthyl *o*-nitromandelates. E. B. Abbot, A. McKenzie, and P. A. Stewart (Ber., 1937, **70**, [*B*], 456—462).—Esterification of *r*-*o*-nitromandelic acid (I) by *l*-menthol and HCl at 100° gives a non-homogeneous product from which (−)-*menthyl* (+)-o-*nitromandelate* (II), m.p. 83—85°, $[\alpha]_{5893}^{20}$ +152·7°, $[\alpha]_{5791}^{20}$ +161·9°, $[\alpha]_{5461}^{20}$ +201·5° in $COMe_2$, $[\alpha]_{5893}^{20}$ +172·7°, $[\alpha]_{5791}^{20}$ +184·1°, $[\alpha]_{5461}^{20}$ +227·2° in EtOH, is isolated by repeated crystallisation from EtOH. (−)-*Menthyl* (−)-o-*nitromandelate* (III), obtained by esterification of the acid, has m.p. 66°, $[\alpha]_{5893}^{20\cdot5}$ −320°, $[\alpha]_{5791}^{20\cdot5}$ −339°, $[\alpha]_{5461}^{20\cdot5}$ −407° in $COMe_2$, $[\alpha]_{5893}^{20}$ −336·5°, $[\alpha]_{5791}^{20}$ −355·9°, $[\alpha]_{5461}^{20}$ −427·3° in EtOH. Admixture of equal amounts of (II) and (III) affords (−)-*methyl* dl-o-*nitromandelate* (IV), m.p. 65—67°, $[\alpha]_{5893}^{20}$ −81° in EtOH, which could not be crystallised unchanged. Esterification of (−)-*o*-nitromandelic acid with *dl*-menthol (V) yields a product separated into (+)-*menthyl* (−)-o-*nitromandelate* (VI), m.p. 83—85°, $[\alpha]_{5893}^{20\cdot5}$ −153·4°, $[\alpha]_{5461}^{20\cdot5}$ −201·8° in $COMe_2$, and (III). Hydrolysis of (VI) yields (+)-menthol, m.p. 41—42°, $[\alpha]_{5893}^{14}$ +50°. (+)-*Menthyl* (+)-o-*nitromandelate* (VII), obtained by esterification, has m.p. 66° $[\alpha]_{5893}^{20}$ +319°, $[\alpha]_{5791}^{20}$ +339°, $[\alpha]_{5461}^{20}$ +407° in $COMe_2$. (IV) undergoes asymmetric catalytic racemisation in presence of KOH–EtOH. The product of the esterification of (I) by (V) in presence of HCl is separated by crystallisation into the α-*ester* (VIII), rhombic plates, m.p. 88—89°, also obtained by admixture of equal amounts of (III) and (VII), and the β-*ester* (IX), m.p. 74—75°. Admixture of equal amounts of (II) and (VI) gives a non-homogeneous product from which the γ-ester (X), needles, m.p. 90°, is derived. Equal quantities of (VIII) and (X) readily give (IX). At >75° the products of the interaction of (I) and PCl_5 explode. H. W.

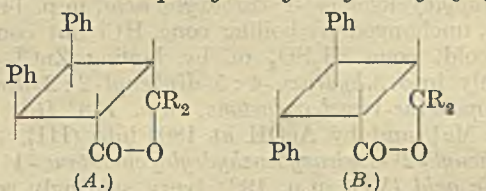
Modifications in the spectra of aqueous solutions of phenylpyruvic acid as a function of p_H and time.—See A., I, 236.

Derivatives of 1-hydroxy-2-naphthoic acid. III. Arylamides and their bromination products. G. V. Jadhav, S. N. Rao, and N. W. Hirwe (J. Univ. Bombay, 1936, **5**, Part II, 137—141; cf. this vol., 149).—Anilides, toluidides, and anisidides of 1 : 2-OH·$C_{10}H_6$·CO_2H are brominated first in the 4-position of the $C_{10}H_6$ and then in the Ph. Structures are proved by synthesis from the Br-acid and/or Br-amine. The following are described: 1-*hydroxy*-2-*naphth*-anilide, new m.p. 155—156°, -m-, m.p. 118—119°, -o-, m.p. 89—90°, and -p-*toluidide*, m.p. 148—149°, -o-, m.p. 161—162°, and -p-*anisidide*, m.p. 129—130°, -o-, m.p. 141—142°, and -p-*phenetidide*, m.p. 154—155°; 4-*bromo*-1-*hydroxy*-2-*naphth*-o-, m.p. 180—181°, and -p-*anisidide*, m.p. 155—156°, -o-, m.p. 190—191°, and -p-*phenetidide*, m.p. 179—180°, -p-*bromoanilide*, m.p. 197—198°, -5′-*bromo*-o-, m.p. 177—178°, -4′-*bromo*-m-, m.p. 171—172°, and -2′-*bromo*-p-*toluidide*, m.p. 213—214°, -??-*dibromo*-o-, m.p. 233—234°, and 4′-*bromo*-p-*anisidide*, m.p. 196—197°, -??-*dibromo*-o-, m.p. 227—228°, and -4′-*bromo*-p-*phenetidide*, m.p. 201—202°. R. S. C.

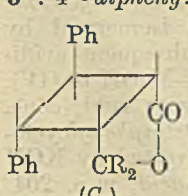
Configuration of the diphenylcyclobutanonecarboxylic acids. XXI. R. Stoermer and H. Starck (Ber., 1937, **70**, [*B*], 479—482).—Successive treatments of the 3-*iso*propylidene-2 : 4-diphenylcyclobutane-1-carboxylic acid (I) (*Me* ester, m.p. 108—109°) derived from γ-truxillic acid (A., 1936, 71) with morphine and brucine in MeOH give with some uncertainty the corresponding (+)-acid (II), m.p. 144—145°, $[\alpha]_D$ +67·5° in EtOH [(?) hydrated *morphine* salt, m.p. 117—118°], and (−)-*acid* (III), m.p. 143—144°, $[\alpha]_D$ −62·75° in EtOH (*brucine* salt; *Me* ester, m.p. 86—87°). (II) has therefore the constitution *A* (R = CMe_2). Ozonisation of (II) in EtOAc yields (−)-2 : 4-*diphenyl*-cyclo*butan*-3-*one*-1-*carboxylic acid* (IV), m.p. 143—144°, $[\alpha]_D$ −33·4° in AcOH, whilst the corresponding (+)-*acid* (V), m.p. 143—144°, $[\alpha]_D$ +37·4° in AcOH, is derived similarly from (III). The *r*-acid (*loc. cit.*) has therefore the structure *A* (R = O). Treatment of (IV) or (V) with hot aq. media, AcOH, or EtOH gives the isomeric diphenylcyclobutanonecarboxylic acid, m.p. 98° (*loc. cit.*), the Me ester, m.p. 72°, of which results when either acid is subjected to CH_2N_2. H. W.



Ring enlargement in the truxinic acid series. XXII. R. Stoermer, G. Starck, and H. E. Anker (Ber., 1937, **70**, [*B*], 483—498).—Et H β-truxinate is converted by MgMeBr in Et_2O into 3ᵗ : 4ᵗ-*diphenyl*-2ᶜ-*hydroxyisopropyl*cyclo*butane*-1ᶜ-*carboxylactone* (*A*; R = Me), m.p. 120—121°, which could not be converted into the corresponding OH-acid, isomerised by heating with acid or alkali, or converted into the anilide or amide by heating with NH_2Ph or NH_3 at 250°. 3ᵗ : 4ᵗ-*Diphenyl*-2ᶜ-*hydroxybenzhydryl*cyclo-

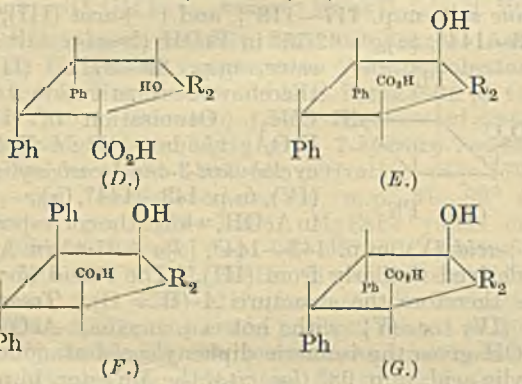


butane-1ᶜ-*carboxylactone*, prepared similarly, has m.p. 189°. Et H ζᶜ-truxnate (I) and MgMeBr afford 3ᶜ : 4ᵗ-*diphenyl*-*h*-*iydroxyisopropyl*cyclo*butane*-1ᶜ-*carboxylactone*-a (*C*; R = Me), m.p. 130°, whereas the isomeric ζ-*truxin*-b-*dimethyl*-*lactone* (*B*; R = Me), m.p. 120°, is derived from Me H ζ-truxinate (II); both lactones are readily hydrolysed to the corresponding OH-acids, from which they are spontaneously regenerated within 24 hr. (I) and MgPhBr give the expected moderately stable OH-acid



(Na salt) converted by boiling Ac_2O into 3^c : 4^t-*diphenyl*-2^c-*hydroxybenzhydryl*cyclo*butane*-1^c-*carboxylactone* (*C*; R = Ph), m.p. 222°. Similarly (II) yields the expected OH-*acid* which is too unstable to permit recrystallisation and readily passes into *γ-truxin*-b-*diphenyl-lactone* (*B*; R = Ph), m.p. 164°.

The following examples of ring enlargement are cited. The products are very resistant towards oxidation and, under drastic conditions, give only BzOH and $COPh_2$ which have no diagnostic val. The configurations are based on analogy with the behaviour of the truxinic acids towards isomerising agents and on the experience of the corresponding ring contraction. Et H neotruxinate *b* and MgMeBr give 3^c : 4^c-*diphenyl*-2^t-*hydroxy*isopropylcyclo*butane*-1^c-*carboxylic acid*, m.p. 165—167°, converted by P_2O_5 in boiling AcOH into 3-*hydroxy*-4 : 5-*diphenyl*-2-gem*dimethyl*-cyclo*pentane*-1-*carboxylactone* (III) (cf. *D*; R = Me),



m.p. 146°; similarly MgPhBr yields 3^c : 4^c-*diphenyl*-2^t-*hydroxybenzhydryl*cyclo*butane*-1^c-*carboxylic acid*, m.p. 210° (very sparingly sol. *Na* salt; *Me* ester, m.p. 170°), whence 3-*hydroxy*-2 : 2 : 4 : 5-*tetraphenyl*cyclo-*pentane*-1-*carboxylactone* (IV) (cf. *D*; R = Ph), m.p. 131—132°. Et H neotruxinate *a* affords 3^t : 4^t-*diphenyl*-2^t-*hydroxybenzhydryl*cyclo*butane*-1^c-*carboxylic acid*, m.p. 222—223° (*NH*$_4$ salt; *Me* ester, m.p. 165°), whence the 3-*hydroxy*-2 : 2 : 4 : 5-*tetraphenyl*-cyclo*pentane*-1-*carboxylactone* (V) (cf. *E*; R = Ph), m.p. 163—164°. *Me H δ-truxinate*, m.p. 109—110°, (*Na* and *Ca* salts), gives 3^c : 4^t-*diphenyl*-2^t-*hydroxy*-isopropylcyclo*butane*-1^c-*carboxylic acid*, m.p. 142° (*Na* salt), unchanged by boiling conc. HCl but converted by cold, conc. H_2SO_4 or by boiling $ZnCl_2$–AcOH mainly into 3-*hydroxy*-4 : 5-*diphenyl*-2 : 2-*dimethyl*-cyclo*pentane*-1-*carboxylactone*, m.p. 159° [(?) cf. *F*; R = Me], and by AcOH at 180° into (III). 3^c : 4^t-*Diphenyl*-2^t-*hydroxybenzhydryl*cyclo*butane*-1^c-*carboxylic acid* (VI), m.p. 192° (very sparingly sol. *Na*, *K*, and *NH*$_4$ salts; *Me* ester, m.p. 152°), is transformed by P_2O_5 in boiling C_6H_6 or AcOH into 3-*hydroxy*-2 : 2 : 4 : 5-*tetraphenyl*cyclo*pentane*-1-*carboxylactone* (cf. *G*; R = Ph), m.p. 163—164°, isomerised by hydrolysis with KOH–MeOH and subsequent acidification or by contact with cold KOH–MeOH to (IV). (VI) is transformed by trituration with cold, conc. H_2SO_4 into the 3-*hydroxy*-2 : 2 : 4 : 5-*tetraphenyl*cyclo-*pentanecarboxylactone*, m.p. 228°, converted by KOH in boiling $(CH_2{\cdot}OH)_2$ into a cis-OH-*acid*, m.p. 204° (decomp.) (*Na* salt), which passes into an isomeric *lactone*, m.p. 256°. These lactones are not isomerised by KOH–$(CH_2{\cdot}OH)_2$ whereas (IV) and (V) [probably with intermediate formation of (IV)] yield two trans-*forms* of 3-hydroxy-2 : 2 : 4 : 5-tetraphenyl*cyclo*-pentane-1-carboxylic acid, m.p. 192° (*Na*, *K*, and *NH*$_4$ salts; *Me* ester, m.p. 152°) and m.p. 180—181° (*NH*$_4$ salt; *Me* ester, m.p. 123—124°), neither of which can be lactonised. During the prep. of (III), 3^c : 4^c-*diphenyl*-2^t-iso*propenyl*cyclo*butane*-1^t-*carboxylic acid*, m.p. 141° (*Na* salt), is produced. Its constitution follows from its ozonisation to 2^t-*acetyl*-3^c : 4^c-*diphenyl*-cyclo*butane*-1^c-*carboxylic acid*, m.p. 167° (*semicarbazone*, m.p. 231°), which is degraded by NaOBr to neotruxinic acid. Similarly, 3^c : 4^t-*diphenyl*-2^t-iso-*propenyl*cyclo*butane*-1^c-*carboxylic acid* is ozonised to 2^t-*acetyl*-3^c : 4^t-*diphenyl*cyclo*butane*-1^c-*carboxylic acid*, m.p. 145° [*semicarbazone*, m.p. 192° (decomp.)].

The following compounds are incidentally described: 3^c : 4^c-*diphenyl*-1^c : 2^t-*dihydroxy*isopropylcyclo*butane*, m.p. 230°; 3^c : 4^t-*diphenyl*-1^c : 2^c-*dihydroxydiphenylmethyl*cyclo*butane*, m.p. 204°, converted by Ac_2O into an *anhydride*, $C_{42}H_{35}O$, m.p. 150°; 1^c : 2^t-*dibenzoyl*-3^c : 4^c-*diphenyl*cyclo*butane*, m.p. 250°, which does not yield a semicarbazone. H. W.

Detection of quinic acid in presence of shikimic acid in the carpels of *Illicium verum*, Hook., and the preparation of quinic acid derivatives. A. Boldt (Pharm. Zentr., 1937, **78**, 157—166).—After removal of oil and protocatechuic acid from the solvent extract of the carpels of *I. verum*, quinic acid can be isolated from its mixture with shikimic acid in the residue and characterised by formation of triacetylquinide, m.p. 134—135°. *Triacetylquinic acid*, m.p. 188°, tribenzoylquinide, m.p. 151°, and quinide (prep. by heating quinic acid in $C_2H_2Cl_4$) are described. E. H. S.

Alkyl methylphthalates. M. Hayashi and S. Tsuruoka (J. Chem. Soc. Japan, 1935, **56**, 999—1007). —*Me*$_1$, m.p. 114·5—115°, and *Et*$_1$, m.p. 86—87°, 3-*methylphthalate* are described. Ch. Abs. (*r*)

Condensation of succinic anhydride with α- and β-naphthyl methyl esters. R. D. Desai and M. A. Wali (J. Univ. Bombay, 1936, **5**, Part II, 73—76).—$(CH_2{\cdot}CO)_2O$, α-$C_{10}H_7{\cdot}OMe$, and $AlCl_3$ in $PhNO_2$ give *γ-keto-γ-4-methoxy-1-naphthylbutyric acid*, m.p. 177—178° (reduced in poor yield to the known 1-$C_{10}H_7{\cdot}[CH_2]_3{\cdot}CO_2H$), but in CS_2 much (?) 4-*methoxy-naphthalenedithiocarboxylic acid*, m.p. 225°, is also formed. β-$C_{10}H_7{\cdot}OMe$ in $PhNO_2$ gives mainly γ-keto-γ-6-methoxy-2-, m.p. 148° (cf. Fieser and Peters, A., 1933, 67) (oxidised to 6 : 2-$OMe{\cdot}C_{10}H_6{\cdot}CO_2H$), and some γ-keto-γ-2-methoxyl-1-naphthylbutyric acid, m.p. 136—137°, the latter acid being the main product (with some thio-acid) in CS_2. R. S. C.

Naphthalylmalonic and *peri*-naphthindandionecarboxylic esters. J. Suszko and M. Wdowicki (Bull. Acad. Polonaise, 1936, **A**, 293—298).—$CHNa(CO_2Et)_2$ with 1 : 8-$C_{10}H_6(COCl)_2$ in C_6H_6 affords *Et*$_2$ *naphthalylmalonate* (I), m.p. 143°, hydrolysed (boiling KOH) to the dicarboxylic acid, but with NH_3 in warm EtOH converted into naphthalimide, which indicates that (I) has un unsymmetrical structure. (I) with conc. H_2SO_4 affords CO_2 and *Et peri-naphthindandionecarboxylate*, m.p. 139—140°, which with boiling 5% KOH affords the *acid*, m.p. 268—

269° (decomp.), decarboxylated at 260°/20 mm. to give *peri*naphthindandione. J. L. D.

Phenylglutaric acids. I. ββ-Diphenylglutaric acid. N. L. Phalnikar and K. S. Nargund (J. Univ. Bombay, 1936, **5**, Part II, 105—108).—CPh_2Cl_2 and $CH_2(CO_2Et)_2$ in NaOEt–EtOH give $CPh_2(OEt)_2$, but with Na in C_6H_6 at 100° give crude oily Et_4 ββ-diphenylpropane-αα*γγ*-tetracarboxylate (I), converted by NaOH–EtOH into the corresponding crude *acid*, m.p. 110—120°, which at 140—150° gives CO_2 and ββ-*diphenylglutaric acid* [better obtained from (I) and hot conc. HCl], m.p. 162—163° (*Ag* salt; *Me*, b.p. 210°/30 mm., and *Et*$_2$ ester, b.p. 253°/7 mm.; *diamide*, m.p. 172°; *dianilide*, m.p. 185°; *imide*, m.p. 188°; anhydride not obtainable). R. S. C.

Catalytic oxidation of phenanthrene by air. J. S. Salkind and V. V. Kesarev (J. Appl. Chem. Russ., 1937, **10**, 99—104).—Phenanthraquinone and solid acids [chiefly *o*-$C_6H_4(CO_2H)_2$ (I), together with $(o\text{-}C_6H_4{\cdot}CO_2H)_2$ (II) and $(CH{\cdot}CO_2H)_2$ (III)] are obtained when phenanthrene (IV)–air mixtures are passed over pumice–V, –V–Mo, or –V–Mo–U catalysts, at 400°. The reaction is represented: (IV) → (II) → (I) → BzOH → (III) → CO_2. R. T.

Condensations of benzoylformic acids. P. Dreyfuss (Atti V Congr. Naz. Chim., 1936, **1**, 358—361).—Veratroylformic acid condenses with veratrole in H_2SO_4 to 2 : 3 : 6 : 7-tetramethoxyfluorene-9-carboxylic acid. This and similar internal condensations of benzilic acids to fluorene derivatives are discussed on the basis of alternate polarities. E. W. W.

Salt effect in rearrangement of benzil-*o*-carboxylic acid. F. H. Westheimer (J. Org. Chem., 1936, **1**, 339—346).—The bimol. velocity coeff. at 100·04° for the alkali-catalysed rearrangement of benzil-*o*-carboxylic acid (I) increases considerably with increasing ionic strength, qualitatively in agreement with Brønsted's theory for reaction between two similarly charged ionic reactants. At high, const. ionic strength, however, in presence of K salts only, the velocity coeff. increases with increasing [KOH], and differs from that obtained when the K salts are replaced by Na salts of the same ionic strength; there is no difference between NaOH and KOH at low ionic strengths (about 0·1). The rearrangement of benzil is, on the contrary, strictly bimol. with a small salt effect only. The foregoing deviations from the bimol. coeff. for the rearrangement of (I) are attributed to the medium effect. H. G. M.

New hydroxycarboxylic acid [from 4-hydroxypyrocatechol ethylene ether].—See B., 1937, 218.

Aldehydes and hydroxyaldehydes of the polymethylene series. III. Transformations of *cyclo*pentanealdehyde. IV. Isomeric transformations of α-hydroxy*cyclo*pentanealdehyde. V. Bromo- and hydroxy-hexahydrobenzaldehyde. E. D. Venus-Danilova (J. Gen. Chem. Russ., 1936, **6**, 1757—1765, 1784—1795, 1863—1869).—III. *cyclo*Pentanealdehyde (I) and conc. H_2SO_4 at −16° yield *cyclo*hexanone (II), *cyclo*hexylidene- and di*cyclo*hexylidene-*cyclo*hexanone, and dodecahydrotriphenylene; the same products are obtained from (II) under analogous conditions, whence it is concluded that the first product of the reaction is (II).

IV. (I) and Br in CS_2 at 0° yield the 1-*Br*-derivative, m.p. 212—215° (decomp.), converted by hydrolysis with aq. $BaCO_3$ into 1-*hydroxy*cyclo*pentanealdehyde* (III), b.p. 94—99°/10 mm., which with semicarbazide yields 2-*keto*-6-cyclo*pentyl*-1 : 3 : 4-*triazine*, m.p. 216—218° (decomp.), and gives a *dimeride*, m.p. 96—97°, on keeping. (III) isomerises when heated with dil. H_2SO_4 (135°; 5 hr.), to yield 2-hydroxy*cyclo*hexanone, also obtained with aq. KOH and $Pb(OH)_2$, or $Cu(OH)_2$, at 100°. In the latter case, *cyclo*pentanecarboxylic acid and its 1-OH-derivative, and 1-hydroxy*cyclo*pentylmethyl alcohol are also obtained as by-products.

V. *cyclo*Hexanealdehyde and Br in CS_2 yield 1-*bromo*cyclo*hexanealdehyde*, b.p. 87—92°/20 mm. (*trimeride*, m.p. 146—147°), converted by Ag_2O in EtOH at 80° into *cyclo*hexanecarboxylic acid, and by aq. $BaCO_3$ into 1-*hydroxy*cyclo*hexanealdehyde* (IV), b.p. 102—108°/10 mm. (*dimeride*, m.p. 126—127°), and Δ^1-*cyclo*hexenealdehyde (V) (*semicarbazone*, m.p. 212°). (IV) yields 1-hydroxy*cyclo*hexanecarboxylic acid when oxidised ($KMnO_4$ in C_5H_5N), and a *semicarbazone*, m.p. 159—160°, with semicarbazide in aq. EtOH at 35°; at 110° the product is 2-*keto*-6-cyclo*hexyl*-1 : 3 : 4-*triazine*, decomp. at 221—223°. (IV) or (V) and *p*-nitrophenylhydrazine yield 4 : 5-*hexahydrobenzo*-1-*p*-*nitrophenylpyrazole*, m.p. 184°. R. T.

Velocity of the Cannizzaro reaction. E. L. Molt (Rec. trav. chim., 1937, **56**, 233—246).—The Cannizzaro reaction with PhCHO in MeOH is termol., retarded by MeOH and accelerated by EtOH (in which solvent much MeCHO is formed). KOH and NaOH have equal effects on the velocity of the reaction, which increases 2·2 times per 10° temp. rise. *p*-OMe·C_6H_4·CHO and *p*-C_6H_4Me·CHO react more slowly, and *p*-C_6H_4Cl·CHO more rapidly, than PhCHO. J. D. R.

Velocity of reaction of benzaldehyde with acetone and acetophenone.—See A., I, 249.

Glucovanillin and a colorimetric reaction for vanillin. W. V. Thorpe and R. T. Williams (J.C.S., 1937, 494).—Vanillin (I) and β-glucose pentaacetate with *p*-C_6H_4Me·SO_3H or $ZnCl_2$ give vanillin-β-glucoside tetra-acetate, m.p. 142—143°, $[\alpha]_D$ −48·3° in $CHCl_3$ (2 : 4-*dinitrophenylhydrazone*, m.p. 202—203°), hydrolysed by NaOMe to vanillin-β-glucoside, m.p. 189—190°, $[\alpha]_D^{21}$ −86·6° in H_2O (2 : 4-*dinitrophenylhydrazone*, m.p. 260—264°). Of 63 phenols examined only (I) (0·002% solution) and vanillic acid give a stable purple colour or, in conc. solution, a ppt., when boiled with 2 drops of Millon's reagent. R. S. C.

Syntheses of *o*-homoveratraldehyde and a new method of preparing *o*-veratraldehyde. F. Mauthner (J. pr. Chem., 1937, [ii], **148**, 95—100).—Guaiacol is converted by CH_2:$CH{\cdot}CH_2Br$ and K_2CO_3 in boiling $COMe_2$ into guaiacol allyl ether (I); CH_2:$CH{\cdot}CH_2Cl$ gives poorer yields but CH_2:$CH{\cdot}CH_2Cl$ + NaI is somewhat more advantageous. (I) in boiling $NPhMe_2$ passes into *o*-allylguaiacol (II), b.p. 130°/10 mm., which with NaOH and Me_2SO_4 gives *o*-allylveratrole, b.p. 122—123°/14 mm. This is ozonised

in anhyd. EtOAc at −20° and the ozonide is decomposed by steam with production of o-*homoveratraldehyde* [2 : 3-*dimethoxyphenylacetaldehyde*] (III), isolated as the p-*nitrophenylhydrazone*, m.p. 157—158°, and 2 : 3-dimethoxyphenylacetic acid (IV), m.p. 82—83°. *o*-Veratraldehyde (V), $CH_2Cl{\cdot}CO_2Et$, and Na wire in abs. EtOH give *Et* 2 : 3-*dimethoxyphenylglycidate*, b.p. 195°/14 mm., hydrolysed and isomerised to (III), which is isolated as the *oxime*, m.p. 92—93°. (II) is converted by boiling NaOH–EtOH into *o-iso*eugenol, which is treated with NaOH and Me_2SO_4 and then ozonised in EtOAc at −20° to (V) in good yield. Treatment of (V) with hippuric acid and anhyd. NaOAc in Ac_2O at 100° gives the *azlactone*, $C_{18}H_{15}O_4N$, m.p. 169—170°, converted by NaOH and H_2O_2 into BzOH and (IV). H. W.

Reaction between toluquinone and cinnamaldehyde under the influence of light. A. Angeletti [with C. Migliardi] (Atti V Congr. Naz. Chim., 1936, 1, 280—283).—Toluquinone and CHPh:CH·CHO in C_6H_6 exposed to light give $CHPh{:}CH{\cdot}CO_2H$, toluquinol, and 5-(or 6-)*hydroxy*-o-(or p-)*tolyl cinnamate*, m.p. 163°. E. W. W.

Oxidation of *cyclo*hexanone and suberone by Caro's acid. R. Robinson and L. H. Smith (J.C.S., 1937, 371—374).—Oxidation of suberone (improved prep.) with $K_2S_2O_8$ and H_2SO_4 in aq. EtOH, followed by treatment of the product with EtOH–H_2SO_4, affords Et ζ-hydroxyheptoate (*phenylurethane*, m.p. 64—65°; *hydrazide*, m.p. 121—123°) and (?) ε-*carbethoxyhexyl* ζ-*hydroxyheptoate*, b.p. 193°/0·5 mm. By similar oxidation, *cyclo*pentanone gives *Et* δ-*hydroxyvalerate*, b.p. 114°/14 mm. (*hydrazide*, m.p. 105—106°), and *cyclo*hexanone yields Et ε-hydroxyhexoate (*phenylurethane*, m.p. 50—51°), reduced (Na–EtOH) to $OH{\cdot}[CH_2]_6{\cdot}OH$, δ-*carbethoxyamyl* ε-*hydroxyhexoate*, b.p. 158—160°/0·05 mm., and, in some cases, cyclo*hexanone peroxide*, m.p. 128°. J. D. R.

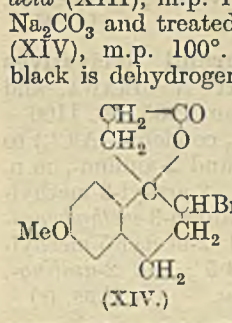
Action of alkaline reagents on some nitroso-α-arylaminoketones and their oximes. J. C. Earl and S. J. Hazlewood (J.C.S., 1937, 374—376).—The nitrosochlorides of ethylenic compounds are converted by primary amines into α-aminoketoximes, converted by HNO_2 into nitroso-α-aminoketoximes and hydrolysed to α-aminoketones, which with HNO_2 afford nitroso-α-aminoketones. The following are described. From methyl-Δ^1-*cyclo*hexene, 2-*anilino*-2-*methyl*-, m.p. 139°, and 2-*nitrosoanilino*-2-*methyl*-cyclo*hexanoneoxime*, m.p. 148·5°, 2-*anilino*-2-*methyl*-, m.p. 91—92°, and 2-*nitrosoanilino*-2-*methyl*-cyclo*hexanone*, m.p. 102°; from $CMe_2{:}CHMe$, α-*nitroso*-o-*toluidinomethyl* Pr^{β} *ketoxime*, m.p. 148°, α-*nitroso-anilino*- (I), b.p. 157°/2 mm., and -p-*toluidino-methyl* Pr^{β} *ketone*, b.p. 145°/0·8 mm.; from α-terpineol, 2-*nitrosoanilino*-2-*methyl*-5-α-*hydroxy*isopropylcyclo*hexanoneoxime*, m.p. 144·5°, and from α-pinene, 2-*nitrosoanilino*-2 : 4 : 4-*trimethyl*-3 : 5-*methylene*cyclo*hexanoneoxime*, m.p. 100·5°. With NaOH and β-$C_{10}H_7{\cdot}OH$, the nitrosoanilino-ketoximes (but not -ketones) afford $PhN_2{\cdot}C_{10}H_6{\cdot}OH$-β; the oxime of (I) also yields a *substance*, $C_{16}H_{24}O_3N_4$, m.p. 130—131°. J. D. R.

Synthesis of substances related to the sterols. XIV. Simple synthesis of certain octalones and ketotetrahydrohydrindenes which may be of angle-methyl-substituted type. A theory of the biogenesis of the sterols. E. C. du Feu, F. J. McQuillin, and R. Robinson. **XV. (IX continued.)** R. Robinson and J. Walker. **XVI. 4-Keto-7-*m*-methoxyphenylheptoic acid and some derivatives.** K. H. Lin, J. Resuggan, R. Robinson, and J. Walker (J.C.S., 1937, 53—60, 60—67, 68—72).—XIV (Cf. A., 1935, 1498). Dicyclic ketones are obtained by condensation of cyclic ketones with substances which readily decompose giving an unsaturated ketone; alternatively the double linking may be produced in the appropriate cyclic ketone. Suitable substances ($R{\cdot}CO{\cdot}CHR'{\cdot}CH_2{\cdot}NMeEt_2$}I) were obtained by methylation of the condensation product of the appropriate ketone ($R{\cdot}CO{\cdot}R'$) with CH_2O and $NHEt_2$ (cf. Mannich, A., 1917, i, 634). 2-Diethylaminomethyl*cyclo*hexanone methiodide when refluxed with $CHAcNa{\cdot}CO_2Et$–EtOH gives 2-*keto*-$\Delta^{1:9}$-*octalin* (I), b.p. 101—102°/2—3 mm. (*semicarbazone*, m.p. 208°; 2 : 4-*dinitrophenylhydrazone*, m.p. 168°), also obtained by hydrolysis of *Et* 2-*keto*-$\Delta^{1:9}$-*octalin*-10-*carboxylate*, b.p. 175—176°/10 mm., formed from Et *cyclo*hexanone-2-carboxylate, NaOEt–EtOH, and δ-diethylaminobutan-β-one methiodide (II). (I) is hydrogenated (H_2–Pd–$SrCO_3$) to *cis*-β-decalone (2 : 4-*dinitrophenylhydrazone*, m.p. 155—156°) and possibly also some of the *trans*-isomeride, and is dehydrogenated to β-$C_{10}H_7{\cdot}OH$. 2-Methyl*cyclo*hexanone (III), $NHEt_2$,HCl, CH_2O, and *cyclo*hexanol when heated at 110° during 2 hr. afford 2-*methyl*-6-*diethylaminomethyl*cyclo*hexanone* (IV), b.p. 95—98°/3 mm., the crude hydrochloride of which decomposes when heated giving 2-*methyl*-6-*methylene*cyclo*hexanone*, b.p. 62°/9 mm. (condensation *product*, m.p. 155°, with 2 : 4-dinitrophenylhydrazine), hydrogenated to 2 : 6-dimethyl-*cyclo*hexanone and dehydrogenated to *m*-2-xylenol. 2 : 6-Dibenzylidene*cyclo*hexanone is conveniently converted into 2 : 6-dibenzylphenol (V) in 75—80% yield by bubbling H_2 through a mixture with Pd–C at 200—250° until the colour is discharged and then heating at 325—330° (9 hr.). The 4-NO_2-derivative, m.p. 124° (*Na* salt; *Me* ether, m.p. 70—71°), of (V) gives on reduction and subsequent oxidation 2 : 6-*dibenzyl*-1 : 4-*benzoquinone*, m.p. 76—77°; 2 : 6-*di*-p-*anisylphenol*, m.p. 66—67°, is similarly obtained. The methiodide of (IV) when refluxed (4 hr.) with $CHAcNa{\cdot}CO_2Et$–NaOEt–EtOH gives 2-*keto*-8-*methyl*-$\Delta^{1:9}$-*octalin*, b.p. 102°/2—3 mm. (*semicarbazone*, m.p. 210—211°; 2 : 4-*dinitrophenylhydrazone*, m.p. 172°), dehydrogenated to 1 : 7-$C_{10}H_6Me{\cdot}OH$. (III) when treated with $NaNH_2$ in Et_2O and (II) in EtOH gives 2-*keto*-10-*methyl*-$\Delta^{1:9}$-*octalin* (VI), b.p. 139°/15 mm. (*semicarbazone*, m.p. 203·5—204°; 2 : 4-*dinitrophenylhydrazone*, m.p. 169°), also obtained from (III), $NaOPr^{\beta}$–$Pr^{\beta}OH$ (or NaOEt–EtOH), and δ-chlorobutan-β-one. (VI) is dehydrogenated (Se; 300—315° for 4 hr. and then 330—340° for 18 hr.) to β-$C_{10}H_7{\cdot}OH$, and hydrogenated (H_2; Pd–$SrCO_3$) to 2-*keto*-10-*methyldecalin*, m.p. 47°, b.p. 95—96°/3 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 152—152·5°). 2-Methyl*cyclo*pentanone (VII), $NHEt_2$,HCl, CH_2O, and EtOH when heated (steam-bath; 4 hr.) afford 2-*methyl*-5-*diethylaminomethyl*cyclo*pentanone*, b.p. 112—114°/17 mm., the methiodide of which when

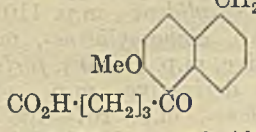
refluxed with $CH_2Ac{\cdot}CO_2Et$–NaOEt–EtOH gives *5-keto-6-carbethoxy-3-methyl-*$\Delta^{4:9}$*-tetrahydrohydrindene*, b.p. 120—125°/3 mm., hydrolysed to impure *5-keto-3-methyl-*$\Delta^{4:9}$*-tetrahydrohydrindene* (*semicarbazone*, m.p. 196—197°; 2 : 4-*dinitrophenylhydrazone*, m.p. 159—160°). (VII) when treated with $NaNH_2$, Et_2O, and (II) yields *5-keto-8-methyl-*$\Delta^{4:9}$*-tetrahydrohydrindene*, b.p. 112°/4 mm. (*semicarbazone*, m.p. 205°; 2 : 4-*dinitrophenylhydrazone*, m.p. 153°). Similarly, *trans*-β-decalone, $NaNH_2$, Et_2O, and (II) give *2-keto-*$\Delta^{1:13}$*-dodecahydroanthracene*, b.p. 152°/3 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 197—198°), dehydrogenated (Se; 290—300°; 6 hr.) to anthracene and β-anthranol. A plausible elaboration of the ring skeleton of the sterols from $COMe_2$ and CH_2O or their biological equivs. is discussed.

XV (Cf. A., 1936, 989). Et 1-keto-7-methoxy-2-methyl-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthrene-2-carboxylate gives a homogeneous *semicarbazone*, m.p. 197—199°. 1-Keto-7-methoxy-1 : 2 : 3 : 4 : 9 : 10-hexahydrophenanthrene (VIII) [*phenylhydrazone*, m.p. 162°; *semicarbazone*, m.p. 238—239° (decomp.)] with $Et_2C_2O_4$ and NaOEt–Et_2O gives its *2-ethoxyoxalyl* derivative $(\cdot CO{\cdot}CO_2Et)_2$, m.p. 90—91°, which reverts to (VIII) when heated. Me δ-keto-η-*m*-methoxyphenyloctoate with conc. H_2SO_4 at —10° gives *Me γ-6-methoxy-3 : 4-dihydro-1-naphthylbutyrate*, b.p. 175—178°/0·2 mm., hydrolysed by KOH–MeOH to the *acid*, which softens at 123° and collapses at 129—130° and when converted into the acid chloride and then treated with $AlCl_3$–*cyclo*hexane–CS_2 gives *1-keto-7-hydroxy-1 : 2 : 3 : 4 : 9 : 10-hexahydrophenanthrene*, m.p. 220—221°, and (VIII). Et 2-methyl*cyclo*hexanone-2-carboxylate (IX) is reduced by $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ giving a mixture, b.p. 118—122°/15 mm., of Et and Pr^{β} *2-methylcyclohexan-1-ol-2-carboxylate* (3 : 5-*dinitrobenzoate*, m.p. 92—93°, of the Pr^{β} ester), which could not be smoothly converted into the corresponding chloride or bromide. With PCl_5 in light petroleum an unsaturated *ester*, b.p. 88—95°/15 mm., was obtained. Other methods for building an additional ring have been examined, and indications of reactions between (IX) and C_2H_2 in presence of K were obtained. (IX) with MgEtI–Et_2O gives a mixture of esters contaminated with the *sec.*-alcohol produced by reduction of the keto-group of (IX). (IX) with $OMe{\cdot}[CH_2]_3{\cdot}MgI$–$Et_2O$ gives an unsaturated substance, b.p. 129°/14 mm., and *Et 2-methyl-1-γ-methoxypropylcyclohexan-1-ol-2-carboxylate*, b.p. 158—168°/13 mm., dehydrated by $KHSO_4$ at 175° to an unsaturated *compound*, b.p. 140—147°/17 mm., hydrogenation of which gives an impure *product*, b.p. 140—144°/13 mm. (IX) with $CH_2Cl{\cdot}CH_2{\cdot}CO_2Et$–Mg–PhOMe–$C_6H_6$ gives a *substance*, b.p. 142—152°/0·3 mm., probably *Et* β-*6-carbethoxy-6-methyl-*$\Delta^{1:2}$*-cyclohexenylpropionate*, and with $COMe_2$ and $NaNH_2$ gives *Et* ζ0*-diketo-α-methyldecoate*, b.p. 138—142°/0·3 mm., which boiled with NaOEt–EtOH gives methyl*cyclo*hexanone and a little $CH_2Ac{\cdot}CO_2Et$. Condensation of Me γ-*m*-methoxyphenylbutyrate (X) with γ-carbomethoxybutyryl chloride (XI) in presence of $AlCl_3$ in CS_2, followed by treatment with Me_2SO_4–KOH, gives *Me γ-[5-methoxy-2-(γ-carbomethoxybutyryl)phenyl]butyrate*, b.p. 205—210°/0·6 mm., cyclised when refluxed with KOMe–C_6H_6 (4 hr.) to Me 1-keto-7-methoxy-1 : 2 : 3 : 4 : 9 : 10-hexahydrophenanthrene-2-carboxylate, hydrolysed to 1-keto-7-methoxy-1 : 2 : 3 : 4 : 9 : 10-hexahydrophenanthrene (A., 1935, 1499). Some 7-hydroxy-1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene was obtained as a by-product of cyclisation. Oxidation of 7-methoxy-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthrol to the corresponding ketone is best achieved by means of CuO at 280—300°.

XVI. *γ-Keto-ζ-m-methoxyphenylheptoic acid*, m.p. 49—51° [*semicarbazone*, m.p. 117—118°; *Me* ester (XII), b.p. 174°/0·3 mm.], obtained by the method of G. M. and R. Robinson (cf. A., 1930, 742) from *γ-m*-methoxyphenylbutyryl chloride and Et sodioacetosuccinate, is reduced by hot Na–EtOH to the *lactone*, b.p. 178°/0·15 mm., of *γ-hydroxy-ζ-m-methoxyphenylheptoic acid*. (XII) when treated with H_2SO_4 at —10° gives *Me* β-(*6-methoxy-3 : 4-dihydro-1-naphthyl)propionate*, m.p. 60—61°, hydrolysed to the *acid* (XIII), m.p. 115°, which when dissolved in aq. Na_2CO_3 and treated with Br–H_2O gives a Br-lactone (XIV), m.p. 100°. (XIII) when heated with Pt-black is dehydrogenated to β-(*6-methoxy-1-naphthyl)-propionic acid* (XV), m.p. 159° (*Na* salt), and is reduced in MeOH by H_2–Pd–$SrCO_3$ to β-(*6-methoxy-1 : 2 : 3 : 4-tetrahydro-1-naphthyl)propionic acid* (XVI), m.p. 77°, the Me ester of which does not react with (XI) in presence of $AlCl_3$. (XII) when treated at 0° with $AlCl_3$–CS_2 yields (XIII), (XV), and (XVI), but when treated at 0° with excess of (XI) in presence of $AlCl_3$–CS_2 and then with Me_2SO_4–NaOH gives (XV) and the *acids*, $C_{19}H_{20}O_6$, m.p. 210°, and $C_{19}H_{24}O_6$, m.p. 144°. Both acids are stable to $KMnO_4$ and react with 2 : 4-dinitrophenylhydrazone, but only the former is unaffected by boiling Ac_2O–NaOAc, and probably is (XVII). Treatment of (X) and phenylethylcarbamyl chloride with $AlCl_3$ in CS_2 followed by hydrolysis of the product affords *γ-(2-carboxy-5-methoxyphenyl)butyric acid*, m.p. 173° after sintering at 165°, which when boiled with Ac_2O is converted into 6-methoxytetralone. The prep. of γ-cyano-α-methylbutyrate (cf. J.C.S., 1900, 77, 947) and its conversion into *γ-carbethoxyvaleryl chloride*, b.p. 134—142°/15—16 mm., are described. *γ-Carbethoxyvalero-β-naphthylamide* has m.p. 76·5—77·5°. H. G. M.



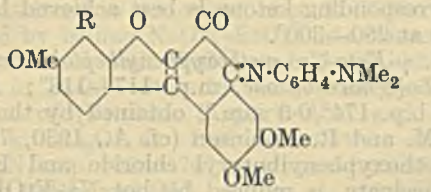
(XIV.)



(XVII.)

Behaviour of open and cyclic ketones towards nitroso-compounds. P. Pfeiffer and H. Böttcher (J. pr. Chem., 1937, [ii], **148**, 126—134; cf. A., 1935, 1369).—Treatment of $COMe{\cdot}CH_2Ph$ with *p*-$NO{\cdot}C_6H_4{\cdot}NMe_2$ and KOH gives *benzylidene-p-dimethylaminoaniline* (I), m.p. 99—100°, whilst indecisive results are obtained with PhNO. (I) accompanied by $CH_2Ph{\cdot}CO_2H$ is also obtained from

p-NO·C_6H_4·NMe_2 and $CO(CH_2Ph)_2$; similar results are obtained with CH_2PhBz and CH_2Ph·CO·CH_2·O·C_6H_4·OMe-*p*. $CO(CH_2Ph)_2$ and PhNO give NHPhBz and CH_2Ph·CO_2H, whilst NHPhBz accompanied by BzOH and *p*-OMe·C_6H_4·O·CH_2·CO_2H, respectively, are derived from CH_2PhBz and CH_2Ph·CO·CH_2·O·C_6H_4·OMe-*p*. Trimethylbrasilone is converted by *p*-NO·C_6H_4·NMe_2



(II.)

into the *compound* (II, R = H), converted by *o*-$C_6H_4(NH_2)_2$ into the *phenazine* derivative, $C_{25}H_{18}O_4N_2$, m.p. 261·5°. Similarly, tetramethylhæmatoxylone yields the *anil* (II; R = OMe) transformed into the *phenazine* derivative, $C_{26}H_{20}O_5N_2$, m.p. 279°. H. W.

Condensation of acetoanthranil derivatives with benzene. M. Hayashi, H. Namikawa, and I. Morikawa (J. Chem. Soc. Japan, 1935, **56**, 1106—1111).—Acetylanthranil and C_6H_6 condense ($AlCl_3$) to yield 2-amino-, m.p. 109—110°, and 2-anilino-, m.p. 121·5—122°, -benzophenone; 2-acetyl-3-methylanthranil similarly affords 2-*anilino*-3-*methylbenzophenone*, m.p. 123—123·5°, and 2-acetyl-5-methylanthranil, 2-*amino*-, m.p. 64—64·5°, and 2-*anilino*-, m.p. 163·5°, -5-*methylbenzophenone*. Ch. Abs. (*r*)

Dihydroresorcinols. IV. Condensation of phenyldihydroresorcinol with aromatic aldehydes. R. D. Desai and M. A. Wali (J. Indian Chem. Soc., 1936, **13**, 735—739).—In presence of $C_5H_{11}N$, phenyldihydroresorcinol (I) with the appropriate aldehyde gives the bis-derivative, dehydrated to the xanthen derivative: *salicylidene*-, m.p. 169—170° (*Ac* derivative, m.p. 145°; 2 : 7-*diphenyl*-4 : 5-*diketo*-9-o-*hydroxyphenyloctahydroxanthen*, m.p. 230°), *benzylidene*-, m.p. 110° (*xanthen* derivative, m.p. 228°), *cinnamylidene*-, m.p. 155—156° (*xanthen* derivative, m.p. >280°), *furfurylidene*-, m.p. 122° (*xanthen* derivative, m.p. >280°), *p*-*dimethylaminobenzylidene*-, m.p. 107—108° (*xanthen* derivative, m.p. 200°), 3 : 4-*methylenedioxybenzylidene*-m.p. 148° (*xanthen* derivative, m.p. >280°), 4-*hydroxy*-3-*methoxybenzylidene*-, m.p. 116° (*xanthen* derivative, m.p. >280°), and *o*-*nitrobenzylidene*-*bisphenyldihydroresorcinol*, m.p. 160° (*xanthen* derivative, m.p. 272°). (I) and *o*-OH·C_6H_4·CHO with HCl yield 2-*phenyl*-4-*keto*-1 : 2 : 3 : 4-*tetrahydrobenzopyranol anhydrochloride*, m.p. >360° (*anhydrobase*, m.p. >360°). With chloral hydrate, (I) yields 1-*phenyl*-4-(α-*hydroxy*-βββ-*trichloroethyl*)cyclo*hexane*-3 : 5-*dione*, m.p. 145—146°, and with $SOCl_2$ affords the *oxide* of 2 : 7-*diphenyl*-4 : 5-*diketo*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydrophenothioxin* (?), m.p. 216°. Similarly dimethyldihydroresorcinol gives the *oxide* of 2 : 2 : 7 : 7-*tetramethyl*-4 : 5-*diketo*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydrophenothioxin* (?), m.p. 181—182°, 1 : 1-*dimethyl*-4-(α-*hydroxy*-ββββ-*trichloroethyl*)cyclo*hexane*-3 : 5-*dione*, m.p. 120°, and *furfurylidene*-, m.p. 160° (*xanthen* derivative, m.p. >280°), and p-*dimethylaminobenzylidene*-*bisdimethyldihydroresorcinol*, m.p. 114° (*xanthen* derivative, m.p. 220°). F. R. S

Transformation of oximinoacetophenone. F. Angelico and S. Cusmano (Gazzetta, 1936, **66**, 791—796).—COPh·CH:N·OH (I) boiled with dil. HCl gives the substance, $C_{16}H_{12}O_3N_2$ (II), m.p. 220°, which is obtained from BzCHO and NH_2OH,HCl (A., 1890, 51), and by other methods (A., 1901, i, 549, etc.). This, previously regarded (A., 1891, 287) as O<CHBz-N:CPh>C:N·OH (III) or, improbably, as O<CBz:N-N:CH->CPh·OH (A., 1907, i, 1086), is now regarded as 4-*oximino*-3-*benzoyl*-5-*phenyl*-4 : 5-*dihydroisooxazole*, O<N:CBz-CHPh>C:N·OH, and as being derived from 2 mols. of (I). BzCHO and NH_2OH,HCl do not give OH·CHBz·COBz [formerly regarded (A., 1897, i, 497) as an intermediate to structure (III), and now found not to yield (II) with NH_2OH,HCl], but (I) and (II). Phenylglyoxime and dil. HCl also give (I). E. W. W.

Manufacture of 3 : 5-di-iodo-4-hydroxyacetophenone and its derivatives substituted in the hydroxyl group.—See B., 1937, 218.

Chelation. V. Hydroxyacetylhydrindene. VI. Hydroxy-derivatives of acetylnaphthalenes, benzonitrile, and carboxylic esters. W. Baker. **VI.** W. Baker and G. N. Carruthers (J.C.S., 1937, 476—479, 479—483; cf. A., 1936, 727).—V. Fixation of the ethylenic linkings in hydrindenes is confirmed by the fact that 5-*hydroxy*-6- (I) is more fully chelated than 5-*hydroxy*-4-*acetylhydrindene* (II); both are chelated, but (I) is more sol. in C_6H_6 and light petroleum, and (I) is volatile and (II) non-volatile in steam. The prep. of 5-acetylhydrindene, its oxime, 5-acetamido-, 5-amino-, and thence 5-hydroxyhydrindene (III) is described. 5-*Acetoxyhydrindene*, b.p. 136°/18 mm., and $AlCl_3$ in CS_2 give readily (I), m.p. 59° (*Ac* derivative, m.p. 88°; *Cu* salt, sol. in $CHCl_3$). 6-*Bromo*-5-*acetoxyhydrindene*, b.p. 169°/16 mm., and $AlCl_3$ in CS_2 give slowly 6-*bromo*-5-*hydroxy*-4-*acetylhydrindene*, m.p. 102—103°, stable to KOH–EtOH at 100°, and, in one case, an *isomeride*, m.p. 115°, both converted by Zn–2% NaOH into (II), m.p. 124·5° (*Cu* salt, sol. in $CHCl_3$).

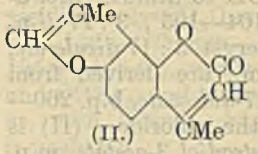
VI. 2 : 1-, m.p. 101°, 1 : 2-, m.p. 64°, and 2 : 3-$C_{10}H_6$Ac·OH (IV), m.p. 112° (preps. described), are much more chelated than the 1 : 4 compound. (IV) gives a (? 1-)*Br*-derivative, m.p. 150°, and does not add maleic anhydride. Its chelation shows it to contain abnormally a $C_{(2-3)}$ ethylenic linking, possibly explicable by resonance. *o*-, *m*-, and *p*-OH·C_6H_4·CN are not chelated, probably owing to the linear nature of the CN. *Et*$_2$ *quinol*-2 : 3-*dicarboxylate*, m.p. 85°, is surprisingly less chelated than the 2 : 5-dicarboxylate, m.p. 133°, and Et_2 resorcinol-4 : 6-dicarboxylate, new m.p. 140°; for this also resonance may provide an explanation. R. S. C.

Application of 2-nitroindan-1 : 3-dione to the isolation and identification of organic bases. G.

Wanag and A. Lode (Ber., 1937, **70**, [*B*], 547—559).—2-Nitroindan-1 : 3-dione (I) yields *salts* with the following bases, usually obtained from the hydrochloride of the bases and (I) in H_2O or EtOH : NH_2Me, m.p. 203—205°; NH_2Et, m.p. 203°; NH_2Pr^{α}, m.p. 184—185°; NH_2Bu^{β}, m.p. 178°; *n*-heptylamine, m.p. 149—150°; *n*-heptadecylamine, m.p. 118—119°; allylamine, m.p. 180—181°; $CH_2Ph{\cdot}NH_2$, m.p. 180°; $CHPhMe{\cdot}NH_2$, m.p. 207°; $CH_2Ph{\cdot}CH_2{\cdot}NH_2$, m.p. 169°; $CHPh_2{\cdot}NH_2$, m.p. 205°; *cyclo*hexylamine, m.p. 213°; camphylamine, m.p. 169°; bornylamine, m.p. 211°; $C_2H_4(NH_2)_2$, m.p. 204—205°; $NHMe_2$, m.p. 210°; $NHEt_2$, m.p. 180—181°; $NHPr^{\alpha}_2$, m.p. 210°; $NHBu^{\beta}_2$, m.p. 231°; di*iso*amylamine, m.p. 190°; $NH(CH_2Ph)_2$, m.p. 203°; NMe_3, m.p. 162°; NEt_3, non-cryst.; NBu^{β}_3, m.p. 111°; *o*-, m.p. 183°, and *p*-$C_6H_4Et{\cdot}NH_2$, m.p. 181°; 1 : 3 : 4-, m.p. 192°, 1 : 3 : 2-, m.p. 185°, 1 : 4 : 2-, m.p. 196°, and 1 : 3 : 5-, m.p. 218°, -xylidine; *o*-, m.p. 183°, and *m*-$C_6H_4Ph{\cdot}NH_2$, m.p. 198° (much decomp.); α-, m.p. 209—210°, and β-$C_{10}H_7{\cdot}NH_2$, m.p. 193°; α-aminofluorene, m.p. 195°; *o*-, m.p. 172—174°, *m*-, m.p. 200°, and *p*-$C_6H_4(NH_2)_2$, m.p. 261—263°; *p*-$NH_2{\cdot}C_6H_4{\cdot}NHAc$, m.p. 212°; 1 : 2 : 4-tolylenediamine, m.p. 183°; benzidine, decomp. 213°; *o*-tolidine, m.p. 216°; $CH_2(C_6H_4{\cdot}NH_2)_2$-4 : 4′, m.p. 248°; 2 : 7-diaminofluorene, m.p. 240° (indef.); $NHPhEt$, m.p. 183°; $NHPhPr^{\alpha}$, m.p. 190—191°; $NHPhBu^{\alpha}$, m.p. 209°; $NHPhBu^{\beta}$, m.p. 207°; *o*-$C_6H_4Me{\cdot}NHMe$, m.p. 190°; *o*-, m.p. 192°, and *p*-$C_6H_4Me{\cdot}NHEt$, m.p. 164°; *o*-$C_6H_4Me{\cdot}NMe_2$, m.p. 150°; *p*-$C_6H_4Me{\cdot}NEt_2$, m.p. 149°; α-$C_{10}H_7{\cdot}NMe_2$, m.p. 153°; *ar*-tetrahydro-α-naphthylamine, m.p. 204°; *ac*-tetrahydro-β-naphthylamine, m.p. 233°; C_5H_5N, m.p. 168°; α-picoline, m.p. 161°; collidine, m.p. 146°; piperidine; quinoline, m.p. 155°; quinaldine, m.p. 157°; 8-methylquinoline, m.p. 160°; acridine, m.p. 183°; 2-aminopyridine, m.p. 197°; quinine, m.p. 186°; strychnine, m.p. 226° (indef.); brucine, m.p. 185°; acetamidine, m.p. 240°; benzamidine, m.p. 195°; guanidine, m.p. 258° (indef.). H. W.

Action of bromine on phenyl *o*-hydroxystyryl ketone. A. Mangini (Gazzetta, 1937, **67**, 39—46).—This ketone and Br in MeOH or AcOH give *Ph* α*β-dibromo*-β-3 : 5-*dibromo*-2-*hydroxyphenylethyl ketone* (I), m.p. 152° (decomp.) (cf. A., 1896, i, 302), oxidised ($KMnO_4$–H_2O) to BzOH or ($KMnO_4$–$COMe_2$) to 3 : 5-dibromosalicylic acid. With KOH–MeOH, (I) is converted (rate of debromination studied) into 5 : 7-*dibromo*-2-*benzoylcoumarone*, m.p. 167—169° (*oxime*, m.p. 200—200·5°; p-*nitrophenylhydrazone*, m.p. 248—249°), also obtained from 3 : 5-dibromosalicylaldehyde (prep. improved) and CH_2BzBr. E. W. W.

Syntheses of 2-acylresorcinols by the Nidhone process. II. 2-Acetylresorcinol. Proof of its constitution. D. B. Limaye and D. D. Gangal (Rasāyanam, 1936, **1**, 64—68; cf. A., 1934, 298).—The orientation of 2-acetylresorcinol [prep. from 8-acetyl-4-methylumbelliferone (I)], m.p. 157° (*Me ether*, m.p. 60°; *semicarbazone*, m.p. 220°; *phenylhydrazone*, m.p. 153°; Bz_2 derivative, m.p. 106°), is proved by oxidation of its Me_2 *ether*, m.p. 73°, by $KMnO_4$ to 2 : 6-*dimethoxyphenylglyoxylic acid*, $+H_2O$, m.p. 98° [*semicarbazone*, m.p. 210° (decomp.)], and thence by H_2O_2 to 2 : 6-$(OMe)_2C_6H_3{\cdot}CO_2H$. This proves also the structure of (I) and of 8-acetyl-7-carbethoxymethoxy-4-methylumbelliferone and the derived acid, m.p. 212°, and ang.-3′ : 4-*dimethyl*-7 : 8-*furocoumarin* (II), m.p. 177°, derived therefrom.

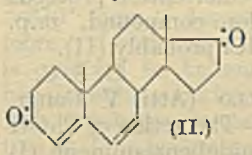


(II.)

R. S. C.

Sexual hormones. XX. Preparation of oxides from Δ^5-cholestenone and Δ^5-androstenedione. XXI. Doubly unsaturated ketones of the androstane series. L. Ruzicka and W. Bosshard (Helv. Chim. Acta, 1937, **20**, 244—249, 328—332).—XX. Cholesterol (I) is oxidised by BzO_2H in $CHCl_3$ at room temp. to α-*cholesterol oxide*, m.p. (impure) 137°, oxidised by CrO_3 in AcOH to 5-*hydroxycholestane*-3 : 6-*dione*, m.p. 246—248°, converted at 250° into Δ^4-*cholestene*-3 : 6-*dione*, m.p. 132°. Cholesteryl acetate is transformed by BzO_2H in $CHCl_3$ into the corresponding *oxide*, m.p. 111—112°, converted by HCl in $CHCl_3$ into 6-*chloro*-5-*hydroxy*-3-*acetoxycholestane*, m.p. 191°. (I) is transformed into the dibromide, which is oxidised and then debrominated by $NaHCO_3$ and Zn dust in boiling EtOH to Δ^5-cholesten-3-one. This is oxidised by BzO_2H to α-, m.p. 202°, and β-, m.p. 122°, -5 : 6-*oxidocholestan*-3-*one*, the latter of which is hydrolysed by $2N$-H_2SO_4 in dioxan to cholestane-3 : 6-dione. Δ^5-Androstenedione gives 5 : 6-*oxidoandrostane*-3 : 17-*dione*, m.p. 265°.

XXI. *trans*Dehydroandrosterone is transformed by Br in AcOH into the dibromide, which when boiled with anhyd. NaOAc in abs. EtOH gives 6-bromoandrostenedione, converted by boiling anhyd. C_5H_5N into $\Delta^{4:6}$-*androstadiene*-3 : 17-*dione* (III), m.p. 173° (corr.). Similarly, Δ^5-androstenediol 17-monobenzoate is transformed into 6-*bromotestosterone benzoate*, m.p. 176—177° (corr.), and thence into *dehydrotestosterone benzoate*, m.p. 246° (corr.). Δ^5-Androstene-3-*trans*-17-diol 17-propionate analogously gives Δ^6-*dehydrotestosterone propionate*, m.p. 134° (corr.). H. W.



(II.)

Biochemical transformation of Δ^4-androstenedione into Δ^4-testosterone. Genesis of the male sexual hormone. L. Mameli and A. Vercellone (Ber., 1937, **70**, [*B*], 470—471).—Addition of Δ^4-androstenedione in EtOH to a fermenting mixture of sugar and yeast gives Δ^4-testosterone. H. W.

Esters of the follicle hormone series. K. Miescher and C. Scholz (Helv. Chim. Acta, 1937, **20**, 263—271).—Œstrone (I) is transformed by the requisite acid anhydride in hot C_5H_5N into the *propionate*, m.p. 134—135·5°, n-*butyrate*, m.p. 101—102·5°, and *valerate*, m.p. 100—101°; the *decoate*, m.p. 71—71·5°, and *palmitate*, m.p. 75·5—76°, are obtained by use of the acid chloride in C_5H_5N at room temp. Œstrone acetate (II) is converted by the Adams catalyst in EtOH into (I); the change appears due to adsorbed alkali since it is not observed

if the catalyst suspension, after pre-reduction, is exactly neutralised by HCl–EtOH to litmus. *Œstradiol* 3 : 17-*dipropionate*, m.p. 104—105°, 3 : 17-*di*-n-*butyrate*, m.p. 64—65°, and non-cryst. 3 : 17-*divalerate*, b.p. 220—230° (bath)/0·05 mm., are derived from the acid anhydride and the 3 : 17-*didecoate*, b.p. 260—265° (bath)/0·001 mm., from the chloride. (II) is reduced (PtO_2 in EtOAc) to *œstradiol* 3-*acetate*, m.p. 136·5—137·5°; the 3-*propionate*, m.p. 124·5—125·5°, and 3-*palmitate*, m.p. 69—71°, are obtained analogously. Œstradiol 17-acetate, m.p. 215—217·5°, is obtained by shaking the diacetate in abs. EtOH at room temp. with freshly reduced PtO_2 catalyst containing alkali. The 17-*monopropionate*, m.p. 198—200°, is obtained similarly, by the action of K_2CO_3 in 90% MeOH or of 0·5*N*-HCl–EtOH. The 17-*monobutyrate* has m.p. 166·5—167°. Œstradiol 3-benzoate is transformed by the requisite acid anhydride in C_5H_5N at 100—105° into *œstradiol* 3-*benzoate* 17-*acetate*, m.p. 172—173°, 17-*propionate*, m.p. 167—167·5°, and 17-n-*butyrate*, m.p. 128·5—129°. The physiological action of the hormone can be greatly increased by suitable esterification. H. W.

Oxonium compounds. Complexes of quinones with hydrochloric, phosphoric, and acetic acids, and their chlorination. V. V. Tschelincev (Compt. rend. Acad. Sci. U.R.S.S., 1937, **14**, 289—291).—Benzoquinone forms dioxonium salts in conc. acids and its reactions are influenced by this fact. Thus, Cl_2 in $CHCl_3$ gives indefinite products : at 0° a substance, m.p. 102°, and at 10° a substance (Cl 19·84%), m.p. 122°. In HCl 2 : 3-di- (I) (*diphenylimide*) or tetra-chlorobenzoquinone (II), or benzoquinone tetrachloride, m.p. 226°, is formed according to the concn. of HCl. In 86% H_3PO_4 (I) is formed more slowly, but in H_3PO_4–HCl chlorination proceeds further. In AcOH a polychloro-compound, m.p. 272°, is formed, and in AcOH–HCl probably (II). R. S. C.

Phenoquinones. M. Covello (Atti V Congr. Naz. Chim., 1936, **1**, 337—345).—The action of PhOH or of quinol on 2 : 6-diphthalimidobenzoquinone (I) in AcOH, EtOH, or $COMe_2$ is studied; quinhydrone and 2 : 6-diphthalimidoquinol are isolated, but no phenoquinones are obtained. This supports the view that in the latter the phenol has become attached to the nucleus, and not to the 1 : 4 O atoms, which in (I) are free to react. E. W. W.

Review of the semiquinone problem. L. Michaelis (Trans. Electrochem. Soc., 1937, **71**, Preprint 17, 185—201).—A review of the evidence for two-stage oxidation–reduction processes of quinonoid substances, and its significance in biology. H. J. E.

Dyes of the anthracene group and their photosensitive capacity.—See A., I, 169.

Spectrographic and chemical study of some aliphatic terpenes. I. Myrcene and its hydrogenation products. G. Dupont and V. Desreux (Bull. Soc. chim., 1937, [v], 4, 422—435).—Mainly a detailed account of work already reported (A., 1936, 1514; this vol., 27). A fraction of lemongrass oil, believed to be methylheptenone, was >50% β-myrcene (I), the purification of which is detailed. With H_2–PtO_2 no H_2-product could be isolated from (I), 2 H_2 being absorbed *en bloc*. Structures are determined mainly by Raman spectra. R. S. C.

Citronellal-terpene. I. Existence of a new terpene, $C_{10}H_{16}$. H. Otsuki (J. Chem. Soc. Japan, 1935, **56**, 1213—1220).—With 50% H_2SO_4 at room temp. citronellal affords *monogene*, $C_{10}H_{16}$, b.p. 184—186°, $[\alpha]_D^{17}$ +49·11° (*nitrosate*, m.p. 154·5—155°), which may be $\Delta^{2:4(8)}$-*p*-menthadiene. Ch. Abs. (*r*)

Isomeration and hydration of pinene. R. W. Charlton and A. R. Day (Ind. Eng. Chem., 1937, 29, 92—95).—Terpinolene, terpineol, terpene hydrate, dipentene (I) and *p*-cymene are identified amongst the acid (H_2SO_4–EtOH) isomerisation and hydration products of α-pinene (II). The vapour-phase isomerism of (II) (ThO_2; 380—425°) affords 55—65% of (I) and camphene. F. N. W.

Constitution of sulphocamphylic acid. J. R. Lewis and J. L. Simonsen (J.C.S., 1937, 457—459).—Bromodihydro-β-camphylic acid (Perkin, J.C.S., 1898, **73**, 827; improved prep.) is 4-*bromo*-2 : 3 : 3-*trimethyl*-Δ^1-cyclo*pentenecarboxylic acid*, since O_3–EtOAc at 0° converts it into liquid $CMe_2Ac{\cdot}CHBr{\cdot}CH_2{\cdot}CO_2H$ (*semicarbazone*, m.p. 190°), further oxidised by NaOBr at 0° to $CHBr_3$ and *trans*-αα-dimethylglutaconic acid. Sulphocamphylic acid (I) is therefore 4-*sulpho*-2 : 3 : 3-*trimethyl*-Δ^1-cyclo*pentene*-1-*carboxylic acid*, and its oxidation product, sulphopimelic acid, is β-*sulpho*-αα-*dimethylglutaric acid*, converted by pyrolysis at 160—170°/reduced pressure into a mixture of *cis*- and *trans*-$CO_2H{\cdot}CMe_2{\cdot}CH{:}CH{\cdot}CO_2H$, and not, as stated by Koenigs *et al.* (A., 1893, i, 363; 1894, i, 47), into terebic acid. (I) with O_3 gives an oil ($CHBr_3$ with NaOBr), converted by heating at 130—140° into an *acid*, $C_{16}H_{20}O_4$, m.p. 145—147°. Ozonolysis of the Me ester of (I) gives an *ozonide*, m.p. 83—85°, from which no cryst. products could be isolated. J. W. B.

Reactivities of α- and β-campholides. Preparation of the corresponding hydroxycampholic acids. F. Salmon-Legagneur and J. Vene (Bull. Soc. chim., 1937, [v], **4**, 448—462).—When α- and β-campholide (modified preps.) are heated with alkali, cooled, and then treated with acid (excess avoided; Congo-red), α-, m.p. 119°, $[\alpha]_D^{15}$ +56·8° in EtOH, and β-*hydroxycampholic acid*, m.p. 116—117°, $[\alpha]_D^{15}$ +54·8° in EtOH, are obtained. The rate of hydrolysis of the α-lactone is 4 times that of the β-lactone. The rate of lactonisation of the β-acid is 7 times that of the α-acid, $H^{\cdot}$ being a potent catalyst. R. S. C.

Optical activity and chemical constitution. III. Optically acids and bases. Mahan Singh and Manohar Singh (J. Indian Chem. Soc., 1936, **13**, 744—746).—Camphoric anhydride and aminodimethylanilines condense to 4′-, m.p. 193°, 3′-, m.p. 120°, and 2′-*dimethylaminocamphoranilic acid*, m.p. 152—153°, and *camphoro*-o-*dimethylaminophenylimide* (I), m.p. 149°. The rotatory powers of these substances have been determined in MeOH, EtOH, and $COMe_2$. The addition of HCl to the 2′-acid increases [α] considerably; addition of HCl to the 4′-acid decreases, and that of NaOH slightly increases, [α]. In MeOH,

$[\alpha]_D$ is: 4′- +69·82°; 3′- +55·7°; 2′-acid 0°; (I), +14·35°. F. R. S.

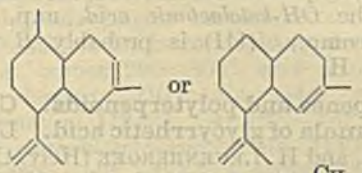
Contact changes of camphor. Y. FUJITA (J. Chem. Soc. Japan, 1935, **56**, 1210—1212).—Camphor vapour passed through a Cu tube containing active C at 480—500° gives carvenone, carvacrol, *o*-cresol, *p*-cymene, and cumene. CH. ABS. (*r*)

Sulphonation of camphor. Y. ASAHINA [in part with K. YAMAGUTI] (Proc. Imp. Acad. Tokyo, 1937, **13**, 38—40).—The formation of camphor-ω-sulphonic acid (I) is explained as due to addition of H_2SO_4 to the $C{:}CH_2$ of 1-hydroxycamphene (II), derived through a retropinacolin inversion of camphor in the *o*-ketonic form; (I) can be prepared in good yield from (II). Formation of camphor-π-sulphonic acid is ascribed to addition of H_2SO_4 to 4-hydroxycamphene (formed by interchange of OH with a *gem*-Me, followed by loss of H_2O), after which the *gem*-Me migrates back, with ring-isomerisation. The racemisation of camphor, but not of α-bromocamphor, during sulphonation, is ascribed to hindrance by the Br of addition of H_2SO_4 to the camphor-enol, which, it is suggested, precedes a Wagner change. E. W. W.

Reduction products of 2 : 6-diketocamphane. Y. ASAHINA and T. TUKAMOTO (Ber., 1937, **70**, [*B*], 584—588).—Reduction of 2 : 6-diketocamphane (I) with Zn dust in well-cooled HI gives only 6-*hydroxycamphor*, m.p. 130°, [α] ±0° in EtOH (*semicarbazone*, m.p. 200°), purified through the 3 : 5-*dinitrobenzoate*, m.p. 146°, and oxidised by CrO_3 in AcOH to α-camphol-onic acid (II). Reduction of 2 : 6-diketocamphanedi-oxime (Pd–C in AcOH) affords 2 : 6-*diketocamphane-monoxime*, m.p. 170°, converted by dil. KOH into the oxime of (II) and by $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$ into the *oxime-semicarbazone*, m.p. 219°, of (I). (I) with Zn dust and HI gives the *ketimine hydriodide*, $C_{10}H_{18}N_2I_2$, m.p. 232—235°, converted by the successive action of alkali and warm dil. HCl into (II). α-Nitro-camphene (III) is transformed by KOH–EtOH into iso*nitrocamphene* (III), m.p. 114° (corresponding *ψ-nitrole*, m.p. 112—113°), which immediately de-colorises $KMnO_4$ and passes when melted into (IV). Oxidation of (III) gives α-camphenone (V), the semi-carbazone, m.p. 213·5°, of which is converted by NaOEt–EtOH at 160° into camphene. (V) with 95% HCO_2H at 120—125° affords *hydroxydihydro-β-campholenolactone*, m.p. about 35°, and with Na–EtOH it yields 6-*hydroxycamphene* (VI), m.p. 114°. Attempted hydration of (VI) by 50% H_2SO_4 in AcOH at 60° leads to 6-*acetoxycamphene*, b.p. 70—72°/14 mm., and a *substance*, b.p. 180°/14 mm., which is stable to $KMnO_4$, decolorises Br in $CHCl_3$, and is probably a product of the polymerisation of α-hydroxycamphene. H. W.

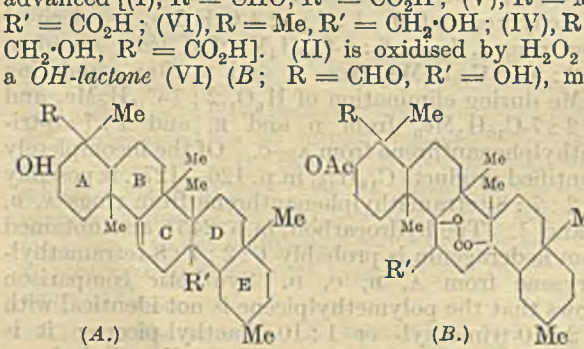
Reversal of optical rotation in the camphene rearrangement. S. S. NAMETKIN and A. I. SCHAV-RIGIN (J. Gen. Chem. Russ., 1937, **7**, 3—5).—Polemical in reply to Houben *et al.* (A., 1936, 729). R. T.

Essential oil of *Lantana camara*, L. II, III. K. KAFUKU, T. IKEDA, and C. HATA (J. Chem. Soc. Japan, 1935, **56**, 1184—1191).—From the oil are isolated *camerene* (I), b.p. 263°, n_D^{30} 1·500, $[\alpha]_D^{27}$ +6·74°, oxidation of which (O_3) yields CH_2O and $COMe_2$ and a non-volatile residue containing succinic acid iso*camerene*, b.p. 253°, n_D^{30} 1·4925, $[\alpha]_D^{27}$ −11·21° yielding only CH_2O on oxidation, and *micranene* (II), b.p. 126—8°/5 mm., n_D^{30} 1·5050 (*hydrochloride*, m.p. 105·5—106·5°), which on oxidation (O_2) gives CH_2O and $COMe_2$, and a residue yielding a salt $C_{14}H_{21}O_4Ag$ or, with $KMnO_4$, hexahydromellophanic acid. (II) is probably



CH. ABS. (*p*)

Polyterpenes and polyterpenoids. CX. Trans-formation of gypsogenin into hederagenin. L. RUZICKA and G. GIACOMELLO (Helv. Chim. Acta, 1937, **20**, 299—309; cf. A., 1936, 1514).—The more freely sol. acetate, m.p. 176—177°, from gypsogenin (I) now designated *acetylgypsogenin* (II) is transformed by HCl–AcOH at 100° into iso*acetylgypsogeninolactone*, m.p. 331—332° (decomp.), $[\alpha]_D^{20}$ +33°, and is hydro-lysed by conc. HCl in MeOH–$CHCl_3$ to (I), which, like the original material, has m.p. 268—271° (corr.) after softening at 240° and from which by sublim-ation at 210°/high vac. a small amount of material, m.p. 272—276° (corr.), is derived. Analyses of this material, which is monobasic, agree well with the formula $C_{30}H_{46}O_4$. The sparingly sol. acetate, m.p. 262° (*loc. cit.*), now termed "*acetylgypsogeninolactone*" (III), is neutral and is formed in small amount when (II) is boiled with MeOH or EtOH; it gives non-cryst. products when hydrolysed. Oxidation of the Br-lactone (*loc. cit.*) of (II) in AcOH by CrO_3 in presence of H_2SO_4 yields an *acid*, $C_{32}H_{47}O_6Br$, m.p. >310° (corr.; decomp.) [*Me* ester, m.p. 238—240° (corr.; decomp.)]. (I) therefore contains ·CHO. It is oxidised to hedragone so that it is a dehydro-hederagenin containing ·CHO in place of $\cdot CH_2{\cdot}OH$. This conclusion is confirmed by the catalytic reduc-tion of (I) to hederagenin (IV). The conversion of (I) into oleanolic acid (V) and (IV) and Zimmermann's oxidation of erythrodiol (VI) to (V) establish the close relationship of the four natural triterpenes, which are stereochemically alike and differ in the structure of two side-chains. The structure *A* is therefore advanced [(I), R = CHO, R′ = CO_2H; (V), R = Me, R′ = CO_2H; (VI), R = Me, R′ = $CH_2{\cdot}OH$; (IV), R = $CH_2{\cdot}OH$, R′ = CO_2H]. (II) is oxidised by H_2O_2 to a *OH-lactone* (VI) (*B*; R = CHO, R′ = OH), m.p.



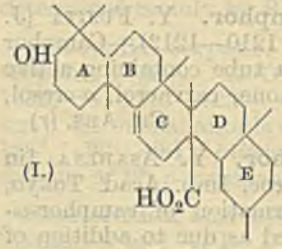
(*A.*) (*B.*)

276—278° (corr.; decomp.), which is neutral, does not give a yellow colour with $C(NO_2)_4$, and gives a Ac_2 derivative, m.p. 226—228° (corr.). (VI) is oxid-

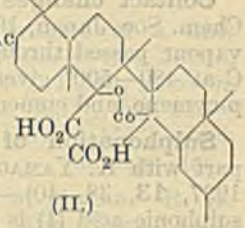
ised by CrO_3 in AcOH to the *ketolactone* (*B*; R = CHO, R′ = :O), m.p. 245° (corr.; decomp.), $[\alpha]_D^{16}$ +29° in $CHCl_3$ [*dioxime*, m.p. 226° (corr.; decomp.)], and by CrO_3 in presence of H_2SO_4 to the *acid* (VII) (*B*; R = CO_2H; R′ = :O), m.p. 309—311° (corr.), which neutralises 3 mols. of KOH in boiling EtOH, and gives an *oxime*, m.p. 239—240° (corr.; decomp.), and a *Me* ester, m.p. 277—280° (corr.); (VII) is hydrolysed to the *OH-ketolactonic acid*, m.p. 329—332° (corr.; decomp.). (III) is probably *B* with R = CHO, R′ = H. H. W.

Polyterpenes and polyterpenoids. CXI. Empirical formula of glycyrrhetic acid. L. Ruzicka, M. Furter, and H. Leuenberger (Helv. Chim. Acta, 1937, **20**, 312—325; cf. this vol., 68).—New analytical data confirm the formula $C_{30}H_{46}O_4$ for glycyrrhetic acid (I). The authors' results are considered in conjunction with those of Voss *et al.* (this vol., 87) and Bergmann *et al.* (A., 1934, 328; this vol., 203). Hydrolysis of glycyrrhizin to (I) is readily achieved with conc. HCl at 50°. (I) is isolated in two forms which are regarded as cryst. modifications, not isomerides. Analyses are recorded of (I), its Me ester (II), acetylglycyrrhetic acid (III) and its Me ester (IV). Prolonged hydrolysis of (II) or (IV) with 0·1*N*- and 0·5*N*-KOH–EtOH give the vals. leading to the formula $C_{30}H_{46}O_4$ when the more conc. alkali is used; with the dil. alkali a part of the ester remains intact. Titrations of (I) and (III) also establish $C_{30}H_{46}O_4$ for (I). Rast's method of determining the mol. wt. is regarded as inapplicable to (I) on account of its very sparing solubility and re-calculation of Bergmann's röntgenographic data leads to the val. 468·8±24, in good agreement with the calc. val. for $C_{30}H_{46}O_4$. (I) does not give a semicarbazone or oxime and (III) is unchanged when boiled with Ac_2O and C_5H_5N. (I) does not accept O when titrated with BzO_2H. Since a double linking has not been detected in (I) the presence of 6 rings is probable. (I) is dehydrogenated by Se to sapotalin, 2 : 7-$C_{10}H_6Me_2$, and a polymethylpicene, m.p. 306°. H. W.

Polyterpenes and polyterpenoids. CXII. Structure of the rings C—E of the pentacyclic triterpenes. L. Ruzicka, M. W. Goldberg, and K. Hofmann (Helv. Chim. Acta, 1937, **20**, 325—328).—The modified constitution (I) is advanced for oleanolic acid. Of the isolated and identified products of dehydrogenation 1 : 2 : 3 : 4-$C_6H_2Me_4$ is derived from ring A, 1 : 5 : 6 : 2-$C_{10}H_4Me_3$·OH from A and B, 1 : 2 : 5 : 6-$C_{10}H_4Me_4$ from A and B after wandering of Me during elimination of H_6O, 2 : 7-$C_{10}H_6Me_2$ and 1 : 2 : 7-$C_{10}H_5Me_3$ from D and E, and 1 : 7 : 8-trimethylphenanthrene from A—C. Of the incompletely identified products $C_{18}H_{18}$, m.p. 126—127°, is possibly 1 : 2 : 7 : 8-tetramethylphenanthrene from rings A, B, C, and ?. The hydrocarbon, m.p. 245°, also obtained from hederagenin is probably 1 : 2 : 7 : 8-tetramethylchrysene from A, B, C, D. Synthetic comparison shows that the polymethylpicene is not identical with 1 : 2 : 10-trimethyl- or 1 : 10-dimethyl-picene; it is probably 1 : 2 : 8-trimethyl- or 1 : 8-dimethyl-picene or a mixture of these substances. Dehydrogenation of amyrin gives a *hydroxypicene*, $C_{24}H_{18}O$, m.p. 330—331°, the *Me ether*, m.p. 358—359°, of which is provisionally regarded as 2-methoxy-1 : 8-dimethylpicene. Very significant for the constitution is the



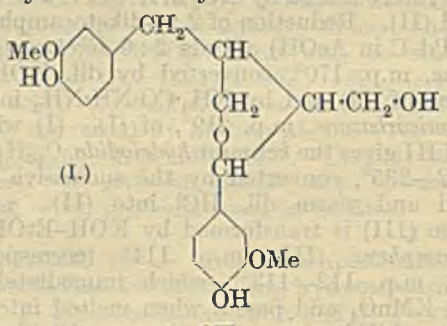
(I.)



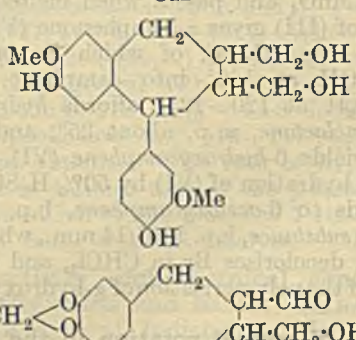
(II.)

conversion of (I) into the acetyl-lactonedicarboxylic acid, to which structure (II) is assigned; this readily explains its dehydrogenation to 2 : 7-$C_{10}H_6Me_2$. The previous location of the double linking in ring E was due to the observation of Schicke and Wedekind (A., 1933, 612) that acetyloleanolic acid is oxidised to "acetylviscolic acid" with loss of 5 C; repetition of this work shows that the sole acidic product is (II). (I) in rings A—C contains an ordered chain of four isoprene residues such as is present in most diterpenes whereas the remaining two residues which constitute rings D and E are irregularly arranged. H. W.

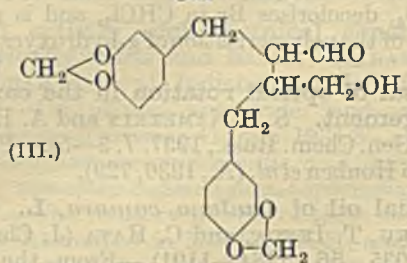
Constituents of natural phenolic resins. VIII. Lariciresinol, cubebin, and some stereochemical relationships. R. D. Haworth and W. Kelly (J.C.S., 1937, 384—391).—Lariciresinol (I), $C_{20}H_{24}O_6$, m.p. 167—168°, $[\alpha]_D^{14}$ +19·7° in $COMe_2$, forms a *Me*$_2$ *ether*, m.p. 79—80°, a *Et*$_2$ *ether*, m.p. 103—104°, and is readily isomerised by dil. acids to iso*lariciresinol*



(I.)



(II.)



(III.)

(II), m.p. 112°, $[\alpha]_D^{14}$ +69·4° in $COMe_2$ [*Me ether*, m.p. 134—135°; *Ac*$_4$ derivative, m.p. 162°; *Me*$_2$ *ether*

(+H_2O), m.p. 166—167°; *Et_2 ether*, m.p. 168°, and its *Ac_2* derivative, m.p. 114—115°, $[\alpha]_D^{15}$ +21·7° in $COMe_2$]. (I) with MeOH–HCl yields *anhydroisolariciresinol*, m.p. 209—210°, $[\alpha]_D^{14}$ +7·9° in AcOH (*Me_2 ether*, m.p. 146—147°, $[\alpha]_D^{16}$ −33·4° in $COMe_2$; *Et_2 ether*, m.p. 132—133°). Oxidation ($KMnO_4$) of the Me_2 and Et_2 ethers of (I) and also of the Me_2 and Et_2 ethers of (II) affords respectively veratric and 3-methoxy-4-ethoxybenzoic acids, and 2-veratroylveratric and 5-methoxy-4-ethoxy-2-(3′-methoxy-4′-ethoxybenzoyl)benzoic acids. Conversion of (I) into (II) involves cyclisation of a diarylbutane into a 1-$C_{10}H_7Ph$ derivative. Oxidation (NaOBr) of the Me_2 ether of (II) gives *l*-conidendrin Me_2 ether, identified by dehydrogenation to the lactone of 6:7-dimethoxy-1-(3′:4′-dimethoxyphenyl)-2-hydroxymethylnaphthalene-3-carboxylic acid. These results are in agreement with the structures assigned. Cubebin, m.p. 132°, $[\alpha]_D^{14}$ −17·1° in $COMe_2$ (*semicarbazone*, m.p. 144°), is (III). It is suggested that matairesinol, hinokinin, arctigenin, olivil, and 1-phenylnaphthalene derivatives, *e.g.*, conidendrin, have a *trans*-configuration, whilst (I) and pinoresinol are *cis*-isomerides. F. R. S.

Constitution of soloric acid. G. Koller and H. Russ (Monatsh., 1937, **70**, 54—72).—Extraction of the thalli of *Solorina crocea*, L., with Et_2O and crystallisation of the product from C_6H_6 followed by sublimation in a high vac. gives soloric acid (I), m.p. 203·5° (vac.), $[\alpha]$ ±0°, which is uniform according to chromatographic analysis (Al_2O_3). It contains 1 OMe. (I) is transformed by Ac_2O containing conc. H_2SO_4 at 100° into the *triacetate*, m.p. 147°, hydrolysed by KOH–MeOH to (I), and by Me_2SO_4–KOH into the *Me_3 ether*, m.p. 130·5° (vac.), and therefore contains 3 OH. Distillation of (I) with Zn dust affords 2-methylanthracene. (I) with Zn dust and boiling AcOH affords the corresponding *anthranol*, $C_{21}H_{22}O_6$, m.p. 173° (vac.), oxidised by air in alkaline solution to (I). (I) with NH_2OH in boiling EtOH yields *soloric acid oxime*, m.p. 223° (vac.; decomp.); the behaviour of other tetrahydroxyanthraquinones shows that the quinone grouping remains intact under these conditions. Treatment of (I) with PhOH and HI (*d* 1·7) at 150° affords MeI, *n*-hexoic acid (II), and 1 : 3 : 6 : 8-tetrahydroxyanthraquinone (III), m.p. 334° [*tetra-acetate*, m.p. 196° (vac.; decomp.); *Me_4* derivative, m.p. 241—242°]. (III) is transformed into anthracene by distillation with Zn dust and into a *compound*, $C_{14}H_8O_6$, m.p. >360°, by atm. oxidation. Drastic oxidation of (I) by $KMnO_4$ gives (II), whilst milder treatment appears to yield a little MeCHO. Hydrogenation (Pd–C in AcOH) of (I) gives probably a *methoxyhexatetradecahydroanthracene* (IV), m.p. 166° after softening at 165°, an *isomeride*, b.p. 125—132°/0·001 mm., and possibly a *hexylperhydroanthracene* (V), $C_{20}H_{36}$, b.p. 99—116°/0·001 mm. Analogous treatment of 1 : 4 : 5 : 8-tetrahydroxyanthraquinone shows that the ring is affected since the *compound*, $C_{14}H_{18}O_3$, m.p. 168°, is produced. Dehydrogenation of perhydroanthracene by Se at 260—290° gives anthracene but analogous treatment of (IV) and (V) gives ill-defined results. (I) is therefore 1 : 3 : 8-*trihydroxy*-6-*methoxy*-2-n-*hexoylanthraquinone*. H. W.

I (A., II.)

Bitter principles of Colombo root. V. Methylation of columbin. F. Wessely and K. Jentzsch (Monatsh., 1937, **70**, 30—36; cf. A., 1936, 1515).—Treatment of columbin (I) or *iso*columbin (II) with Me_2SO_4 and NaOH affords *methylcolumbin* (III), $C_{21}H_{24}O_6$, m.p. 225° (decomp.), $[\alpha]_D^{16}$ +64·52° in C_5H_5N, in which the function of the O is similar to that in (I) or (II) except as concerns OMe. The action of alkali on (III) depends largely on conditions and, under drastic conditions, leads to unchanged (III), a *substance*, m.p. about 290—300°, and a dibasic *acid*, $C_{21}H_{26}O_7$, decomp. 210° (*Me_2* ester, m.p. 119·5° after softening at 116·5°). At 190—210° (III) yields CO_2 and *methyldecarboxycolumbin* (IV), $C_{20}H_{24}O_4$, m.p. 205—204°, $[\alpha]_D^{14}$ −383·7° in anhyd. C_5H_5N, which cannot be obtained by methylation of decarboxycolumbin or *-iso*columbin (V). (IV) reacts with the amount of NaOH required for one lactone group and the solution when acidified yields (V). This unusual hydrolysis of OMe is not observed when (III) is treated similarly. H. W.

Sapogenins. II. Sarsasapogenin and smilagenin. S. N. Farmer and G. A. R. Kon (J.C.S., 1937, 414—420).—Sarsasapogenin (I) forms a *Me ether*, m.p. 153—155°, and its Ac derivative is oxidised (H_2CrO_4) to the *acetate* of a lactone (II), $C_{24}H_{36}O_4$, m.p. 184—185°, $[\alpha]_D^{25}$ −32° in $CHCl_3$ (also obtained by oxidation of smilagenin acetate), a *lactone*, $C_{20}H_{30}O_4$, m.p. 220°, and a *Me* ester, $C_{30}H_{44}O_{11}$, m.p. 199—200°. (II) with HBr affords a *lactone*, $C_{24}H_{34}O_3$, m.p. 201°, and a *lactone*, $C_{22}H_{32}O_2$, m.p. 99°. Hydrolysis (KOH–EtOH) of (II) yields the *OH-lactone*, $C_{22}H_{34}O_3$, m.p. 202°, $[\alpha]_D^{25}$ −36·2° in $CHCl_3$, oxidised (H_2CrO_4) to a *keto-lactone*, m.p. 184·5°, which is reduced (Clemmensen) to a deoxy-lactone, m.p. 133·5° (cf. Jacobs *et al.*, A., 1935, 1130). The deoxylactone with MgPhBr gives a *diphenylcarbinol* (+$COMe_2$), m.p. 205·5°, oxidised (H_2CrO_4) to an *acid*, $C_{37}H_{42}O_2$, m.p. 212—213°, and ætiobilianic acid. Dehydration with $SOCl_2$–C_5H_5N of 3-*methylcholestan*-3-*ol*, m.p. 147°, from β-cholestanone, gives 3-*methyl*-$\Delta^{3(?)}$-*cholestene*, m.p. 81—82°, but dehydration with Se yields 3-*methylcholestane*, m.p. 96—97°, or under different conditions a *dimethylcyclopentenophenanthrene*, m.p. about 165° [*s*-$C_6H_3(NO_2)_3$ *complex* (III), m.p. 165°]. A sample of a hydrocarbon prepared by Se dehydrogenation affords a $C_6H_3(NO_2)_3$ *complex*, m.p. 174—175°, from which an impure hydrocarbon, a methylcyclopentenophenanthrene, regenerated forms a *picrate*, m.p. 145—146°, *s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 181—182°, and *styphnate*, m.p. 175—176°. Sarsasapogenone with MgMeI gives *methylsarsasapogenin*, m.p. 185°, dehydrogenated to an impure *hydrocarbon*, $C_{19}H_{16}$, m.p. 215—216° (?), the *s*-$C_6H_3(NO_2)_3$ complex of which is identical with (III); a portion of the hydrocarbon yields a *s*-$C_6H_3(NO_2)_3$ *complex*, m.p. 161—163°. (I) belongs to the coprostane series and the side chain is attached to ring IV at $C_{(17)}$ and one of the oxide rings to $C_{(16)}$. F. R. S.

Glycyrrhetic acid. E. Bergmann and F. Bergmann (Helv. Chim. Acta, 1937, **20**, 207—208; cf. Ruzicka *et al.*, this vol., 202).—The isolation of a trimethylpicene, $C_{25}H_{20}$, from the products of the dehydrogenation of glycyrrhetic acid excludes the

possibility of the author's formula $C_{23}H_{36}O_5$. Treatment of $(NH_4)_2$ glycyrrhizate with NaOH and Me_2SO_4 gives the *Me H* ester, decomp. 263—264°, whereas the *Me*$_3$ ester, decomp. 267°, is obtained by use of CH_2N_2. H. W.

Resin alcohol, $C_{25}H_{41}O_2$·OH, + 0·5EtOH, m.p. 272·5° (acetate, m.p. 188·5°), from *Periploca aphylla*.—See A., III, 191.

Eloxanthin, a new carotenoid pigment from the pondweed *Elodea canadensis*. D. Hey (Biochem. J., 1937, **31**, 532—534).—*Eloxanthin*, $C_{40}H_{56}O_3$, m.p. 182·5—183°, $[\alpha]_{Cd}^{18}$ +225° in C_6H_6, from the leaves of *E. canadensis*, contains 3 active H atoms (Zerevitinov) and 11 double linkings of which 9 are in conjugation (suggested by absorption data) and is isomeric with flavoxanthin but gives no colour reaction with 25% HCl. It is accompanied with carotene but lutein could not be detected. P. W. C.

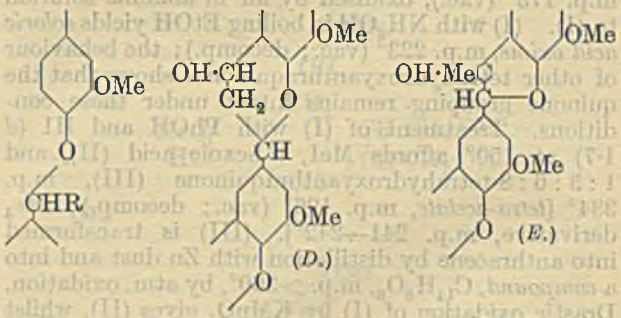
Limonin, the bitter principle of orange kernels. II. G. Koller and H. Czerny (Monatsh., 1937, **70**, 26—29; cf. A., 1936, 857).—Limonin (I) has m.p. 280°, $[\alpha]_D^{20}$ −142·85° in CH_2Cl_2. Fresh determinations of the mol. wt. of hexahydrolimonic acid are recorded. (I) is very probably identical with Feist's citrolimonin (A., 1936, 995). H. W.

Constitution of ammoresinol. H. Raudnitz, K. Lanner, and E. Deutschberger (Ber., 1937, **70**, [*B*], 463—465; cf. A., 1936, 1259).—Repetition of the work of Späth (A., 1936, 1119) on the dissolution of diacetylhexahydroammoresinol (I) in warm 5% KOH and its subsequent oxidation with $KMnO_4$ (≡ 9 O) at room temp. shows the product to be γηλ-trimethyl-*n*-tridecoic acid, b.p. 140°/0·15 mm. (*Me* ester, m.p. 120—125°/0·15 mm.; p-*bromophenacyl* ester, m.p. about 25°). (I) gives a distinct yellow colour with $C(NO_2)_4$ in $CHCl_3$ and hence does not contain a latent double linking. H. W.

Occurrence of acetone and syringic aldehyde as degradation products of lignin substances. A. Bell, W. L. Hawkins, G. F. Wright, and H. Hibbert (J. Amer. Chem. Soc., 1937, **59**, 598).—Stepwise oxidation or ozonolysis of HCO_2H-spruce lignin gives $COMe_2$, whilst alkaline fission of sulphite liquor from yellow birch wood affords syringic aldehyde. H. B.

"Cuproxam" lignins. Action of Schweitzer's reagent on wood and other components of plants. R. S. Hilpert and Q. S. Woo (Ber., 1937, **70**, [*B*], 413—421).—Prolonged treatment of pine wood with Schweitzer's reagent (I) dissolves about 80% of the material. The residue contains 8% OMe and 1·8% N which is so firmly retained that it is not removed by boiling 1% H_2SO_4 although 24% of the substance is dissolved; treatment of it with 72% H_2SO_4 leaves 47% of material with 15% OMe and 1·7% N. It is impossible by this method to obtain a N-free substance. Reaction between wood and NH_3 occurs in absence of Cu compounds but only about 0·5% of N is retained in the product. The dissolved portion is not homogeneous cellulose (II) since it is incompletely pptd. by acids and the ppt. contains 2·1—2·6% OMe and N. White beech behaves similarly. When treated with (I), straw, jute, and sisal leave only a small residue which contains an increased % of C and OMe and about 1% of N or 2·2% in the case of straw. Asparagus fibre (III) is largely dissolved and the residue is richer in C and H but not in N; the first ppt. contains 9% N, but this may be due to a component, rich in N, of the original material since the composition of the subsequent ppts. is similar to that from straw and jute. The product of the action of $NaHSO_3$ on (II) is almost completely sol. in (I) and the undissolved portion differs in C and H content from (II) or lignin. The dissolved material is closely similar to (II) and contains very little N. The product (IV) obtained from (III) and $NaHSO_3$ when treated with (I) leaves a residue richer in C and H than any product similarly prepared; the material pptd. by acid has the same C–H content as (IV) but the N content is increased from 0·27% to 1·12%. Union with N under the influence of (I) is a general phenomenon of the treatment of all parts of plants. The N content of the insol. product usually increases with the C content. The precipitable product has the composition of (II) only when this is possessed by the initial product (V); otherwise the composition lies between those of (II) and (V). It cannot therefore be assumed that (II) is present in the free form in the greater part of the skeleton matter of plants. The bearing of the experiments on the genesis of coal is discussed. H. W.

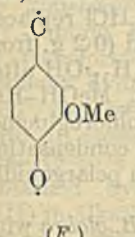
Lignin. XVI. Pine lignin. K. Freudenberg, M. Meister, and E. Flickinger (Ber., 1937, **70**, [*B*], 500—514).—Lignin (I) is composed of simple units united by etherification. The side-chain of the unit consists of the biologically equiv. forms, OH·CH_2·CH(OH)·CH(OH)·, CHO·CH_2·CH(OH)·, or COMe·CH(OH)·, and the nucleus is of the type of vanillin, piperonyl, or, possibly, *iso*vanillin. The assumption that etherification is concerned only with the primary OH is unnecessary and uniformity is secured in the sense, *A*—*C*. The physiological or



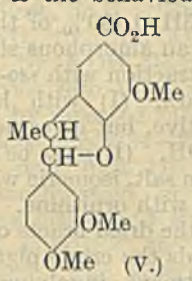
A. R = ·CH(OH)·CH_2·OH. *B*. R = CH_2·CHO.
C. R = COMe.

post-mortal condensation to *D* or *E* is thus readily explained. From the % CH_2O obtained from (I) it appears that (I) is composed of about 7 units in ethereal linking according to *A*, *B*, and *C* and probably exists thus in the primary lignin of young wood. Condensation according to *D* or *E* takes place in the wood and, postmortally or under the influence of chemical reagents, condensation of CO of *B* and *C* with terminal CO of *D* or *E* occurs with production of three-dimensional products of high mol. wt. Moderated treatment of (I) with alkali followed by methyl-

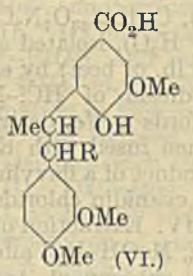
ation and oxidation gives veratric (II) (10%), *iso*-hemipinic (III) (3%), and 2 : 3 : 2′ : 3′-tetramethoxydiphenyl-5 : 5′-dicarboxylic acid (IV). It is uncertain whether (IV) exists pre-formed in (I) or is formed during the degradation. (III) does not appear to be derived from (IV). Degradation, ethylation, and oxidation of (I) affords 3-methoxy-4-ethoxybenzoic acid in 10% yield. Protocatechuic acid and (II) are therefore derived from the arrangement *F*. Lignin-sulphonic acid, purified through the quinoline salt and by electrodialysis, when methylated and oxidised gives 1—2% of (II) and nearly 1% of (III). Lignin-thiolacetic acid does not give aromatic acids when oxidised. When methylated and then oxidised it yields 4% of (II) and 3% of (III); (IV) is not produced. As model experiment for the production of (III) from *D* or *E* the behaviour of Erdtman's acid



(*F*.)



(V.)



(VI.)

(V) has been investigated. When oxidised it gives exclusively (II) in 32% yield (calc. 53%). When treated successively with alkali and CH_2N_2 and then oxidised it yields 21% of (II) and 5% of (III). (V) is converted by SO_3'' into the non-cryst. *sulphonic acid* (VI; R = SO_3H); the non-cryst. *Me* ester is oxidised to 17% of (II) and 4% of (III), thus closely resembling methylated ligninsulphonic acid. (V) and $SH{\cdot}CH_2{\cdot}CO_2H$ yield a product containing the *analogue* (VI; R = $\cdot S{\cdot}CH_2{\cdot}CO_2H$) which when methylated, hydrolysed, and then oxidised affords 7·4% of (II) and 3% of (III). Holmberg's model experiments with $CHPhMe{\cdot}OH$ and $CHPh_2{\cdot}OH$ and $SH{\cdot}CH_2{\cdot}CO_2H$ are discussed. The actions of alkali, SO_3'', and $SH{\cdot}CH_2{\cdot}CO_2H$ on (I) are reviewed. H. W.

Alkaline degradation of pine wood. II. R. S. Hilpert and O. Peters (Ber., 1937, 70, [*B*], 514—517).—Successive treatments of pinewood with NaOH–H_2O and CH_2PhCl give a *CH_2Ph* derivative which very closely resembles benzylcellulose and is extensively sol. in conc. HCl. The presence of benzyl-lignin is not detectable. Lignin obtained from wood by acids is therefore a reaction product and not a component thereof. Pine wood is converted by NaOH followed by CS_2 into a *xanthate* which is completely sol. in H_2O. Addition of acid to the solution ppts. a material (yield 50%) with 4·7% OMe and the composition of a cellulose anhydride, $2C_6H_{10}O_5 - H_2O$. The sol. portion appears further degraded. Cellulose is obtained from the xanthate only when used as initial material. Free cellulose is not present in the wood. H. W.

Mercuriation of wood, straw, and lignin. Evidence against the presence of aromatic components. R. S. Hilpert, E. Littmann, and R. Weinbeck (Ber., 1937, 70, [*B*], 560—567).—Distinction between mercuriation at a double linking and in the C_6H_6 nucleus is effected by treating the products with $(NH_4)_2S$ whereby, in the former case, HgS is ppt. usually immediately but sometimes gradually, whereas in the latter case the products are stable provided that only one residue has entered the nucleus. Hot, dil. mineral acid usually causes decomp. of the former but not of the latter class of compound. Vanillin is transformed by $Hg(OAc)_2$ in AcOH into a product with about 1·5 atoms of Hg which is stable to prolonged heating with 5% HCl. Under similar conditions pine wood gives a material with 8% Hg which is completely removed by $(NH_4)_2S$ or dil. HCl. With boiling 1% AcOH, pine wood, rye straw, and wheat straw slowly yield products with 28—30% Hg which is readily removed. With raw and bleached cotton and cellulose there appears a relationship between the extent of mercuriation and the content of "apparent" lignin, but there is no evidence of nuclear substitution. The ability of Ph, even if chemically united in wood, to give typical Hg compounds is established by comparison of $BuCO_2{\cdot}CH_2Ph$, which yields a product containing 2 Hg part of which is removable by HCl leaving a stable residue, with benzylcellulose or benzyl-pine wood each of which gives a product with about 20% Hg which is not removed by $(NH_4)_2S$ or dil. HCl. Straw lignin and pine lignin in boiling 1% AcOH slowly give products with (max.) 43% Hg which can be removed with the exception of 4—6% Hg by dil. HCl. The substances obtained from fructose and xylose under the conditions of the lignin determination with H_2SO_4 behave analogously. The small residue of Hg can be attributed to aromatic components which must then be contained in the products derived from the sugars. According to behaviour on mercuriation, it is very improbable that wood and straw contain aromatic components. Addition appears to occur at a double linking, the character of which is not yet defined. The aromatic compounds from wood are therefore the products of chemical action. H. W.

Preparation of gliadin and zein.—See A., III, 191.

Velocity of reaction between furfuraldehyde and acetophenone.—See A., I, 249.

Synthesis of benzalfurfuralazine. S. A. Tebinov (J. Gen. Chem. Russ., 1936, 6, 1902—1903).—PhCHO, furfuraldehyde, and N_2H_4 yield *NN′-benzylidenefurfurylideneazine*, m.p. 99—100°. R. T.

Preparation of substituted xanthones and xanthhydrols. A. Lespagnol and J. Dupas (Bull. Soc. chim., 1937, [v], 4, 541—548).—The standard methods of prep. of xanthones give increasing amounts of "disalicyde," $C_6H_4\langle^{CO{\cdot}O}_{O{\cdot}CO}\rangle C_6H_4$, as the wt. of the substituents increases. The prep. of 4 : 5-dimethyl-, 1-*methyl*-4-iso*propyl*- (from *o*-$OH{\cdot}C_6H_4{\cdot}CO_2H$, thymol, and Ac_2O), m.p. 169°, and 1 : 5-*dimethyl*-4-iso*propyl-xanthone* (from *m*-cresotic acid, thymol, and Ac_2O), m.p. 165° (with 75—80% of "*di*-o-*cresotide*," m.p. 234°), is detailed. 1 : 8-Dimethyl-4 : 5-di*iso*propylxanthone could not be obtained from thymotic acid, only "*di*-o-*thymotide*," m.p. 212°, being formed. Zn–NaOH–EtOH gives

the corresponding xanthhydrols. 2 : 7-Dibromoxanthone (prep. erratic) could not be reduced without elimination of Br. R. S. C.

Reactions of o-hydroxybenzylideneacetophenones. VII. Flavylium salts from dihydrochalkones. A. D. Harford and D. W. Hill (J.C.S., 1937, 41—42).—4-*Methoxy*-, m.p. 64—65° (*phenylhydrazone*, m.p. 140—141°; O-*Ac* derivative, m.p. 84—85°), and 3′ : 4-*dimethoxy*-, m.p. 89—90° (*phenylhydrazone*, m.p. 145—146°; O-*Ac*-derivative, m.p. 55—56°), -ω-*salicylacetophenone*, obtained by reduction (H_2–Pt) of the appropriate salicylideneacetophenone, and ω-salicylacetophenone (O-*Ac* derivative, m.p. 65°), when treated with $FeCl_3$–HCl–AcOH yield, respectively, without the aid of an oxidising agent, the corresponding flavylium ferrichlorides. The salicylacetophenones are unaffected by HCl–EtOH and when refluxed with AcOH, but were acetylated by Ac_2O (cf. salicylacetone, A., 1935, 985). H. G. M.

Constitution of tannins. V. Synthesis of some flavpinacols. A. Russell and J. Todd (J.C.S., 1937, 421—424).—*o*-Benzoyloxyacetophenone and vanillin benzoate with HCl give 2 : 4′-*dibenzoyl*-3′-*methoxychalkone*, m.p. 118—119°, hydrolysed to the 2 : 4′-*dihydroxy*-compound, m.p. 128°, which with Zn–HCl yields *bis*-(4′-*hydroxy*-3′-*methoxy*)*flavpinacol*. Similar reactions with the appropriate reagents lead to 2 : 4 : 4′-*tribenzoyloxy*-, m.p. 148°, and 2 : 4 : 4′-*trihydroxy*-3′-*methoxychalkone*, m.p. 210°, *bis*-(7 : 4′-*dihydroxy*-3′-*methoxy*)*flavpinacol*; 2 : 4 : 6 : 4′-tetrahydroxy-3′-methoxychalkone, m.p. 214° (Bz_4 derivative), *bis*-(5 : 7 : 4′-*trihydroxy*-3′-*methoxy*)*flavpinacol*; 2 : 3 : 4 : 4′-*tetrahydroxy*-3′-*methoxychalkone*, m.p. 199—200° (Bz_4 derivative, m.p. 95°), *bis*-(7 : 8 : 4′-*trihydroxy*-3′-*methoxy*)*flavpinacol*; 2 : 4′-*dihydroxychalkone*, m.p. 145° (Bz_2 derivative, m.p. 120°), *bis*-(4′-*hydroxy*)*flavpinacol*; 2 : 4 : 4′-*trihydroxychalkone*, m.p. 187—188° (Bz_2 derivative, m.p. 114—115°), *bis*-(7 : 4′-*dihydroxy*)*flavpinacol*; 2 : 3 : 4 : 4′-*tetrahydroxychalkone*, m.p. 117° (Bz_4 derivative, m.p. 105°), *bis*-(7 : 8 : 4′-*trihydroxy*)*flavpinacol*; 2 : 4 : 6 : 4′-*tetrahydroxychalkone*, m.p. 205° (Bz_4 derivative), and *bis*-(5 : 7 : 4′-*trihydroxy*)*flavpinacol*. Derivatives of the parent flavpinacol bearing free OH have been compared with others in which the 3′-OH has been eliminated or replaced by OMe. The two latter series of flavpinacols are not directly comparable with natural phlobatannins, but the properties of the first group show that free OH in the 3′ : 4′ positions suffice for the reproduction of full tanning properties in a substance of this type. 2 : 4 : 6 : 3′ : 4′-Pentahydroxy- and 2 : 4 : 6 : 4′-tetrahydroxy-3′-methoxy-chalkone have been prepared and converted into the corresponding flavanones, which have been shown to be identical with eriodictyol and homoeriodictyol, respectively. F. R. S.

Constitution of fustin. V. Synthesis of 3-hydroxy-4′-methoxyflavanone. T. Oyamada (J. Chem. Soc. Japan, 1935, 56, 980—983).—Synthetic 3-hydroxy-4′-methoxyflavanone is identical with methylfustin. Ch. Abs. (*r*)

Colouring matters of Grimes Golden, Jonathan, and Stayman Winesap apples. C. E. Sando (J. Biol. Chem., 1937, **117**, 45—56).—3-*Galactosidylquercetin*, m.p. 236·5—237·5°, hydrolysed to *d*-galactose and quercetin, and, after methylation, to 3-hydroxy-5 : 7 : 3′ : 4′-tetramethoxyflavone, has been isolated from the skins of Grimes Golden and Jonathan apples, and idaein (3-β-galactosidylcyanidin) from Jonathan and Stayman Winesap apples. H. G. M.

Nitrogenous anthocyanins. III. Preliminary experiments with betanidin. A. D. Ainley and R. Robinson. IV. Colouring matter of *Bougainvillæa glabra*. J. R. Price and R. Robinson. **V. Synthesis of substituted aminoflavylium salts.** A. D. Ainley and R. Robinson (J.C.S., 1937, 446—449, 449—453, 453—456).—III. Aq. extracts of beet undergo fermentation when kept (9—11 days), liberating *betanidin chloride* (I), $C_{20}H_{19-23}O_7N_2Cl,3H_2O$ (30% of the HCl replaced by H_2O), isolated as an amorphous solid (0·2 g. from 56 lb. of beet) by extraction with *iso*-C_5H_{11}·OH after addition of HCl–NaCl. (I) with hot MeOH–HCl affords a Me_2 derivative, but gives no phloroglucinol when fused with KOH. (I) may be a condensation product of a flavylium salt, isomeric with pelargonidin or cyanidin chloride, with ornithine.

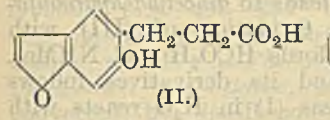
IV. Extraction of the dried bracts of *B. glabra* with 1% MeOH–HCl affords the crude pigment, separated by subsequent treatment involving shaking with saturated brine–BuOH–conc. HCl and chromatographic adsorption on Al_2O_3 into a glucosidic portion, quercetin, and *bougainvillæidin chloride* (absorption spectrum in the visible region is plotted; distribution no. between *n*-C_5H_{11}·OH–0·5% HCl = 50). Analytical data suggest that the isolated anthocyanidin is a mixture of approx. 2 parts of bougainvillæidin (betaine), $C_{22}H_{23}O_8N + 2H_2O$, and 1 part of its Me ester chloride, $C_{23}H_{26}O_8NCl + 2H_2O$.

V. $CH_2Br·CO_2Et$–NaI in $COMe_2$ with *p*-$NH_2·C_6H_4·CO·CH_2·OAc$ give 4-*carbethoxymethylamino*-ω-*acetoxyacetophenone*, m.p. 113°, which condenses with β-resorcylaldehyde in dry dioxan–HCl and with 2-*O*-benzoylphloroglucinaldehyde in EtOAc–HCl at 0° to give, respectively, 4′-*carbethoxymethylamino*-3 : 7-*dihydroxyflavylium chloride* and its 5-*OBz*-derivative: a similar *chloride* is obtained from *o*-vanillin. s-$C_6H_3(OH)_3$ and $NH_2·CH_2·CO_2Et$ in EtOH (N_2) afford *Et* 3 : 5-*dihydroxyanilinoacetate*, m.p. 153·5—154°, which with chloranil–EtOH–HCl and OH·CBz:CH_2 or OH·CBz:CHPh gives, respectively, 5-(or 7-)*carbethoxymethylamino*-3 : 7-(or 3 : 5-)*dihydroxyflavylium chloride* +$3H_2O$, and its 4-*Ph* derivative +$2·5H_2O$. The following were prepared in connexion with abandoned syntheses: *Et* 4-*carbethoxyanilinoacetate*, m.p. 63—63·5° (from the acid); ω-*chloro*-4-p-*toluenesulphonamido*-, m.p. 184°, and 4-p-*toluenesulphonamido*-ω-*acetoxy-acetophenone*, m.p. 179—179·5° (from the NH_2-compound and *p*-$C_6H_4Me·SO_2Cl$), which with $CH_2Br·CO_2Et$–Et_2O–aq.NaOH affords the -ω-*hydroxyacetophenone*, m.p. 202—204° (decomp.); p-*acetoxypropiophenone*, m.p. 59°, from the OH-compound and Ac_2O. J. W. B.

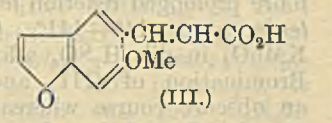
Natural coumarins. XXIV. Synthesis of bergapten. E. Späth, F. Wessely, and G. Kubiczek (Ber., 1937, 70, [*B*], 478—479).—The product

obtained by successive treatments of 3 : 4 : 6-triacetoxycoumarin with Et sodioformylacetate and CH_2N_2 is separated into *allo*bergapten and bergapten, m.p. 188—190°. H. W.

Derivatives of psoralene. H. S. Jois and B. L. Manjunath (Ber., 1937, 70, [*B*], 434—438).—Psoralene (I) is converted by HNO_3 (*d* 1·52) in cold AcOH into *nitropsoralene*, m.p. 278—279° (decomp.),



(II.)



(III.)

in small yield. Treatment of (I) with dil. NaOH followed by reduction with Na–Hg affords the *acid* (II), m.p. 133—134°, readily lactonised at 155°/vac. to *dihydropsoralene*, m.p. 105—106°, and oxidised by fuming HNO_3 to $(CH_2{\cdot}CO_2H)_2$. (I) in $COMe_2$ is transformed by KOH–Me_2SO_4–EtOH and subsequent hydrolysis into the *acid* (III), m.p. 163—166°, converted by repeated sublimation in high vac. into an *isomeride*, m.p. 234—235°, and reduced by Na–Hg to a H_2-*acid*, m.p. 116°, identical with that obtained by methylation of (II). Oxidation of (III) in alkaline solution by $KMnO_4$ at 40—50° yields an *acid*, $C_9H_8O_4$, m.p. 182°, the constitution of which is not established. The absorption spectra of (I), *iso*psoralene, pimpinellin, *iso*pimpinellin, and *iso*bergapten are recorded. H. W.

Reactivity of chlorine in 1 : 1-dioxy-3-chloro-4-methyl-Δ³-thia*cyclo*pentene. H. J. Backer and S. van der Baan (Rec. trav. chim., 1937, 56, 181—185).—β-Chloro-γ-methylbutadiene and SO_2 in Et_2O afford 3-*chloro*-4-*methyl*-Δ³-*thia*cyclo*pentene* 1 : 1-*dioxide* (I), m.p. 145—147° (decomp.), converted by NaSMe in EtOH into 4-*methylthiol*-3-*methyl*-Δ³-*thia*cyclo*pentene* 1 : 1-*dioxide*, m.p. 101°, which is oxidised (H_2O_2–AcOH) to 4-*methylsulphonyl*-3-*methyl*-Δ³-*thia*cyclo*pentene* 1 : 1-*dioxide*, m.p. 192·5° (decomp.), and by NaSBu$^\gamma$ to 4-tert.-*butylthiol*-3-*methyl*-Δ³-*thia*cyclo*pentene* 1 : 1-*dioxide*, m.p. 74—75°, oxidised to 4-tert.-*butylsulphonyl*-3-*methyl*-Δ³-*thia*cyclo*pentene* 1 : 1-*dioxide*, m.p. 193° (decomp.). With K_2S in EtOH (I) affords 4 : 4′-*bis*-(3-*methyl*-Δ³-*thia*cyclo*pentene* 1 : 1-*dioxide*) *sulphide*, m.p. 163—164°, oxidised to the *sulphone*, m.p. 192°; H_2–Pt in AcOH reduce (I) to 3-*methylthia*cyclo*pentane* 1 : 1-*dioxide*, b.p. 100—102°/2 mm., m.p. 0—1°. J. D. R.

Tetramethylmethanetetrasulphonic acid. H. J. Backer and N. Evenhuis (Rec. trav. chim., 1937, 56, 174—180).—Na_2S_4 and $C(CH_2Br)_4$ in EtOH afford 2 : 3 : 7 : 8-*tetrathia*-5-spiro*nonane* 2 : 7-*disulphide* (I), m.p. 182—184°, converted by Na or Cu in boiling PhMe into 2 : 3 : 7 : 8-*tetrathia*-5-spiro*nonane* (II), m.p. 80—80·5° ($HgCl_2$ *compound*, m.p. 132°), and by K_2S into 2 : 3 : 7 : 8-*tetrathia*-5-spiro*nonane* 2-*sulphide*, m.p. 117·5—118°. (I) or (II) with H_2O_2–AcOH affords *tetramethylmethanetetrasulphonic acid* [*tetrachloride*, by PCl_5; *Na* salt, m.p. 217° (decomp.)]. J. D. R.

Configuration of heterocyclic compounds. V. Thianthren and phenoxthionine derivatives. G. M. Bennett, M. S. Lesslie, and E. E. Turner (J.C.S., 1937, 444—446).—Thianthren with NPhEt·COCl–$ZnCl_2$ at 160—170° and hydrolysis with aq. EtOH–NaOH gives *thianthren*-2(?)-*carboxylic acid* (I), m.p. 224° (*amide*, m.p. 227°; *anilide*, m.p. 200—201°; l-α-*phenylethylamine* salt, m.p. 286—288°, $[\alpha]_{5461}$ −3·8° in MeOH). 3-Thiol-*p*-tolyl carbonate (improved prep.) in boiling aq. EtOH–KOH with 2 : 3 : 5-$C_6H_2Cl(NO_2)_2{\cdot}CO_2H$–KOH gives 3-*nitro*-8-*methylphenoxthionine*-1-*carboxylic acid* (II), m.p. 253—254° (*brucine* salt, $[\alpha]_{5791}$ −3·4° in $CHCl_3$). Phenoxthionine (improved prep.) with NPhEt·COCl–$ZnCl_2$ at 190—200° affords its 2-(or 1-)*carboxylic acid* (III), m.p. 230—238° (*strychnine*, m.p. 178—179°, $[\alpha]_{5461}$ −10·9° in $CHCl_3$, and l-α-*phenylethylamine*, m.p. 188—189°, $[\alpha]_{5791}$ −3·25° to −4·6° in MeOH, salts). No resolution of (I), (II), or (III) could be effected. J. W. B.

Exchange of hydrogen between pyrrole and water.—See A., I, 250.

Catalytic formation of heterocyclic compounds. G. G. Schneider, H. Bock, and H. Hausser (Ber., 1937, 70, [*B*], 425—429).—Passage of $NH_3 + C_2H_2$ over SiO_2 gel activated by Al_2O_3–CdO (I), Al_2O_3, or Fe_2O_3 at 400° and 480°, 420°, and 420°, respectively, affords pyrrole (II) in small yield. (II) in H_2 is decomposed by (I) at 430°, 510°, and 620° with formation of HCN and NH_3 whilst C_2H_2 and C_2H_4 could not be detected. The intermediate formation of a hydrocarbon with conjugated double linkings in the production of (II) is rendered probable by the better yield obtained when butadiene (III) and NH_3 are passed over Pt–asbestos, Cu, Ni, or (best) over (I); oxidising catalysts are not more effective. Further improvement in yield is observed when nascent NH_3 [(III) and NO] is employed. The catalytic action of C_2H_2 and NH_3 can result in the formation of (II) through a conjugated system, the production of C_5H_5N through C_2H_2 and HCN, or the formation of derivatives of C_5H_5N through aldehydeammonias. (III) and H_2S in presence of pyrites yield thiophen but not its homologues; reaction occurs at a higher temp. than that required by $C_2H_2 + H_2S$. H. W.

Action of nitroprusside on pyrroles. G. Scagliarini (Atti R. Accad. Lincei, 1936, 24, 294—299).—1-Phenyl-, 1-methyl-2 : 5-diethyl-, 5-carbethoxy-2-methyl-, 5-propionyl-2-methyl-4-ethyl-, and 2 : 3 : 5-trimethyl-4-ethyl-pyrrole, pyrrole-2-aldehyde, and 2 : 4-dimethylpyrrole-5-aldehyde do not react with nitroprusside, which with pyrrole, and 2 : 4-dimethyl- and 3-methyl-4-ethyl-pyrrole gives colorations, with 2 : 5-dimethylpyrrole yields a ppt., and with 2-methyl- and 2-acetyl-pyrrole forms the *compounds* $K_4[Fe(CN)_5{\cdot}NO{\cdot}C_4H_2N{\cdot}Me],4H_2O$ and $K_4[Fe(CN)_5{\cdot}NO{\cdot}C_4H_2N{\cdot}Ac],2H_2O$. E. W. W.

Preparation of acetoanthranil derivatives. M. Hayashi, I. Morikawa, and H. Namikawa (J. Chem. Soc. Japan, 1935, 56, 1102—1105).—Preps. of a no. of anthranil derivatives are described. Ch. Abs. (*r*)

Adrenaline and adrenochrome. D. E. Green and D. Richter (Biochem. J., 1937, 31, 596—616).—Malic acid is rapidly oxidised by a system comprising coenzyme, CN′, adrenaline (I), and heart muscle malic acid dehydrogenase. The initiation of the reaction

depends on the primary oxidation of (I) to a red pigment. A similar red pigment, *adrenochrome* (II), $C_9H_9O_3N$, m.p. 115—120° (decomp.) {*oxime*, m.p. 278°; *Br*- and *I*-derivatives; reduction product, *leucoadrenochrome* (III) $[\alpha]_D^{18}$ +79·2°}, was isolated by the action of pyrocatechol oxidase on (I) and shown to be 3-hydroxy-*N*-methyl-2 : 3-dihydroindole-5 : 6-quinone. (II) is probably identical with the red compound formed in the malic dehydrogenase system in that it behaves equally well as O_2 carrier when added thereto and gives the same quant. results. Oxidising agents [cytochrome *C* (IV) and H_2O_2] accelerate and reducing agents (ascorbic acid and glutathione) retard its formation. The primary formation of (II) from (I) is probably effected by a hæmatin compound similar to (IV) shown spectroscopically to be present in the enzyme prep. In the absence of CN′, (I) and (III) are readily oxidised by the indophenol-oxidase–cytochrome system. P. W. C.

Heterocyclic compounds containing nitrogen. XXVII. Preparation of 2-phenylisatogen and 6-carbethoxy-2-phenylisatogen. P. Ruggli, E. Caspar, and B. Hegedüs (Helv. Chim. Acta, 1937, **20**, 250—263).—Decarboxylation of *o*-$NO_2{\cdot}C_6H_4{\cdot}CH{:}CPh{\cdot}CO_2H$ affords *cis-o*-$NO_2{\cdot}C_6H_4{\cdot}CH{:}CHPh$ (I), isomerised when heated with I in $PhNO_2$ into *trans-o*-$NO_2{\cdot}C_6H_4{\cdot}CH{:}CHPh$ (II). Chlorination of (I) gives *o*-nitrostilbene dichloride (III), m.p. 122°, whereas that of (II) gives the isomeride (IV), m.p. 77—79°. Treatment of (III) and (IV) with NaOH–EtOH affords *o*-nitrotolane (V) in 36% and 74—90% yield, respectively. Irradiation of (III) or (IV) by sunlight or artificial light leads so slowly to 2-phenylisatogen (VI) that the change is not practical although accompanied by little resinification. Reaction occurs still more slowly with (V). The best synthesis of (VI) is from (V) and PhNO in $CHCl_3$ in the dark, change occurring slowly at room temp. A reaction mechanism is suggested. In attempts to prepare *o*-$NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2Ph$, *o*-$NO_2{\cdot}C_6H_4{\cdot}COCl$ is condensed with $CN{\cdot}CPhNa{\cdot}CO_2Et$ to *Et cyano-o-nitrobenzoylphenylacetate*, m.p. 118°, which regenerates the initial materials when hydrolysed by alkali and either suffers the same change slowly or is unaffected when treated with acids. Similarly *o*-$NO_2{\cdot}C_6H_4{\cdot}COCl$ and $CPhNa(CO_2Et)_2$ yield *Et*$_2$ *o-nitrobenzoylphenylmalonate*, m.p. 104°, which could not be satisfactorily hydrolysed. The best method for the prep. of 6-carbethoxy-2-phenylisatogen consists in converting 2-nitro-4-cyanostilbene dichloride by Na_2CO_3 in boiling EtOH–H_2O into 2 : 4-$NO_2{\cdot}C_6H_3(ON){\cdot}CCl{:}CHPh$, which is slowly hydrolysed by boiling HCl–EtOH to 4 : 2-$CO_2Et{\cdot}C_6H_3(NO_2){\cdot}CCl{:}CHPh$; the latter substance is irradiated in C_5H_5N by a 300-watt Osram lamp. H. W.

Toad poisons. X. Constitution of bufothionin. H. Wieland and T. Wieland (Annalen, 1937, 528, 234—246).—Bufothionin (I), isolated from *Bufo arenarum*, is converted by dil. HCl into H_2SO_4 and dehydrobufotenin hydrochloride (II) (corresponding *picrate*, m.p. 186°), transformed by TlOEt in abs. EtOH into *dehydrobufotenin* (III), $C_{12}H_{14}ON_2$, m.p. 218° or (+1·5H_2O) m.p. 199° (decomp.). Exhaustive treatment of (II) with MeI and TlOEt in abs. EtOH gives the *methiodide*, m.p. 208° (corresponding *picrate*, m.p. 103—104°), of the methoxylated base which is not hydrogenated (PtO_2 in H_2O) and is converted by KOH at 160°/high vac. into dehydrobufotenin Me ether in good yield. Short treatment of (II) with boiling Ac_2O appears to yield an Ac_1 derivative, m.p. 265° (decomp.), whereas more prolonged reaction leads to *diacetyldehydrobufotenin*, m.p. 140—141°. Oxidation of (III) with $KMnO_4$ in dil. H_2SO_4 affords HCO_2H and $NHMe_2$. Bromination of (III) and its derivatives follows an obscure course whereas (I) in H_2O reacts with exactly 4 Br and gives the *compound*, $C_{12}H_{13}ON_2BrSO_4$, m.p. 186·5° (decomp.), hydrolysed by CO_2–H_2O to the *substance*, $C_{12}H_{14}ON_2BrSO_4$, m.p. 171—172° (decomp.), which does not give the colour reactions of indole. Removal of H_2SO_4 is effected by HCl–MeOH or 3*N*-HBr, thus leading to the *hydrochloride*, m.p. 241° (decomp.), and *hydrobromide*, m.p. 210—211° (decomp.), of *5-hydroxy-2-keto-3-dimethylaminoacetyl-2 : 3-dihydroindole*, the constitution of which is established by its fission by alkali to *β-keto-γ-dimethylamino-α-2-amino-5-hydroxyphenyl-n-butyric acid*, m.p. 218° (decomp.), which can be diazotised and then coupled with β-$C_{10}H_7{\cdot}OH$. Hydrogenation of (III) does not occur in basic or neutral solution whereas in an acid medium bufotenin (IV) is produced. (III) is therefore *5-hydroxy-3-β-dimethylaminovinylindole*. (IV) gives a yellow monopicrate (V), which at 140° passes into the red monopicrate (VI), m.p. 178°. The red compound, m.p. 177—178°, of Hoshino and Shimodaira (A., 1935, 1378) is a *dipicrate* (VII). (VII) is converted into (V) when boiled with C_6H_6 and into (VI) when crystallised from H_2O containing $NaHCO_3$. H. W.

Reduction of the pyridine ring by formic acid. F. R. Mayo (J. Org. Chem., 1936, **1**, 496—503).—C_5H_5N, HCO_2H, and MeOH (or CH_2O), which at 100° give only traces of a quaternary salt, at 175—200° give up to 60% of 1 : 1-*dimethylpiperidinium formate*, m.p. 140—180° deliquescent (corresponding *chloride*, decomp. 330—340°). 1-Methylpyridinium formate and 1-methylpiperidine are intermediate products. 1-Methylpyridinium chloride and HCO_2H–MeOH do not react until HCO_2K is added; with HCO_2K, but without MeOH, the yield is poor. E. W. W.

Action of nitrobenzoyl chlorides on pyridine. B. M. Bogoslovski (J. Gen. Chem. Russ., 1937, **7**, 255—257).—C_5H_5N and *o*-, *m*-, and *p*-$NO_2{\cdot}C_6H_4{\cdot}COCl$ yield quinonoid additive *products*, m.p. 149—150°, 124—125°, and 228—230°, respectively, in which the N is tervalent, and Cl is substituted in position 2 or 4 of the quinonoid ring. R. T.

2 : 4-Diketo-3 : 3-dialkyltetrahydropyridines.—See B., 1937, 289.

Enol-betaines. III. Detection of reactive hydrogen atoms. F. Kröhnke and H. Kübler (Ber., 1937, 70, [*B*], 538—542; cf. A., 1936, 1510).—Further evidence of the presence of active H atoms in "methine-enol-betaines," $R{\cdot}\bar{C}O{:}CH{\cdot}\overset{+}{N}{:}$, is adduced. The enol-betaine from phenacylpyridinium bromide is

converted by PhNCO into (ω-*phenylcarbamylphenacyl*)-*pyridinium enol-betaine*, $PhCO{\cdot}C(CO{\cdot}NHPh){\cdot}NC_5H_5$, decomp. >210°, which gives a red-brown colour with $FeCl_3$ in EtOH and a negative reaction with chloranil and picryl chloride. It gives a *bromide*, $COPh{\cdot}CH(CO{\cdot}NHPh){\cdot}N(C_5H_5)Br$, m.p. 177—179°, *perchlorate*, m.p. 172—173°, and *picrate*, m.p. 174°. It is hydrolysed to N-*phenylcarbamylmethylpyridinium bromide*, m.p. 203—204° after softening at 201°, also obtained from $CH_2Br{\cdot}CO{\cdot}NHPh$ and C_5H_5N in boiling EtOH. ω-*Phenylcarbamyl*-p-*bromophenacylpyridinium enol-betaine*, m.p. 210° (decomp.), is converted by distillation/high vac. into C_5H_5N, PhNCO, and a *substance*, m.p. 231—234°; the *perchlorate*, m.p. about 160°, gives p-$C_6H_4Br{\cdot}CO_2H$ when crystallised from H_2O. ω-*Phenylcarbamyl*-2 : 4 : 6-*trimethylphenacylpyridinium enol-betaine*, m.p. 210—211° (decomp.) [*bromide*, m.p. 250—251° (decomp.) after much darkening], is not hydrolysed by boiling *N*-NaOH or *N*-HBr. α-*Naphthylcarbamylphenacylpyridinium enol-betaine* has m.p. 211° (decomp.). ω-*Phenylthiocarbamylphenacylpyridinium enol-betaine*, decomp. 172° (*perchlorate*, m.p. 171°), gives PhNCS when heated at 180—190°/0·6 mm.; it is hydrolysed by 2*N*-HBr to BzOH and (with $HClO_4$) N-*phenylthiocarbamylmethylpyridinium perchlorate*, m.p. 200—201° (decomp.). The active H of the methines is also detected by Zerevitinov's method. *p*-Bromophenacylpyridinium enol-betaine, PhN_2Br, and NaOH in EtOH readily afford ω-*phenylhydrazino*-p-*bromophenacylpyridinium enol-betaine*, m.p. 108—109° (*bromide*, m.p. 219—220°). H. W.

Enol-betaines. IV. New type of enol-betaines. F. Kröhnke [with A. Schulze] (Ber., 1937, **70**, [*B*], 543—547).—The possibility that the formation of enol-betaines from compounds, $\cdot CO{\cdot}[CH_2]_n{\cdot}$N-cyclic residue, is general provided that CH_2 vicinal to CO contains a sufficiently labile H atom is not supported by the observation that propiophenonylpyridinium chloride is converted by cold NaOH or Na_2CO_3 or by warm H_2O into Ph vinyl ketone. Definite evidence of the production of an enol-betaine is not obtained when C_5H_5N is replaced by $NAlk_3$. C_5H_5N and $CHBr(CO_2Et)_2$ readily yield *dicarbethoxymethylpyridinium perchlorate*, m.p. 152° after softening, converted by K_2CO_3 into the *enol-betaine* $(C_5H_5)N{\cdot}C(CO_2Et){:}C(O){\cdot}OEt$, m.p. 170—171° (*bromide*, m.p. 70—71° after softening). C_5H_5N and $CMeBr(CO_2Et)_2$ do not appear to react in C_6H_6 at 36°. *Dicarbethoxymethyl*isoquinolinium *enol-betaine*, m.p. 195°, yields a *perchlorate*, m.p. 91—92°. The production of a betaine requires the presence of two strongly negative groups. Thus *carbethoxymethylpyridinium bromide*, m.p. 135—136°, does not give a coloured base with K_2CO_3 and $CHCl_3$. *Phenylcarbethoxymethylpyridinium bromide*, m.p. 159—160° (decomp.), from C_5H_5N and $CHPhBr{\cdot}CO_2Et$, becomes pale red when treated with K_2CO_3 and the colour passes into $CHCl_3$ so that possibly an equilibrium exists between a colourless carbinol base and a coloured form. *Phenylcarbethoxymethyl*isoquinolinium *bromide*, m.p. 104—105°, gives a *perchlorate*, m.p. 159—160°, and a nitrate. H. W.

Hydrolysis of azlactones with alcoholic potassium hydroxide. E. T. Stiller (J.C.S., 1937, 473—476).—2-Phenyl-4-(*o*-carbomethoxybenzylidene)-oxazolone (Bain *et al.*, J.C.S., 1914, **105**, 2397) with KOH–MeOH or KOH–EtOH gives BzOH and, respectively, *Me* (I), m.p. 134—135° (K + 3·5H_2O derivative) or *Et* 1-*keto*-1 : 2-*dihydro*isoquinoline-3-*orthoformate*, m.p. 183—185°, converted by boiling 2*N*-KOH into *iso*carbostyril-3-carboxylic acid [*Me* (II), m.p. 161—162°, and *Et* (III), m.p. 147—148°, esters; *amide*, m.p. 289°] and by dil. HCl into (II) and (III), respectively. (I) in MeOH with Et_2O–CH_2N_2 affords *Me* 1-*keto*-2-*methyl*-1 : 2-*dihydro*isoquinoline-3-*orthoformate*, m.p. 87—88°, converted by warm dil. HCl into the corresponding -3-*carboxylate*, m.p. 132—133°. The formation of orthoformates seems to be dependent on the presence of CO_2Alk on the adjacent nuclear C since MeOH–KOH and 2-phenyl-4-benzylideneoxazolone (Bain *et al.*, *loc. cit.*) give α-benzamidocinnamic acid, and 2-phenyl-4-indolylideneoxazolone similarly affords indole-3-(α-benzamido)acrylic acid. J. W. B.

Condensation reactions of quinolinealdehydes. C. E. Kwartler and H. G. Lindwall (J. Amer. Chem. Soc., 1937, **59**, 524—526).—Oxidation (SeO_2 in xylene at 135°) of 4-methylquinoline gives *quinoline-4-aldehyde*, m.p. 51—53° [*hydrate* (I), m.p. 84—84·5°; *oxime*, m.p. 181—182°; p-*nitrophenylhydrazone*, m.p. 261—262°], and/or quinoline-4-carboxylic acid. 6-*Methoxyquinoline*-4-*aldehyde*, m.p. 96—98° (*oxime*, m.p. 214—216°), is similarly prepared. (I), $MeNO_2$, and EtOH–$NHEt_2$ afford α-*nitro*-β-*hydroxy*-β-4-*quinolylethane*, m.p. 133—136°; the hydrate (II) of quinoline-2-aldehyde (oxime, m.p. 188—190°; 2 : 4-*dinitrophenylhydrazone*, m.p. 251—253°) similarly gives α-*nitro*-β-*hydroxy*-β-2-*quinolylethane*, m.p. 110—113°. (I), COPhMe, and cold aq. EtOH–NaOH yield 4-*diphenacylmethylquinoline*, m.p. 144—146° (*dioxime*, m.p. 204—205°), whilst (II) similarly affords *Ph* β-*hydroxy*-β-2-*quinolylethyl ketone*, m.p. 114—116° (also formed using $NHEt_2$ as the condensing agent). (II) and $COMe_2$ in aq. EtOH–NaOH give β-*hydroxy*-β-2-*quinolylethyl Me ketone*, m.p. 164—167°; in EtOH–$NHEt_2$, *di*-(β-*hydroxy*-β-2-*quinolylethyl*) *ketone*, m.p. 208—210°, results. H. B.

Calcium salts of substituted quinolinecarboxylic acids.—See B., 1937, 290.

Quinoline derivatives.—See B., 1937, 289.

(A) Condensation of acetylene with esters of aminobenzoic acids. (B) Condensation of acetylene with *p*-nitroaniline. New synthesis of 6-nitroquinaldine. N. Kozlov and P. Fedoseev (J. Gen. Chem. Russ., 1937, **7**, 51—53, 54—55).—(A) p-$NH_2{\cdot}C_6H_4{\cdot}CO_2Et$ in EtOH and C_2H_2, in presence of $HgCl_2$, yield cis- (I), m.p. 168—169° and trans-γ-4-*carbethoxyanilino*-α-4-*carbethoxyanilobutane*, m.p. 184°. (I) decomposes when heated yielding Et quinaldine-6-carboxylate (*picrate*, m.p. 196°). *o*-$NH_2{\cdot}C_6H_4{\cdot}CO_2Me$ similarly yields γ-2-carbomethoxyanilino-α-2-carbomethoxyanilobutane, which gives on hydrolysis the corresponding 2 : 2′-*dicarboxylic acid*, decomp. 110—150° to yield quinaldine.

(B) p-$NH_2{\cdot}C_6H_4{\cdot}NO_2$ in EtOH and C_2H_2 in pres-

ence of $HgCl_2$ yield *cis*-, m.p. 195°, and *trans*-*αγ-di-p-nitroanilino-Δ*$^{\alpha}$*-butene*, m.p. 231°, both converted by heating above the m.p. into 6-nitroquinaldine. R. T.

Manufacture of quinaldine compounds.—See B., 1937, 290.

Catalytic hydrogenation of 2-cyano-1-benzoyl-1 : 2-dihydroquinoline (Reissert's compound). I. H. Rupe, R. Paltzer, and K. Engel [with, in part, Gassmann and H. von Bidder] (Helv. Chim. Acta, 1937, **20**, 209—218).—2-Cyano-1-benzoyl-1 : 2-dihydroquinoline (I) (Reissert, A., 1905, i, 247) is hydrogenated (Ni) at 80—90°/100 atm. in EtOAc to *2-benzamidomethyl-1 : 2 : 3 : 4-tetrahydroquinoline* (II), m.p. 138—139° (*NO*-derivative, m.p. 156°), hydrolysed by HCl–EtOH–H_2O to *2-aminomethyl-1 : 2 : 3 : 4-tetrahydroquinoline* (III), b.p. 168°/11 mm. (*perchlorate*, explodes when melted; *picrate*, m.p. 183°; *H oxalate*, m.p. 159°; *tartrate*, m.p. 152°; *citrate*, m.p. 184°). (II) is converted by BzCl in anhyd. C_5H_5N into *1-benzoyl-2-benzamidomethyl-1 : 2 : 3 : 4-tetrahydroquinoline*, m.p. 164°, also obtained similarly from (III). (III) yields a *phenylthiocarbamide*, $C_{17}H_{19}N_3S$, m.p. 130°, and a *:CHPh* derivative, m.p. 70—71° after softening at about 65°. (II) is transformed by MeI in MeOH at 100° into *1-methyl-2-benzamidomethyl-1 : 2 : 3 : 4-tetrahydroquinoline methiodide*, m.p. 166°, converted by HCl into MeI and *1-methyl-2-aminomethyl-1 : 2 : 3 : 4-tetrahydroquinoline* (IV), b.p. 153—155°/11 mm. (*hydrochloride*; *perchlorate*; *picrate*, m.p. 171°; *citrate*, m.p. 164°), also obtained from *1-methyl-2-benzamidomethyl-1 : 2 : 3 : 4-tetrahydroquinoline*. Treatment of (III) with NaOH and Me_2SO_4 gives ill-defined results whereas MeI and KOH in MeOH give *1-methyl-2-dimethylaminomethyl-1 : 2 : 3 : 4-tetrahydroquinoline methiodide* (V), *1-methyl-2-dimethylaminomethyl-1 : 2 : 3 : 4-tetrahydroquinoline* (VI), b.p. 144°/11 mm. (*picrate*, m.p. 122°), and (IV). Hydrolysis of (VI) with HCl gives (IV). (IV) is converted by MeI and KOH at 100° into (V) and (VI). Hydrogenation (Pd-black) at 80—90°/115 atm. of (I) gives (II) and (?) the *compound*, $\left(\begin{matrix}CH_2—CH_2\\ C_6H_4\cdot NBz\end{matrix}>CH\cdot CH_2\right)_2NBz$, m.p. 210°. H. W.

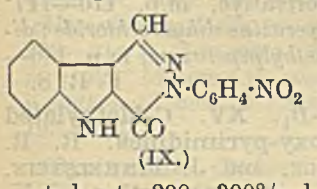
Synthesis of dihydrocarbostyril and homodihydrocarbostyril by ring enlargement and a synthesis of tetrahydroquinoline. L. H. Briggs and G. C. De Ath (J.C.S., 1937, 456—457).—The action of N_3H–conc. H_2SO_4 on cyclic ketones (Schmidt, A., 1924, i, 721) has been extended to the aromatic series. Thus COPhMe gives NHPhAc; α-hydrindone —5% N_3H–conc. H_2SO_4 in C_6H_6 at 40° give dihydrocarbostyril (68% yield), and 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene (in $CHCl_3$) similarly gives homodihydrocarbostyril (70% yield), hydrolysed (91% yield) by hot conc. HCl into *γ-o*-aminophenylbutyric acid. This with N_3H gives a 44% yield of *γ-o*-aminophenylpropylamine, the dihydrochloride of which affords a 50% yield of tetrahydroquinoline when distilled. J. W. B.

Rupture of cyclic azomethines. Opening of the ring of 6 : 7-dimethoxy*iso*quinoline. M. I. Kabat schnik and A. I. Zitzer (J. Gen. Chem. Russ., 1937 7, 162—168).—6 : 7-Dimethoxy*iso*quinoline (I) an 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$ in Et_2O yield 6 : 7-*dimethoxy-N-2′* : *4′-dinitrophenyl*isoquinoline *chloride* (II), m.p. 154—155°, converted by aq. NH_3 into *1-hydroxy-6 : 7-dimethoxy-2-(2′ : 4′-dinitrophenyl)-1 : 2-dihydro*isoquinoline, m.p. 162—163° (1-O-*Me*, m.p. 116—118°; 1-O-*Et* derivative, m.p. 145—148°). The appropriate bases with (II) yield (I) and 2 : 4-dinitro- or 2 : 4-dinitro-4′-methyl-diphenylamine, or *N-2′* : *4′*-dinitrophenylpiperidine. R. T.

Reactions of 2 : 4-dimethylacetophenone with compounds of the thiocarbanilide type. K. Dziewonski and J. Moszew (Bull. Acad. Polonaise, 1936, **A**, 258—265; cf. A., 1933, 836).—2 : 4-$C_6H_3Me_2\cdot$COMe (I) with $CS(NHPh)_2$ at 220° affords *4-anilino-2-m-xylylquinoline*, m.p. 221° [*hydrochloride*, m.p. 184—185° (decomp.); *picrate*, m.p. 235—236°; *methiodide*, m.p. 246—248° (decomp.); *NO*-, m.p. 141—142° (decomp.), N-*Ac*, m.p. 143—144°, and N-*Me*, m.p. 149°, derivatives], which with boiling EtOH–KOH under pressure gives *4-hydroxy-2-m-xylylquinoline*, m.p. 255°. (I) with *s*-di-*p*-tolylthiocarbamide at 180—220° affords *4-p-toluidino-2-m-xylyl-6-methylquinoline*, m.p. 191° [*hydrochloride*, m.p. 289°; *picrate*, m.p. 245°; *methiodide*, m.p. 233—234°; N-*Me*, m.p. 157—158°, and *-Ac* derivative, m.p. 163°], which with EtOH–KOH at 200° gives *4-hydroxy-2-m-xylylquinoline*, m.p. 237°. (I) with *s*-di-*m*-xylylthiocarbamide at 180—220° affords *4-m-xylidino-2-m-xylyl-6 : 8-dimethylquinoline*, m.p. 192° (*picrate*, m.p. 187—188°; N-*Ac* derivative, m.p. 164°), converted by EtOH–KOH at 220° into *4-hydroxy-2-m-xylyl-6 : 8-dimethylquinoline*, m.p. 234—235°. J. L. D.

Synthesis of norharmancarboxylic acid and its bearing on the constitution of lysergic acid. H. King and E. T. Stiller (J.C.S., 1937, 466—473).—Me indole-2-carboxylate with $Zn(CN)_2$–HCl in Et_2O and subsequent hydrolysis gives *2-carbomethoxyindole-3-aldehyde*, m.p. 209—210°, isolated as its *anil*, m.p. 163—164°. 2-Carbomethoxy- and 2-carbethoxy-indole-3-aldehyde with $NHBz\cdot CH_2\cdot CO_2H$–NaOAc–$Ac_2O$ afford, respectively, *2-phenyl-4-(2′-carbomethoxyindolylidene)oxazolone* (I), m.p. 253—254°, and the corresponding carbethoxy-azlactone (II), m.p. 249—250° [lit., m.p. 242° (decomp.)]. Hydrolysis of (II) with 8% aq. KOH gives *2-carboxyindole-3-(α-benzamido)-acrylic acid*, + EtOH (III), m.p. 223—224°, and + AcOH, m.p. 233—234° [*Et*$_2$, m.p. 198—199°, and *Me*$_2$, m.p. 230—231° (decomp.), esters, by hydrolysis of (II) with ROH–anhyd. Na_2CO_3]. (II) with EtOH–aq. NH_3 gives *2-carbethoxyindole-3-(α-benzamido)acrylamide*, m.p. 246—247°, resolidifying at 249°, converted by hot 2*N*-NaOH into the *Na* salt + $3H_2O$ of *5-keto-2-phenyl-4-(2′-carboxyindolylidene)-4 : 5-dihydroglyoxaline*, which is obtained by acidification. Hydrolysis of (I) or (II) with boiling MeOH–KOH or with NaOMe–MeOH affords *2-keto-2 : 3-dihydro-β-carboline-4-carboxylic acid* (IV), m.p. 365° (decomp.) (separates at its *K* salt; *Me*, m.p. 272—273°, and *Et*, m.p. 260—261°, esters), *Me 2-keto-2 : 3-dihydro-β-carboline-4-orthoformate* (V), dimorphous, + EtOH, m.p. 233—234° (decomp.) and m.p. 232—233° [*K*, + $6H_2O$ (VI), and *Na*, + $6H_2O$, derivatives], (III), BzOH, and, probably, 2-carboxy-

indole-3-pyruvic acid. (V) with CH_2N_2 or (VI) with MeI gives *Me* 2-*keto*-3-*methyl*-2 : 3-*dihydro*-β-*carboline*-4-*orthoformate*, m.p. 262—263° (decomp.) (? m.p. 283—284°), converted by warm dil. HCl into the -4-*carboxylate*, m.p. 256—258°, but (V) with Me_2SO_4–K_2CO_3 in dry $COMe_2$ affords *Me* 2-*keto*-1 : 3-*dimethyl*-2 : 3-*dihydro*-β-*carboline*-4-*carboxylate*, m.p. 160—161°. Similar products are obtained from (II) and EtOH–KOH, *Et* 2-*keto*-2 : 3-*dihydro*-β-*carboline*-4-*orthoformate* + 0·5EtOH having m.p. 192—193°. (IV) with PCl_5–$POCl_3$ and treatment of the product with MeOH gives *Me* 2-*chloro*-β-*carboline*-4-*carboxylate* (VII), m.p. 244—245° [*hydrochloride*, m.p. 231—232° (decomp.); hydrolysed by hot 2*N*-NaOH to the free *acid* + H_2O, m.p. 246—247° (decomp.)], and the *dihydrochloride*, m.p. 213—214° (decomp.), of a *base*, $C_{25}H_{20}O_4N_4$, m.p. 333—334° (decomp.). (VII) with HI (*d* 1·7)–red P–KI at 180° gives *norharmancarboxylic acid* + 1·5AcOH (VIII), m.p. 309—310° (decomp.) [*Me* ester, m.p. 262° (decomp.)], decarboxylated by heating with $Ca(OH)_2$ to norharman, and converted by MeOH–Et_2O–CH_2N_2 into *Me* 1-*methyl*-β-*carboline*-4-*carboxylate*, m.p. 256—257°. The p-*nitrophenylhydrazone*, m.p. 274—275° (decomp.), of 2-carbethoxy- and of 2-carbomethoxyindole-3-aldehyde, crimson converted into colourless needles without melting at 287—292°, are converted at 290—300°/reduced pressure into 2-p′-*nitrophenylindolo*-(2′ : 3′ : 4 : 5-)*pyridaz*-3-*one* (IX), m.p. >365°. (VIII) does not give the usual indole reactions and lysergic acid probably does not contain a β-carboline skeleton. J. W. B.



(IX.)

Reaction between anthranilic acid and *cyclo*pentanone. B. K. Blount and S. G. P. Plant (J.C.S., 1937, 376—377).—Anthranilic acid (I) and *cyclo*pentanone at 265° afford 12-*keto*-3-cyclo*pentylidene*-2 : 3 : 5 : 12-*tetrahydro*-β-*quinindene*, (II), m.p. 285°, also formed from (I) and *cyclo*pentylidene*cyclo*pentanone. With $POCl_3$, (II) affords 12-*chloro*-3-cyclo*pentylidene*-2 : 3-*dihydro*-β-*quinindene*, m.p. 110°, whilst 12-keto-2 : 3 : 5 : 12-tetrahydro-β-quinindene gives 12-*chloro*-2 : 3-*dihydro*-β-*quinindene*, m.p. 70°. J. D. R.

Meso-derivatives of acridine. VII. Preparation of 5-*p*-dimethylaminophenylacridines. N. S. Drozdov (J. Gen. Chem. Russ., 1937, 7, 219—226).—5-Chloroacridine and $NPhMe_2$ in presence of $AlCl_3$ (3 hr. at 100°) yield 5-p-*dimethylaminophenylacridine* (I), m.p. 290°. The 3-Me derivative of (I) is prepared analogously. 1 : 3-Dinitroacridone, $NPhMe_2$, and $POCl_3$ (100°; 3 hr.) yield 1 : 3-*dinitro*-5-p-*dimethylaminophenylacridine*, m.p. 268—270° (decomp.). 4-Nitro-4′-methyldiphenylamine-2-carboxylic acid and $POCl_3$ in xylene (130—170°) yield 5-*chloro*-7-*nitro*-3-*methylacridine*, m.p. 199—200°, converted by heating with PhOH into 7-*nitro*-5-*phenoxy*-3-*methylacridine*, m.p. 189—190°, and with aq. NaOH into 7-*nitro*-3-*methylacridone*, m.p. >300°, which with $NPhMe_2$ and $POCl_3$ gives 7-*nitro*-5-p-*dimethylaminophenyl*-3-*methylacridine*, m.p. 259—260°. R. T.

2 : 8-Dialkoxy-10-alkylacridinium derivatives with various kinds of amino-group on the 5-carbon atom. XV. Synthesis of 2 : 8-diethoxy-5-alkylamino-10-ethylacridinium derivatives. K. Ishihara (J. Chem. Soc. Japan, 1935, **56**, 1164—1173).—The following 5-alkyl derivatives are described: *Iodides*: *Me*, m.p. 227°; *Et*, m.p. 224°; *Pr*$^{\alpha}$, m.p. 207°, *Bu*$^{\beta}$, m.p. 230°, iso-C_5H_{11}, m.p. 227°. *Hydroxides*: *Me*, m.p. 126°; *Et*, m.p. 115°; *Pr*$^{\alpha}$, m.p. 105°; *Bu*$^{\beta}$, m.p. 122°; iso-C_5H_{11}, m.p. 101°. *Chlorides*: *Me*, m.p. 225°; *Et*, m.p. 216°; *Pr*$^{\alpha}$, m.p. 230°; *Bu*$^{\beta}$, m.p. 194°; iso-C_5H_{11}, m.p. 152°. *Oxalates*: *Me*, m.p. 195°; *Et*, m.p. 180°; *Pr*$^{\alpha}$, m.p. 174°; *Bu*$^{\beta}$, m.p. 199°; iso-C_5H_{11}, m.p. 172°. Ch. Abs. (*r*)

Differences in absorption curves of groups of unsaturated hydantoins. M. K. Seikel (J. Amer. Chem. Soc., 1937, **59**, 436—439).—The characteristic ultra-violet absorption spectrum of anisylidenehydantoin is not appreciably affected by 3(*N*)-substitution; such compounds may exist largely in the enolic forms. Distinct changes occur with 1(*N*)-substitution irrespective of the presence or absence of a 3-substituent. The stable and labile geometrical isomerides of the 1 : 3-disubstituted derivatives also show differences. The uniformity of absorption of each group parallels chemical and other physical properties. H. B.

Synthesis of 4-(or 5-)carbamidoglyoxaline. G. Hunter and I. Hlynka (Biochem. J., 1937, **31**, 488—489).—4-(or 5-)Nitroglyoxaline was reduced with Na–Hg and the aminoglyoxaline treated, without isolation, with HCNO. The product had the same m.p. and mixed m.p. as that obtained from guanine (A., 1936, 999, 1000). P. W. C.

Iminazoles. IV. Derivatives of glyoxaline. R. Weidenhagen, R. Herrmann, and H. Wegner (Ber., 1937, **70**, [*B*], 570—583; cf. A., 1936, 1523).—The synthesis (*loc. cit.*) is extended to ketols with *sec.* OH. Thus, furoin, CH_2O, $Cu(OAc)_2$, and conc. NH_3 in MeOH yield 4 : 5-*difurylglyoxaline*, m.p. 162—163° (decomp.) [*Cu* salt; *hydrochloride*, m.p. 196° (decomp.); *picrate*, m.p. 222—223° (decomp.) after darkening]. Analogously, furfuraldehyde (I) yields 2 : 4 : 5-*trifurylglyoxaline*, m.p. 202° (darkening) [*hydrochloride*, m.p. 141°]. Acetoin gives 4 : 5-dimethylglyoxaline (*hydrochloride*, m.p. 285°) and 2 : 4 : 5-trimethylglyoxaline (*hydrochloride*, m.p. 310—311°; *picrate*, m.p. 157°). Benzoin affords 4 : 5-diphenylglyoxaline [*picrate*, m.p. 231—232° (lit. m.p. 135°)] and 2 : 4 : 5-triphenylglyoxaline (*picrate*, m.p. 235°). Fructose and CH_2O afford 4(5)-hydroxymethylglyoxaline in almost 40% yield owing to preliminary fission into $CO(CH_2{\cdot}OH)_2$ and $OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CHO$, which is further oxidised; glucose and invert sugar act similarly. *p*-$C_6H_4Me{\cdot}CO{\cdot}CH_2{\cdot}OAc$ and CH_2O yield 4(5)-p-*tolylglyoxaline*, m.p. 116—117° (*picrate*, m.p. 210°). 4(5)-p-*Ethylphenylglyoxaline*, m.p. 127—128° (*picrate*, m.p. 197°), is described. p-iso*Propylbenzoylcarbinyl acetate*, m.p. 40—41°, is hydrolysed to the corresponding carbinol, which affords 4(5)-p-iso*propylphenylglyoxaline*, m.p. 114—115° (*picrate*, m.p. 186—187°). The halogens in 4(5)-p-*chlorophenyl*-, m.p. 147° (*picrate*, m.p. 219—220°), and -p-*bromo*-

phenyl-, m.p. 142° (*picrate*, m.p. 216°), *-glyoxaline* do not react with Mg in Et_2O or *iso*amyl ether or with Na_3AsO_3 under pressure. 2-$C_{10}H_7$·CO·CH_2·OH gives 4(5)-2′-*naphthylglyoxaline* (II), m.p. 170—171° [*hydrochloride*, m.p. 219—220° after softening; *nitrate*, m.p. 185° (decomp.); *picrate*, m.p. 215°]. CH_2Bz·OH and (I) afford 2-*furyl*-4(5)-*phenylglyoxaline*, m.p. 180° (decomp.) [*hydrochloride*, m.p. 275—276°; *picrate*, m.p. 204° (decomp.)]. 4(5)-*p*-Carboxyphenylglyoxaline in NaOH is converted by gradual addition of the requisite amount of I into *iodo-*, m.p. 240° (decomp.), and *di-iodo-*, m.p. 234—235° (decomp.), -4(5)-p-*carboxyphenylglyoxaline*. Glyoxaline-4(5)-*p*-phenylsulphonic acid is iodinated to 2 : 5(4)-*di-iodoglyoxaline*-4(5)-p-*phenylsulphonic acid*, decomp. 327°; an I-derivative could not be obtained. Entry of I into glyoxaline-4(5)-carboxylic acid is accompanied by loss of CO_2 and gives 2 : 4 : 5-triiodoglyoxaline. (II) and fuming H_2SO_4 (10% SO_3) at 100° yield 4(5)-2′-*naphthylglyoxalinesulphonic acid*. 4(5)-Phenylglyoxaline is transformed by pyridinium-1-sulphonic acid into 4(5)-*phenylglyoxaline*-1-*sulphonic acid*, decomp. >300° after becoming transparent at 210° (*K* salt, anhyd. and +0·5H_2O). 4(5)-2′-*Naphthylglyoxaline*-1-*sulphonic acid*, becoming gelatinous at 200—210° (*K* salt), and *benziminazole*-1-*sulphonic acid*, m.p. 221—222° (*K* salt), are obtained analogously. H. W.

Method for protecting the iminazole ring of histidine during certain reactions and its application to the preparation of *l*-amino-*N*-methylhistidine. V. DU VIGNEAUD and O. K. BEHRENS (J. Biol. Chem., 1937, **117**, 27—36).—*l*-Histidine monohydrochloride when treated in dry liquid NH_3 with Na then with CH_2PhCl yields 1(or 3)-*benzyl*-l-*histidine* (I), m.p. 248—249°, $[\alpha]_D^{24}$ +20·5° in H_2O + 1 equiv. of HCl, and some *amino*-N-*benzyl*-1(or 3)-*benzyl*-l-*histidine*, m.p. 193—195°, $[\alpha]_D^{24}$ +34·5° in H_2O + 1 equiv. of HCl. *p*-C_6H_3Me·SO_2Cl–NaOH with (I) gives N-p-*toluenesulphonyl*-1(or 3)-*benzyl*-l-*histidine* (II), m.p. 198°, which on methylation (MeI–NaOH–H_2O; 68—70°; 40 min.) gives p-*toluenesulphonyl*-1(or 3)-*benzyl*-N-*methyl*-l-*histidine* (III), m.p. 118—122°. Na in liquid NH_3 reduces (I) and (II) to histidine without racemisation. Similarly, (III) is reduced in good yield to l-*amino*-N-*methylhistidine*, m.p. 266°, $[\alpha]_D^{20}$ −13·5° in H_2O (*mono-*, m.p. 268°, and *di-*, m.p. 124—127°, *-hydrochloride*; *dipicrate*, m.p. 61°). All m.p. are corr. Other applications of the protection of the glyoxaline ring by benzylation followed by debenzylation are suggested. H. G. M.

***l*-Histidine anhydride dihydrochloride, decomp. 270—280°, $[\alpha]_D^{20}$ + 48·1°.**—See A., III, 141.

Rearrangement of pyrazolones and of their derivatives. I. A. KOCWA (Bull. Acad. Polonaise, 1936, A, 266—275).—Equimol. amounts of 1-phenyl-5-methylpyrazol-3-one (I) with $CO(NHPh)_2$ or PhNCO at 250—260° afford 4-*carbanilido*-1-*phenyl*-5-*methylpyrazolone* (II), m.p. 258°. Similarly, (I) with $CS(NHPh)_2$ or PhNCS affords 4-*thiocarbanilido*-1-*phenyl*-5-*methylpyrazolone*, m.p. 238°, which with NH_3 under pressure at 150—160°, or with PCl_5 at 130°, affords (II). α-$C_{10}H_7$·NCO and (I) similarly afford 4-*carb*-α-*naphthylamido*-1-*phenyl*-5-*methylpyrazolone*, m.p. 231—232°. 1-Phenyl-2 : 3-dimethylpyrazolone (III) with $CO(NHPh)_2$ and $ZnCl_2$ at 260° affords 4-*carbanilido*-1-*phenyl*-2 : 3-*dimethylpyrazolone* (IV), m.p. 250°, also prepared from (III), PhNCO, and $AlCl_3$. With an equimol. amount of $CS(NHPh)_2$ or PhNCS at 230° (III) affords 4-*thiocarbanilido*-1-*phenyl*-2 : 3-*dimethylpyrazolone* (V), m.p. 199°, which when hydrolysed (NH_3, EtOH–HCl) or oxidised (warm Cr_2O_3, H_2O_2 or HNO_3) affords (IV) and with HNO_3 (*d* 1·48) gives a NO_2-compound, m.p. 240°. Et 1-phenyl-2 : 3-dimethylpyrazolone-4-carbithionate when boiled with NH_2Ph affords 1-*phenyl*-2 : 3-*dimethyl*-4-*anilothiolmethylpyrazolone*, R·C(NPh)·SH, m.p. 148°, isomeric with (V) and converted by hot EtOH–KOH into (IV). J. L. D.

Thiobarbituric acid compounds.—See B., 1937, 290.

Stereoisomeric 2 : 3 : 5 : 6-tetramethylpiperazines. V. F. B. KIPPING (J.C.S., 1937, 368—369). Separation of commercial 2 : 3 : 5 : 6-tetramethylpiperazine gives 99—99·5% of the α- and β-isomerides, with some δ- and ε-compounds, the last-named isolated as the $(NO)_2$-derivative, m.p. 116—117° (ε-2 : 3 : 5 : 6-*tetramethylpiperazine dihydrochloride*; *dibenzoyl*-ε-2 : 3 : 5 : 6-*tetramethylpiperazine*, m.p. 146—147°). F. R. S.

Crystalline vitamin-B_1. XV. *C*-Methylated 6-amino- and 6-hydroxy-pyrimidines. R. R. WILLIAMS, A. E. RUEHLE, and J. FINKELSTEIN. **XVI. Identification of pyrimidine portion.** J. K. CLINE, R. R. WILLIAMS, A. E. RUEHLE, and R. E. WATERMAN (J. Amer. Chem. Soc., 1937, **59**, 526—530, 530—533).—XV. Oxidation (H_2O_2 at >90°) of 4-methyl-2-thiouracil, thiothymine, and 6-*hydroxy*-4 : 5-*dimethyl*-2-*thiopyrimidine*, m.p. >255° [from CHMeAc·CO_2Et and $CS(NH_2)_2$ in EtOH–NH_3], gives 6-hydroxy-4-methyl-, m.p. 148—149°, -5-*methyl-*, m.p. 153—154°, and -4 : 5-dimethyl-, m.p. 202—203°, -pyrimidine, respectively. 6-Amino-4-methyl-, m.p. 194—195°, -5-methyl-, m.p. 175—176°, and -4 : 5-dimethyl-, m.p. 229—231°, -pyrimidines are prepared from the respective 6-Cl-derivatives and EtOH–NH_3 at 110—120°. 6-*Hydroxy*-2 : 5-*dimethylpyrimidine*, m.p. 174° (from Et sodioformylpropionate and acetamidine hydrochloride in H_2O), is similarly converted through the 6-Cl-derivative into 6-*amino*-2 : 5-*dimethylpyrimidine*, m.p. 201—202° (*picrate*, m.p. 222°). Ultra-violet absorption spectra of 6-hydroxy- and 6-aminopyrimidines and their 2-, 4-, and 5-Me, and 2 : 4-, 2 : 5-, and 4 : 5-Me_2 derivatives are given; the effect of acid and alkali on the NH_2-derivatives is discussed.

XVI. A more detailed account of work previously reviewed (A., 1936, 1159). The base, $C_6H_{10}N_4$, m.p. 211—215° (picrate, m.p. 225°) (cf. Windaus *et al.*, *ibid.*, 253), obtained by cleavage of vitamin-B_1 (I) with liquid NH_3, probably contains 6-NH_2 and a side-chain NH_2. 6-Hydroxy-2-methyl-5-ethoxymethylpyrimidine and aq. $NaHSO_3$ at 144°/sealed tube give the 5-*sulphomethyl* derivative, m.p. >360°, which is identical with the hydroxysulphonic acid previously prepared (A., 1935, 1035) from (I). 4 : 6-Diamino-5-ethylpyrimidine, m.p. 245° (lit. 233—235°) (*dipicrate*, m.p. 165—167°), is obtained from

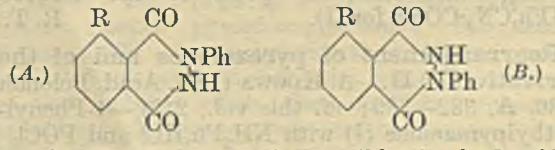
4-iodo-6-amino-5-ethylpyrimidine and EtOH–NH_3 at 220°. 6-Amino-2 : 5-dimethylpyrimidine is formed from the aminosulphonic acid (*loc. cit.*) [from (I)] and Na in liquid NH_3. H. B.

Aryloxy-derivatives of pyrimidines, quinoxalines, and quinolines. (Miss) D. Lockhart and E. E. Turner (J.C.S., 1937, 424—427).—Condensation of 2 : 4 : 6-trichloropyrimidine or 2 : 3-dichloroquinoxaline with the appropriate phenoxide or amine gives 2 : 4 : 6-*tri-phenoxy-*, m.p. 156°, -p-*tolyoxy-*, m.p. 118°, -p-*anisoxy-*, m.p. 120°, and -p-*chlorophenoxy-pyrimidine*, m.p. 107°; 2 : 3-*di-phenoxy-*, m.p. 160°, -p-*tolyloxy-*, m.p. 145—146°, -p-*anisoxy-*, m.p. 193—194°, -p-*chlorophenoxy-*, m.p. 153°, *-anilino-*, m.p. 223°, -m-*toluidino-*, m.p. 225°, and -p-*toluidino-quinoxaline*, m.p. 254°. 4-*Chloro*-6-*ethoxy*-2-*methylquinoline*, m.p. 65°, from the OH-compound, is nitrated to the 4-*chloro*-5-*nitro*-derivative, m.p. 125°, which with the required phenoxide gives 5-*nitro*-4-p-*anisoxy*-6-*ethoxy-*, m.p. 109°, 4-*phenoxy*-2-*ethoxy-*, m.p. 107—108° (*methiodide*, m.p. 210°); 4-p-*anisoxy-*, m.p. 115° (*methiodide*, m.p. 216°), *-tolyloxy-*, m.p. 134° (*methiodide*, m.p. 213°), and *-chlorophenoxy*-6-*ethoxy-*, m.p. 125° (*methiodide*, m.p. 213—214°); 4-m-*nitro-*, m.p. 183—184° [*methiodide*, m.p. 224° (decomp.)], *-amino-*, m.p. 139°, and *-bromo*-p-*methoxyphenoxy*-6-*ethoxy*-2-*methylquinoline*, m.p. 193—194°. F. R. S.

Pyrimidine derivatives. A. Bowman (J.C.S., 1937, 494—495).—The following are prepared by adaptation of known methods: 2 : 4 : 6-*trimethylpyrimidine*, b.p. 160°, and its *dihydrate*, m.p. 47—48° (*compound*, m.p. 169°, with $HgCl_2$), converted by PhCHO–$ZnCl_2$ at 150° into 2 : 4 : 6-*tristyrylpyrimidine*, m.p. 198—199°; 2-*phenylpyrimidine*-4 : 6-*dicarboxylic acid*, decomp. 165°, m.p. dependent on the rate of heating; 2-*phenyl*-4-*methylpyrimidine*-6-*carboxylic acid*, m.p. 112° (decomp.); 2 : 4-*dichloro*-5-*chloromethyl*-6-*methylpyrimidine*, m.p. 38—39°; and 3-(2′ : 4′-*dichloro*-6′-*methylpyrimidyl*-5′-*methyl*)-5-β-*hydroxyethyl*-4-*methylthiazolium chloride*, sinters 201°, m.p. 202·5°, which does not exhibit aneurin-like activity. J. W. B.

Synthesis of 1-*d*-ribosidouracil. Interaction of acetobromo-*d*-ribose and 2 : 4-diethoxypyrimidine. G. E. Hilbert and C. E. Rist (J. Biol. Chem., 1937, **117**, 371—380).—Acetobromo-*d*-ribose with 2 : 4-diethoxypyrimidine (65°; 18 hr.) yields some uracil, 4-*ethoxy*-2-*triacetyl*-d-*ribosidopyrimidine* (I), m.p. 162·5°, $[\alpha]_D^{26}$ −66·2° in $CHCl_3$, and a syrupy product, which on hydrolysis yields some 1-d-*ribosidouracil*, m.p. 257—258°, $[\alpha]_D^{29}$ −140·0° in H_2O {Ac_3 derivative, m.p. 184—185° (when heated slowly), $[\alpha]_D^{26}$ −25·1° in $CHCl_3$}. This is similar in chemical but not in physical properties to uridine (1-*d*-ribosidouracil-furanose form), and probably is a pyranoside. (I) is hydrolysed by 5% HCl giving uracil, and by NaOH–H_2O–$COMe_2$ giving 2-keto-4-ethoxy-1 : 2-dihydropyrimidine. H. G. M.

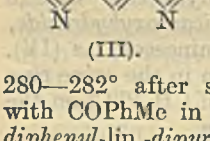
Chemiluminescence of cyclic hydrazides. R. Wegler (J. pr. Chem., 1937, [ii], **148**, 135—160).—The chemiluminescence of hydrazides in presence of H_2O_2 is greatly enhanced by the use of radish or horseradish shavings or expressed juice; it does not quite attain the intensity given by hæmin (I) but persists for several days since decomp. of H_2O_2 is nearly avoided if the materials are pure. (I) causes much more intense luminescence in strongly than in feebly alkaline solution whereas closely related derivatives are inactive. In spite of marked catalytic activity, various Fe oxides do not enhance luminescence. The importance of the oxidisability of *m*-NH_2 in 3-aminophthalhydrazide (II) is established by the observation that 3-*hydrazinophthalhydrazide* (III), m.p. (indef.) 280—300° (decomp.), is more strongly luminescent than (II) whilst the diazonium salt from (II) is intensely luminescent; in each case addition of (I) has little effect. Under all conditions the activity of the :*CHPh* derivative, m.p. 310—312°, of (III) is less marked than that of (III) or (II). In spite of ready oxidisability 3 : 5-diaminophthalhydrazide (obtained impure from 3 : 5-*dinitrophthalhydrazide*, m.p. 306—307°) is less luminescent than (II); *diaminopyromellitdihydrazide*, m.p. 42° and m.p. >250° after re-solidification at 68—69° (obtained from *dinitropyromellithydrazide*, m.p. >260°), is scarcely luminescent. The luminescence of 3-*hydroxyphthalhydrazide*, m.p. about 300° (much decomp.), is intermediate between that of (II) and phthalhydrazide (IV) and > that of 3 : 6-*dihydroxyphthalhydrazide*, m.p. >340°, although the latter is readily oxidised and rapidly becomes coloured when its alkaline solutions are exposed to air. Hydrazides of polycyclic ring systems (*e.g.*, anthraquinone-2 : 3-dicarboxyhydrazide) are less luminescent than (IV). The behaviour of succinhydrazide proves that the saturated character of the azine ring is not an impediment and that the presence of a second ring is not essential for luminescence. Dimethylmaleinhydrazide shows the expected action also exhibited by dimethylmalonhydrazide with a 5-membered ring. *Pyridine*-2 : 3-*dicarboxyhydrazide*, m.p. 309°, is about as strongly luminescent as (IV). In study of the effect of substitution in the azine ring (IV) is transformed by the action of CH_2PhCl on the Ag salt into the O-*benzyl* derivative, $C_6H_4<^{CO\text{———}NH}_{C(O\cdot CH_2Ph):N}$, m.p. 156°, which is highly luminescent; the isomeric N-*benzyl* compound, $C_6H_4<^{CO-NH}_{CO-N\cdot CH_2Ph}$, m.p. 204° [from $CH_2Ph\cdot NH\cdot NH_2$ and o-$C_6H_4(CO)_2O$], is distinctly but feebly active. The ease with which CH_2Ph is eliminated renders these compounds of somewhat doubtful val. Direct treatment of $NO_2\cdot C_6H_3(CO_2H)_2$ with $NHPh\cdot NH_2$ at 210° gives products sol. in alkali and converted by reduction (Zn–AcOH–HCl) into compounds almost insol. in alkali and hence probably consisting of a mixture of the forms *A* and *B* (R = NO_2 or NH_2). The behaviour of these products appears to show



that chemiluminescence is possible in hydrazides substituted at N. The following compounds are incidentally described: 2 : 3-*quinoxalinecarboxyhydraz-*

ide, m.p. >330°; *phthal*-NN'-*dibenzylhydrazide*, m.p. 153—154°; *phthal*-ON-*dibenzylhydrazide*, m.p. 96—97°; 3-*nitrophthalpropylhydrazide*, m.p. 207—210°; 3-*nitrophthaldipropylhydrazide*, m.p. 119°, and the 3-NH_2-compound, m.p. 142°. H. W.

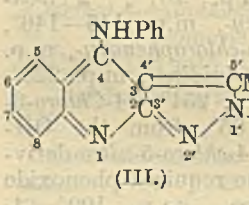
Heterocyclic compounds containing nitrogen. XXVIII. 4 : 6-Dinitro- and -diamino-*iso*phthalaldehyde. P. Ruggli and P. Hindermann (Helv. Chim. Acta, 1937, **20**, 272—282).—4 : 6-Dinitro-*m*-xylene is condensed with *p*-NO·C_6H_4·NMe_2 and Na_2CO_3 in EtOH and the product is oxidised by HNO_3 (*d* 1·12) in C_6H_6 to 4 : 6-dinitro*iso*phthalaldehyde (I), m.p. 129·5—130°. (I) is decomposed by NaOH or Na_3PO_4 and converted by C_5H_5N into a *substance*, decomp. >360°. (I) yields a $(NaHSO_3)_2$ *compound*, a *dianil*, m.p. 164·5—165°, and a *disemicarbazone*, decomp. >360°. Condensation of (I) with $CH_2(CO_2H)_2$ in C_5H_5N at 50—55° gives 4 : 6-*dinitrophenylene*-1 : 3-*diacrylic acid*, m.p. 216°; the Et_2 ester, m.p. 116°, is reduced (Ni–EtOAc–EtOH–H_2O) to Et_2 4 : 6-*diaminophenylene*-1 : 3-*diacrylate*, m.p. 195—196° (*hydrochloride*; Ac_2 derivative, m.p. 244—245°). 4 : 6-*Dinitro*isophthalaldibarbituric *acid* is described. (I) and CH_2N_2 in Et_2O give 4 : 6-*dinitro*-1 : 3-*diacetylbenzene*, m.p. 153—154°. (I) is not reduced satisfactorily in presence of Ni but is readily transformed by $FeSO_4$ and NH_3 into 4 : 6-*diamino*isophthalaldehyde (II), m.p. 208°, in 85% yield. (II) is stable towards NaOH; it gives a *dioxime*, m.p. 219—220° after becoming discoloured at 210°, a *disemicarbazone*, slow decomp. >360°, a *mono*-, m.p. 275—276° (decomp.), and a *di*-, decomp. 337°, -*phenylhydrazone*. (II) is slowly converted by Ac_2O at room temp. into the Ac_1 derivative, m.p. (indef.), 270—272° (decomp.) after softening at 250°, transformed by boiling Ac_2O into 4 : 6-*diacetamido*isophthalaldehyde, decomp. 280—282° after softening at 270°. (II) condenses with COPhMe in presence of KOH–MeOH to 2 : 8-*diphenyl*-lin.-*dipyridinobenzene* (III), m.p. 216—217° (*dipicrate*, incipient decomp. 270°), and with $CH_2Ac·CO_2Et$ to Et_2 2 : 8-*dimethyldipyridinobenzene*-3 : 7-*dicarboxylate*, m.p. 166—167° (*dipicrate*).


(III.)

H. W.

Structure of the product of reaction of αβ-dibromo-β-phenylethyl methyl ketone with salts of azoimide. S. G. Fridman (Mem. Inst. Chem. Ukrain. Acad. Sci., 1936, **3**, 587—604).—The monoazide (I), m.p. 78—79°, previously described (A., 1936, 1109) evolves N_2 and NH_3 when treated with aq. NaOH, yields PhCHO with NaOH or H_2SO_4, and BzOH with $KMnO_4$, and combines with Br or Cl_2 to yield unidentified halogen derivatives, with evolution of N_2. The reactions point to the structure CHPh:CN_3·COMe for (I). R. T.

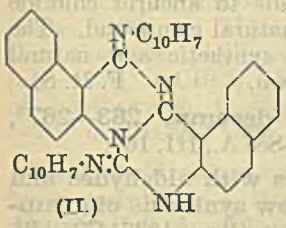
Rearrangement of pyrazolones and of their derivatives. II. A. Kocwa (Bull. Acad. Polonaise, 1936, **A**, 382—389; cf. this vol., 212).—1-Phenyl-5-methylpyrazolone (I) with NH_2Ph,HCl and $POCl_3$ at 260° affords 3-*anilo*-1-*phenyl*-5-*methylpyrazolone* (II), m.p. 146—147° [*picrate*, m.p. 194° (decomp.)], which with an equimol. amount of $CO(NHPh)_2$ or PhNCO at 230—240° affords 4-*anilino*-1'-*phenyl*-5'-*methylpyrazolo*-3' : 4' : 2 : 3-*quinoline* (III), m.p. 198—199° [*hydrochloride*, m.p. 273—274° (decomp.); *picrate*, m.p. 209°]. (III) with EtOH–KOH at 200—220° gives 4-*hydroxy*-1'-*phenyl*-5'-*methylpyrazolo*-3' : 4' : 2 : 3-*quinoline*, m.p. 189° (decomp.). Equimol. amounts of (II) and $CS(NHPh)_2$ or PhNCS at 230—240° afford (III) and 3-*anilo*-4-*thiocarbanilido*-1-*phenyl*-5-*methylpyrazolone*, m.p. 224—225°, which at 100—110° with PCl_5 gives (III). (I) with *p*-$C_6H_4Me·NH_2$,HCl and $POCl_3$ at 260—270° affords 3-*p*-*toluido*-1-*phenyl*-5-*methylpyrazolone*, m.p. 116° (*picrate*, m.p. 203°), which with an equimol. amount of PhNCS at 240—245° gives 4-*anilino*-1'-*phenyl*-5' : 6-*dimethylpyrazolo*-3' : 4' : 2 : 3-*quinoline*, m.p. 192—193°, converted by EtOH–KOH at 200—220° into 4-*hydroxy*-1'-*phenyl*-5' : 6-*dimethylpyrazolo*-3' : 4' : 2 : 3-*quinoline*, m.p. 203° (decomp.). J. L. D.


(III.)

Rearrangement of pyrazolones and of their derivatives. III. A. Kocwa (Bull. Acad. Polonaise, 1936, **A**, 390—402; cf. preceding abstract).—An equimol. mixture of 5-anilo-1-phenyl-3-methylpyrazolone (I) with $CO(NHPh)_2$, $CS(NHPh)_2$, PhNCO, or PhNCS at 245—250° in 0·5 hr. affords 4-*anilino*-1'-*phenyl*-3'-*methylpyrazolo*-4' : 5' : 2 : 3-*quinoline* (II), m.p. 170° [*hydrochloride*, m.p. 265° (decomp.); *picrate*, m.p. 256—257° (decomp.); *NO*-derivative, m.p. 170° (decomp.)], converted by aq. EtOH–KOH at 200—220° into 4-*hydroxy*-1'-*phenyl*-3'-*methylpyrazolo*-4' : 5' : 2 : 3-*quinoline*, m.p. 274°, which when heated with NH_3 under pressure is converted into the 4-NH_2-compound, m.p. 150°. (I) with PhNCO at 260° for 10 min. affords 5-*anilo*-4-*carbanilido*-1-*phenyl*-3-*methylpyrazolone*, m.p. 171—172° [*methiodide*, m.p. 110—115° (decomp.), with boiling 15% NaOH affords 5-*anilo*-4-*carbanilido*-1-*phenyl*-2 : 3-*dimethylpyrazolone*, m.p. 215—216°, which is not converted into a pyrazoquinoline derivative with P_2O_5, but with conc. HCl under pressure gives 5-anilo-1-phenyl-2 : 3-dimethylpyrazolone], converted by P_2O_5 into (II), and with HCl under pressure into (I). (I) with α-$C_{10}H_7$·NCO (III) at 290° affords 4-α-*naphthylamino*-1'-*phenyl*-3'-*methylpyrazolo*-4' : 5' : 2 : 3-*quinoline*, m.p. 198° [*picrate*, m.p. 224° (decomp.); *NO*-derivative, decomp. at 145°], and a *substance*, m.p. 314° (decomp.). 5-*p*-Toluido-1-phenyl-3-methylpyrazolone (IV) with $CO(NHPh)_2$, PhNCO, $CS(NHPh)_2$, or PhNCS at 235—240° affords 4-*anilino*-1'-*phenyl*-3' : 6-*dimethylpyrazolo*-4' : 5' : 2 : 3-*quinoline*, m.p. 174—175° [*hydrochloride*, m.p. 257° (decomp.); *picrate*, m.p. 234° (decomp.); *NO*-derivative, m.p. 174° (decomp.); 4-*OH*-analogue (V), m.p. 258°]. (IV) with an equimol. amount of (III) at 280—285° affords 4-α-*naphthylamino*-1'-*phenyl*-3' : 6-*dimethylpyrazolo*-4' : 5' : 2 : 3-*quinoline*, m.p. 238—239° [*picrate*, m.p. 195°; 4-OH-analogue identical with (V)]. J. L. D.

Reactions of β-naphthylamine with thiocarbamide. K. Dziewoński, L. Sternbach, and A. Strauchen (Bull. Acad. Polonaise, 1936, **A**, 493—500).—β-$C_{10}H_7$·NH·CS·NH_2 or equimol. amounts of β-

$C_{10}H_7{\cdot}NH_2$ and $CS(NH_2)_2$ at 230—240° under reduced pressures afford 2-*thio*-2 : 4-*diketo*-5 : 6-*benzo*-1 : 2 : 3 : 4-*tetrahydroquinazoline*-4-β-*naphthil* (I), m.p. 318°; if the reaction temp. is raised to 300° 4 : 2′-*diketo*-5 : 6 : 5′ : 6′-*dibenzo*-1 : 4 : 1′ : 2′-*tetrahydro*-1 : 2 : 3′ : 4′-*quinazolinoquinazoline*-ββ-*dinaphthil* (II), m.p. 206—207° (*acetate*, m.p. 160—190°; *hydrochloride*, m.p. 308—310°; *nitrite*, m.p. 259°; *picrate*, m.p. 269—270°; *Ac* derivative, m.p. 245·5°), results. (II) is also obtained by heating (I) and $C(:N{\cdot}C_{10}H_7\text{-}\beta)_2$ (III), which indicates that (II) probably arises in the original reaction by way of $CS(NH{\cdot}C_{10}H_7\text{-}\beta)_2$, which yields (III) by loss of H_2S. (I) in boiling AcOH–HCl gives β-$C_{10}H_7{\cdot}NH_2$ and 2-*thio*-2 : 4-*diketo*-5 : 6-*benzo*-1 : 2 : 3 : 4-*tetrahydroquinazoline* (IV), m.p. > 350°; at 220°, however, S is lost and 2 : 4-*diketo*-5 : 6-*benzo*-1 : 2 : 3 : 4-*tetrahydroquinazoline* (V), m.p. 342°, is formed. (II) with KOH–EtOH at 160° affords the 4-β-*naphthil* of (V), m.p. 301·5—302° (*acetate*, m.p. 301·5—302°; *hydrochloride*, m.p. 258—285°), which with conc. HCl at 200° gives (IV). (IV) and PCl_5 when heated yield 2 : 4-*dichloro*-5 : 6-*benzoquinazoline*, m.p. 184°, showing that (IV) can exist in the enolic form. That α-$C_{10}H_7{\cdot}NH_2$ and other primary bases do not react with $CS(NH_2)_2$ in the above manner emphasises the reactivity of the α-H atom adjacent to the NH grouping in β-$C_{10}H_7{\cdot}NH_2$.



(II.)

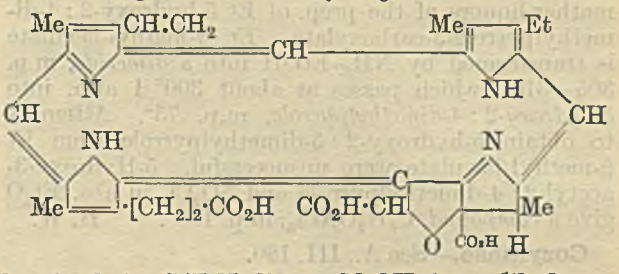
R. F. P.

Synthetic nucleosides. V. Theophylline-*d*-allomethyloside. P. A. Levene and J. Compton (J. Biol. Chem., 1937, **117**, 37—43).—*d*-Allomethylose with Ac_2O–C_5H_5N yields its Ac_4 derivative, m.p. 109—110°, $[\alpha]_D^{25}$ +10·4°, converted by HBr–AcOH into acetobromoallomethylose, which when heated (95—100°; 4 hr.) with Ag theophylline in PhMe gives *theophyllinetriacetyl*-d-*allomethyloside* (I), m.p. 217—218°, $[\alpha]_D^{25}$ +12·5° in MeOH, as an additive *compound*, m.p. 140°, $[\alpha]_D^{25}$ +11·0° in MeOH, with 1 PhMe. $Ba(OMe)_2$–MeOH–H_2O hydrolyses (I) to *theophylline*-d-*allomethyloside*, m.p. 167—168°, $[\alpha]_D^{28}$ −21·9° in H_2O, −6·5° in EtOH, the rate of hydrolysis of which in 0·1*N*-HCl at 100° is recorded. H. G. M.

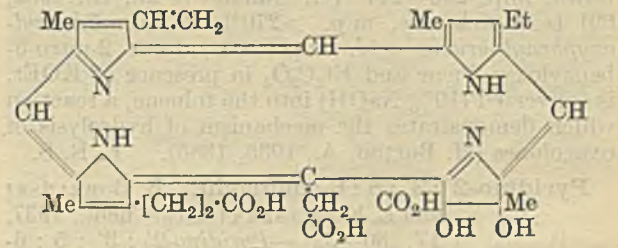
Production of tetrazoles of the camphor group and products therefrom.—See B., 1937, 289.

Preparation of purines and pyrimidines from nucleic acid. G. Hunter and I. Hlynka (Biochem. J., 1937, **31**, 486—487).—Existing methods are shortened by using the difference in solubilities of the hydrochlorides of guanine and adenine on the one hand and of cytosine hydrochloride and uracil on the other. Separation of all four pure substances from nucleic acid is thus effected without intermediate formation of Cu or Ag salts. P. W. C.

Chlorophyll. LXXVI. Dihydroxychlorins and dihydroxyphorbides. H. Fischer and W. Lautsch (Annalen, 1937, **528**, 247—264).—Oxidation of phæophorbide-*a* in C_5H_5N–EtOH by Ag_2O [at room temp. gives purpurin 7 (isolated at the Me_3 ester), to which the following, modified constitution is now assigned. Chlorin-e_6 Me_3 ester is converted



by Ag_2O in C_5H_5N–dioxan–MeOH into *dihydroxychlorin*-e_6 *Me*$_3$ *ester* (I), m.p. 114°. Similarly mesochlorin-e_6 Me_3 ester yields *dihydroxymesochlorin Me*$_3$ *ester* and D.E.E.-chlorin-e_6 Me_3 ester gives *D.E.E.-dihydroxychlorin-e*$_6$ *Me*$_3$ *ester*. These derivatives of chlorin-e_6 are decarboxylated by Na_2CO_3 in boiling C_5H_5N to the corresponding dihydroxyphæophorbide-*a* Me esters. (I) is also obtained from pyrophæophorbide-*a* and Ag_2O. Analytical and spectro-



scopic data are in harmony with the above constitution. ψ-Chlorin-p_6 Me_2 ester is oxidised to *dihydroxy-ψ-chlorin*-p_6 *Me*$_3$ *ester*, m.p. 120°, and chlorin-p_6 Me_3 ester to *dihydroxychlorin*-p_6 *Me*$_3$ *ester*, m.p. 118°, converted into chlorin-p_6 by catalytic hydrogenation or treatment with Na_2CO_3 in boiling C_5H_5N. H. W.

Chlorophyll. LXXVII. Partial synthesis of methylphæophorbide-*a* and -*b*. H. Fischer and W. Lautsch (Annalen, 1937, **528**, 265—275).—Short, energetic treatment of chlorin-e_6 Me_3 ester (I) in C_5H_5N with 10% KOH–MeOH in N_2 gives methylphæophorbide-*a* (II), m.p. 236°, identical with that derived from chlorophyll except in respect of [α]; this is probably due to the intermediate production of an enolic form. (II) is re-converted by CH_2N_2–MeOH into (I). (II) is decarbomethoxylated in boiling C_5H_5N and then converted by CH_2N_2 in Et_2O into pyrophæophorbide-*a* Me ester, m.p. 230°, $[\alpha]_{690-720}^{20}$ −468°, against −352° as max. val. for the natural material. Similarly DEE-chlorin-e_6 Me_3 ester is smoothly transformed into DEE-methylphæophorbide-*a*, m.p. 233°, $[\alpha]_{690-720}^{20}$ −235°. Analogously, rhodin-g_7 Me_3 ester affords methylphæophorbide-*b*, m.p. (indef.) 261°, $[\alpha]_{690-720}^{20}$ −277° (natural product, −128°), whence pyrophæophorbide-*b* Me ester, $[\alpha]_{690-720}^{20}$ −562°. An explanation in the discrepancies of [α] is difficult since, in this series, inactive materials have been isolated which afford inactive derivatives convertible by further treatment into active products.

[With H. Haberland.] Oxidation of opsopyrrolecarboxylic acid by H_2O_2 in C_5H_5N gives a *compound*, $C_8H_{11}O_3N$, m.p. 185—186°, and possibly two further

isomerides. 5-*Hydroxy*-2 : 4-*dimethylpyrrole*-3-*carboxylamide*, m.p. 217—218°, is obtained from the mother-liquors of the prep. of Et 5-hydroxy-2 : 4-dimethylpyrrole-3-carboxylate. Et α-methyl-lævulate is transformed by NH_3–EtOH into a *dimeride*, m.p. 305—310°, which passes at about 300°/1 atm. into 5-*hydroxy*-2 : 4-*dimethylpyrrole*, m.p. 75°. Attempts to obtain 5-hydroxy-2 : 3-dimethylpyrrole from Et β-methyl-lævulate were unsuccessful. 5-Hydroxy-3-acetyl-2 : 4-dimethylpyrrole and SO_2Cl_2 in abs. Et_2O give a *compound*, $C_6H_4ONCl_3$, m.p. 188°. H. W.

Cozymase.—See A., III, 180.

5-Furfuryl-5-*iso*propylbarbituric acid.—See B., 1937, 290.

Alkaline hydrolysis of the azlactones derived from certain *o*-nitrobenzaldehydes. Formation of isatins. H. Burton and J. L. Stoves (J.C.S., 1937, 402—404).—5-Keto-2-phenyl-4-(2′-nitro-4′-acetoxy-3′-methoxybenzylidene)-4 : 5-dihydro-oxazole is hydrolysed (10% NaOH) to 6-*hydroxy*-7-*methoxyisatin*, m.p. 246—247° (cf. Gulland *et al.*, A., 1932, 69) (*semicarbazone*, m.p. >270°). 2-*Nitro*-5-*benzyloxyphenylpyruvic acid*, m.p. 103°, from 2-nitro-5-benzyloxytoluene and $Et_2C_2O_4$ in presence of KOEt, is converted (10% NaOH) into the toluene, a reaction which demonstrates the mechanism of hydrolysis of oxazolones (cf. Burton, A., 1935, 1385). F. R. S.

Pyridino-2′ : 3′ : 5 : 6-coumarin. B. Bobrański and L. Kochańska (Rocz. Chem., 1937, 17, 30—32).—*Pyridino*-2′ : 3′ : 5 : 6-*coumarin*, m.p. 187°, is prepared from 7-hydroxyquinoline, $CH_2(CO_2H)_2$, and H_2SO_4 (100°; 2 hr.), or from 7-hydroxy-8-aldehydoquinoline, NaOAc, and Ac_2O (180°; 2 hr.). R. T.

Preparation and properties of thiazole compounds. H. Erlenmeyer and H. von Meyenburg (Helv. Chim. Acta, 1937, 20, 204—206).—Et chloroformylacetate is converted by $HCS{\cdot}NH_2$ into *Et thiazole*-5-*carboxylate*, b.p. 99—103°/11 mm., hydrolysed to *thiazole*-5-*carboxylic acid* (I), m.p. 196—197° (corr.) (*Na* salt). Analogously, Et_2 chlorooxaloacetate affords *Et*$_2$ *thiazole*-4 : 5-*dicarboxylate*, b.p. 175°/12 mm., whence *thiazole*-4 : 5-*dicarboxylic acid* (II), decomp. 177° with formation of (I) [*Na H* salt (+$1H_2O$); *Ba* salt]. (II) is converted by $SOCl_2$ followed by $NHEt_2$,HCl at 160° into *thiazole*-4 : 5-*dicarboxybisdiethylamide* (III), m.p. 44° (corr.). *Thiazole*-5-*carboxydiethylamide* (IV), b.p. 152°/11 mm., m.p. 28°, is obtained analogously from (I) or from (II) after prolonged boiling with Ac_2O. The physiological properties of (III) and (IV) are described. H. W.

Aneurin. VII. Synthesis of aneurin. A. R. Todd and F. Bergel (J.C.S., 1937, 364—367).—Acetamidine and $OMe{\cdot}CH{:}C(CN){\cdot}CO_2Et$ in EtOH give Et α-cyano-β-acetamidinoacrylate (?), m.p. 108—110°, hydrolysed (NaOH) to 4-*hydroxy*-5-*cyano*-2-*methylpyrimidine*, m.p. 233—235°, which with $POCl_3$ forms the 4-*Cl*-compound, m.p. 63—64°, aminated to the 4-NH_2-derivative (I), m.p. 249° (cf. Grewe, A., 1936, 1566). Acetamidine hydrochloride and Et ethoxymethylenemalonate yield *Et* 4-*hydroxy*-2-*methylpyrimidine*-5-*carboxylate*, m.p. 191°, which is converted through the Cl-compound into the 4-NH_2-derivative, m.p. 120°. The NH_2-ester with aq. NH_3 forms 4-*amino*-2-*methylpyrimidine*-5-*carboxylamide*, m.p. 264—265°, which with $POCl_3$ affords (I). (I) is reduced to 4-amino-5-aminomethyl-2-methylpyrimidine hydrochloride, which with HCS_2K gives 4-*amino*-5-*thioformamidomethyl*-2-*methylpyrimidine*, m.p. 187° (decomp.). Condensation of the thioformyl derivative with Me α-chloro-γ-acetoxypropyl ketone followed by HCl leads to aneurin chloride which is identical with the natural compound. The difference in m.p. between synthetic and natural specimens is due to dimorphism. F. R. S.

Spinazine, $C_9H_{14}O_4N_4$, decomp. 263—267°, from *Acanthias vulgaris*.—See A., III, 167.

Condensations of indoles with aldehydes and secondary amines. I. New synthesis of gramine. H. Kühn and O. Stein (Ber., 1937, 70, [*B*], 567—569).—3-Dimethylaminomethylindole (gramine) is quantitatively obtained from indole, $NHMe_2$, and CH_2O in AcOH at room temp. In alkaline solution the condensation is less complete and an unidentified colourless oil is also produced. 3-*Diethylaminomethylindole*, m.p. 165° (*picrate*, m.p. 124°), and 3-1′-*piperidinomethylindole*, m.p. 161°, are obtained similarly. H. W.

Optical rotation and refractivity of nicotine and nicotine sulphate in dilute aqueous solution.—See A., I, 169.

Constituents of the bark of *Lunasia costulata* (Miq.). H. Dieterle and H. Beyl (Arch. Pharm., 1937, 275, 174—191).—This bark contains (*a*) 0·48% of tannins, (*b*) an oil, *d* 0·9506, acid val. 62·32, sap. val. 164, ester val. 101·7, I val. 118·5, which gives stearic (5·65), palmitic (13·76), oleic (60·38), and linolenic acid (15·66%), and (*c*) 0·083% of alkaloids, including *lunacrine* (I) (0·068%), *lunasine*, $C_{16}H_{21}O_5N$, m.p. 188° (0·009), and *lunacridine*, $C_{18}H_{15}O_4N$, m.p. 230—231° (0·0003%). (I), $CH_2O_2{:}C_{13}H_{12}(OMe){:}NMe$, + H_2O, m.p. 95—96°, (anhyd.) 115—116°, [α] 0 (*hydrochloride*, m.p. 163—164°; *hydrobromide*, m.p. 170—171°; *hydriodide*, m.p. 196—197°; *picrate*, m.p. 208°; *aurichloride*, m.p. 176—177°), gives a *methiodide*, m.p. 130—131°, which with Ag_2O gives a *substance*, $C_{16}H_{20}O_3N$, m.p. 85—86°, insol. in dil. HCl, also obtained from the methosulphate by hot 30% KOH. (I) is very stable; 30% H_2O_2 gives a cryst. product. Photomicrographs of the alkaloids and bark are given. R. S. C.

Properties of the ecgonines and their esters. I, II. A. W. K. de Jong (Rec. trav. chim., 1937, 56, 186—197, 198—201).—I. [α] of *l*-ecgonine in different solutions is discussed, and an optical method for its determination in admixture with a lævorotatory compound, not affected by boiling 20% KOH, is described. The hydrolysis of ecgonine esters with HCl first yields ecgonine, which is then partly transformed into ecgonidine (I); this latter change also occurs with 20% KOH. At room temp. esters of *l*-ecgonine are partly transformed by alkali in EtOH or $COMe_2$ into *d*-ψ-ecgonine (stable to conc. HCl). *l*-Cocaine at 115—120° yields *d*-ecgonine Me

ester and Bz_2O, whilst *d*-cocaine at 115—120° affords, with difficulty, (I). Ecgonines and cocaines when heated to 115—120° with BzOH afford (I).

II. The structural formulæ of the ecgonines are discussed, and arguments are advanced for the position of the double linking being αβ to the CO_2H, and not βγ as suggested by Willstätter (cf. A., 1899, i, 178). J. D. R.

Mitraphylline. Raymond-Hamet and L. Millat (Bull. Sci. pharmacol., 1935, **42**, 602—611; Chem. Zentr., 1936, i, 3145).—Comparative experiments show that mitraphylline, $C_{22}H_{28}O_4N_2$, m.p. 206—216°, $[\alpha]_D$ −23·1° in $CHCl_3$, 2 OMe, is probably the Me ether of mitrinermine, $C_{21}H_{26}O_4N_2$, m.p. 258—267°, $[\alpha]_D$ −7·7° in $CHCl_3$, 1 OMe. H. N. R.

***allo*Quinidine, a carbinol *iso*-base obtained from quinidine.** (Mlle.) R. Ludwiczak and J. Suszko (Bull. Acad. Polonaise, 1936, **A**, 276—292).—Quinidine with H_2SO_4 (*d* 1·60) at 60—70° affords *γ-iso*quinidine and allo*quinidine* (I), m.p. 249—250°, $[\alpha]_D^{20}$ +230° in 96% EtOH [*hydriodide*, m.p. 265—266° (decomp.); *sulphate* + $3H_2O$, m.p. 244—245° (decomp.); *oxalate* + $10H_2O$, m.p. 272° (decomp.); *dihydrochloride* + $\frac{1}{2}EtOH$, m.p. 204—205°; *methiodide* + $4{\cdot}5H_2O$, m.p. 252—253° (decomp.); *dimethiodide* + $1H_2O$, m.p. 227° (decomp.); *Bz* derivative, m.p. 113—115°, hydrolysed to (I); *Ac* derivative, m.p. 166—167°]. With H_2SO_4 at 70—80°, (I) affords β-*iso*quinidine (II). (I) with Br in $CHCl_3$ affords a Br_2-compound (perbromide ?), m.p. 230—231° (decomp.), decomposed by H_2O, dil. HNO_3, or dil. NH_3 to (I). (I) with aq. 48% HBr containing Br affords a Br_3-compound, m.p. 144°, one Br of which may be present as hydrobromide, the others as perbromide. (I) with excess of AcOH at 100° in an atm. of CO_2 affords *allo*quinotoxine, m.p. 117—118° {*oxalate*, m.p. 117—119° (decomp.); N-*NO*-, m.p. about 50°, and N-*Me*, an oil, derivatives [*oxalate*, m.p. 228—229° (decomp.); *methiodide*, m.p. 80—85° (decomp. after sintering at 60°); p-*nitrophenylhydrazone*, m.p. 80—105°]}. (II) with hot dil. AcOH affords β-*iso*quinotoxine [*oxalate*, m.p. 161—162° (decomp.)], the *N*-Me derivative of which affords an *oxalate*, m.p. 157—158° (decomp.). J. L. D.

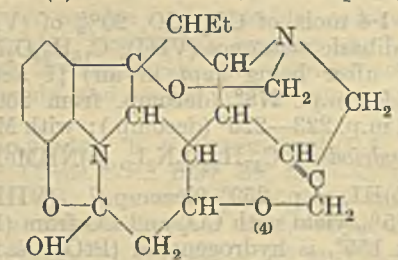
Steric changes in optically active carbinols. I. Complete conversion of quinidine into *epi*quinidine. J. Suszko and F. Szelag (Bull. Acad. Polonaise, 1936, **A**, 403—412; cf. A., 1935, 99).—Quinidine (I) and *p*-$C_6H_4Me{\cdot}SO_2Cl$ in C_6H_6 with 50% NaOH at room temp. afford the *p-toluenesulphonate* (II), m.p. 116—118°, $[\alpha]_D^{21}$ +28·3° in 95% EtOH [*dihydrochloride*, m.p. 183—185° (decomp.)], which with boiling EtOH–KOH affords some (I), but mainly an *oil* [*hydriodide*, m.p. 256—258° (decomp.), affords a *base*, m.p. 167—168°, when hydrolysed]. (II) is resistant to HCl, but when boiled for a short time with dil. tartaric acid, it affords *epi*quinidine (III), m.p. 112—113° (cf. A., 1932, 289) [*dihydrochloride*, m.p. 195—197° (decomp.); *hydriodide*, m.p. 203—205° (decomp.); *methiodide*, m.p. 222—224° (decomp.); *Bz* derivative, m.p. 128—131°, hydrolysed (hot dil. HCl) to (III)]. *epi*Dihydroquinidine, m.p. 123—124°, is formed from (III) in AcOH with Pt–PtO_2–H_2 under slight pressure (cf. A., 1932, 289). A probable interpretation of the results is included. J. L. D.

Quinine and strychnine germano- and zircono-oxalates. A. Tchakirian (Compt. rend., 1937, **204**, 356—358).—Germano-oxalic acid (cf. A., 1930, 177) with quinine oxalate (I) in H_2O affords *quinine germano-oxalate*, $H_2Ge(C_2O_4)_3$,quinine, easily hydrolysed by warm H_2O. The analogous *strychnine* salt, $H_2Ge(C_2O_4)_3$,2strychnine, resists hydrolysis with H_2O. Zircono-oxalic acid with (I) in cold H_2O affords *quinine zircono-oxalate*, $2H_2Zr(C_2O_4)_4$,2quinine, stable to boiling H_2O, as is the analogous *strychnine* salt, $2H_2Zr(C_2O_4)_4$,4strychnine. The four salts are very hygroscopic. J. L. D.

Constitution of strychnine. IV. Action of perbenzoic acid on strychnine and its derivatives. M. Kotake and T. Mitsuwa (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1937, **31**, 217—233).—The product from methoxymethyldihydroneostrychnine and BzO_2H, Robinson's "methoxymethyl*chano*-dihydrostrychnone" (I) (A., 1934, 788), with dil. KOH gives an *isomeride*, $C_{23}H_{28}O_5N_2$, m.p. 268°; on Pd–H_2 reduction (I) loses O to form a *substance*, $C_{23}H_{28}O_4N_2$, which is not explained on Robinson's formula for (I) (*loc. cit.*). Strychnine and BzO_2H give a strychnine *N*-oxide–BzOH *compound*, $C_{21}H_{22}O_3N_2$,BzOH,H_2O (II), decomp. 160°, which is reconverted by H_2SO_3 into strychnine, and is reduced (Pd–H_2) to *dihydrostrychnine benzoate*, $C_{21}H_{24}O_2N_2$,BzOH,H_2O (III), m.p. 115—117°, with some (unexpected) neostrychnine. (II) is also obtained from strychnine *N*-oxide and BzOH, and (III) from dihydrostrychnine. The last and BzO_2H form a *compound*, $C_{21}H_{24}O_3N_2$,BzOH, decomp. 196—198°, which is also obtained from dihydrostrychnine *N*-oxide, and which is reduced (Pd–H_2 or H_2SO_3) to (III). Strychnine and dihydrostrychnine are regenerated by Pd–H_2 reduction of their *N*-oxides. E. W. W.

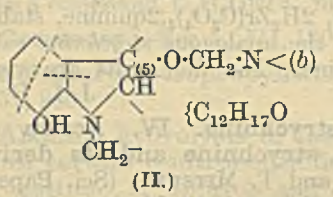
***Strychnos* alkaloids. XVIII. Constitution of vomicine. Degradation of vomicidine.** H. Wieland and L. Horner (Annalen, 1937, **528**, 73—100; cf. this vol., 126).—Reactions described below lead to formula (I) for vomicine, based partly on the

(I.)

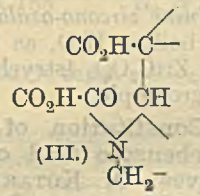


Robinson–Leuchs formula for strychnine. The part of formula (II) given in full is based on the present work, but the $C_{(5)}{\cdot}O_{(3)}{\cdot}CH_2{\cdot}N(b)$ is uncertain. The $O_{(3)}{\cdot}CH_2{\cdot}N(b)$ is postulated because (I), deoxyvomicine, and the base, $C_{22}H_{30}O_2N_2$, show exactly 1 *N*-Me [pure MeI is obtained from (I)]; cholesterol and deoxybilianic acid show only about 0·5 *N*-Me (from the C·Me); strychnine shows about 0·15 *N*-Me (a mixture of MeI and EtI is obtained). $O_{(3)}$ is attached to $C_{(5)}$ in order to account for the steric hindrance of

the CO_2H attached to $C_{(5)}$ and the ready loss of this CO_2H by the action of HCl or heat. Improved CrO_3-oxidation of vomicidine (II) gives, by fission at the dotted lines, the acid (III), new formula $C_{19}H_{24}O_7N_2$, $+2H_2O$ (lost only with decomp.), m.p. 219—220° (decomp.) (slow heating), stable to conc. HNO_3, Br, $Ca(OCl)_2$, H_2O_2, and alkali, hydrogenated with loss of CO_2, and giving no CO reactions. When evaporated with KOH–MeOH at 120°, (III) gives HCO_2H and $H_2C_2O_4$. With CH_2N_2–MeOH (III) gives

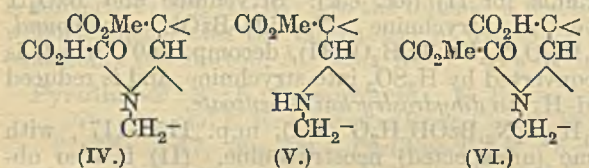


(II.)



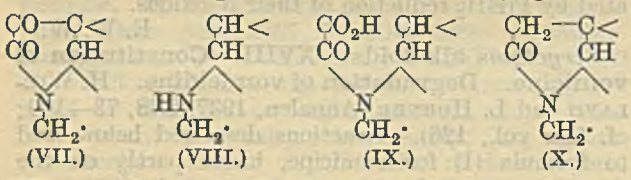
(III.)

the *Me*$_2$ ester, m.p. 235—236° (decomp.), sublimes at 180°/high vac., stable to Ac_2O, hydrogenated (PtO_2) to a *substance*, $C_{19}H_{26}O_4N_2(OMe)_2$, m.p. 136° (presumably by the reaction $C_{(5)}\cdot O\cdot C \rightarrow \geq CH\ CH\leq$), and hydrolysed by *N*-KOH–MeOH to the *H Me* ester (IV), $C_{19}H_{23}O_6N_2\cdot OMe$, m.p. 255° (decomp.) (*hydrochloride*, decomp. 214°). At 235—240°/high



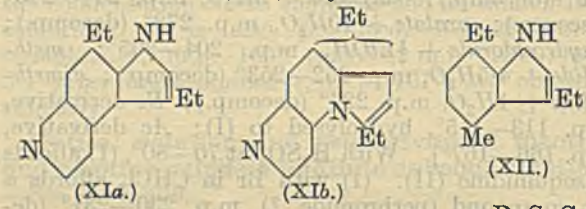
(IV.) (V.) (VI.)

vac. (IV) gives CO_2, CO, and a *base* (V), $C_{18}H_{26}O_4N_2$, m.p. 159—160°. HCl–MeOH and (III) give the *H Me* ester (VI), sinters at 190°, decomp. 276° [*hydrochloride*, m.p. 206° (decomp.)], which at 200°/high vac. gives CO_2 and a *base* (VII), $C_{18}H_{22}O_4N_2$, m.p. 282—284° (decomp. from 250°). At 200°/high vac.



(VII.) (VIII.) (IX.) (X.)

(III) gives 1·4 mols. of CO_2, CO, 20% of (VII), and 15% of a dibasic *substance* (VIII), $C_{16}H_{24}O_2N_2$, m.p. 146° (100° after being kept in air) [1 active H; *hydrochloride*, m.p. 278° (decomp. from 250°); *Ac* derivative, m.p. 223—225° (decomp.); with MeI gives the (?) *dihydriodide*, $C_{17}H_{28}O_2N_2I_2$, (*a*)NHMeI . . . . ·O·CH_2·N(*b*)HI, m.p. 259° (decomp.)]. (VIII) is obtained in 75% yield with CO_2 and CO from (III) and 2*N*-HCl at 155°, is hydrogenated (PtO_2; saturation of the ethylenic linking) in H_2O to a *base*, $C_{16}H_{26}O_2N_2$, $+H_2O$, m.p. 154—155°, stable to H_2-Pt at 120°/100 atm., is reduced by HI–red or –yellow P to a *base*, $C_{16}H_{26}O_2N_2$, m.p. 167°, by fission of the $O_{(4)}$ ring, and resists $SOCl_2$ and PCl_5. (VII) does not react with MeI, is hydrogenated (PtO_2; saturation of the ethylenic linking, $C\cdot O\cdot C \rightarrow \geq CH\ CH\leq$, $C\cdot O\cdot C \rightarrow \geq C\cdot OH\ CH\leq$, and $CO \rightarrow CH_2$) to a *base*, $C_{18}H_{30}O_3N_2$, m.p. 197° (*methiodide*, m.p. 262°, stable to alkali), with hot 10% KOH–MeOH gives the *acid* (IX), $C_{18}H_{24}O_5N_2$, $+5H_2O$, m.p. 214° (decomp.) (<50% yield) (*Me* ester, m.p. 157°), and gives a 2 : 4-*dinitrophenylhydrazone*, m.p. >330°, decomp. from 250°. The *hydrazone*, $+1{\cdot}5H_2O$, m.p. 251° (decomp.), of (VII) with HNO_2 gives N_2O and regenerates (VII) and with hot NaOEt–EtOH affords the *deoxo-base* (X), $C_{18}H_{24}O_3N_2$, $+0{\cdot}5H_2O$, m.p. 186° (decomp.), hygroscopic, stable to 10% KOH–MeOH, reduced (H_2–PtO_2) in H_2O mainly to a *substance*, $C_{18}H_{28}ON_2$, an oil [*hydrochloride*, $+0{\cdot}5H_2O$, m.p. 262° (decomp.; sinters at 250°); *methiodide*, cryst.]. (VIII) is dehydrogenated by Pd at 145—150° (later at 230°), giving *vomipyrine* (XI), $C_{15}H_{16}N_2$, m.p. 105—106° (yellow *hydrochloride*), an oily *base*, (?) $C_{14}H_{14}N_2$, b.p. 164—165°/high vac. (yellow *hydrochloride*, sinters at 220°, m.p. 240°, loses HCl at 80°), and a *base* (XII), $C_{13}H_{17}N$, b.p. 150—160°/12 mm. (XI) is unchanged by H_2–Pd–C, but with Na–C_5H_{11}·OH gives a H_4-*base*, $C_{15}H_{20}N_2$ [*hydrochloride*, m.p. 221° (decomp.; sinters at 200°)]. The last four bases give the pine shaving reaction. (XI) is probably (XI*a*); (XI*b*) would account for the coloured salts, but is less probable for other reasons. (XII) may be as shown.



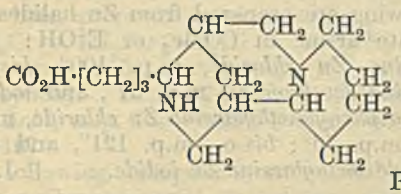
(XI*a*.) (XI*b*.) (XII.)

R. S. C.

α- and β-Hydroxylaudanosines. II. Products of exhaustive methylation. F. E. King and P. L'Ecuyer (J.C.S., 1937, 427—432).—Degradation of α-*hydroxylaudanosine methiodide*, m.p. 168° (efferv.), and *methochloride*, m.p. 165—166° (efferv.), and the β-*methiodide*, m.p. 223—225°, and *methochloride*, m.p. 217—218° (efferv.), with NaOH or Ag_2O gives 4 : 5-*dimethoxy*-2-*vinylbenzyldimethylamine* (I), b.p. 128°/2 mm. [*picrate*, m.p. 158—159°; *methiodide*, m.p. 197—198°; *methochloride*, m.p. 218° (efferv.)], which with dil. acid yields veratraldehyde (2 : 4-*dinitrophenylhydrazone*, m.p. 253—255°). Catalytic reduction of (I) affords 4 : 5-*dimethoxy*-2-*ethylbenzyldimethylamine* (II), b.p. 108°/0·06 mm. [*picrate*, m.p. 110—111°; *methiodide*, m.p. 209°; *methochloride* ($+H_2O$) (III), m.p. 150—151°]. Degradation of (III) by Emde's method gives 4-*methyl*-5-*ethylveratrole*, b.p. 105°/5 mm., demethylated to 4-methyl-5-ethylpyrocatechol (*di*-p-*nitrobenzoate*, m.p. 124—125°), also obtained by synthesis from 4 : 5-dimethoxy-2-methylacetophenone. 5-*Nitro*-4-*ethylveratrole*, m.p. 54—54·5°, prepared by nitration, is reduced to the 5-*amino*-compound, m.p. 63° (*Ac* derivative, m.p. 147°), which yields the 5-*CN*-derivative, m.p. 60°, reduced (Na–EtOH) to (II) [*picrolonate*, m.p. about 235° (decomp.)]. The methiodides of synthetic and natural specimens of (II) are identical. (III) on distillation/high vac. gives 4 : 5-*dimethoxy*-2-*ethylbenzyl chloride*, b.p. 128°/1 mm., m.p. 40°, also obtained from 4-ethylveratrole and CH_2O; the chloride with $NHMe_2$ forms (II). F. R. S.

Lupin alkaloids. XIII. Fission of the piperidone ring of lupanine by fuming hydrochloric

acid. E. Hoffmann, F. W. Holschneider, and K. Winterfeld (Arch. Pharm., 1937, **275**, 65—66; cf. this vol., 125).—The lactam nature of lupanine is confirmed by fission by conc. HCl at 150° to the *acid* (*platinichloride*, $+H_2O$, decomp. 245°, of the *Et* ester), having the structure

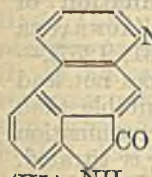


R. S. C.

Alkaloids of ergot. VIII. New alkaloids of ergot: ergosine and ergosinine. S. Smith and G. M. Timmis (J.C.S., 1937, 396—401).—Ergosinine, (I), $C_{30}H_{37}O_5N_5$ (+0·5MeOH), m.p. 220° (decomp.), (*hydrochloride*, decomp. about 206°) (cf. A., 1936, 351, 1131), is degraded by hydrolysis and pyrolysis to lysergic acid, NH_3, ergine, *d*-proline, *l*-leucine, and $AcCO_2H$. (I) is converted (KOH–EtOH) into ergosine (II) [*hydrochloride*, m.p. 235° (decomp.); *hydrobromide*, decomp. 230°; *nitrate*, decomp. 215°; *methiodide*, decomp. 215°]. (I) and (II) form a mol. *compound*, m.p. 200° (decomp.), $[\alpha]_{5461}^{20}$ +164° in $CHCl_3$. (I), heated under reduced pressure, gives with other cryst. products *l-leucyl-d-proline lactam*, m.p. 148°, $[\alpha]_{5461}^{20}$ +105° in H_2O. (I) and (II) differ as regards $[\alpha]$ and their physiological activity in the same sense as do, *e.g.*, ergotamine and ergotaminine.

F. R. S.

Synthesis of substances related to lysergic acid. W. A. Jacobs and R. G. Gould, jun. (Science, 1937, **85**, 248—249; cf. A., 1936, 1277).—Reduction of naphthostyril with Na in BuOH yields 3 : 4-trimethyleneindole (I), with 8-amino-1-hydroxymethyl-1 : 2 : 3 : 4-tetrahydronaphthalene as by-product. (I) exhibits the usual indole reactions, but not the characteristic Keller reaction of the ergot alkaloids. A nearer approach to the synthesis of lysergic acid (II) has been achieved as follows. 3 : 1-NH_2·$C_{10}H_6$·CO_2H by the Skraup reaction gives the corresponding β-naphthoquinolinecarboxylic acid, which is nitrated to a nitro-β-naphthoquinoline carboxylic acid. After reduction of the NO_2 to NH_2, lactamisation occurred forming the substance (III). Reduction of (III) with Na and BuOH yields a mixture which gives colour reactions closely approaching those characteristic of (II) and its derivatives.



(III.)

L. S. T.

Derivatives of berbine. IV. Hydrogenation with amalgamated zinc and an addition of amalgamated cadmium. W. Awe and H. Unger (Ber., 1937, **70**, [*B*], 472—478).—The use of Cd–Hg in the Clemmensen reaction offers no advantage over that of Zn–Hg but mixtures of Zn–Hg and Cd–Hg (3 : 1) allow the change to proceed much more rapidly and with much better utilisation of H. Conc. HCl can be replaced by 30% AcOH containing 2*N*-H_2SO_4. The method is particularly suited for the conversion of *iso*quinoline bases into their H_4-derivatives. The following examples are cited: berberinium H sulphate to 16 : 17-dihydrodeoxyberberine; palmatinium iodide to 16 : 17-dihydrodeoxypalmatine; 9-benzyldeoxyberberine to 11 : 12-dimethoxy-2 : 3-methylenedioxy-9-benzylberbine, m.p. 165—166°, and its ψ-form, m.p. 146°; 9-*o*-tolyl- and 9-*o*-methoxyphenyldeoxyberberine to 11 : 12-dimethoxy-2 : 3-methylenedioxy-9-*o*-tolyl- and -9-*o*-methoxyphenyl-berbine, respectively; *9-phenyldeoxypalmatine hydrobromide* to 2 : 3 : 11 : 12-*tetramethoxy-9-phenylberbine*, m.p. 172°, and (?) *9-phenyl-16 : 17-dihydrodeoxypalmatine*, m.p. 139—140°; papaverine methiodide to *dl*-laudanosine. Codeine appears largely unaffected. H. W.

Alkaloid from Chinese hanfangchi. S. K. Liu, C. Ma, and S. Y. Li (Pharm. Chem. Res. Rept. [China], 1935, **1**, No. 1, 1—11, 13—28).—Extraction with AcOH or EtOH and recrystallisation of the phosphate yields an *alkaloid*, m.p. 215—217°, $[\alpha]_D^{19\cdot2}$ +280·8° in $CHCl_3$, containing 1 double linking, 1 :CO, 2 OMe, and 1 NMe. Ch. Abs. (*r*)

Alkaloid from Japanese hanfangchi. S. K. Liu, C. Ma, S. Y. Li, and C. F. Lo (Pharm. Chem. Res. Repts. [China], 1935, **1**, No. 1, 29—35, 37—49).—Extraction with EtOH followed by recrystallisation of the hydrochloride yields an *alkaloid*, $C_{19}H_{23}O_4N$, m.p. 160—163°, $[\alpha]_D^{16}$ −66° in $CHCl_3$ (*hydrochloride*, m.p. 235—239°), which contains 1 double linking, 1 :CO, 1 phenolic OH, 2 OMe, and 1 NMe.

Ch. Abs. (*r*)

Alkaloids of *Sinomenum* and *Cocculus*. XLIV. Phenolic alkaloid of *C. trilobus*, D.C. 3. Constitution of normenisarine. XLV. Review on the biscoclaurine alkaloids. Consideration from the stereochemical and biogenetic viewpoint. H. Kondo and M. Tomita (J. Pharm. Soc. Japan, 1935, **55**, 911—913, 914—933).—XLIV. *Normenisarine*, $C_{32}H_{22}(OMe)_2(\cdot O\cdot)_3(NMe)(:N)$, m.p. 223°, yields *menisarine*, $C_{33}H_{25}N_2O_3(OMe)_3$, m.p. 164°, on methylation.

XLV. A review. Ch. Abs. (*r*)

Rotatory power of some alkaloids. C. Lormand and P. Gesteau (XIV Congr. Chim. ind. Paris, 1934, Comm. 2, 3 pp.; Chem. Zentr., 1936, i, 3145).—$[\alpha]^{20}$ for λ 5893, 5780, 5460, 4358, and 4046 are recorded for cocaine hydrochloride, codeine, heroine hydrochloride, picrotoxin, emetine hydrochloride, pilocarpine hydrochloride and nitrate, scopolamine hydrobromide, and eserine and its salicylate.

H. N. R.

Arsinic acids. F. F. Blicke and G. L. Webster (J. Amer. Chem. Soc., 1937, **59**, 534—537).—PhAsO (in aq. NaOH) and *m*-NO_2·C_6H_4·N_2Cl (neutralised) give m-*nitrodiphenylarsinic acid*, m.p. 154—155°, reduced ($FeSO_4$, aq. NaOH) to the m-NH_2-*acid*, m.p. 210—212°, which is converted (diazo-method) into the m-*OH-acid*, m.p. 230—232°, and thence by Me_2SO_4 + aq. NaOH into m-*methoxydiphenylarsinic acid*, m.p. 120—121°. o-*Hydroxy-*, m.p. 221—223°, and o-*methoxy-*, m.p. 187—188°, *-diphenylarsinic acids* are similarly prepared. p-*Bromodiphenylarsinic acid*, m.p. 184—185°, is obtained from PhAsO and *p*-C_6H_4Br·N_2Cl. *p*-Nitrodiphenylarsinic acid (in conc. H_2SO_4) with HNO_3 (*d* 1·42) + conc. H_2SO_4 at 0—3° give the 3 : 4′-(NO_2)$_2$-*acid*, m.p. 230—232°,

reduced (method : A., 1934, 312) to the 3 : 4′-$(NH_2)_2$-*acid*, m.p. 176—178°, which is converted (diazo-method) into 3 : 4′-*dihydroxydiphenylarsinic acid*, m.p. 210—211°. 3 : 3′-*Dinitro*-4-*hydroxydiphenylarsinic acid*, m.p. 195—196°, is obtained by similar nitration of *p*-hydroxydiphenylarsinic acid. 3-*Nitro*-4-*methoxyphenylarsine oxide*, m.p. 247—248° (decomp.), and MeI in aq. MeOH–NaOH give 3-*nitro*-4-*methoxyphenylmethylarsinic acid*, m.p. 216—217°. 3-Amino-4-hydroxyphenylmethylarsinic acid, m.p. 233—234° (lit. 206—207°), is prepared by reduction ($FeSO_4$, aq. NaOH) of the 3-NO_2-acid (Bertheim, A., 1915, i, 331). The prep. of *p*-$C_6H_4Br{\cdot}AsO_3H_2$ is improved. The following are obtained from the requisite acids by the usual methods : *p*-$NO_2{\cdot}C_6H_4{\cdot}AsCl_2$, which with piperidine *N*-pentamethylenedithiocarbamate gives p-*nitrophenylarsylene N-pentamethylenedithiocarbamate*, m.p. 177—178° ; o-*nitrodiphenyliodoarsine*, m.p. 113—114° ; o- (I) and m-, m.p. 173—175°, *aminodiphenylchloroarsine hydrochlorides* ; 3-*amino*-4-*hydroxyphenylmethyl-chloroarsine hydrochloride*, m.p. 178—180°, and -*iodoarsine hydriodide*, m.p. 136—137° ; o-*methoxydiphenyliodoarsine*, m.p. 68—69° ; *p*-$OMe{\cdot}C_6H_4{\cdot}AsCl_2$, m.p. 49—50°. (I) and aq. NH_3 give 2 : 2′-diaminotetraphenylarsyl oxide, the Ac_2 derivative (+1·5AcOH), m.p. 180—181°, of which with aq. HI affords o-*acetamidodiphenyliodoarsine*, m.p. 147—148° (the m-*isomeride*, m.p. 146—147°, is similarly prepared). *o*-$OH{\cdot}C_6H_4{\cdot}AsCl_2$ and aq. Na_2CO_3 give (cf. Kalb, A., 1921, i, 375) an anhydride, m.p. 181—182°, of *o*-$OH{\cdot}C_6H_4{\cdot}As(OH)_2$. H. B.

Synthesis of *p*-benzylthiolbenzenearsinic acid. T. Takahashi (J. Pharm. Soc. Japan, 1935, **55**, 875—879).—*p*-$NO_2{\cdot}C_6H_4{\cdot}SH$, m.p. 77°, from *p*-$C_6H_4Cl{\cdot}NO_2$ with KOH and H_2S, yields, with KOH and CH_2PhCl, 4-*nitrophenyl benzyl sulphide*, m.p. 123°, reduced to 4-*aminophenyl benzyl sulphide* (*hydrochloride*, m.p. 256° ; *Ac* derivative, m.p. 133° and 105° ; *Bz* derivative, m.p. 182°), which, on diazotisation and treatment with Na_3AsO_3, yields p-*benzylthiolphenylarsinic acid*, decomp. 250°.

Ch. Abs. (*r*)

Compounds formed by mercury salts with tertiary arsines. J. J. Anderson and G. J. Burrows (J. Proc. Roy. Soc. New South Wales, 1936, **70**, 63—68).—The following are prepared from Hg^{II} halides and $AsPh_2Me$ in boiling EtOH : *diphenylmethylarsine Hg*^{II} *chloride*, m.p. 186°, *bromide*, m.p. 142°, and *iodide*, m.p. 116° ; below 50° the reaction products are *bisdiphenylmethylarsine Hg*^{II} *chloride*, m.p. 131°, *bromide*, m.p. 100·5°, and *iodide*, m.p. 83°. $AsPhMe_2$ and Hg^{II} halides in boiling EtOH yield *phenyldimethylarsine Hg*^{II} *chloride*, m.p. 201°, *bromide*, m.p. 171°, and *iodide*, m.p. 144°, and below 50°, *bisphenyldimethylarsine Hg*^{II} *chloride*, *bromide*, m.p. 115°, and *iodide*, m.p. 104°. J. D. R.

Co-ordination compounds of cadmium with tertiary arsines. G. J. Burrows and A. Lench (J. Proc. Roy. Soc. New South Wales, 1936, **70**, 218—221).—The following are prepared by interaction of Cd halide with the appropriate arsine in hot EtOH : *phenyldimethylarsine Cd chloride*, m.p. 220°, *bromide*, m.p. 186°, *iodide*, m.p. 108° ; *diphenylmethylarsine Cd chloride*, m.p. 292°, *bromide*, m.p. 257° ; *bisdiphenylmethylarsine Cd chloride*, m.p. 100° ; *bis*-o-, m.p. 187°, and -p-, m.p. 126°, -*tolyldimethylarsine Cd iodide*. J. D. R.

Derivatives of zinc halides with tertiary arsines. G. J. Burrows and A. Lench (J. Proc. Roy. Soc. New South Wales, 1936, **70**, 222—224).—The following are prepared from Zn halides and the appropriate arsine in $COMe_2$ or EtOH : *phenyldimethylarsine Zn chloride*, m.p. 100°, *bisphenyldimethylarsine Zn bromide*, m.p. 67°, and *iodide*, m.p. 92° ; bis-*diphenylmethylarsine Zn chloride*, m.p. 128°, *bromide*, m.p. 76° ; *bis*-o-, m.p. 121°, and -p-, m.p. 115°, -*tolyldimethylarsine Zn iodide*. J. D. R.

Preparation of camphor-10-dichloroarsine from camphor-10-sulphinic acid. J. D. Loudon (J.C.S., 1937, 391—392).—Camphor-10-sulphinic acid and $AsCl_3$ give *camphor*-10-*dichloroarsine* (I), m.p. 89—90°, also obtained from biscamphor-10-mercury and $AsCl_3$. (I) is hydrolysed (NaOH) to *camphor*-10-*arsinous acid*, m.p. 100° (decomp.), and oxidised (Cl_2 or H_2O_2) to the -*arsinic acid*, m.p. 210°. F. R. S.

Complex compounds formed by the reaction between phenyldichlorostibine and benzenediazonium chloride. A. B. Bruker (J. Gen. Chem. Russ., 1936, **6**, 1823—1827).—Aq. PhN_2Cl, AcOH, and $SbPhCl_2$ or $SbPh{\cdot}OCl$ in AcOH, at 0°, yield the *complex*, $PhN_2Cl,SbPhCl_2$, decomp. at 58—60° to give $SbPh_2Cl_3$ and N_2. R. T.

Reaction of organic bismuth compounds with mercuric chloride. L. G. Makarova (J. Gen. Chem. Russ., 1937, **7**, 143—147). The following reactions are described : $BiPh_3Cl_2$ (I) + $HgCl_2$ + H_2O → HgPhCl (II) + BiOCl + $2C_6H_6$ + Cl_2 ; (I) + $3HgCl_2$ + H_2O → 3(II) + BiOCl + Cl_2 + 2HCl ; $BiPh_2Cl$ (III) + $HgCl_2$ + H_2O → (II) + BiOCl + C_6H_6 + HCl ; (III) + $2HgCl_2$ + H_2O → 2(II) + BiOCl + 2HCl. R. T.

Aromatic phosphorus halides and their suitability for the volumetric determination of water. J. Lindner, W. Wirth, and B. Zaunbauer (Monatsh., 1937, **70**, 1—19 ; cf. A., 1931, 1257).—Further examination of P aryl halides does not lead to the discovery of a material more suitable than $C_{10}H_7{\cdot}POCl_2$ (A., 1925, ii, 901) for the determination of H_2O by conversion into HCl, which is titrated. Ph_2, PCl_3, and $AlCl_3$ give *P diphenylyl dichloride* (mixture of isomerides), transformed by Cl_2 in CCl_4 into *P diphenylyl tetrachloride*, which with SO_2 affords the corresponding *oxychloride*, b.p. 220°/10—11 mm., m.p. 90° after softening at 70°. $PPhCl_2$, b.p. 221°/1 atm., m.p. −51°, best obtained from C_6H_6 and PCl_3 at 600°, is converted by Cl_2 in CCl_4 into $PPhCl_4$, m.p. 73°, and the *compound*, $PPhCl_4,PCl_5$, m.p. >200°, also obtained from $PPhCl_2$, PCl_3, and Cl_2 in CCl_4. Cl_2 and $PPhCl_4$ in CCl_4 yield the *substance*, $PPhCl_4,Cl_2$, which readily loses 2Cl. The analogous *compound*, $PPhCl_4,Br_2$, m.p. 134° (decomp. ; sealed capillary), is more stable. The behaviour of the compounds when heated in air and the effects of light are described. H. W.

Structure of hypophosphorous acid. I. Reaction of aryldiazonium salts with hypophosphites. II. Reaction of arylhydrazines with

hypophosphites. III. Reaction of aryldiazonium salts with phosphorus trichloride and sodium di*iso*propyl phosphite. IV. Reaction of hypophosphites with alkyl halides. V. M. PLETZ (J. Gen. Chem. Russ., 1937, 7, 84—89, 90—92, 270—272, 273—276).—I. The following arylphosphinic acids have been prepared by the reaction NaH_2PO_2 (I) + $R{\cdot}N_2Cl \rightarrow [H_2PO{\cdot}O{\cdot}N_2R] \rightarrow RH_2PO_2 + N_2$: phenyl-, o-, m.p. 115°, and p-*tolyl*-, o-, m.p. 157°, and p-*nitrophenyl*-, m.p. 134°, α- and β-*naphthylphosphinic acid*, m.p. 175°, and *diphenyldiphosphinic acid*, m.p. 167°.

II. The following compounds are obtained from (I) and various hydrazines in aq. solution, in presence of $CuSO_4$, by the reaction $NHR{\cdot}NH_2$ + (I) → $NHR{\cdot}NH{\cdot}PH_2{:}O$ (II) + NaOH; (II) + O → $RH_2PO_2 + N_2 + H_2O$: phenyl-, *p*-bromophenyl-, and *p*-nitrophenyl-phosphinic acid.

III. PCl_3 or $NaPr^{\beta}_2PO_3$ do not react with benzenediazonium compounds.

IV. (I) and EtBr or EtI in H_2O react as follows: $3(I) + 3EtX \rightarrow 3NaX + PH_2Et + 2EtH_2PO_2$. The reaction with $CH_2Cl{\cdot}CO_2Et$ involves intermediate production of $H_2PO_2{\cdot}CH_2{\cdot}CO_2H$, which readily eliminates CO_2, to yield MeH_2PO_2. R. T.

Review on the organic compounds of phosphorus. V. M. PLETZ (Uspechi Chim., 1935, 4, 573—609).—A comprehensive survey. In the presence of Cu, PhN_2Cl reacts with PCl_3 and $PhPCl_2$ to give $PPhCl_4$ and PPh_2Cl_3, respectively. CH. ABS. (*r*)

(A) Structure of products of addition of mercury salts to unsaturated compounds by the arylation method. A. N. NESMEJANOV and R. C. FREIDLINA. **(B) Reaction of diazomethane with β-bromomercuriethyl alcohol, and the structure of the products of addition of mercuric salts to olefines.** R. C. FREIDLINA, A. N. NESMEJANOV, and F. A. TOKAREVA (J. Gen. Chem. Russ., 1937, 7, 43—50, 262—266).—(A) $OH{\cdot}CH_2{\cdot}CH_2{\cdot}HgBr$ (I) in C_6H_6 and PhNCO yield β-*bromomercuriethyl phenylcarbamate* (II), m.p. 124—126° (decomp.). (I) in aq. alcoholic KOH and di-*p*-tolyldichlorostannane afford β-*hydroxyethyl*-p-*tolylmercury* (III), m.p. 52·5—53·5°. $Hg(OAc)_2$ and *cyclo*hexene (IV) in H_2O yield 2-*acetomercuri*cyclo*hexanol*, m.p. 112·5—113·5°, which reacts with $SnPh_2Cl_2$ (V) in EtOH–KOH, at the b.p., to afford 2-*phenylmercuri*cyclo*hexanol* (VI), m.p. 101—102°. $Hg(OAc)_2$ and (IV) in EtOH give 1-*ethoxy*-2-*acetomercuri*cyclo*hexane*, m.p. 76°, converted by boiling with NaOH and (V) in EtOH into *Hg phenyl* 2-*ethoxy*cyclo*hexyl* (VII). 1-Chloromercurimethyl-1 : 2-dihydrobenzfuran, NaOH, and (V) in EtOH, at the b.p., afford 1-*phenylmercurimethyl*-1 : 2-*dihydrobenzfuran*, m.p. 60—61°. This, similarly to (II), (III), (VI), and (VII), is decomposed by 15% HCl, with production of unsaturated hydrocarbon and Hg aryl chloride. The reactions support the structure given above for (I), rather than one involving residual valencies, of the type $C_2H_4{,}HgBrOH$.

(B) (I) and CH_2N_2 in Et_2O yield β-bromomethylmercuriethyl alcohol, which decomposes at room temp. with production of C_2H_4, Hg, *bromomethylmercuric bromide* (VIII), m.p. 124—125°, CH_2O, and N_2. $HgBr_2$ and CH_2N_2 in Et_2O yield (VIII) and *Hg dibromodimethyl*, m.p. 42—43°. (VIII) and aq. NaOH yield Hg, CH_2O, and HBr. R. T.

Lead organic compounds containing the carbethoxy-group. K. A. KOTSCHESCHKOV and A. P. ALEXANDROV (J. Gen. Chem. Russ., 1937, 7, 93—96).—K Et malonate in EtOH and $PbPh_3Cl$ in $COMe_2$ yield *Et triphenylplumbyl malonate*, m.p. 159—160° (decomp.), converted by heating at 160—165° in vac. into *Et triphenylplumbiacetate*, m.p. 59—60°. K Et benzylmalonate similarly gives *Et triphenylplumbyl benzylmalonate*, m.p. 131—132° (decomp.), and *Et γ-phenyl-α-triphenylplumbibutyrate*, m.p. 82—84°. R. T.

Reduction of organic mercury compounds by tin alkyl compounds, as a method of synthesis of hydroxy- and amino-aryl tin compounds. A. N. NESMEJANOV, K. A. KOTSCHESCHKOV, and V. P. PUZIREVA (J. Gen. Chem. Russ., 1937, 7, 118—121).—The following compounds have been prepared, by the reactions $Sn_2Et_6 + RHgCl \rightarrow SnEt_3Cl + SnREt_3 + Hg$; $Sn_2Et_6 + HgR_2 \rightarrow 2SnREt_3 + Hg$: $SnPhEt_3$, p-*dimethylaminophenyl*- (I), b.p. 172—173°/3 mm., and o-*hydroxyphenyl-triethylstannane*, b.p. 197—200°/3 mm. (I) with $HgCl_2$ yields *p*-$NMe_2{\cdot}C_6H_4{\cdot}HgCl$ and $SnEt_3Cl$, and with Br gives *p*-$C_6H_4Br{\cdot}NMe_2$ and $SnEt_3Br$. $SnEt_2$ yields $SnEt_2Cl_2$ and Hg with $HgCl_2$, and $SnPh_2Et_2$ and Hg with $HgPh_2$. R. T.

Relative reactivities of organometallic compounds. XV. Organoalkali compounds. H. GILMAN and R. V. YOUNG (J. Org. Chem., 1936, 1, 315—331).—The prep. of the *compounds* $CPh{:}CM$ (M = *MgBr*, *Li*, Na, *K*, *Rb*, and *Cs*) in Et_2O is described, and the times required for reaction with PhCN under comparable conditions given, no significant reaction with Et_2O being observed. The reactivity of these compounds increases in the above order, which accords with the reactivity sequences obtained from the metalation of dibenzfuran (I) by EtM (M = Li, Na, and K) and the reaction with Bu^tCl of the benzophenone alkali compounds of K, Rb, and Cs. Further, EtLi in light petroleum at room temp. gives only monometalation of (I), whilst NaEt and in greater amounts KEt also give dimetalation. Na–K alloy reacts with $CMe_2Ph{\cdot}OMe$ giving CMe_2PhK, and similarly only organo-K compounds are obtained from $CPh_3{\cdot}OEt$, $CHPh_2{\cdot}OMe$, $(CHPh_2)_2$, and $CHPh_3$. Only Na adds to $(CPh_2)_2$ giving $(CNaPh_2)_2$, but Na–K and Na–Rb alloys give the corresponding K and Rb compounds, respectively. 4-Dibenzfuryl-sodium and -potassium split Et_2O to an appreciable extent; they react more rapidly with PhF than with PhCl, and immediately with *o*-$C_6H_4Me{\cdot}CN$, but in the case of PhCl the Na- is more reactive than the K-compound. The reaction of CPh_3Li and CPh_3Na with PhCl and PhBr is also anomalous in that the Li- reacts more rapidly than the Na-compound, but with $C_6H_4Me{\cdot}CN$ the Na-compound is the more reactive. All the foregoing organoalkali compounds are satisfactorily carbonated at room temp. except the Li-compounds which are better carbonated at low temp. or with solid CO_2. Conductivity results and electromotive series are

shown to be of limited use for predicting relative reactivities of organometallic compounds. H. G. M.

Organometallic compounds of styrene. G. F. Wright (J. Org. Chem., 1936, **1**, 457—463).—The reported prep. of *cis*- and *trans*-phenylbutadienes (A., 1931, 349) is not confirmed. *cis*- (I) and *trans*-β-bromostyrene (II) react with pure Mg (in absence of I and of O_2) to form, after an induction period, *cis*- and *trans*-Mg styryl bromide. The former with solid CO_2 gives 9% *trans*- and 19% *cis*-, and the latter 30% *trans*- and 20·5% *cis*-cinnamic acid, together with 3% and 11% *trans-trans*-αδ-diphenylbuta-αγ-diene (III), respectively. The yield of 12% of *cis*-acid from the equilibrium mixture of (I) and (II) [largely (II)] shows that isomerisation has not occurred in the halide itself, but in the Mg compound. With MeCHO, both Mg derivatives give mixed isomeric methylstyrylcarbinols. With Mg and $HgBr_2$, the above equilibrium mixture yields *styrylmercuric bromide*, m.p. 202—203° (converted by I into β-iodostyrene). Either (I) or (II) with Li yields *Li styryl*, converted by solid CO_2 into a 4 : 1 mixture of *trans*-cinnamic and phenylpropiolic acids, with (III). A new flask for the Grignard reaction, of inverted conical shape, is described. E. W. W.

Rhizopenin.—See A., III, 144.

Structure of proteins. Ox hæmoglobin, ovalbumin, ox fibrin, and gelatin.—See A., III, 168.

Quantitative organic micro-analysis. H. Lieb and A. Soltys (Mikrochem., Molisch Festschr., 1936, 290—300).—Points of technique as to wt. calibration, and the determination of C, H, N, halogens, Ac, and mol. wts. (Rast method) are discussed. J. S. A.

Pressure regulator for carbon and hydrogen determination. H. Roth (Mikrochem., Molisch Festschr., 1936, 373—374).—Apparatus is described. J. S. A.

Refinement of micro-carbon–hydrogen determination by improved weighing technique. A. Friedrich and H. Sternberg (Mikrochem., Molisch Festschr., 1936, 118—124).—An improved form of absorption tube is described. J. S. A.

Qualitative tests for nitrogen in organic substances. J. B. Robertson (J. S. African Chem. Inst. 1937, **20**, 17—20).—The addition of Fe filings (equal in bulk to the substance) to the Na fusion increases the amount of $[Fe(CN)_6]''''$ formed, and improves the sensivity of the test. J. S. A.

Detection of elements in organic compounds. R. H. Baker and C. Barkenbus (Ind. Eng. Chem. [Anal.], 1937, **9**, 135—136).—A fusion mixture of anhyd. K_2CO_3 and Mg powder (2 : 1) is substituted for Na in the ordinary test for elements. The sample is distilled over the strongly heated fusion mixture in an atm. of Et_2O. J. L. D.

Organic oxidation equivalent analysis. I. Theory and applications. R. J. Williams. **II. Use of iodate (micro and "sub-micro" methods).** R. J. Williams, E. Rohrman, and B. E. Christensen. **III. General method using dichromate.** B. E. Christensen, R. J. Williams, and A. E. King (J. Amer. Chem. Soc., 1937, **59**, 288—290, 291—293, 293—296).—I. The mol. formula of a compound can be calc. from its mol. wt. [suitably corr. if N and/or S (both in reduced condition) are present] and the amount of O necessary for its complete oxidation; equations for compounds containing C, H, and O are given. Possible applications are discussed.

II. The amount of O necessary for complete oxidation can often be determined by treatment with KIO_3 in conc. H_2SO_4 at 185° and back-titration of unused KIO_3; micro (3—4 mg.) and "sub-micro" (0·4—0·6 mg.) methods are detailed (cf. Strebinger, A., 1919, ii, 350; Stanek and Nemes, A., 1932, 529). Phthalates are oxidised with difficulty, whilst nicotinic acid is almost unaffected. Oxidation of N is largely avoided under the conditions used.

III (cf. Snethlage, A., 1935, 1140, 1390). The substance (0·05—0·15 g.) is oxidised with $K_2Cr_2O_7$ in conc. H_2SO_4–H_2O (5 : 1 vol.) at 165—200°, the mixture is then diluted with 6*N*-H_2SO_4 and boiled gently for 5 min. [to decompose any $HCrO_5$ or $Cr_2(SO_4)_5$], and the excess of $K_2Cr_2O_7$ is determined iodometrically; correction for evolved O_2 is necessary. In some cases (*e.g.*, carbohydrates) CO is produced; this is oxidised with the evolved O_2 over a Pt spiral. The apparatus used is described and the advantages of the method (compared with combustion) are indicated. H. B.

Apparatus for micro-hydrogenation by a volumetric method.—See A., I, 267.

Apparatus for determination of the hydrogenation index. A. Castille (Bull. Soc. chim. Belg., 1937, **46**, 5—9).—An apparatus for the accurate determination of the hydrogenation index (100 × wt.-% of H_2 absorbed by the unsaturated compound), by measurement of the H_2 absorbed by approx. 1 g. of the substance in presence of Pt, is described. J. W. B.

Sensitivity of colour reactions for phenols. V. M. Platkovskaja and S. G. Vatkina (J. Appl. Chem. Russ., 1937, **10**, 202—207).—Min. concns. of substance giving a detectable blue colour with phosphomolybdic acid and aq. NH_3 are: PhOH, *o*- and *m*-$C_6H_4(OH)_2$, 1 : 2 : 3- (I), 1 : 2 : 4- (II), and 1 : 2 : 5-$C_6H_3(OH)_3$ (III), α-$C_{10}H_7$·OH, and *iso*eugenol 0·0005; cresol and quinol 0·00005; β-$C_{10}H_7$·OH, thymol, and adrenaline 0·005; guaiacol carbonate 0·05; vanillin 0·1; salicylic acid 0·5%. The vals. with phosphotungstic acid and aq. NH_3 are: *o*- and *p*-$C_6H_4(OH)_2$ and (I) 0·0005; *m*-$C_6H_4(OH)_2$ and (II) 0·005; PhOH 0·5%, and with Millon's reagent: PhOH and cresol 0·0005; *o*-$C_6H_4(OH)_2$ 0·05; (I) 0·5; (III) 5%. R. T.

Turbidity in determination of uric acid with the photo-electric colorimetric.—See A., III, 192.

Sodium cupricyanate. Reaction for cyanuric acid.—See A., I, 256.

Colour reactions of rare earths with alkaloids. III.—See A., I, 263.

Determination of magnesium.—See A., I, 199.