BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

JUNE, 1938.

Electrochemical synthesis of organic compounds. N. N. MELNIKOV (Uspechi Chim., 1937, 6, 4—41).—A review. R. T.

Asymmetric synthesis. R. BOUSSET (Bull. Soc. chim., 1938, [v], 5, 479—493).—Theoretical. If a racemic substance, *A*, yields *B* by the agency of, or combination with, an active substance which is regenerated unchanged, and the activity and yield of *B* are such that *B* would be active even if all material unaccounted for had been of opposite rotation, then an asymmetric synthesis will have been achieved. Known reactions, *e.g.*, of bacteria, Kuhn's and McKenzie's reactions, are merely resolutions. R. S. C.

Purification and characterisation of substances of high mol. wt. A. TISELIUS (Svensk Kem. Tidskr., 1938, 50, 58—68).—A review with special reference to electrophoretic methods. A. LI.

Decomposition of hydrocarbons.—See A., 1938, I, 330.

Methylene. T. G. PEARSON, R. H. PURCELL, and G. S. SAIGH (J.C.S., 1938, 409—424).—Decomp. of keten by light (cold Hg arc), and of CH_2N_2 by heat (400°) or by light, yields CH_2, detected by combination with Te (at 70°) or Se mirrors. Gaseous CH_2Te and CH_2Se are formed, and polymerise in small yield on cooling to two solids in each case. In presence of CH_2N_2, CH_2 has a half-val. period of 5×10^{-3} sec., but in pure keten it shows no measurable decay in 50×10^{-3} sec. Its stability in CH_2N_2 is increased by dilution with keten, Et_2O, or N_2. CH_2 behaves as a reactive mol. rather than a free radical, and undergoes a bimol. reaction with CH_2N_2. Measurements of the rate of removal of mirrors by CH_2 from CH_2N_2 heated at different temp. show the activation energy in the production of CH_2 to be 22 kg.-cal. A. LI.

[Rates of] condensation of ethane, propane, butane, and propylene.—See A., 1938, I, 317.

Polymerisation of unsaturated hydrocarbons. H. I. WATERMAN and J. J. LEENDERTSE (J. Inst. Petroleum Tech., 1938, 24, 16—37).—Aliphatic olefines (C_2—C_{16}) and cyclic unsaturated hydrocarbons (pinene, *cyclo*hexene, and tetrahydronaphthalene) were polymerised with $AlCl_3$, and in a few cases with BF_3 or Al_2O_3, at −78° to 70°. Polymerisation products were fractionated and hydrogenated and the fractions then examined for cyclisation by the sp. refraction–mol. wt. method. Some ring formation was evident in every case except with hexadecene. When polymerising cyclic unsaturated hydrocarbons ring-opening was observed in some cases. By varying the base material and conditions practically any desired composition can be obtained.

By comparing the composition of saturated hydrocarbon mixtures as derived from sp. refraction and sp. parachor (based on at. parachors of Mumford and Phillips) a qual. idea of the degree of branching of the hydrocarbon mixtures can be obtained, particularly of aliphatic hydrocarbon mixtures. The sp. parachor–mol. wt. method gives information as to the degree of cyclisation, but the sp. parachor is also dependent on the branching of the mol. The difference between the no. of rings calc. from the parachor and the true no. of rings found by the sp. refraction–mol. wt. method gives an indication of the amount of branching in the saturated hydrocarbons. C. C.

Addition of hydrogen chloride to butadiene. M. S. KHARASCH, J. KRITCHEVSKY, and F. R. MAYO (J. Org. Chem., 1938, 2, 489—496).—At −80° or 25° HCl and butadiene alone give 35% or in AcOH 50—80% of a mixture containing 75—80% of $CH_2{:}CH{\cdot}CHMeCl$ (I), b.p. 64°/750 mm., and 25—20% of $CHMe{:}CH{\cdot}CH_2Cl$ (II), b.p. 84°/750 mm., but no $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2Cl$. Anhyd. $FeCl_3$ rapidly rearranges (I) or (II) to a 1 : 1 mixture. H_2O and peroxides are without effect. 1 mol. of HCl slowly gives a mixture containing 70—75% of (I) and 30—25% of (II); $FeCl_3$–HCl gives the same mixture much more rapidly. At 100° more (II) is formed. At −80° HCl alone has practically no effect. CuCl–HCl also catalyses the change. It is concluded that the mixture obtained from butadiene and HCl is not determined by isomerisation. Similarly the products obtained by HBr under anaërobic conditions are a primary mixture; the effect of peroxides or HBr is to isomerise this mixture. R. S. C.

Thermal polymerisation of butadiene.—See A., 1938, I, 315.

Conjugated systems. IV. Reactions of divinyl with hypochlorous acid and its esters. V. Reactions of divinyl with hypobromous acid and with alkyl hypobromites. A. A. PETROV (J. Gen. Chem. Russ., 1938, 8, 131—141, 142—150).—IV. Divinyl (I) at −12° and 10% aq. $NH_2{\cdot}CO{\cdot}NHCl$ yield *α-chloro-β-hydroxy-*Δ^{γ}*-butene* (II), b.p. 144—147°, (*acetate*, b.p. 163—166°), converted by heating with aq. KOH into divinyl α-oxide (III), from which *γ-hydroxy-δ-methoxy-*, b.p. 143—144° (*acetate*, b.p. 159—162°), *-δ-ethoxy-*, b.p. 153—157°, or *-δ-isobutoxy-*Δ^{α}*-butene*, b.p. 173—180°, are obtained by boiling with the appropriate alcohol. (II) and Br in $CHCl_3$ yield *α-chloro-γδ-dibromo-β-hydroxybutane*, b.p. 129—

130°, oxidised by $Na_2Cr_2O_7$ in dil. H_2SO_4 to *α-chloro-γδ-dibromo-β-ketobutane*, b.p. 132—133°. (I) when shaken with EtOH and $PhSO_2{\cdot}NCl_2$ yields *α-chloro-β-ethoxy-Δ$^{\gamma}$-butene*, b.p. 137·5—138·5°, which, with Br in $CHCl_3$, gives *α-chloro-γδ-dibromo-β-ethoxybutane*, b.p. 114—115°/10 mm.

V. (I) and aq. NHAcBr give *α-bromo-β-hydroxy-Δ$^{\gamma}$-butene*, b.p. 161—162·5° (*acetate*, b.p. 72°/10 mm.), which yields (III) as above, and with Br in $CHCl_3$ at −10° gives *αγδ-tribromo-β-hydroxybutane*, b.p. 141—141·5°/10 mm. (*acetate*, b.p. 146°/10 mm.); this is oxidised to *αγδ-tribromo-β-ketobutane*, b.p. 121°/10 mm. R. T.

Isomerisation of diallyl. J. M. Slobodin (J. Gen. Chem. Russ., 1938, **8**, 188—189).—Levina's conclusion that Al_2O_3 is a more active catalyst of isomerisation of diallyl than is floridin (A., 1938, II, 48) is questioned. R. T.

Spectrographic and chemical study of some aliphatic terpenes. III. *allo*Ocimene and [its] hydrogenation products. G. Dupont, R. Dulou, V. Desreux, and R. Picoux. **IV. Ocimene.** G. Dupont and V. Desreux (Bull. Soc. chim., 1938, [v], **5**, 322—336, 337—339; cf. A., 1937, II, 200; 1938, II, 80).—III. When prepared by pyrolysis of pinene (A., 1935, 1127) *allo*ocimene (I) consists of βζ-dimethyl-Δ$^{\beta\delta\zeta}$-octatriene (cf. A., 1917, i, 111), with no significant amount of the isomeric Δ$^{\alpha\delta\eta}$-compound. This is shown by the Raman spectrum (which is discussed), by the formation of a single *compound*, m.p. 81—82°, with maleic anhydride (II), and by the following reactions. With O_2–O_3, (I) gives $COMe_2$, HCO_2H, $H_2C_2O_4$, Ac_2, and OH·CHMe·COMe, and not CH_2O or AcOH. Reduction of (I) gives mixed products, except with Na–NH_3, which yields *βζ-dimethyl-Δ$^{\nu\epsilon}$-octadiene* (III), b.p. 57—58°/12 mm., shown by Raman spectrum to be homogeneous. This with (II) gives a *3-methyl-3-ethyl-6-isopropyl-Δ$^{4:5}$-tetrahydrophthalic acid*, m.p. 158—160°, and a *compound*, b.p. 112—115°/12 mm., with CH_2:CH·CHO. Further reduction of (III) by H_2–Ni gives trans-*βζ-dimethyl-Δ$^{\delta}$-octene*, b.p. 45—46°/12 mm.; using Na–NH_3, the cis-*form* is also obtained. Reduction of (I) by Na–EtOH yields an equal mixture of (III) with *βζ-dimethyl-Δ$^{\beta\epsilon}$-octadiene* (IV), b.p. 59—59·5°/12 mm., of which the structure is established by the Raman spectrum, and by ozonolysis to $COMe_2$ and COMeEt; with H_2–Ni (III) in the mixture is hydrogenated and (IV) remains unchanged. With H_2–Ni at room temp., (I) gives a mixture of *βζ-dimethyl-Δ$^{\epsilon}$-* with some *-Δ$^{\zeta}$-octene* (ozonised). Using H_2–Pt, a similar product is obtained.

IV. From its Raman spectrum, and its reduction by Na–EtOH to dihydromyrcene (A., 1937, II, 27), ocimene is regarded not as a Δ$^{\alpha\epsilon\eta}$-compound (A., 1926, 619) but as *βζ-dimethyl-Δ$^{\beta\epsilon\eta}$-octatriene*. E. W. W.

Photodecomposition of methyl and ethyl iodides.—See A., 1938, I, 318.

Allylic rearrangements. VII. Action of metals on crotyl and methylvinylcarbinyl bromides. W. G. Young, N. Kaufman, A. Loshokov, and D. Pressman (J. Amer. Chem. Soc., 1938, **60**, 900—903; cf. A., 1938, II, 2).—Identical products are obtained by treating CHMe:CH·CH_2Br or CH_2:CH·CHMeBr with metals in 80% EtOH. For Al–Hg, Zn, Cr, Cd, and Sn the yield (41—96%) of Δ$^{\alpha}$-butene ∝ the mol. reduction potential of the metal, the bivalent metals and Cr–Al forming distinct series. The ratio, *cis-* : *trans-*Δ$^{\beta}$-butene (1·2—5·6), of the product ∝ the mol. reduction potential independently of the valency. Equilibration is due to equilibration of the organometallic halide or to resonance between CHMe:CH·CH_2^+ and CH_2:CH·$CHMe^+$ at the moment of reaction with the metal. R. S. C.

Effect of groups on reaction rate. Reaction of αβ-dibromides with sodium iodide. T. L. Davis and R. Heggie (J. Org. Chem., 1938, **2**, 470—479).—The reaction of 0·3M-NaBr with 0·015M-$(CH_2Br)_2$, $CH_2Br{\cdot}CHBr{\cdot}CH_2{\cdot}OH$, $CH_2Br{\cdot}CHBr{\cdot}CO_2H$ (I), $CH_2Br{\cdot}CHBr{\cdot}CO_2Et$, $CHMeBr{\cdot}CHBr{\cdot}CO_2H$, and *trans-*$(CHBr{\cdot}CO_2H)_2$ in EtOH, usually at 25·3°, 37·2°, and 56·3°, and with $CHPhBr{\cdot}CHBr{\cdot}CO{\cdot}C_6H_4X$ (X = H, *p*-NO_2, and *m*-Cl), $CHPhBr{\cdot}CHBr{\cdot}COMe$, and (I) in $COMe_2$ at suitable temp. between 0° and 25·3°, gives good *k* for second order or *ψ*-unimol. reactions. $CHMeBr{\cdot}CH_2Br$ and $CHPr^{\alpha}Br{\cdot}CH_2Br$ do not give good *k*. Using second-order *k*, *E* and *P* are calc. from the relation, $k = PZe^{-E/RT}$, *Z* being taken as 2×10^{11}. *P* may be ⩾1 and so needs liberal interpretation. Me, Pr, and $CH_2{\cdot}OH$ increase *E*; $(CO_2H)_2$ and $CO_2Et > CO_2H$ decrease *E*; the effect of CO_2H is > that of Me. A CO_2H reduces *P*, but a second CO_2H partly restores it. COPh greatly increases *k*. Reaction of (I) is much faster in $COMe_2$ than in EtOH. Individual results are further discussed. R. S. C.

Stereoisomerides of αβ-dichloro-αβ-dibromoethylene. H. van de Walle and J. Pens (Bull. Soc. chim. Belg., 1938, **47**, 217—220).—trans-*αβ-Dichloro-αβ-dibromoethylene*, m.p. −12·2°, b.p. 165°, easily polymerised, prepared by refluxing $(CClBr_2)_2$ with Zn–EtOH for 20 hr., is much less stable to KOEt (10 min.) than the *cis*-form (cf. A., 1921, i, 491); the latter is obtained from KOEt and $CHBr_2{\cdot}CCl_2Br$. A. T. P.

Detection of methyl alcohol. E. Eegriwe (Mikrochim. Acta, 1938, **2**, 329—331).—A drop of the solution to be tested is acidified with 0·05 c.c. of 5% H_3PO_4 and about 0·065 c.c. of 5% $KMnO_4$ is added. After 1 min. finely powdered solid $NaHSO_3$ is added slowly until the solution is colourless, and 4 c.c. of H_2SO_4 (150 c.c. of 96% H_2SO_4 to 100 c.c. of H_2O) are then added, together with finely ground chromotropic acid, and the solution is heated for 10 min. at 60°. A violet-pink colour is produced if the initial MeOH content of the drop is $< 3{\cdot}5 \times 10^{-6}$ g. Org. compounds which are found not to affect the test are listed. $5{\cdot}3 \times 10^{-6}$ g. of MeOH can be detected in presence of $6{\cdot}1 \times 10^{-3}$ g. of EtOH. J. W. S.

Allylic rearrangements. V. Mechanism of the reaction of crotyl alcohol and methylvinylcarbinol with solutions of hydrogen bromide. W. G. Young and J. F. Lane (J. Amer. Chem. Soc., 1938, **60**, 847—853; cf. A., 1937, II, 480).—Reaction of CHMe:CH·CH_2·OH and CH_2:CH·CHMe·OH with HBr is assumed to occur mainly by way of a resonat-

ing mixture of $CHMe{:}CH{\cdot}CH_2^+$ and $CH_2{:}CH{\cdot}CHMe^+$, which gives the equilibrium mixture of bromides, and to a smaller extent by direct replacement. The thermal equilibrium mixture of the bromides in 48% HBr at 25° with or without addition of H_2SO_4 is determined. The amounts of the alcohols reacting by each process are then determined from the results of Young and Lane (*loc. cit.*) and from new data for HBr–AcOH at 0°. 2·9—11·9% reacts by direct replacement. R. S. C.

Resolution of *n*-propylpropenylcarbinol. Refractivity and optical rotatory dispersion of substituted allyl alcohols. C. L. Arcus and J. Kenyon (J.C.S., 1938, 312—318).—*dl-n*-Propylpropenylcarbinol (*acetate*, b.p. 63—64·5°/12 mm.; *benzoate*, b.p. 146°/12 mm.; *Me ether*, b.p. 135°/760 mm.) was resolved through the strychnine salt of its H phthalate. (+)-n-*Propylpropenylcarbinyl H phthalate* has m.p. 74—75°, $[\alpha]_{5461}^{16}$ +22·85° in EtOH ([α] for various λ in EtOH, C_6H_6, $CHCl_3$, and CS_2 at room temp. are recorded), and is hydrolysed (NaOH) with slight racemisation to the (+)-alcohol (I), b.p. 63·5°/15 mm., α_{5461}^{16} +4·58° (*l*, 0·5) [benzoate, b.p. 158°/16 mm., α_{5461}^{20} +11·16° (*l*, 0·5); acetate, b.p. 74°/16 mm., α_{5461}^{21} −21·98° (*l*, 0·5): vals. for other λ also given for both of these derivatives] (cf. A., 1934, 1088), which shows no mutarotation. Vals. for α of (−)-*n*-propylpropenylcarbinyl Me ether for various λ at 26°, and for α of (I) for various λ and temp., and for [α] in C_6H_6, $CHCl_3$, CS_2, and C_5H_5N for various λ at room temp. are recorded. Catalytic reduction of (I) and its esters gave optically inactive $CHPr^a_2{\cdot}OH$ and its esters respectively, indicating the absence of the isomeride, $CHPr^a{:}CH{\cdot}CHMe{\cdot}OH$, and its esters. The $[R]_D$ and optical rotatory dispersion of (I) and the optically active forms of $CHMe{:}CH{\cdot}CHMe{\cdot}OH$, $CHPh{:}CH{\cdot}CHMe{\cdot}OH$, $CHMe{:}CH{\cdot}CHPh{\cdot}OH$, and $CMe_2{:}CH{\cdot}CHMe{\cdot}OH$ are compared. These alcohols are considered to have the *trans*-configuration. The rotatory dispersion of the alkylallyl alcohols in complex, but that of the phenylallyl alcohols is simple, and it is suggested that a large proportion of the rotatory power of the latter is due to induced dissymmetry of the Ph. H. G. M.

Preparation of anhydrous pinacol. K. A. Krasuki and S. Mamedov (J. Gen. Chem. Russ., 1938, **8**, 67—70).—The m.p. of anhyd. pinacol is 43°, and of the hexahydrate 45—46°; the lowest m.p. obtained for mixtures of the two is 29—30° (19% of hexahydrate). R. T.

Rate of hydrolysis of enol ethers.—See A., 1938, I, 316.

Synthesis of disodium phenyl phosphate. H. F. Freeman and C. W. Colver (J. Amer. Chem. Soc., 1938, **60**, 750—751).—$POCl_2{\cdot}OPh$ [modified prep. in 70·4% yield with 8·2% of $POCl(OPh)_2$], b.p. 240°, with H_2O, followed by Na_2CO_3, gives a 68·2% yield of pure Na_2PhPO_4. R. S. C.

Synthesis of 5-phospho-*d*-arabinose. P. A. Levene and C. C. Christman (J. Biol. Chem., 1938, **123**, 607—611).—Interaction of *iso*propylidene-*d*-arabinose and $POCl_3$ in C_5H_5N, followed by hydrolysis (0·3N-H_2SO_4), yields d-*arabinose-5-phosphoric acid* (*Ba* salt, $[\alpha]_D^{26}$ −18·8° in 0·1N-HCl; *di-brucine* salt, $[\alpha]_D^{26}$ −48·6° in 50% aq. C_5H_5N). J. D. R.

Action of selenium sulphur protochloride and sulphur selenium protochloride on ethyl mercaptan and on ethyl selenomercaptan. A. Baroni (Atti R. Accad. Lincei, 1937, [vi], **26**, 456—459).—$S{:}Se{:}Cl_2$ (A., 1938, I, 42) with EtSH or EtSeH in CS_2 gives the *compounds* $(EtS)_2Se{:}S$, b.p. 102°, and $(EtSe)_2Se{:}S$, b.p. 105°; similarly $Se{:}S{:}Cl_2$ (A., 1933, 241) gives the *compounds* $(EtS)_2S{:}Se$, b.p. 104°, and $(EtSe)_2S{:}Se$, b.p. 107°. With $Pb(OH)_2$–NaOH, these yield PbS or PbSe, with $(EtS)_2Se$ etc. E. W. W

Selenoglycerols. A. Baroni (Atti R. Accad. Lincei, 1937, **26**, 460—463; cf. A., 1936, 704).—NaSeH, from NaOEt and H_2Se, in EtOH, with $OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2Br$ gives *selenoglycerol*, $OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}SeH$, b.p. 185°/20 mm. Similarly with $OH{\cdot}CH(CH_2Br)_2$ and $CHBr(CH_2Br)_2$, *di-*, $OH{\cdot}CH(CH_2{\cdot}SeH)_2$, b.p. 114°/20 mm., and *tri-selenoglycerol*, $SeH{\cdot}CH(CH_2{\cdot}SeH)_2$, b.p. 140°/20 mm, are obtained; the last is insol. in H_2O E. W. W.

Pyrolysis of esters in presence of aluminium chloride. H. Gault and E. Beloff (Bull. Soc. chim., 1938, [v], **5**, 295—304).—When distilled with $AlCl_3$, Bu^aOAc gives Bu^aCl, with HCl, CO_2, CO, CH_4, C_4H_8, etc.; the reaction is primarily that of chlorolysis, not of catalytic decomp. Cetyl palmitate reacts similarly with $AlCl_3$, but the non-volatile products are decomposed on heating, giving a mixture of ethylenic hydrocarbons. E. W. W.

Preparation of diacyloxy-derivatives of ketones, and a new method of preparation of acid anhydrides. V. V. Evlampiev [with N. P. Gurianov] (J. Gen. Chem. Russ., 1937, **7**, 2934—2940).—Ac_2O and $CMeR(OEt)_2$ (R = Me or Et), at room temp. or at the b.p., yield EtOAc and AcOH, but not the expected $CMeR(OAc)_2$. CPh_2Cl_2 and $R{\cdot}CO_2M$ (R = Me, Pr, Ph, $C_{17}H_{35}$; M = Na, Ag) or $(\cdot CH_2{\cdot}CO_2Na)_2$ react at 100—130° as follows: $CPh_2Cl_2 + 2R{\cdot}CO_2M \rightarrow (R{\cdot}CO_2)_2CPh_2 \rightarrow COPh_2 + (R{\cdot}CO)_2O$. R. T.

Preparation of acetic anhydride by interaction of nitrogen peroxide and sodium acetate. V. M. Rodionov and T. A. Oblitzeva (Trans. VI Mendeleev Congr. Chem. 1932, 1935, **2**, Pt. 1, 1002—1003).—The reaction is $2NaOAc + 2N_2O_4 = Ac_2O + 2NaNO_3 + N_2O_3$. N_2O_3 does not act on NaOAc. Ch. Abs. (*c*)

Allylic transposition. VII. γ-Chloro-Δ$^\alpha$-propenyl acetate. A. Kirrmann (Bull. Soc. chim., 1938, [v], **5**, 256—260).—$CH_2Cl{\cdot}CH_2{\cdot}CHCl{\cdot}OAc$ (I) and AgOAc–AcOH give $CH_2Cl{\cdot}CH_2{\cdot}CH(OAc)_2$ (cf. A., 1936, 191), which can be distilled, b.p. 110—112°/11 mm., and is thus not an intermediate in the formation of $CH_2Cl{\cdot}CH{:}CH{\cdot}OAc$ (II) from $CH_2{:}CH{\cdot}CH(OAc)_2$ (III) and HCl (A., 1937, II, 175); similarly (I) is too stable to be an intermediate. The actual intermediate, *α-chloro-Δ$^\beta$-propenyl acetate* (IV), b.p. 37°/12 mm., prepared from AcCl and $CH_2{:}CH{\cdot}CHO$, spontaneously isomerises into (II), accompanied by some (I). With HCl at 0°, (IV) gives (I) and (II); with HBr, followed by HNO_3, (IV) gives $CH_2Br{\cdot}CH_2{\cdot}CO_2H$. The presence of (IV) in the reaction product from (III)

is shown by the b.p. and Raman spectrum of the fraction of b.p. 30—40°/12 mm. E. W. W.

Vapour-phase photolysis of propionic acid.—See A., 1938, I, 318.

β-Methyl-α-propylvaleric acid and αβ-dimethylhexoic acid. M. S. KONDAKOVA and M. M. KATZNELSON (Compt. rend. Acad. Sci. U.R.S.S., 1938, **18**, 271—274).—*Propyl*-sec.-*butylmalonic acid*, m.p. 134—136° [from *sec.*-Bu bromide and $CHPr^{\alpha}(CO_2Et)_2$], when heated yields β-*methyl-α-propylvaleric acid*, b.p. 233—234° (*Me* ester, b.p. 183—184°; *chloride*, b.p. 97—100°/37 mm.; *amide*, m.p. 125°; *anilide*, m.p. 110—111°). *αβ-Dimethylpentane-αα-dicarboxylic acid*, m.p. 139—140° [from MeI and $CHMePr^{\alpha}{\cdot}CH(CO_2Et)_2$] (*Ag* salt), gives *αβ-dimethylhexoic acid*, b.p. 223—224° (*Ag* salt; *Me* ester, b.p. 175—176°; *chloride*, b.p. 80°/25 mm.; *amide*, m.p. 121°). A. LI.

Addition of hydrogen bromide to undecenoic acid in toluene. I. Effect of reduced nickel. Y. URUSHIBARA and M. TAKEBAYASHI (Bull. Chem. Soc. Japan, 1938, **13**, 331—335; cf. A., 1937, II, 43; 1938, II, 48).—Addition of HBr to undecenoic acid in PhMe in presence of H_2 or in a vac. gives ι-bromodecoic acid with about 1% of the κ-bromo-acid (I), irrespective of dilution. In presence of either air or reduced Ni the proportion of (I) is greatly increased. The effect with air is > with Ni, and in both cases increases with dilution. F. L. U.

Unsaturated acids of natural oils. VII. Docosahexaenoic acid, abundant highly unsaturated acid of cod-liver oil. E. H. FARMER and F. A. VAN DEN HEUVEL (J.C.S., 1938, 427—430).—The C_{22} fraction isolated as Me ester from the unsaturated acids of cod-liver oil by evaporative distillation below 110° is a structurally homogeneous acid, $C_{22}H_{32}O_2$. Its mol. refraction shows it to be unconjugated, whilst complete reduction yields pure behenic acid. Oxidation with $KMnO_4$ and with O_3 shows that it has four $:CH{\cdot}CH_2{\cdot}CH:$ groups between the end-groups $CHMe:$ and $:CH{\cdot}[CH_2]_2{\cdot}CO_2H$. A. LI.

Substitution of iodine in enols by means of iodine and hydrogen peroxide. Preparation of ethyl α-iodoacetoacetate, s-iodoacetylacetone, and α-iodotetronic acid. W. D. KUMLER (J. Amer. Chem. Soc., 1938, **60**, 855—856).—With I and H_2O_2 in aq. EtOH $CH_2Ac{\cdot}CO_2Et$, tetronic acid, and $CH_2Ac{\cdot}COMe$ give $CHIAc{\cdot}CO_2Et$ (I), *α-iodotetronic acid*, decomp. 160°, m.p. 170—175° (decomp.), and s-*iodoacetylacetone*, respectively. The products are unstable, especially in H_2O or when heated, and oxidise KI quantitatively. Only 1 I could be introduced. (I) is stable in H_2O_2. R. S. C.

Condensation of formaldehyde with ethyl acetate. I, II. H. GAULT and J. BURKHARD (Bull. Soc. chim., 1938, [v], **5**, 385—409, 409—429).—I. CH_2O, $CH_2Ac{\cdot}CO_2Et$, and aq. K_2CO_3 under most conditions give known products, but condensation at −10° to 0° and removal of all H_2O at −15° yields *Et αα-di(hydroxymethyl)acetoacetate*, an oil, which is stable when kept at room temp., but decomposes when heated to yield CH_2O. This product gives a *diacetate*, b.p. 172°/14 mm., and a *ketimine*, m.p. 185°, but with PhNCO gives only $CO(NHPh)_2$ and with $NHPh{\cdot}NH_2$ gives $CH_2{:}N{\cdot}NHPh$; with N_2H_4 it yields (?) *αα-di(hydroxymethyl)acetoacethydrazidephenylhydrazone* (I), m.p. >300°; in boiling H_2O it liberates CH_2O and (?) $CH_2{:}CAc{\cdot}CO_2Et$, and a similar decomp., followed by hydrolysis, is effected by hot, dil. H_2SO_4; KOH probably gives $CHAc(CH_2{\cdot}OH)_2$. Unsuccessful attempts to prepare $OH{\cdot}CH_2{\cdot}CHAc{\cdot}CO_2Et$ are described.

II. According to the temp. 1 mol. each of (I) and $CH_2Ac{\cdot}CO_2Et$ or CH_2O and $CH_2Ac{\cdot}CO_2Et$ with aq. K_2CO_3 give α-, m.p. 87° [*Ac* derivative (II), m.p. 79°; gives only oils with CO-reagents], and β-*ethers*, $C_{14}H_{22}O_7$, an oil, decomp. at the b.p./20 mm., which are possibly stereoisomeric forms of *Et*$_2$ 3-*methyl*-6-*hydroxymethyl*-Δ^3-cyclo*hexenone*-4 : 6-*dicarboxylate*. With NH_3 or $NHPh{\cdot}NH_2$ the β-ether gives derivatives of $CH_2(CHAc{\cdot}CO_2Et)_2$ (III). CH_2O and (III) or 2 mols. of $CH_2Ac{\cdot}CO_2Et$ and 3 mols. of CH_2O with aq. K_2CO_3 give a *γ-ether*, $C_{15}H_{24}O_8$, m.p. 101°, which with CO-reagents gives derivatives of (III), with AcCl–C_5H_5N gives (II), and may be *Et*$_2$ 3-*hydroxy*-3-*methyl*-4 : 6-*di(hydroxymethyl)*cyclo*hexanone*-4 : 6-*dicarboxylate*. The ethers may have derived dicyclic structures since none of them gives a colour with $FeCl_3$ or shows CO bands in the Raman spectra. R. S. C.

Dissociation relationships of disubstituted succinic acids. H. BODE and K. PETERSEN (Ber., 1938, **71**, [*B*], 871—879).—Re-examination of the dissociation consts. of a series of symmetrical, disubstituted succinic acids shows that the relationship of Kuhn *et al.* (A., 1928, 507) does not exist. Examination of the models suggests that the quotient of the dissociation const. of symmetrically disubstituted succinic acids is smaller with the *meso*- than with the racemic form or the same for each. This is true for the halogeno- or alkyl-acids. If ring formation or internal subsidiary valency union prevents or greatly hampers free rotation the relationships may be displaced as shown experimentally and by model with *cyclo*hexane derivatives and assumed to explain the abnormal relationships of the tartaric acids. H. W.

Interaction of maleic acid with thiol compounds. E. J. MORGAN and E. FRIEDMANN (Biochem. J., 1938, **32**, 733—742).—Maleic acid (I) forms an additive *compound*, $CO_2H{\cdot}CH_2{\cdot}CH(CO_2H){\cdot}S{\cdot}CH_2{\cdot}CO_2H$, m.p. 140·5°, with $SH{\cdot}CH_2{\cdot}CO_2H$ (II), and similar *compounds* with cysteine (III), m.p. 134—135°, and with glutathione (IV), 151—152° (decomp.). In the course of reaction of (I) with (II) and (IV) fumaric acid (V) is formed. With increasing reaction concn. formation of the additive compound is more complete and less (V) is formed. Interaction of (I) with (III) is complete and no (V) is formed. A. T.

Synthesis of polyene fatty acids. J. BALTES (Fette u. Seifen, 1938, **45**, 196—198).—A lecture. The synthesis of long-chain polyethylenic (fatty) acids is discussed with special reference to the work of R. Kuhn and collaborators. E. L.

Quantitative precipitation of citric acid. A. C. KUYPER (J. Biol. Chem., 1938, **123**, 405—407).—When a citrate solution containing $Ca^{\cdot\cdot}$ and PO_4''' is made alkaline, quant. pptn. of citrate occurs if the $Ca^{\cdot\cdot}$ present are in excess of those required to react

with PO_4''' and citrate. The ppt. is thought to be a complex of $Ca^{\cdot\cdot}$, PO_4''', and citrate. C. R. H.

Dissociation constants of some enols related to ascorbic acid. Tetronic, α-chloro-, -bromo-, -iodo-, and -hydroxy-tetronic acids, and ethyl α-iodoacetoacetate. W. D. KUMLER (J. Amer. Chem. Soc., 1938, **60**, 859—864).—The following vals. of pK_a are determined: α-chloro- 2·13, α-bromo- 2·23, α-iodo- 2·31, and α-hydroxy-tetronic (I) 4·37, and tetronic acid (II) 3·76; $CHIAc{\cdot}CO_2Et$ 7·0. The strong acidities relative to ascorbic acid and $[:C(OH){\cdot}CO_2Et]_2$ are not due to fission of the lactone ring, since there is no second dissociation const., Na α-iodotetronate contains no extra H_2O, and *p-nitrobenzyl α-bromotetronate*, m.p. 177°, is not acidic. The results are ascribed to resonance between $CH_2<\overset{C(\cdot O^-):C(OH)}{O\text{———}}>CO$ and $CH_2<\overset{CO{\cdot}C(OH)}{O\text{———}}>C{\cdot}O^-$, which also accounts for $C_{(3)}$ carrying the acidic OH and for (I) being weaker than (II). R. S. C.

Behaviour of halogen-substituted enols. Preparation of α-chlorotetronic acid. W. D. KUMLER (J. Amer. Chem. Soc., 1938, **60**, 857—859).—α-Iodotetronic acid (I), $CHIAc{\cdot}CO_2Et$, and $CHIAc{\cdot}COMe$ react quantitatively with KI in strong acid solution, the reaction depending on one of the changes, $\cdot C(OH):CI{\cdot}CO\cdot + H^+ \rightarrow \cdot C(OH):CH{\cdot}CO\cdot + I'$ or $\cdot C(OH):CI{\cdot}CO\cdot + H_2O \rightarrow \cdot C(OH):CI{\cdot}CO\cdot + HOI$. $CHIAc{\cdot}CO_2Et$ and (I) oxidise Fe^{II} to Fe^{III}, but α-bromotetronic acid (II) does so only in presence of KI (by replacement of the Br by I). By Kurt Meyer's method $CHIAc{\cdot}CO_2Et$ contains 20% of enol, or after 72 hr. in abs. EtOH 49%. Tetronic acid absorbs 20—35% more Br than corresponds with 100% of enol and α-Br- and α-I-derivatives apparently contain 20—35 and 50—70%, respectively, of enol. With HCl–abs. EtOH (II) gives *α-chlorotetronic acid*, m.p. 205° (decomp.), which slowly liberates I from KI (3% after 5 min.; 55% after 1 week), doubtless by replacement of Cl by I. The tenacity of the C–Hal linking is determined by the avidity of the halogen for its electron pair and thus on the size of the halogen atom; this determines the relative reactivities of the compounds. R. S. C.

Cacothelin as a reagent for ascorbic acid.—See A., 1938, III, 506.

Physico-chemical properties of ascorbic acid. J. C. GHOSH (J. Indian Chem. Soc., 1938, **15**, 1—14).—Thiol and other compounds inhibit the auto-oxidation of synthetic acid. Potentiometric examinations of the alkali titrations of ascorbic (I) and dehydroascorbic acids and of the reversible (I) oxidation–reduction system are discussed in relation to mol. structures. The circular dichroism of (I) is investigated. M. R.

Titrimetric determination of thionyl compounds. E. LARSSON (Svensk Kem. Tidskr., 1937, **49**, 264—271).—The equilibrium in the reaction: $S([CH_2]_n{\cdot}CO_2H)_2 + Br + H_2O \rightleftharpoons OS([CH_2]_n{\cdot}CO_2H)_2 + HBr$ lies far to the left in AcOH containing $>0{\cdot}2\%$ of H_2O, and may be used for the determination of thionyl acids by addition of KI and titration with $Na_2S_2O_3$. The kinetics of the reaction have been studied. *Benzylthionylacetic*, m.p. 124°, *β-thionyldipropionic*, m.p. 114°, and *r-β-thionyldibutyric*, m.p. 112°, acids have been prepared. M. H. M. A.

Thioketonic esters. V. S. K. MITRA (J. Indian Chem. Soc., 1938, **15**, 31—36; cf. A., 1934, 57).—$CHAc(CO_2Et)_2$ and H_2S–EtOH give *Et₂ thioacetylmalonate*, b.p. 120°/4 mm., converted by $NHPh{\cdot}NH_2$ into Et 1-phenyl-3-methyl-5-pyrazolone-4-carboxylate. $CHMeAc{\cdot}CO_2Et$ and H_2S–EtOH give *Et methylthioacetoacetate* (I), b.p. 95°/10 mm. *Et isobutylthioacetoacetate*, b.p. 122°/5 mm., is similarly prepared. As expected, $SNa{\cdot}CMe{:}CH{\cdot}CO_2Et$ does not react with $CHPh{:}CH{\cdot}CO_2Et$, but with $(:C{\cdot}CO_2Et)_2$ or $CMeCl{:}CH{\cdot}CO_2Et$ gives *di-β-carbethoxyisopropyl sulphide*, b.p. 155°/12 mm., converted by $NHPh{\cdot}NH_2$ into 4-1′-phenyl-3′-methyl-4′ : 5′-dihydropyrazolidene-1-phenyl-3-methyl-5-pyrazolone; this proves the attachment of the Na to S. The Na salt of (I) with Me_2SO_4 in hot EtOH gives the S-*Me*, b.p. 225°/750 mm. (from which HCl liberates MeSH), with EtI in C_6H_6 gives the S-*Et*, b.p. 220°/7 mm., and with $CH_2Cl{\cdot}CO_2Et$ in C_6H_6 the S-*$CH_2{\cdot}CO_2Et$*-derivative, b.p. 160°/6 mm. With H_2S–HCl–EtOH (I) gives *di-γ-carbethoxy-Δ^β-β-butenyl disulphide*, b.p. 180°/6 mm., also obtained by direct oxidation. The Na derivative of Et_2 thioacetonedicarboxylate (II) with Me_2SO_4 gives *Et_2 β-methylthiolglutaconate*, b.p. 135°/6 mm., and with $CH_2Cl{\cdot}CO_2Et$ the S-*$CH_2{\cdot}CO_2Et$*-derivative, b.p. 170°/6 mm. With Ac_2O (II) gives the S-*Ac* derivative, b.p. 150°/9 mm., but with $MgBu^aI$ merely liberates C_4H_{10}. R. S. C.

Formaldehyde from percarbonate.—See A., 1938, I, 319.

Reactivity of formaldehyde in presence of various bases.—See A., 1938, I, 316.

Aldol condensation products. M. M. PLANT (J.C.S., 1938, 536—541).—The action of CaO on crude aldol yields H_2O-sol. products, with reducing properties which appear to be due neither to unsaturation nor to CHO groups. Methylation followed by acetylation and fractionation yields *acetates*, $C_9H_{16}O_4$, b.p. 107°/21 mm., and $C_{13}H_{22}O_6$, b.p. 83°/0·15 mm. Structural formulae are suggested. A. LI.

Enolisation and aldol condensation. K. F. BONHOEFFER and W. D. WALTERS (Z. physikal. Chem., 1938, **181**, 441—448).—The aldol from MeCHO in presence of D_2O contains only a trace of D. The $(CH_2{\cdot}CHO)^-$ ion formed in the enolisation of MeCHO reacts with MeCHO to form aldol before it can revert to MeCHO. This enolisation is the rate-determining step in Bell's measurements (A., 1937, I, 622). Similarly the product of the condensation of glyceraldehyde (I) alone, or of its mixture with dihydroxyacetone (II), to give ketohexoses contains only a trace of D if the reaction is carried out in D_2O. The ion $(OH{\cdot}CH_2{\cdot}CO{\cdot}CH{\cdot}OH)^-$ reacts further before it can re-form (I) or (II). In the aldol condensation of $COMe_2$ on the other hand, the keto–enol equilibrium is established more rapidly than is the condensation equilibrium. H. J. E.

Treatment of the keto–enol equilibrium according to the theories of prototropy and mesomerism. C. GUSTAFSSON (Finska Kem. Medd., 1938, 67, 12—18).—A theoretical discussion of the keto–enol equilibrium. M. H. M. A.

Interaction of ketones, carbon monoxide, and steam. D. V. N. HARDY (J.C.S., 1938, 464—468).—With CO and steam at 200 atm. pressure in presence of H_3PO_4, $COMe_2$ (or CMe_2:CH·COMe) yields AcOH, $Bu^{\gamma}CO_2H$ (ratio 2 : 1), and hydrocarbons, whilst COMeEt yields AcOH, $EtCO_2H$, $CMe_2Et{\cdot}CO_2H$, $CMe_2Pr{\cdot}CO_2H$, $CMeEt_2{\cdot}CO_2H$, and a neutral oil. With N_2 or H_2 instead of CO, $COMe_2$ gives AcOH with an increased yield of neutral oil, hydrogenation of which gives a fraction (b.p. <200°) having an octane no. of 81. The mechanism of the reaction is discussed. A. LI.

α-Chloroketones. G. RICHARD (Bull. Soc. chim., 1938, [v], 5, 286—294).—Theoretical. The greater reactivity of Cl in CHRCl·CO·CH_2R' (I) than in COR·CHCl·CH_2R' (II) is ascribed to enolisation of the former; various reactions are discussed, including the action of KCN. In the formation of $\overset{CPh_2}{O}\!>\!CMe{\cdot}CN$ from $CPh_2Cl{\cdot}COMe$, an intermediate *cyanohydrin*, $CPh_2Cl{\cdot}CMe(OH){\cdot}CN$, m.p. 197°, is isolated. With gaseous HCl, compounds of type $\overset{CHR}{O}\!>\!C(CN){\cdot}CH_2R'$ and $\overset{CN{\cdot}CR}{O}\!>\!CH{\cdot}CH_2R'$ regenerate the chloroketones (I) and (II). With EtOH–HCl, (I) can give compounds of type CHRCl·C(OH)(CO_2Et)·CH_2R'. Some chloroketones with NaOPh give compounds of type COR·CH(OPh)·CH_2R', some of which when heated give *cyclo*butadiones. E. W. W.

Influence of radicals on isomeric transformations of *tert.* α-keto-alcohols. I. A. M. CHALETZKI (J. Gen. Chem. Russ., 1938, 8, 164—174).—γ-Keto-ββδ-trimethylhexane in H_2O and Br at 60° yield *δ-bromo-γ-keto-ββδ-trimethylhexane* (I), b.p. 82—83°/10 mm., which at 100° with 10% K_2CO_3 gives *γ-hydroxy-ββδ-trimethylhexane γδ-oxide* (II), b.p. 62—63°/10 mm. (I) and KOAc in EtOH (6 hr. at the b.p.) yield *γ-keto-δ-acetoxy-ββδ-trimethylhexane*, b.p. 72—74°/12 mm., hydrolysed to (II) by 10% aq. K_2CO_3. (II) when heated for 8 hr. with EtOH and H_2SO_4 at 120° yields β-*keto-γ-hydroxy-δδ-dimethyl-γ-ethylpentane*, b.p. 61—62°/10 mm. (*semicarbazone*, m.p. 198—199°), which is oxidised by K_2CrO_4 to AcOH and $COEtBu^{\gamma}$, and is reduced by Na in EtOH to *γ-hydroxy-ββδ-trimethylhexane*, b.p. 168—170° (*phenylurethane*, m.p. 78—79°). R. T.

Amino-acid catalysis of the mutarotation of glucose. F. H. WESTHEIMER (J. Org. Chem., 1938, 2, 431—441).—17 NH_2-acids, containing primary, *sec.*, *tert.*, or quaternary N, catalyse the mutarotation of glucose, their effects being approx. in accord with the Brønsted equation. Picoline and quinoline accord less well. R. S. C.

Dimethyl acetal of *d*-glucose. M. L. WOLFROM and S. W. WAISBROT (J. Amer. Chem. Soc., 1937, 60, 854—855).—Glucose Et_2 mercaptal penta-acetate, $CdCO_3$, and $HgCl_2$ in hot MeOH give d-*glucose* Me_2 *acetal penta-acetate*, m.p. 71—72°, $[\alpha]_D^{20}$ +12° in $CHCl_3$, converted by 0·4N-NaOMe at 0° into d-*glucose* Me_2 *acetal*, m.p. 94—95°, $[\alpha]_D^{20}$ +15° in H_2O. R. S. C.

4 : 6-Dimethylaltrose and 2 : 4 : 6-trimethylaltrose from glucose. G. J. ROBERTSON and H. G. DUNLOP (J.C.S., 1938, 472—476).—4 : 6-Benzylidene-2 : 3-anhydro-α-methylalloside (I) (Robertson and Griffith, A., 1935, 1225) is hydrolysed by very dil. HCl in $COMe_2$ to a mixture of two α-*methylhexoside chlorohydrins*, m.p. 160—162° and 136—138°, $[\alpha]_D^{15}$ +113·1° and +157·2° in MeOH, respectively. The mixture yields a *triacetate* with Ac_2O in C_5H_5N, and with Ag_2O gives 2 : 3-*anhydro-α-methylalloside*, m.p. 105—107°, $[\alpha]_D^{15}$ +153° in MeOH, also obtained by hydrolysing (I) with $H_2C_2O_4$ in aq. $COMe_2$. Methylation of this (MeI+Ag_2O) gives 4 : 6-dimethyl-2 : 3-anhydro-α-methylalloside, hydrolysed by KOH to 4 : 6-*dimethyl-α-methylaltroside* (identified by complete methylation), b.p. 130—135°/0·5 mm., $[\alpha]_D^{15}$ +145·7° in $CHCl_3$. Further hydrolysis (dil. HCl) affords 4 : 6-*dimethylaltrose*, m.p. 158—160°, $[\alpha]_D^{15}$ +102·9° in H_2O (*osazone*, m.p. 139—141°). NaOMe converts the Me_2 anhydroalloside into 2 : 4 : 6-trimethyl-α-methylaltroside, b.p. 105°/9·1 mm., $[\alpha]_D^{15}$ +144·9° in $CHCl_3$, hydrolysed (dil. HCl) to 2 : 4 : 6-*trimethylaltrose* (a syrup), $[\alpha]_D^{15}$ +79·3° in $CHCl_3$, which yields the same osazone as 4 : 6-dimethylaltrose. A. LI.

Esters of methanesulphonic acid in the sugar group. B. HELFERICH and A. GNÜCHTEL (Ber., 1938, 71, [*B*], 712—718).—$MeSO_2{\cdot}$, like *p*-$C_6H_4Me{\cdot}SO_2{\cdot}$, derivatives of sugars crystallise readily and are well suited to identifications. Since the reactivity of $MeSO_2Cl$ is > that of *p*-$C_6H_4Me{\cdot}SO_2Cl$, the former gives many more derivatives than the latter and also reacts more readily. $MeSO_3Na$ is converted by PCl_5 into $MeSO_2Cl$, from which the difficult removal of the last traces of P compounds is unnecessary. All esters of $MeSO_3H$ give the Beilstein test for halogens by reason of the volatility of $(MeSO_3)_2Cu$ in the Bunsen flame. Esterification of individual OH-groups in presence of Ac or other groups is demonstrated by the production of β-d-*glucose* 1 : 2 : 3 : 4-*tetra-acetate* 6-*methanesulphonate* (*mesylate*) (I), m.p. 156°, $[\alpha]_D^{18}$ +10·3° in $CHCl_3$ (whence *bromoglucose triacetate* 6-*methanesulphonate*, m.p. 91—93°, $[\alpha]_D^{18}$ +189°), *glucose* 1 : 2 : 3 : 6-*tetra-acetate* 4-*methanesulphonate* (II), m.p. 175—176°, $[\alpha]_D^{19}$ −20·1° in $CHCl_3$, 3 : 5-*benzylidene*-1 : 2-iso*propylideneglucofuranose* 6-*methanesulphonate*, m.p. 132—133°, $[\alpha]_D^{22}$ +12·8° in C_5H_5N, and α-*methyl*-d-*glucoside* 2 : 3 : 4-*triacetate* 6-*methanesulphonate*, m.p. 113—114°, $[\alpha]_D^{20}$ +139° in C_5H_5N, from the requisite OH-compound and $MeSO_2Cl$ in C_5H_5N. The possibility of the introduction of several $MeSO_2$ groups is established by the prep. of 1 : 2-iso*propylideneglucofuranose* 3 : 5 : 6-*trimethanesulphonate*, m.p. 165°, $[\alpha]_D^{20}$ −24·2° in C_5H_5N, and of α-d-*methylglucoside* 2 : 3 : 4 : 6-*tetramethanesulphonate* (III), m.p. 145—146°, $[\alpha]_D^{19}$ +92·2° in $CHCl_3$, in almost quant. yield. In this respect $MeSO_2Cl$ is superior to *p*-$C_6H_6Me{\cdot}SO_2Cl$. Acetobromoglucose and $MeSO_3Ag$ in C_6H_6 afford *glucose* 2 : 3 : 4 : 6-*tetra-acetate* 1-*methanesulphonate*, m.p. 112—113°, $[\alpha]_D^{19}$ +121·4° in $CHCl_3$, which reduces warm Fehling's solution, decomposes slowly when kept in a desiccator, and is transformed by $CaCO_3$ and

boiling MeOH into β-methylglucoside tetra-acetate. α-Glucose, $MeSO_2Cl$, and C_5H_5N smoothly give 1-*chloroglucose* 2 : 3 : 4 : 6-*tetramethanesulphonate*, m.p. 168—169°, $[\alpha]_D^{20}$ +110° in EtOAc. KOAc and (III) in boiling Ac_2O give almost quantitatively α-*methylglucoside* 6-*acetate* 2 : 3 : 4-*trimethanesulphonate*, m.p. 146—147° (corr.), $[\alpha]_D^{20}$ +90·6° in C_5H_5N. With NaI in boiling $COMe_2$ or KI in boiling H_2O (III) yields α-*methylglucoside* 6-*iodohydrin* 2 : 3 : 4-*trimethanesulphonate*, m.p. 144—145°, $[\alpha]_D^{20}$ +82·4° in C_5H_5N. Similarly (I) and NaI in $COMe_2$ at room temp. slowly yield β-d-glucose 6-iodohydrin 1 : 2 : 3 : 4-tetra-acetate and (II) with NaI in $COMe_2$ at 135° gives *glucose* 4-*iodohydrin* 1 : 2 : 3 : 6-*tetra-acetate*, m.p. 199—200° (slight decomp.) after softening at 190°, $[\alpha]_D^{20}$ +51·8° in C_5H_5N. Hydrolysis of the sugar methanesulphonates does not proceed smoothly with the customary reagents. The marked discoloration suggests the elimination of $MeSO_3H$ with production of unsaturated compounds. H. W.

Application of periodate to the volumetric determination of ketoses (monosaccharides). II. F. Rappaport and I. Reifer (Mikrochim. Acta, 1938, **2**, 273—279; cf. A., 1937, II, 530).—The ketose is oxidised with aq. KIO_4 at 100°, and the excess of IO_4' is titrated iodometrically after buffering with K_2HPO_4 to prevent deposition of I from the IO_3'. For a ketose containing n C atoms, $n-2$ mols. of KIO_4 are consumed per mol. of ketose, as against $n-1$ mols. in the case of aldoses and alcohols. Oxidation of 1 mol. of alcohol or ketose yields 2 mols. of CH_2O and $n-2$ mols. of HCO_2H, as compared with 1 mol. of CH_2O and $n-1$ mols. of HCO_2H formed from 1 mol. of aldose. The method therefore affords distinction between the three classes of compounds. J. W. S.

Bromine oxidation and mutarotation measurements with α-*d*-β-mannoheptose and α-*d*-α-guloheptose. H. S. Isbell (J. Res. Nat. Bur. Stand., 1938, **20**, 97—108).—With NaCN–$CaCl_2$ mannose gives much *d*-α- (*Pb*, $+H_2O$, and *K*, $[\alpha]_D^{20}$ +5·4° in H_2O, salts; best isolated as Ba or Ca salt) and some *d*-β-mannoheptonic acid [best isolated as *Pb* salt, $[\alpha]_D^{20}$ +2·6° in H_2O; *K* salt, $[\alpha]_D^{20}$ +0·3° in H_2O; *γ-lactone*, (I), m.p. 130°, $[\alpha]_D^{20}$ −35·7° → (slowly) −27·9° in H_2O], epimerised in C_5H_5N. Na–Hg reduces (I) to α-d-β-*mannoheptose* (II), $+H_2O$, m.p. 83°, $[\alpha]_D^{20}$ +45·7° → +14·5° in H_2O (cf. Ettel, A., 1933, 47). α-*d*-α-Mannoheptose, m.p. (anhyd.) 140° and ($+H_2O$) 107°, is described. Equilibration of crude *d*-α-mannoheptose in H_2O yields β-d-α-*mannoheptose*, $+H_2O$, m.p. 104°. Mutarotation of (II) involves a fast reaction to an unstable isomeride, followed by a slow reaction. The temp. coeff. for the fast reaction is similar to that for the fast reactions of similar sugars, *e.g.*, talose, that for the slow reaction corresponding with the normal α ⇌ β change. Br-oxidation of (II) and α-*d*-α-guloheptose consists of fast, followed by slow, reactions (cf. talose), the amounts of readily oxidisable forms indicated being 38 and 33%, respectively. The peculiarities of mutorotation and oxidation are determined by the configuration of the C of the pyranose ring, thus showing the advantage of the author's system of classification. R. S. C.

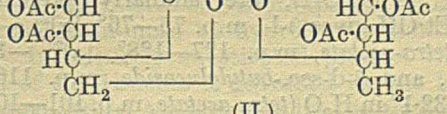
Acetylation of perseulose. Y. Khouvine and G. Arragon (Compt. rend., 1938, **206**, 917—919; cf. A., 1909, i, 634).—Perseulose (I) and Ac_2O–C_5H_5N at room temp. for 24 hr. give a *hexa-acetate* (II), m.p. 105°, $[\alpha]_{578}^{20}$ +0·57° in $CHCl_3$, +20·8° in C_6H_6, −2·85° in MeOH, which shows a strong absorption band at 2800 A., characteristic of C:O. (I) and Ac_2O–$ZnCl_2$, at room temp. for 24 hr., give (II) and a *hexa-acetate*, m.p. 112°, $[\alpha]_{578}^{20}$ −113·4° in $CHCl_3$, −113·2° in C_6H_6, −106·5° in MeOH, which shows no characteristic absorption band and probably has a cyclic structure. An *alcohol*, m.p. 91°, $[\alpha]_{578}^{20}$ −12° in $CHCl_3$, −7·42° in C_6H_6 (Ac_7 derivative), is recorded. A. T. P.

Influence of neutral salts on inversion of sucrose.—See A., 1938, I, 316.

Inhibition in inversion of sucrose.—See A., 1938, I, 316.

Synthesis of crystalline 6-β-*d*-glucosido-α-*d*-mannose, the epimeride of gentiobiose, and its octa-acetate. H. J. Dauben, jun., and W. L. Evans (J. Amer. Chem. Soc., 1938, **60**, 886—890).—β-Gentiobiose octa-acetate, m.p. 196°, $[\alpha]_D^{24}$ −6·8°, yields 57% of acetobromogentiobiose and thence by Zn–75% AcOH at 0° 96% of gentiobial hexa-acetate, m.p. 121—122°, $[\alpha]_D^{18}$ −7·4° in $CHCl_3$. With $Ba(OMe)_2$ this gives 65% of gentiobial, m.p. 191—192°, oxidised by BzO_2H in 68% yield to 6-β-d-*glucosido*-α-d-*mannose*, m.p. ($+H_2O$) 137—138°, (anhyd.) 167·5—168°, $[\alpha]_D^{20}$ −5·09° → −11·06° in about 2 hr. in H_2O, which by acid hydrolysis gives glucose and mannose and with C_5H_5N–Ac_2O at 0° affords the *octa-acetate*, dimorphic, m.p. 114° and 142—143°, respectively, $[\alpha]_D^{21}$ +26° in $CHCl_3$. M.p. are corr. [α] agree with Hudson's rules. R. S. C.

Action of mercury salts on acetohalogenosugars. XI. Synthesis of derivatives of β-1-*l*-rhamnosido-6-*d*-galactose. G. Zemplén, A. Gerecs, and H. Flesch (Ber., 1938, **71**, [*B*], 774—776).—Galactosan triacetate is converted by $TiCl_4$ in $CHCl_3$ into 1-*chlorogalactopyranose* 2 : 3 : 4-*triacetate* (I), m.p. 132°, $[\alpha]_D^{21}$ +207·8° in $CHCl_3$, transformed by acetobromorhamnose and $Hg(OAc)_2$ in abs. C_6H_6 at 50° into α-1-*chloro*-β-6-l-*rhamnosido*-d-*galactopyranose hexa-acetate* (II), m.p. 166·5—167·5°, $[\alpha]_D^{21}$ +67·59° in



(II.)

$CHCl_3$, whence, by Ac_2O and AgOAc, a *rhamnosido-galactose hepta-acetate*, m.p. 84—85° after softening at 71°, $[\alpha]_D^{21}$ −9·90° in $CHCl_3$. Successive treatments of (I) with $Hg(OAc)_2$ in C_6H_6 at 50°, Ag_2CO_3 in boiling MeOH, and Ac_2O–NaOAc afford β-1-*methyl*-β-6-l-*rhamnosido*-d-*galactopyranose hexa-acetate*, m.p. 161·5—162·5°, $[\alpha]_D^{17}$ −39·21° in $CHCl_3$, identical with a fraction obtained by crystallisation of β-1-methylrobinobiose hexa-acetate. H. W.

Methylation of raffinose. K. Hess and K. H. Lung (Ber., 1938, **71**, [*B*], 827—829).—Anhyd.

raffinose is converted by Ac_2O in C_5H_5N at room temp. into the hendeca-acetate, m.p. 99·8°, $[\alpha]_D^{20}$ +104·6° in $CHCl_3$. This is pre-methylated by Me_2SO_4 and 30% NaOH at 50° and the product is treated with Na in liquid NH_3 and then with MeI, thus giving hendeca-methylraffinose, b.p. 155—165°/0·001 mm., $[\alpha]_D^{22}$ +124·1° in H_2O, without appreciable amounts of more volatile fractions. It therefore appears that saccharide linkings are not sensitive to Na–NH_3. H. W.

Decomposition products of sugars. Caramel and humin. A. Schweizer (Rec. trav. chim., 1938, 57, 345—382).—The literature of caramel and humin is reviewed. Sugar-humin [$(C_{24}H_{10}O_9)_n$ or $(C_{12}H_8O_4)_n$] (I) (Cl_4- and Br_4-derivatives) is a highly dehydrated carbohydrate, highly polymerised, with the hexane skeleton intact. A mechanism of formation from hymatomelanic acid or *iso*saccharosan (II) is discussed. (I) and H_2O_2–KOH yield CO_2 and a product, $C_{12}H_{10}O_5$ (III) (structure suggested) (cf. hymatomelanic acid, Bergius, Naturwiss., 1928, **16**, 4) [*Pb* and *K* salts; $NHPh{\cdot}NH_2$ compound; *Ac*$_2$ derivative; *Br*$_2$-derivative (Br in N_2 for 6 hr.)], which with HNO_3 (*d* 1·52) at −5° gives a substance (V), $C_{12}H_{11}O_8N$, decomp. explosively about 160°, $H_2C_2O_4$, and saccharomonolactone. (V) [also obtained from (I)] and HNO_3 (*d* 1·4), or H_2O_2–KOH, give saccharic and oxalic acids. (I) and HNO_3 (*d* 1·52) at below 60° afford $H_2C_2O_4$ and saccharodilactone, and HNO_3 (*d* 1·26) gives a gluconolactone, m.p. 143° (*Ac*$_3$ derivative, m.p. 115°). Caramel is a mixture of (I) and (II), as also are caramelan, caramelen, and caramelin. A. T. P.

Synthesis and properties of β-alkylglucosides. II. Glucosides of five butyl alcohols and of tertiary amyl, hexyl, and heptyl alcohol. S. Veibel and H. Lillelund (Bull. Soc. chim., 1938, [v], **5**, 494—502; cf. A., 1936, 318).—Acetobromoglucose, Bu^cOH, and Ag_2CO_3 give β-n-*butylglucoside tetra-acetate*, m.p. 65·5—66·5°, $[\alpha]_D^{20}$ −26·8° in EtOH, hydrolysed to β-*n*-butylglucoside, m.p. 68—69°, $[\alpha]_D^{20}$ −36·9° in H_2O, not hygroscopic when pure. β-*tert.*-Butyl-, m.p. 164—166°, $[\alpha]_D^{20}$ −19° in H_2O (*tetra-acetate*, m.p. 145—146°, $[\alpha]_D^{20}$ −19·3° in EtOH), -dimethylethylcarbinyl-, m.p. 127—128°, $[\alpha]_D^{20}$ −18° in H_2O (*tetra-acetate*, m.p. 122·5—123·5°, $[\alpha]_D^{20}$ −17·7° in EtOH), -methyldiethylcarbinyl- (*tetra-acetate*, m.p. 96—97°, $[\alpha]_D^{20}$ −14·5° in EtOH), and -triethylcarbinyl-glucoside, $+H_2O$ (*tetra-acetate*, m.p. 94—95°, $[\alpha]_D^{20}$ −10·3° in EtOH), are similarly prepared. *dl*-CHMeEt·OH gives β-l-, m.p. 75—76°, $[\alpha]_D^{20}$ −44·5° in H_2O (*tetra-acetate*, m.p. 127—128°, $[\alpha]_D^{20}$ −36·6° in EtOH), and β-d-sec.-*butylglucoside*, m.p. 116—117°, $[\alpha]_D^{20}$ −32·1° in H_2O (*tetra-acetate*, m.p. 101—103°, $[\alpha]_D^{20}$ −18·5° in EtOH), the synthesis being slightly asymmetric; hydrolysis yields pure *l*- and *d*-CHMeEt·OH (p-*nitrobenzoates*, m.p. 17·5—18°, $[\alpha]_D^{20}$ 30·2° in abs. EtOH). dl-sec.-*Bu* p-*nitrobenzoate* has m.p. 25—26°. R. S. C.

Enzymic hydrolysis of triethylcarbinol-β-*d*-glucoside. Steric hindrance: its significance in the hydrolysis of glucosides. S. Veibel and H. Lillelund (Z. physiol. Chem., 1938, **253**, 55—63; cf. A., 1936, 1235; 1937, III, 30).—In the hydrolysis, at 30° and 20°, by emulsin (I) of triethylcarbinol-β-*d*-glucoside (II) $k \times 10^4$ decreases from 2·98 and 0·905 at the start to 1·32 and 0·45, respectively, at 49 hr. The affinity of (I) for (II) is approx. 25 times that of (I) for trimethylcarbinol-β-*d*-glucoside (III) and (II) is hydrolysed by (I) approx. 4 times as rapidly as is (III). The concn. of (III) required to bind a given percentage of (I) is 25 times that of (II). Methyldiethylcarbinol-β-*d*-glucoside is hydrolysed by (I) approx. 15 times as rapidly as is (III). Steric hindrance is not a cause of the slow hydrolysis of the glucosides of *tert.* alcohols. W. McC.

Attempted separation of the isomorphous glucosides of *Digitalis lanata*. C. Mannich and F. Borkowsky (Arch. Pharm., 1938, **276**, 234—242).—The possibility of converting the glucosides into non-isomorphous derivatives which can be separated from one another by crystallisation and from which the parents can be readily regenerated has been examined. The crude glucoside (I) is readily dissolved by $COMe_2$ containing 0·3% of HCl (H_2SO_4 and $CuSO_4$ behave similarly) but dissolution is accompanied by rapid hydrolysis although the material is relatively stable towards 0·3% HCl–H_2O or 0·3% HCl–EtOH. If, immediately after dissolution of (I) in 0·3% HCl–$COMe_2$, the solution is diluted with H_2O, the products are a trisaccharide acetate hydrolysed to AcOH, digilanidobiose, and digitoxose (II) and a portion sol. in $CHCl_3$ which contains unchanged (I) and some genin but is mainly glucosidic since it gives (II) when hydrolysed. H. W.

Attempted syntheses of hydroxyflavanone-glucosides. S. Fujise and S. Mitui (Ber., 1938, **71**, [*B*], 912—915).—7-Hydroxyflavonone, acetobromoglucose, Ag_2O, and quinoline in C_6H_6 give 7-*hydroxyflavanoneglucoside tetra-acetate*, m.p. 149·5—150°, $[\alpha]_D^{21·5}$ −21·0° in dioxan, hydrolysed by NaOH in MeOH–$CHCl_3$ to 7-*hydroxyflavanone*-7-*glucoside* ($+1H_2O$), m.p. 183—184°, $[\alpha]_D^{18·5}$ −102·63° in dioxan or (anhyd.), $[\alpha]_D^{24·5}$ −121·34° in dioxan. Similarly 5 : 7-dihydroxyflavanone (I) gives 5 : 7-*dihydroxyflavanone*-7-*glucoside tetra-acetate* (II), m.p. 173—173·5°, $[\alpha]_D^{21}$ −29·1° in dioxan, the constitution of which follows from its indifference towards CH_2N_2, which readily converts (I) into 5-hydroxy-7-methoxyflavanone. Ac_2O and C_5H_5N transform (II) into 7-*hydroxy*-5-*acetoxyflavanone*-7-*glucoside tetra-acetate*, m.p. 160·5—161°, reconverted into (II) by HBr–AcOH. 5 : 7-*Dihydroxyflavanone*-7-*glucoside* ($+1H_2O$), has m.p. 134—135° (decomp.), $[\alpha]_D^{14·5}$ −36·0° in $CHCl_3$. H. W.

Synthesis of quinacetophenone methyl ether glucoside. F. Mauthner (J. pr. Chem., 1938, [ii], **150**, 197—198).—Addition of aq. NaOI to 3 : 6-OMe·C_6H_3(OH)·COMe and acetobromoglucose in $COMe_2$ at 5° gives 2-*aceto*-4-*methoxyphenylglucoside tetra-acetate*, m.p. 159—160°, converted by 6% aq. $Ba(OH)_2$ into the free glucoside, m.p. 139—140° (cf. Goris and Canal, A., 1935, 1041). R. S. C.

Structure of dextran. F. E. Brauns (Canad. J. Res., 1938, **16**, B, 73—75).—Re-examination of the data recorded by Fowler *et al.* (A., 1938, II, 55) for the dextran synthesised by the action of *Leuconostoc mesenteroides* on sucrose reveals the impossibility of thus deciding definitely whether it is a 1 : 2 : 1, 1 : 3 : 1, or 1 : 4 : 1 polymeride. H. W.

Pectic substances. I. The araban and pectic acid of the peanut. E. L. Hirst and J. K. N. Jones (J.C.S., 1938, 496—505).—The polysaccharides of *Arachis hypogœa* contain starch, cellulose, and a complex of pectic acid and araban. Partial methylation (Tl derivative with MeI) of the complex yields the methylated araban, hydrolysed by 1% MeOH–HCl to 3 products: (*a*) 2 : 3 : 5-*trimethylmethyl*-l-*arabinoside*, b.p. 87—90°/0·001 mm., $[\alpha]_D^{21}$ −60° in H_2O, hydrolysed by dil. HCl to the trimethylarabinose, oxidised (Br) to the γ-arabonolactone, converted by MeOH–NH_3 into the arabonamide; (*b*) 2 : 3-*dimethylmethyl*-l-*arabinoside*, b.p. 115—122°/0·001 mm., $[\alpha]_D^{21}$ +14° in H_2O, hydrolysed to 2 : 3-*dimethyl*-l-*arabinose*, $[\alpha]_D^{20}$ +106° in H_2O, oxidised to the *γ-lactone*, b.p. 145—155°/0·003 mm., $[\alpha]_D^{20}$ −34° in H_2O, giving an *amide*, m.p. 160°, $[\alpha]_D^{20}$ +17° in H_2O, which gives a negative Weerman test; and (*c*) 3-*methylmethyl*-l-*arabinoside*, b.p. up to 200°/0·001 mm., $[\alpha]_D^{21}$ +46° in H_2O, giving the 3-*methylarabinose* (impure), $[\alpha]_D^{20}$ +96° in H_2O, *γ-lactone*, b.p. 175°/0·003 mm., $[\alpha]_D^{21}$ −36° in H_2O, and *amide*, $[\alpha]_D^{21}$ +31° in H_2O, the hydrazodicarbonamide from which (Weerman) was identical with an authentic sample. The structure of the araban is discussed. A. Li.

Degradation of limit dextrins and starch by acetyl bromide. II. Constitution of limit dextrins and of starch. K. Myrbäck (Svensk Kem. Tidskr., 1937, **49**, 271—274; cf. A., 1937, II, 446).—Zulkowski starch and maltose when treated with AcBr–AcOH and then with Ag_2CO_3 in Et_2O give maltose hepta-acetate (I) in good yield; under identical conditions (I) is not obtained from a limit dextrin of mol. wt. about 610. Similar observations are recorded with a sol. starch and a limit dextrin of mol. wt. about 810. A part of the starch mol. therefore is not formed from maltose residues and the limit dextrins arise from the portions of the mol. which are not constructed according to Haworth's formula. H. W.

Degradation products of starch produced by α-amylase. J. Blom, B. Braal, and A. Bak (Z. physiol. Chem., 1938, **252**, 261—270).—Potato starch is hydrolysed by α-amylase yielding dextrins and maltose (I). The quantity of (I), which is determined by the difference in the reducing power of the sugars before and after fermentation with yeast, increases with degree of degradation and reaches a max. of 23% of the theoretical quantity when 40% of the starch is hydrolysed. The hydrolysis by α-amylase is inhibited by increasing quantities of (I). J. D. R.

Periodic acid oxidation of starches and dextrins as a means of determining molecular size. C. G. Caldwell and R. M. Hixon (J. Biol. Chem., 1938, **123**, 595—606).—HIO_4 consumed in oxidation of starches and dextrin fractions varies inversely with the fat and P content. Hydrolysis of oxidised starch (0·004N-H_2SO_4) gives $(CHO)_2$, indicating cleavage of the non-terminal glucose units between $C_{(2)}$ and $C_{(3)}$. Correlation between the amount of CH_2O formed in oxidation and the reducing power of nine dextrins shows that both methods are reliable for the determination of reducing terminal groups, and it is concluded that starches have chain-lengths > the 25 units proposed by Haworth. J. D. R.

Starch. IX. Constitution of starch on the basis of the determination of the terminal group. K. Hess and K. H. Lung (Ber., 1938, **71**, [*B*], 815—826; cf. A., 1937, II, 326).—Treatment of potato starch with Me_2SO_4 and 45% NaOH in H_2 gives methylstarch with 42—43% OMe which, when examined by the terminal group method of Hess and Neumann (*ibid.*, 232), shows an end-group content of 1·88—1·90%, indicating a degree of polymerisation of 52—52·4. The viscosity of trimethylstarch in $CHCl_3$ indicates a 30- to 60-fold greater degree of polymerisation. The discrepancy leads to the examination of the "comb formula" for starch by determination of the less highly methylated sugars formed by hydrolysis and also by measurements of viscosity; the comparison gives little support to the formula. Other possibilities for the constitution of starch are discussed. H. W.

Viscosimetric behaviour of solutions of methylstarch. W. Philippoff and K. Hess (Ber., 1938, **71**, [*B*], 841—847).—The viscosities of the trimethylstarches of Hess and Lung (preceding abstract) have been determined in $CHCl_3$. The observed vals. are > any recorded previously and are very similar to those of the starch triacetate of Sakurada and Lee. This is attributed to the very mild conditions during extraction of the starch and prep. of the derivatives. Typical micellary solutions such as those of soap colloids and of methylstarch (I) in which according to Hess and Lung (*loc. cit.*) individual mols. cannot be present have mechanical properties exactly similar to those of cellulose derivatives and caoutchouc. Although the flow behaviour of solutions of (I) and methylcellulose is closely similar the latter gives normal films of high tenacity whereas the former usually gives only very brittle and powdery films. In harmony with results obtained with the ultracentrifuge, starch, in contrast with cellulose, appears highly heterodisperse. H. W.

Action of nucleotides in disruptive phosphorylation of glycogen.—See A., 1938, II, 510.

Mechanism of cellulose reactions. H. M. Spurlin (Trans. Electrochem. Soc., 1938, **73**, Preprint 30, 411—423).—Cellulose reactions are classified as (*a*) formation of derivatives of OH groups and (*b*) degradation of the chain-mols. by hydrolysis, oxidation, or decomp. In a partly substituted product the distribution of substituents is governed by the laws of chance, modified to some extent by the tendency of particular groups to react more rapidly than the remainder in certain reactions (*e.g.*, etherification) and also by the degree of swelling of the cellulose, the rate of diffusion of the reagents, and the solubility of the product. When swelling is low the reaction proceeds in bands from visible starting points on the surface. In solution, or with rapid intramicellar swelling, the reaction is uniform throughout. When intermicellar swelling occurs, although the reaction is not visibly heterogeneous, the *X*-ray diagram of the original cellulose persists for a long time. W. A. R.

Terminal group question of cellulose in cotton hairs. II. E. Leckzyck (Ber., 1938, **71**, [*B*], 829—841).—Re-examination of the "terminal group" method of Hess and Neumann (A., 1937, II, 232) with mixtures of tetra- (I) and tri-methylmethylglucoside shows that it is sufficiently sensitive for chain-lengths up to 10,000 C_6 and could be extended to longer chains by working at greater dilutions. The purification of the cotton hairs is effected under the conditions used by Hess and Neumann (*loc. cit.*) but with inclusion of a final treatment with 9% NaOH. The fibre thus obtained gives a "terminal group prep." in very small amount; this is very extensively decomposed by repeated distillation over Na and appears to consist mainly of the Me ester of a methoxycarboxylic acid. The more complete removal of the "accompanying matter" by the NaOH is accompanied therefore by the formation of decomp. products in small amount. The extracted material when treated with alkali and Me_2SO_4 gives a product with low OMe content which cannot be distilled unchanged over Na; it does not appear to be related to the carbohydrate group and probably arises from the fat–wax phase of the cotton hairs. A "terminal group prep." obtained from cotton exposed to air during preliminary purification and methylation is found to consist largely of a Me trimethoxybutan(?)onecarboxylate. A second prep. in which methylation at any rate was accomplished with exclusion of air gave, after hydrolysis, small amounts of tetramethylglucose, so that (I) in small amount can result from secondary decomp. The experimental results prove the necessity of excluding all formulæ for cellulose which have a chain-length up to 10,000 C_6. The possibilities remain that the cellulose chain is so highly polymerised that the terminal group cannot be detected by the method of Hess and Neumann (degree of polymerisation $>10^4$ C_6), that the terminal group is a glucose group with "anhydride closure" with respect to $C_{(4)}$, or that cellulose has not a chain but a ring structure. In the second case dimethylglucose must be formed by hydrolysis of the methylcellulose; this is not experimentally excluded but the required structure is regarded as unlikely. H. W.

Reduction of aminosorbitol hydrochloride with hydriodic acid. P. A. Levene and C. C. Christman (J. Biol. Chem., 1938, **123**, 77—82; cf. A., 1937, II, 139, 447).—Reduction of aminosorbitol (I) hydrochloride by HI yields β-*aminohexene oxide* (*platinichloride*; *hydrochloride*, m.p. 217—218°, $[\alpha]_D^{25}$ −5·9° in EtOH; *Ac* derivative, m.p. 142—143°, $[\alpha]_D^{25}$ +4·1° in EtOH) which cannot be hydrogenated. The hexa-acetate of (I) with HI in AcOH gives a β-*aminohexanol*, m.p. 86—88° (*Ac* derivative, m.p. 77—78°, $[\alpha]_D^{26}$ +39·7° in $CHCl_3$). E. G. B.

Effect of heating amino-acids in neutral or acid solution in the autoclave. N. I. Gavrilov, N. V. Elaguina, N. V. Dudikina, and I. V. Kornilov (Bull. Soc. chim., 1938, [v], **5**, 442—454).—Arginine and $(NH_2)_1$-acids, except cystine, yield only traces of NH_3 in H_2O at 180°/10 atm. Glycine anhydride and alanylglycine yield slightly more NH_3 than do the component acids and glutamic acid gives its lactam. These changes are reduced by increasing acidity. Histidine yields NH_3 with fission of the ring, the change being favoured by acid. R. S. C.

Bacterial deamination of glycine. F. Egami (Bull. Soc. Chim. biol., 1938, **20**, 301—304; cf. A., 1936, 113, 640).—An organism isolated from garden soil deaminates and dehydrogenates glycine with formation of $CHO{\cdot}CO_2H$. J. N. A.

Determination of arginine and histidine. G. Mourot and O. Hoffer (Bull. Soc. Chim. biol., 1938, **20**, 274—292).—Three methods for separation and determination of arginine (I) and histidine (II) are described: (*a*) (II) is pptd. by AgOAc in presence of $Ba(OH)_2$ whilst (I) remains in solution; (*b*) when (I) and (II) are heated with dil. alkali in sealed tubes, (I) is decomposed into NH_3 and ornithine, whilst (II) is unattacked; (*c*) arginase or the crude enzyme prep. from liver decomposes (I) into $CO(NH_2)_2$ and ornithine, without affecting (II). The three methods are applicable to protein hydrolysates; (*a*) and (*b*) can be applied only after a quant. separation of (I) and (II) from the other NH_2-acids, whilst (*c*) can be used directly. In the last case the errors are 1% for (I) and 2% for (II). J. N. A.

Reduction of glucosamic acid with hydrogen iodide in glacial acetic acid. P. A. Levene and C. C. Christman (J. Biol. Chem., 1938, **123**, 83—85; cf. A., 1903, i, 74; 1935, 1228).—Reduction of glucosamine by HI in AcOH yields *α-amino-γ-hydroxyhexoic acid*, $[\alpha]_D^{25}$ −16·4° in 20% HCl. E. G. B.

Oxazolines and thiazolines. IV. β-Chloroethylthiourethane. P. G. Sergeev and B. S. Kolitschev (J. Gen. Chem. Russ., 1937, **7**, 2863—2867).—$CH_2Cl{\cdot}CH_2{\cdot}CNS$ (I) in Et_2O–EtOH and HCl at 0° yield β-*chloroethylthiourethane* (II), m.p. 106—107°, regenerating (I) when distilled from P_2O_5 in vac. and identical with the product obtained previously (A., 1938, II, 32) from $OH{\cdot}CH_2{\cdot}CH_2{\cdot}CNS$ and HCl at 80°. (II) is also synthesised from $CH_2Cl{\cdot}CH_2{\cdot}S{\cdot}COCl$ and NH_3. R. T.

Thiocarbamyl ethers. M. Battegay and R. Krebs (Compt. rend., 1938, **206**, 919—921).—Anhyd. $Pr^{\alpha}OH$ and NH_4CNS at <10° and H_2SO_4,H_2O give the *compound*, $OPr^{\alpha}{\cdot}CS{\cdot}NH_2$, m.p. 35°; if the reaction mixture is not neutralised and alcohol removed in presence of mineral acid, conversion (at about 80°) into the *substance*, $SPr^{\alpha}{\cdot}CO{\cdot}NH_2$, m.p. 91°, occurs. A. T. P.

Reduction of nitrous acid by cysteine and glutathione. M. Lemoigne, P. Monguillon, and R. Désveaux (Compt. rend., 1938, **206**, 947—949).—At p_H 3 cysteine and glutathione rapidly reduce HNO_2 to NH_2OH and NH_3, whilst at p_H 7 <30% of the HNO_2 is reduced by glutathione. P. G. M.

Synthesis of tetradeuterohomocystine and dideuteromethionine. W. I. Patterson and V. du Vigneaud (J. Biol. Chem., 1938, **123**, 327—334; cf. A., 1935, 1486).—C_2D_2, from CaC_2 and D_2O, is reduced ($CrCl_2$) to $C_2H_2D_2$, brominated to $C_2H_2D_2Br_2$ (yield from D_2O, 63%). The latter is condensed with $CH_2Ph{\cdot}SH$ to *αβ-dideutero-β-benzylthiolethyl bromide*, b.p. 118—123°/1 mm. (yield 41%), which with

$CHNa(CO_2Et)_2$ yields 65% of *βγ-dideuterobenzylthiolethylmalonic acid*, m.p. 119—120°. By successive bromination and amination this yields 66% of *βγ-dideutero-S-benzylhomocysteine*, indistinguishable from *S*-benzylhomocysteine. This compound by successive reduction and oxidation (cf. A., 1935, 737) yields 90% of *ββ′γγ′-tetradeuterohomocystine*, and by successive reduction (Na) and methylation (MeI) in liquid NH_3, 78% of *βγ-dideuteromethionine*. The last two compounds contain theoretical amounts of D, indicating stability of D in these positions.

E. G. B.

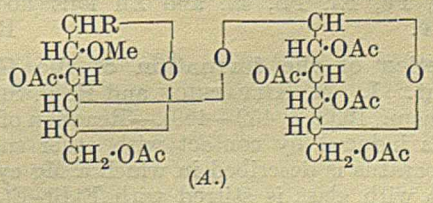
Guanidine structure and hypoglycæmia. Branched-chain analogue of synthalin. C. E. Braun and B. J. Ludwig (J. Org. Chem., 1938, **2**, 442—446).—Et γ-cyano-εη-dimethyloctane-γ-carboxylate (prepared from $CHMeBu^{\beta}\cdot CH_2Br$ and $CN\cdot CHEt\cdot CO_2Et$), b.p. 99—105°/3—4 mm., gave the corresponding *cyano-amide*, m.p. 74°, by way of the acid and acid chloride, but not directly by NH_3 etc. Distillation with P_2O_5 then yields *ζζ-dicyano-βδ-dimethyloctane*, b.p. 124—128°/15 mm., reduced by Na–EtOH to *ζζ-diamino-βδ-dimethyloctane* (*picrate*, m.p. 129°), the *dihydrochloride*, m.p. 242° (decomp.), of which with $NH_2\cdot CN$ in hot, dry EtOH gives *δδ-diguanidino-βδ-dimethyloctane dihydrochloride*, decomp. 112—113° (*picrate*, m.p. 214—215°). This salt has no hypoglycæmic action and is not toxic, even in doses of 75 mg. per kg., to rabbits. R. S. C.

Synthesis of homoarginine. J. P. Greenstein (J. Org. Chem., 1938, **2**, 480—483).—*Dicarbobenzoyloxylysine*, m.p. 104°, with PCl_5 in cold, dry $CHCl_3$ gives the acid chloride, converted by evaporation at 50°/vac. into the *anhydride*, m.p. 92°, and thence by HCl–$COMe_2$ into *ε-carbobenzoyloxy-*dl*-lysine*, m.p. 263°. Pd-hydrogenation of the *Bz* derivative (prepared by BzCl–NaOH) thereof in 5N-HCl gives *α-benzoyl-*dl*-lysine*, m.p. 211°, which with $NH_2\cdot C(NH)\cdot OMe$ and NaOMe in MeOH gives *ε-guanidino-α-benzoyl-*dl*-lysine*, m.p. 273°, hydrolysed by hot 5N-HCl to *ε-guanidino-*dl*-lysine* [*homoarginine*] [*sulphate*, $+1{\cdot}5H_2O$, decomp. 127° after sintering at 112°; *benzylidene* derivative, m.p. 248° (decomp.)], unaffected by arginase at 40° and p_H 8. R. S. C.

Geometrical isomerism in the epoxynitrile series. R. Gerbaux (Bull. Acad. roy. Belg., 1938, [v], **24**, 88—91).—Interaction of $COMe\cdot CHMeCl$ (I) with aq. KCN affords β-cyano-βγ-oxidobutanes, b.p. 155—156°/758 mm. (35%) (II) and b.p. 142—143°/758 mm. (65%) (III). Neither affords a semicarbazone, but either with conc. HCl affords two β-chloro-α-hydroxy-α-methylbutyric acids, m.p. 75° and 92°. (II) and (III) with HCl (gas) afford isomeric *γ-chloro-β-cyanobutan-β-ols*, b.p. 93·4—93·6°/10 mm. (IV) and b.p. 99·8—100°/10 mm., respectively. In slightly alkaline solutions (II) and (III) afford isomeric *β-cyanobutane-βγ-diols*, m.p. 94·4—95·4° and 107·4—108·4°, respectively. (I) with anhyd. HCN and a little KCN gives a mixture of two chlorocyanohydrins with (IV) preponderating. J. L. D.

Reactions of β-keto-nitriles with hydrogen. R. H. Wiley and H. Adkins (J. Amer. Chem. Soc., 1938, **60**, 914—918).—Partial hydrogenation of keto-nitriles, $R\cdot CO\cdot CHR\cdot CN$, in presence of Raney Ni at 35—40°/120 atm. gives 10—60% of unstable keto-amine if R = Pr^{β}, but not if R = Bu^{α}, the nature of R′ also influencing the yield. At 150—200°/270 atm. 23—58% of NH_2-ketones are obtained with 20—40% of tetrahydropyrans and/or other products of hydrogenolysis, which often occurs extensively. At intermediate temp. indefinite products are obtained. At 130° some dialkylamine is formed. Condensation of $Pr^{\beta}CO_2Et$ with the appropriate nitrile by NaOEt, first at 90—100° and then at 120—130° (3—4 days), gives about 40% yields of *β-keto-αγ-dimethyl-*, b.p. 95—96°/24 mm., *-γ-methyl-α-ethyl-*, b.p. 96·5°/17 mm., *-γ-methyl-α-*n*-propyl-*, b.p. 91°/7 mm., and *-γ-methyl-α-*n*-butyl-valeronitrile*, b.p. 128°/24 mm.; $Bu^{\gamma}CO_2Et$ and $Bu^{\alpha}CN$ give only 6% of *β-keto-γγ-dimethyl-α-*n*-propyl-valeronitrile*, b.p. 122°/12 mm. Addition of $Bu^{\alpha}CN$ (2 mols.) to powdered Na in boiling Et_2O gives 45% of *β-imino-α-*n*-propyl-*n*-heptonitrile*, b.p. 125—126°/3 mm., hydrolysed by hot 10% H_2SO_4 to *β-keto-α-*n*-propyl-*n*-heptonitrile*, b.p. 127°/17 mm. By hydrogenation were obtained *γ-keto-δ-methyl-β-*n*-propyl-*, m.p. 79—80°, *-δ-methyl-β-ethyl-*, m.p. 104—105°, and *-βδ-dimethyl-*n*-amylamine*, m.p. 140—141°, *γ-hydroxy-δ-methyl-*n*-amylamine*, b.p. 104°/23 mm. (p-*nitrobenzoyl* derivative, m.p. 132—133°), *γ-hydroxy-βδ-dimethyl-*n*-amylamine*, b.p. 105°/25 mm. (p-*nitrobenzoyl* derivative, m.p. 181—182°), *γ-hydroxy-δ-methyl-β-ethyl-*, b.p. 107°/16 mm., and *-*n*-propyl-*n*-amylamine*, b.p. 120°/17 mm., *γ-benzamido-ε-methyl-*n*-octan-δ-ol*, m.p. 99—100°, *δ-benzamido-ζ-methyl-*n*-octan-ε-ol*, m.p. 107—108°, δ-p-*nitrobenzamidomethyl-*n*-heptan-γ-ol*, m.p. 137—138°, *di-γ-keto*iso*hexylamine hydrochloride*, m.p. 194—196°, *di-(γ-keto-β-ethyl*iso*hexyl)amine hydrochloride*, m.p. 185—187°, cyclic *ethers*, $C_9H_{16}O$, b.p. 66—67°/22 mm., $C_{10}H_{18}O$, b.p. 80—81°/22 mm., and $C_{10}H_{18}O$, b.p. 88—89°/22 mm., the *Bz* derivative, m.p. 71·5—73·5°, of an O-free base from $COPr^{\beta}\cdot CHPr\cdot CN$, and the p-*nitrobenzoyl* derivative, m.p. 97·5—98·5°, of an O-free base from $COBu\cdot CHPr\cdot CN$. M.p. are corr. R. S. C.

Transformation of nitriles of the sugar series. G. Zemplén, E. Balassa, and M. Gárdonyi (Ber., 1938, **71**, [*B*], 768—774).—Cellobiononitrile octa-acetate (I) is transformed by HBr–AcOH at room temp. into *cellobionamide octa-acetate* (II), m.p. 164·5°, $[\alpha]_D^{18}$ +32·65° in $CHCl_3$, reconverted into (I) by $POCl_3$ at 75°. With NaOMe in MeOH (II) gives *cellobionamide*, hydrolysed by boiling $Ba(OH)_2$ to non-cryst. *cellobionic acid*, isolated as the *Ca* salt. Similarly gluconamide penta-acetate gives gluconamide, m.p. 145—145·5°, $[\alpha]_D^{18}$ +31·11° in H_2O. Galactonitrile penta-acetate is converted by HBr–AcOH into *galactonamide penta-acetate*, m.p. 177—177·5°, $[\alpha]_D^{18}$ +26·80° in $CHCl_3$, whence *galactonamide*, m.p. 170—



(*A.*)

171°. Acetobromocellobiose and AgCN in boiling xylene yield *cellobiosido-*1*-nitrile hepta-acetate* (III)

(*A*; R = ON), m.p. 172·5°, $[\alpha]_D^{20}$ −6·25° in $CHCl_3$, converted by AgOAc and Ac_2O at 100° into β-cellobiose octa-acetate, m.p. 194°, $[\alpha]_D^{20}$ −12·58° in $CHCl_3$, and hydrolysed by boiling $Ba(OH)_2$ to non-cryst. *cellobiosido-1-carboxylic acid*, isolated as the *Ca* salt. HBr–AcOH and (III) afford *cellobiosido-1-carboxylamide*, m.p. 189°, $[\alpha]_D^{19}$ +0·84° in $CHCl_3$, converted by NH_3–H_2S in EtOH at 70° into *cellobiosido-1-thiocarboxylamide hepta-acetate*, m.p. 188—189°, $[\alpha]_D^{22}$ ±0° in $CHCl_3$. H. W.

Change in optical rotation of gluconitrile. P. E. Papadakis and H. J. Cohen (J. Amer. Chem. Soc., 1938, **60**, 765—768).—The forms, m.p. 145° and 120·5°, of gluconitrile are obtained by crystallising from AcOH or abs. EtOH, respectively. The former has $[\alpha]_D$ +9·96° (const.) in H_2O, +6·27° in C_5H_5N. The latter has $[\alpha]_D$ +6·03° in C_5H_5N, about +10° in H_2O, changing first to a negative and then again to a small positive val. The m.p. of mixtures is intermediate. R. S. C.

Phosphorus analogues and homologues of choline and betaine. Onium compounds. XVII. R. R. Renshaw and R. A. Bishop (J. Amer. Chem. Soc., 1938, **60**, 946—947; cf. A., 1937, II, 488). —PMe_3 and $CH_2Cl{\cdot}CH_2{\cdot}OH$ in abs. EtOH at 90—100° give *trimethyl-β-hydroxyethylphosphonium chloride*, hygroscopic. $Br{\cdot}[CH_2]_2{\cdot}PMe_3Br$ and hot KOH–EtOH (1 mol.) give PMe_3 and *ethylenebis(trimethylphosphonium bromide)*. PEt_3 (prep. in 70% yield by the Grignard reagent) with $Br{\cdot}[CH_2]_2{\cdot}OH$ at 50°, $CH_2Br{\cdot}CH_2{\cdot}OAc$ at 40°, or $CH_2Br{\cdot}CO_2Et$ at room temp., yields *triethyl-β-hydroxyethyl-*, m.p. 223° (corr.), *triethyl-β-acetoxyethyl-*, m.p. 74·6° (corr.), and *carbethoxymethyltriethyl-phosphonium bromide*, m.p. 83·2° (corr.), respectively. Very little PMe_3 is obtained by the Grignard reaction. R. S. C.

Separation of α- and β-lecithin.—See A., 1938, III, 546.

Co-ordination of silver ion with unsaturated compounds. S. Winstein and H. J. Lucas (J. Amer. Chem. Soc., 1938, **60**, 836—847).—By the distribution technique (A., 1937, I, 135) $CHMe{:}CMe_2$, Δ^{β}-pentene, Δ^{α}-hexene, *cyclo*hexene, $CHMe{:}CHPh$, $(CHMe{:}CH)_2$, $(CH_2{:}CH{\cdot}CH_2)_2$ (I), $CH_2{:}CH{\cdot}CH_2{\cdot}OH$, $CH_2{:}CH{\cdot}CHO$, $CH_2{:}CH{\cdot}CO_2H$, and PhOH are shown to co-ordinate with $Ag^{\cdot}$. (I) and di*cyclo*pentadiene give solid compounds with $AgNO_3$. Equilibrium consts. are measured. *cis-* and *trans-*Δ^{β}-Butene are not equilibrated by $Ag^{\cdot}$. The resulting co-ordination compounds are assigned resonance formulæ and similar structures are assigned to compounds of unsaturated substances with, *e.g.*, Pt, Al, Fe, and Zn salts, Fe carbonyls, and NO_2-compounds. Cd, Co, Cr, Cu, Fe, Ni, Pb, Tl, and Zn ions do not co-ordinate. R. S. C.

Kinetics of the formation of the Grignard reagent. I. M. Kilpatrick and H. P. Simons (J. Org. Chem., 1938, **2**, 459—469).—Reaction of Mg with EtBr is induced by contact with other substances. An apparatus is described in which a Mg cylinder in contact with glass is stirred with EtBr–Et_2O. The rate of reaction ∝ [EtBr] after an induction period during which C_4H_{10}, but no MgEtBr, is formed. I decreases the induction period, but has no effect on the subsequent reaction rate. R. S. C.

Co-ordination compounds of palladous chloride. M. S. Kharasch, R. C. Seyler, and F. R. Mayo (J. Amer. Chem. Soc., 1938, **60**, 882—884).—Reaction of $PdCl_2$ with PhCN yields $(PhCN)_2PdCl_2$, from which *compounds* containing 1 mol. of C_2H_4, *iso*butene, *cyclo*hexene (I), or styrene (II) per mol. of $PdCl_2$ have been obtained by the action of C_2H_4 derivatives. The compounds appear to be bimol.; a general structural formula has been proposed. The stability decreases in the order (I), C_2H_4, (II). E. S. H.

Organic chemistry of gold and production of gold mirrors. C. S. Gibson (Compt. rend. XVII Cong. Chim. Ind., 1937, 877—880).—A summary of work previously published by Gibson and collaborators. F. N. W.

Complex compounds of platinum metals with thio-, seleno-, and telluro-ethers.—See A., 1938, I, 322.

Homologues of *cyclo*propane. Methyl*cyclo*propane. I. Preparation. W. A. Lott, W. G. Christiansen, and L. F. Shackell (J. Amer. Pharm. Assoc., 1938, **27**, 125—128).—Reduction of αγ-dibromobutane with Zn in 85% EtOH affords methyl*cyclo*propane (yield 81%, *iso*butylene content 0·68%); similar reduction of αγ-dichloro*iso*butane yields practically pure *iso*butylene. The reduction products of various dihalogeno-propanes and -butanes are discussed. F. O. H.

Catalytic dehydrogenation of *cyclo*hexane in presence of oxides of chromium and vanadium. H. S. Taylor and L. M. Yeddanapalli (Bull. Soc. chim. Belg., 1938, **47**, 162—171).—The Cr_2O_3 is obtained as a hard, black, vitreous gel by boiling a solution of $Cr(NO_3)_3{,}9H_2O$ with NH_4OAc, cooling, adding NH_3, and again boiling. The product is washed with H_2O; dried at 100—300°, and then heated *in situ* in H_2 at 400°. The activity of the catalyst in the dehydrogenation of *cyclo*hexane at 383—444° is reproducible. The gas evolved contains >95% of H_2. The apparent energy of activation is 24 kg.-cal. per mol. V_2O_3 is obtained by slowly evaporating a solution of NH_4VO_3 and $H_2C_2O_4$ to dryness, gradually raising the temp. of the residue to 400°, and reducing the product in H_2 *in situ* at 400°. It is inferior to Cr_2O_3 as catalyst. Mixtures of Cr_2O_3 and U_2O_3 are intermediate in activity; their apparent energies of activation are of the same order as those of Cr_2O_3. It is suggested that in the case of catalytic gels of Cr_2O_3 the energy of desorption of H determines the magnitude of the observed energy of activation. H. W.

Thermal decomposition of alicyclic compounds. I. Decomposition of *cyclo*hexane and some simpler hydrocarbons. F. O. Rice, P. M. Ruoff, and E. L. Rodowskas (J. Amer. Chem. Soc., 1938, **60**, 955—961).—Investigations designed to isolate the primary products of thermal decomp. are best conducted at low pressures, which retard subsequent bimol. reactions and polymerisation without affecting the rate of the unimol. thermal decomp. A

suitable technique is described. At 700—800°/7—15 mm. *cyclo*hexene (I) gives 90—95% of C_2H_4 and butadiene (II) with 1—2% each of $C_6H_6+2H_2$ and $2C_2H_4+C_2H_2$, but no tar. C_2H_4 and (II) are unaffected under the conditions used, and C_2H_6 and C_4H_{10} are barely affected. (I) slowly removes a Te mirror, giving an unstable compound, but $COMe_2$ gives free radicals much more easily. *cyclo*Hexane and (II) give only traces of free radicals. Dissociation of (I) is assumed to occur by way of the radical, $-CH_2\cdot[CH_2]_2\cdot\dot{C}H\cdot CH{:}CH_2$, *i.e.*, the resonance form common to $-CH_2\cdot[CH_2]_2\cdot CH{:}CH\cdot CH_2-$ and $-CH_2\cdot[CH_2]_2\cdot\dot{C}H\cdot CH{:}CH_2$, this radical being formed in preference to others possible because resonance involves the least energy change and is possible only with this mode of fission; C_2H_4 and (II) are then formed by simple electronic shift. Similarly decomp. of dipentene to isoprene occurs by way of $CH_2{:}CMe{:}CH\cdot CH_2\cdot CH(CMe{:}CH_2)\cdot CH_2-$, and that of α-pinene to *allo*ocimene by way of

$$\text{H}\text{-}CMe_2\rangle C\langle \begin{matrix}CH_2\cdot CH\\ CH_2\cdot CH\end{matrix}\rangle CMe$$

and ocimene.

R. S. C.

Action of aluminium chloride on *cyclo*hexylbenzene. B. B. Corson and V. N. Ipatiev (J. Amer. Chem. Soc., 1938, **60**, 747—749).—With $AlCl_3$ at 80—85° *cyclo*hexylbenzene decomposes to (*a*) C_6H_6 and $C_6H_4(C_6H_{11})_2$ and (*b*) $C_6H_{10}Ph_2$ and C_6H_{12}. The products isolated were C_6H_6, *cyclo*hexane, a mixture of hexane and (?) methyl*cyclo*pentane, 1 : 4-diphenyl-*cyclo*hexane (I), m.p. 169—170°, and a liquid mixture (II) thereof with the 1 : 3-isomeride, and a *hydrocarbon*, $C_{24}H_{30}$, b.p. 330—370°/2 mm. (hydrogenated by H_2–Ni at 240°/100 kg. per sq. cm. to a liquid *tri*cyclo*hexyl*cyclo*hexane*). Hydrogenation of (II) gives 1 : 4- and 1 : 3-*di*cyclo*hexyl*cyclo*hexane*, m.p. 62·5—63·5°, the latter product being also prepared from *m*-$C_6H_4Ph_2$ and H_2–Ni. Hydrogenation of *o*-$C_6H_4Ph_2$ gives 1 : 2-*di*cyclo*hexyl*cyclo*hexane*, m.p. 44·5—46°. Identity of (I) with Kursanov's product (A., 1902, i, 20) and that from C_6H_6–*cyclo*hexene–$AlCl_3$ is proved. R. S. C.

Reaction of *cyclo*paraffins with aromatic hydrocarbons. De*cyclo*alkylation. A. V. Grosse and V. N. Ipatiev (J. Org. Chem., 1938, **2**, 447—458).—"De*cyclo*alkylation," *i.e.*, alkylation of aromatic hydrocarbons by *cyclo*paraffins, is effected in presence of metallic catalysts. The ease and uniformity of reaction depend on the nature of the reactants. In presence of $AlCl_3$ *cyclo*propane converts C_6H_6 at <0° or 25—30° into *n*-propylbenzenes up to *hexa*-n-*propylbenzene*, m.p. 103°, b.p. 332° (photomicrograph); reaction does not occur by way of propylene, which gives Pr^{β}-compounds and none higher than $C_6H_2Pr^{\beta}_4$. Methyl*cyclo*butane gives mixed amylbenzenes, including *iso*amylbenzene, with some *iso*-C_5H_{12} and Ph_2. *cyclo*Pentane reacts only at 150°, the main reaction products, amylbenzenes, being contaminated with products of dealkylation, *e.g.*, PhMe and PhEt, and of side-reactions, *e.g.*, *cyclo*pentylbenzene. In presence of $ZrCl_4$ 2-$C_{10}H_7Me$ and *cyclo*propane at 30—35° give methylpropylnaphthalenes, b.p. 136—138°/9·5 mm., and higher products. R. S. C.

Velocity of hydrogenation of aromatic hydrocarbons.—See A., 1938, I, 317.

Hydrogen fluoride as a condensing agent. J. H. Simons and S. Archer (J. Amer. Chem. Soc., 1938, **60**, 986).—In presence of HF at 0° C_6H_6 with C_3H_6 gives $PhPr^{\beta}$, with $Pr^{\beta}Cl$ gives (?) $C_6H_4Pr^{\beta}_2$, with *iso*-C_4H_8 or $Bu^{\gamma}Cl$ gives $PhBu^{\gamma}$ and $PhBu^{\gamma}_2$, and with $CMe_2{:}CHMe$ or CMe_2EtCl gives products, b.p. 188° and 262—265°, respectively. R. S. C.

Fluorinated derivatives of methane bearing phenyl groups. A. L. Henne and H. M. Leicester (J. Amer. Chem. Soc., 1938, **60**, 864—865).—CPh_2Cl_2 and SbF_3 with or without a little Br at 140° give *difluorodiphenylmethane*, b.p. 125°/10 mm., about 260° (decomp.)/760 mm., m.p. −1·9° to 1·8°, which is more stable than $CHPhF_2$, but less so than $CPhF_3$. CCl_2F_2, C_6H_6, and $AlCl_3$ give HF, $CHPh_3$, and $CPh_3\cdot OH$, derived by decomp. of CPh_3Cl. Ph decreases the stability of $>CF_2$ and $\cdot CF_3$. R. S. C.

Additive products of benzene derivatives and halogen. IX. Nitrobenzene and chlorine. T. van der Linden (Rec. trav. chim., 1938, **57**, 342—344).—$PhNO_2$ and liquid Cl_2 in a sealed tube in sunlight for about 6 months afford 1 : 2 : 3 : 4 : 5 : 6-*hexachloro*-1-*nitro*cyclo*hexane*, m.p. 212—213°; after 7 months, β-*p*-$C_6H_4Cl_2,Cl_6$ (?) (decomposed with KOH–EtOH to C_6HCl_5), ennea- and hepta-chloro-*cyclo*hexane (possibly) are obtained. A. T. P.

Liquid–vapour equilibria of binary systems of nitrotoluenes.—See 1938, A., I, 313.

Preparation of *o*-dinitro-compounds. R. Kuhn and W. van Klaveren (Ber., 1938, **78**, [*B*], 779—780).—*o*-$(NO_2)_2$-Compounds are advantageously obtained by the action of a warm mixture of HNO_3 (*d* 1·4) and 30% H_2O_2 on *o*-nitronitroso-derivatives in AcOH. The active reagent is probably a per-acid since the separate components react much less rapidly. 4 : 5-Dinitro-*o*- and -*m*-xylene, 2 : 3-dinitro-5 : 6 : 7 : 8-tetrahydronaphthalene, and 2 : 3-dinitrohydrindene are obtained in 75%, 78%, 88%, and 62% yield, respectively. H. W.

Cationoid reactivity of aromatic compounds. V. Fission of arylsulphones by means of sodamide and piperidine. W. Bradley (J.C.S., 1938, 458—460; cf. Bradley *et al.*, A., 1932, 622).—When heated with $NaNH_2$ and piperidine, Ph_2SO_2 yields 1-phenylpiperidine (I) (p-*chlorobenzeneazo*-derivative, m.p. 143°) and $PhSO_2H$, $PhSO_2\cdot CH_2Ph$ yields (I) and $CH_2Ph\cdot SO_2H$, while *p*-$MeSO_2\cdot C_6H_4Me$ yields 1-*p*-tolylpiperidine and $MeSO_2H$ (characterised as $MeSO_2\cdot CH_2Ph$). Even in presence of O_2, no nuclear substitution occurs. $(CH_2Ph)_2SO_2$ does not undergo fission. A. Li.

Diphenyl series. XI. Nitration of some 2 : 4′ diphenyl derivatives. C. Finzi and V. Bellavita (Gazzetta, 1938, **68**, 77—87).—2 : 4′-$(C_6H_4Br)_2$ is nitrated ($EtNO_3$, KNO_3, or HNO_3 in H_2SO_4) to a mixture converted by $C_5H_{11}N$ into 2-*bromo*-4 : 3′-*dinitro*-4′-*piperidyldiphenyl*, m.p. 130—131°, and 5 : 3′-*dinitro*-2 : 4′-*dipiperidyldiphenyl*, m.p. 121°; these are also obtained from the dibromodinitro-

diphenyls (A., 1933, 388). With H_2SO_4–$EtNO_3$, 4′ : 2-$C_6H_4Br{\cdot}C_6H_4{\cdot}NO_2$ gives 4′-*bromo*-2 : 3′-*dinitrodiphenyl*, m.p. 148°, which with $C_5H_{11}N$ yields 2 : 3′-*dinitro*-4′-*piperidyldiphenyl*, m.p. 88—89°. 2 : 4′-$C_6H_4Br{\cdot}C_6H_4{\cdot}NO_2$ and H_2SO_4–$EtNO_3$ give 2-*bromo*-5 : 4′-*dinitrodiphenyl*, m.p. 164—165°, converted into 5 : 4′-*dinitro*-2-*piperidyldiphenyl*, m.p. 155°. 2 : 4′-$NO_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH_2$ and H_2SO_4–$EtNO_3$ give 2 : 4-*dinitro*-4′-*aminodiphenyl*, m.p. 138—139° (*Ac* derivative, m.p. 186°) [converted into 2 : 4-$C_6H_3Ph(NO_2)_2$], and 2 : 2′-*dinitro*-4′-*aminodiphenyl*, m.p. 138—139° (converted into 2 : 2′-$NO_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NO_2$). 4′ : 2-$NO_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH_2$ yields 4 : 4′-*dinitro*-2-*aminodiphenyl*, m.p. 208° (*Ac* derivative, m.p. 168—169°) (converted into 4 : 4′-$NO_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NO_2$). 2 : 4′-$NO_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NHAc$ gives 2 : 3′-*dinitro*-4′-*acetamidodiphenyl*, m.p. 160—161°, reduced and acetylated to 2 : 3′ : 4′-$NHAc{\cdot}C_6H_4{\cdot}C_6H_3(NHAc)_2$. E. W. W.

Cumulenes. I. Synthesis of tetraphenylhexapentaene and di-diphenylenehexapentaene. R. Kuhn and K. Wallenfels (Ber., 1938, 71, [*B*], 783—790).—Cumulenes are compounds with an unbroken sequence of C:C linkings whereas the term polyenes is reserved for substances with conjugated double linkings. Tetraphenylbutinenediol in Et_2O is transformed by P_2I_4 into *ααδδ-tetraphenyl-*$\Delta^{\alpha\beta\gamma}$*-butatriene*, m.p. 236·5—237°. Successive addition of CH:C·C:CH and $COPh_2$ to MgEtBr in Et_2O yields *ααζζ-tetraphenyl-*$\Delta^{\beta\beta}$*-hexadi-inene-αζ-diol*, m.p. 140—141°, converted by P_2I_4 in C_5H_5N at 0° into *ααζζ-tetraphenyl-*$\Delta^{\alpha\beta\gamma\delta\epsilon}$*-hexapentaene*, $CPh_2{:}C{:}C{:}C{:}C{:}CPh_2$, m.p. 302° after softening at 290°. It forms scarlet crystals which are not fluorescent when solid or in solution. It gives a brown colour with $SbCl_3$ in $CHCl_3$ but does not react with $C(NO_2)_4$. It is remarkably stable towards O_2 but immediately decomposed by O_3. It readily adds Br and I. It is scarcely affected by $KMnO_4$ in C_5H_5N at 20°. It does not add maleic anhydride or *p*-benzoquinone. It is unchanged by Zn dust in $CHCl_3$ but immediately becomes decolorised on addition of AcOH. With a mild catalyst (PdO) the five double linkings become saturated without affecting the Ph residues whereby the transitory occurrence of an intense green fluorescence is remarkable. Analogously fluorenone affords *αζ-di-diphenylene-*$\Delta^{\beta\beta}$*-hexadi-inene-αζ-diol*, colourless leaflets, m.p. 257°. This with P_2I_4 affords *αζ-di-diphenylenehexapentaene*, m.p. 441—442°, the almost black crystals of which give solutions comparable with $KMnO_4$ in colour. It is not fluorescent. Its solutions in $CHCl_3$ are unchanged by exposure to bright sunlight. With an equal no. of double linkings the absorption of light is displaced more towards longer λ by cumulated than by conjugated double linkings. H. W.

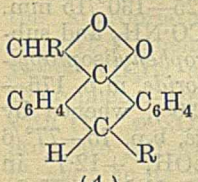
Preparation of 1 : 2 : 7-trimethyl-4-*iso*propylindene and 1 : 2 : 7-trimethyl-4-*iso*propylhydrindene. C. L. Carter and S. N. Slater (J.C.S., 1938, 546).—2 : 7-Dimethyl-4-*iso*propyl-1-hydrindone (Cook *et al.*, A., 1935, 74) with MgMeI gives 1 : 2 : 7-*trimethyl*-4-iso*propyl-indene*, b.p. 154—157°/17 mm., reduced (Pd–norit) to the *-hydrindene*, b.p. 154—155°/29 mm. A. Li.

Synthesis of 1 : 1 : 2 : 6-tetramethyl-1 : 2 : 3 : 4-tetrahydronaphthalene. Constitution of irene. M. T. Bogert and P. M. Apfelbaum (J. Amer. Chem. Soc., 1938, 60, 930—933).—Diagnosis of irene as 1 : 1 : 2 : 6-tetramethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (I) (Ruzicka *et al.*, A., 1933, 1297) is confirmed by synthesis. Oxidation of irene proceeds with loss of 1 C; analogies are cited. *m*-$C_6H_4Me{\cdot}[CH_2]_2{\cdot}OH$ [from *m*-$C_6H_4Me{\cdot}MgBr$ and $(CH_2)_2O$], b.p. 115—118°/10 mm. (*phenylurethane*, m.p. 59—60°), with PBr_3 gives the bromide, b.p. 103—106°/10 mm., the Grignard reagent from which with $COMePr^{\beta}$ gives *ε-m-tolyl-αγ-dimethyl-*n*-pentan-γ-ol*, b.p. 150—152°/10 mm., which with hot H_2SO_4 gives (I), b.p. 120—125°/10 mm. (physical data = those of irene). With Se at 250—280° it gives 1 : 2 : 6-$C_{10}H_5Me_3$. With CrO_3 it gives α-2-*carboxy*-p-*tolyl*iso*propyl Me ketone*, m.p. 154—155° [= "trihydroxydehydroirene" (Tiemann *et al.*, A., 1894, i, 80; 1895, i, 530)], which with NaOHal gives impure α-2-carboxy-p-tolyl*iso*butyric acid. With $KMnO_4$ (I) gives α-2 : 4-dicarboxyphenyl*iso*butyric ["ioniregentricarboxylic"] acid [anhydride, m.p. 214° (corr.)]. R. S. C.

Synthetic experiments with polyterpenes. W. Huber (Ber., 1938, 71, [*B*], 725—734).—The prep. of hydronaphthalene or hydrophenanthrene derivatives with the conjugated linkings in a single ring is difficult by reason of the sensitiveness of these compounds to heat and traces of acid. 2-Keto-10-methyl-$\Delta^{1:9}$-octahydronaphthalene is reduced by $Al(OPr^{\beta})_3$ and $Pr^{\beta}OH$ to 2-*hydroxy*-10-*methyl-*$\Delta^{1:9}$*-octahydronaphthalene* (I), b.p. 68°/0·18 mm. [non-cryst. *benzoate* (II); *dinitrobenzoate*, m.p. 69—69·5°]. When heated at 170° in presence of air (II) gives BzOH and an oil which resinifies with change in absorption spectrum when kept in air. The only homogeneous product which can be obtained by loss of BzOH from (II) in N_2 alone or in presence of $CaCO_3$ or KOH or by loss of H_2O from (I) is 10-*methyl-*$\Delta^{8:9\text{–}1:2}$- or -$\Delta^{7:8\text{–}9:1}$-*hexahydronaphthalene*, b.p. 142°/12 mm., which does not add maleic anhydride (III); the production of 10-*methyl-*$\Delta^{1:9\text{–}2:3}$-*hexahydronaphthalene* is shown by the absorption spectrum of the crude product and the formation of an *adduct*, $C_{15}H_{20}O_4$, b.p. 172°/12 mm., with (III). Addition of *cyclo*hexanone and 2-acetyl-1-methyl-Δ^1-*cyclo*hexene in C_5H_5N to $KOPr^{\beta}$ in Et_2O affords 9-*keto*-13-*methyl-*$\Delta^{10:11}$*-dodecahydrophenanthrene*, b.p. 81°/10^{-4} mm. [2 : 4-*dinitrophenylhydrazone*, m.p. 103—104°; *semicarbazone*, m.p. (indef.) 116—118°], reduced by $Al(OPr^{\beta})_3$ in $Pr^{\beta}OH$ to 9-*hydroxy*-13-*methyl-*$\Delta^{10:11}$*-dodecahydrophenanthrene* (IV), b.p. 79°/0·007 mm. (non-cryst. *benzoate* (V); *dinitrobenzoate*, m.p. 97·5—98°). Elimination of H_2O from (IV) or of BzOH from (V) invariably yields a mixture of hydrocarbons. 13-*Methyl-*$\Delta^{9:14\text{–}10:11}$*-decahydrophenanthrene*, its *adduct*, $C_{19}H_{26}O_4$, b.p. 220°/12 mm., from (III), and 13-*methyl-*$\Delta^{9:10\text{–}11:4(7)}$*-decahydrophenanthrene*, b.p. 76·5°/1 mm., are described. H. W.

Dissociable anthracene oxides. Influence of *meso* aliphatic groups. A. Willemart (Bull. Soc. chim., 1938, [v], 5, 556—564).—Partly a review of work already noted (A., 1938, II, 50). The *oxides* of 9-methyl- (I), 9-ethyl- (II), 9 : 10-dimethyl-, and

9-methyl-10-ethyl-anthracene (III), prepared in CS_2, are described. That of (I) decomposes violently at about 80°, the others at indefinite temp. Insolation of (I) and (II) in Et_2O gives *polymerides*, m.p. >250° (block) and about 275° (block), respectively. The differing amounts of O_2 evolved when alkyl-, 9-aryl-10-alkyl, and 9 : 10-diaryl-anthracene oxides are heated are due to the stabilisation of anthracene by aryl towards oxidation and not to a difference in formula, *e.g.*, (*A*) for alkyl oxides. Thus, all the hydrocarbons have the normal absorption of anthracene derivatives in the ultra-violet, and (III) gives only one oxide.



(*A*.)

R. S. C.

Preparation and photochemical oxidation of 2 : 4-cholestadiene. E. L. Skau and W. Bergmann (J. Amer. Chem. Soc., 1938, **60**, 986—987).—Conversion of cholesterol into 2 : 4-cholestadiene, m.p. 68·5°, $[\alpha]_D^{23}$ +168·5° in Et_2O, is modified to give a 30% yield. Previous material contained cholesterylene. With O_2 in presence of eosin and light the diene gives a stable *peroxide*, $C_{27}H_{44}O_2$, m.p. 118·5—120·5°, $[\alpha]_D^{23}$ +52·8° in $CHCl_3$. R. S. C.

Production of methylcholanthrene from cholic acid. C. Sannié (Bull. Soc. chim., 1938, [v], **5**, 260—261).—The method of Fieser and Newman (A., 1935, 859) is simplified : cholic acid is acetylated, and the crude product oxidised (CrO_3–AcOH) to 12-keto-3 : 7-diacetoxycholanic acid (A., 1933, 158), which by pyrolysis and Se gives methylcholanthrene. E. W. W.

Reduction and hydrogenation of methylcholanthrene. L. F. Fieser and E. B. Hershberg (J. Amer. Chem. Soc., 1938, **60**, 940—946).—The so-called 6 : 7 : 17 : 20 : 22 : 23-hexahydromethylcholanthrene, m.p. 160—160·5°, of Wieland and Dane (A., 1933, 1161) is the 1 : 2 : 3 : 4 : 11 : 14-H_6-derivative (I), for with anhyd. $Na_2Cr_2O_7$–AcOH it gives 6-*methyl*-1′ : 2′ : 3′ : 4′-*tetrahydro*-1 : 2-*benzanthraquinonyl*-5-*acetic acid*, m.p. 283—284° (decomp.), which gives a vat test and is reduced by Zn dust–Cu–aq. NH_3 to 1′ : 2′ : 3′ : 4′-*tetrahydro*-1 : 2-*benzanthracene*-5-*acetic acid*, m.p. 267—269° (decomp.). Attempts to re-form the cholanthrene ring system failed. Hydrogenation of methylcholanthrene (II) [$C_6H_3(NO_2)_3$ additive *compound*, m.p. 203·5—204°] is slow; partial or complete hydrogenation in presence of PtO_2–Pd in EtOAc–AcOH gives a mixture of (I) and the 6 : 7-H_2-compound (III), m.p. 154·5—155° [$C_6H_3(NO_2)_3$ additive *compound*, m.p. 153·4—154·5°], which indicates a dual mode of reaction. Structures assigned are confirmed by absorption spectra, which are detailed on a new system for (I), (II), (III), cholanthrene, 11 : 14-dihydromethylcholanthrene, new m.p. 138—139°, 10-methyl-1′ : 2′ : 3′ : 4′- and -5 : 6 : 7 : 8-tetrahydro-1 : 2-benzanthracene, $C_{10}H_8$, phenanthrene, anthracene, and 2-$C_{10}H_7Ph$, m.p. 102·2—102·7°. R. S. C.

Polycyclic aromatic hydrocarbons. XVII. Completion of the synthesis of the twelve monomethyl-1 : 2-benzanthracenes [and synthesis of 4-*iso*propylchrysene]. J. W. Cook and A. M. G** (A., II.)

Robinson (J.C.S., 1938, 505—513).—Anthracene, $(CH_2{\cdot}CO)_2O$, and $AlCl_3$ in $PhNO_2$ yield a mixture of isomerides containing β-2-*anthroylpropionic acid*, m.p. 220—221° (*Me* ester, m.p. 144·5—145·5°), which is oxidised ($Na_2Cr_2O_7$, then $KMnO_4$) to anthraquinone-2-carboxylic acid, and is reduced (Clemmensen) to γ-2-*anthrylbutyric acid*, m.p. 194—195°, cyclised by $SnCl_4$ or $AlCl_3$ to 1′-*keto*-1′ : 2′ : 3′ : 4′-*tetrahydro*-1 : 2-*benzanthracene*, m.p. 114—114·5°. MgMeI converts this into a carbinol which when boiled with picric acid in EtOH gives the *picrate*, m.p. 120—121°, of 1′-*methyl*-3′ : 4′-*dihydro*-1 : 2-*benzanthracene*, m.p. 74—75°. Dehydrogenation (Pt-black) of this yields 1′-*methyl*-1 : 2-*benzanthracene*, m.p. 137·5—138·5° (*dipicrate*, m.p. 119°; *quinone*, m.p. 188·5—189·5°). $(CH_2)_2O$ and 1 : 4 : 6-OMe·C_6H_3Me·MgBr in Et_2O yield β-4-*methoxy*-m-*tolylethyl alcohol*, m.p. 45—46°; the Grignard compound of the corresponding *chloride*, b.p. 126—127°, reacts with *trans*-β-decahydronaphthalone in Et_2O and PhOMe, giving a carbinol, the 3 : 5-*dinitrobenzoate*, m.p. 117—117·5°, of which when dehydrated ($KHSO_4$) affords 2-β-(4′-*methoxy*-m-*tolyl*)*ethyl*-$\Delta^{2:3}$-*octahydronaphthalene*, b.p. 178—180°/0·5 mm., cyclised by $AlCl_3$ in CS_2 to 4′-*methoxy*-1′-*methyldodecahydro*-1 : 2-*benzanthracene*, m.p. 80·5—81°. The OMe could not be removed. 8-*Methyl*-1 : 2-*benzanthracene* (II) : 3-acetylphenanthrene condenses (Na) with Et succinate giving *methyl*-3-*phenanthryl-itaconic acid*, m.p. 192—193° (*anhydride*, m.p. 203°), reduced by Na–Hg to α-(α′-3-*phenanthrylethyl*)-*succinic acid*, m.p. 183° (*anhydride*, m.p. 145°), cyclised by $AlCl_3$ in $PhNO_2$ to a mixture of 5-*keto*-8-*methyl*-5 : 6 : 7 : 8-*tetrahydro*-1 : 2-*benz*-7-*anthroic acid*, m.p. 214—215° [*semicarbazone*, m.p. 275° (decomp.)], and -*benz*-7-*phenanthroic acid*, m.p. 177—178° (ratio 10 : 1). Reduction (Clemmensen) of the former acid yields 8-*methyl*-5 : 6 : 7 : 8-*tetrahydro*-1 : 2-*benz*-7-*anthroic acid*, m.p. 215—217°, which with Pt-black at 300° gives (II), m.p. 107° [*picrate*, m.p. 161—162°; s-$C_6H_3(NO_2)_3$ *complex*, m.p. 164—165°; *quinone*, m.p. 191—192°]. 1-$C_{10}H_7$Me, α-$C_{10}H_7{\cdot}$COCl, and $AlCl_3$ in CS_2 yield 4-*methyl*-1 : 1′-*dinaphthyl ketone*, m.p. 100—101·5° (*picrate*, m.p. 86—87·5°); both this and the 2-Me ketone, when heated with $AlCl_3$ and NaCl, give 3-*methyl*-1 : 2 : 5 : 10-*dibenz*-9-*anthrone*, m.p. 221°. Oxidation of this (CrO_3) gives 3-*methyl*-1 : 2-*benzanthraquinone*-5-*carboxylic acid*, m.p. 305—306°, reduced ($SnCl_2$ in HCl followed by Zn + NaOH) to 3-*methyl*-1 : 2-*benz*-5-*anthroic acid*, m.p. 320—322° (decomp.) (*Me* ester, m.p. 170—171°), which with Cu-bronze in quinoline affords 3-methyl-1 : 2-benzanthracene (*picrate*, m.p. 153°).

1-$C_{10}H_7{\cdot}[CH_2]_2{\cdot}$MgCl and tetrahydrocarvone in Et_2O yield a carbinol which when dehydrated ($KHSO_4$) gives 2-*methyl*-1-(β-1′-*naphthylethyl*)-5-iso*propyl*-Δ^1-cyclo*hexene*, b.p. 160—165°/0·15 mm., cyclised by $AlCl_3$ in CS_2 to *methyl*iso*propyloctahydrochrysene*, m.p. 108°. This is converted by Se at 320° into 4-iso*propylchrysene*, m.p. 227° (2 : 7-*dinitroanthraquinone complex*, m.p. 241—242°). *Et* α-*methyl*-δ-iso*propylpimelate*, b.p. 110°/0·5 mm. (from tetrahydrocarvone; cf. Simonsen *et al.*, A., 1935, 755), with Na in PhMe yields *Et* 6-*methyl*-3-iso*propyl*cyclo*hexanone*-2-*carboxylate*, b.p. 100°/0·2 mm., the K compound of which does not condense with 1-$C_{10}H_7{\cdot}[CH_2]_2{\cdot}$Cl. A. Li.

Synthesis of perylene from anthracene. I. J. Postovski and N. P. Bednjagina (J. Gen. Chem. Russ., 1937, 7, 2919—2925).—Anthracene, aq. CH_2O, and HCl afford 9 : 10-*di*(*chloromethyl*)*anthracene*, m.p. 263—264° (decomp.), which with $CHNa(CO_2Et)_2$ in boiling xylene yields 9 : 10-*di*-(ββ-*dicarbethoxyethyl*)*anthracene*, m.p. 171°, hydrolysed by NaOH in EtOH to the corresponding *acid*, m.p. 244—246° (*compound* with maleic anhydride, m.p. 280°). This, when heated at 250—265°/10 mm., affords 9 : 10-*di*-(β-*carboxyethyl*)*anthracene*, m.p. 244° (*compound* with maleic anhydride, m.p. 306°), which with $SOCl_2$ gives the corresponding acid *chloride*, m.p. 168—170°. This is heated at 50—60° with $AlCl_3$ in $C_2H_2Cl_4$, to yield 3 : 9-*diketo*-1 : 2 : 7 : 8-*tetrahydroperylene*, m.p. 338—340° (decomp.), from which 3 : 9-*diacetoxy*-1 : 7-*dihydroperylene*, m.p. 280°, is obtained with Ac_2O in C_5H_5N (12 hr. at room temp.), and perylene by distillation from Zn dust. R. T.

Symmetrical derivatives of chrysene. I. G. R. Ramage (J.C.S., 1938, 397—400; cf. A., 1933, 828).—*p*-$C_6H_4Me{\cdot}CH{:}CH{\cdot}CO_2Me$, prepared from *p*-$C_6H_4Me{\cdot}CHO$, MeOAc, and Na, is reduced by Al–Hg in Et_2O to *p*-$C_6H_4Me{\cdot}[CH_2]_2{\cdot}CO_2Me$ and *Me* β*γ*-*di*-p-*tolyladipate*-a, m.p. 150° [corresponding *acid*-a (I), m.p. 320°], and crude isomeride-*b* (II), probably the *meso*- and *r*-forms, respectively, separable by means of Et_2O. Ring-closure of (I) is effected by hot H_2SO_4 (85%, 3 hr.) or by successive treatment with $SOCl_2$ and then $AlCl_3$–$C_2H_2Cl_4$ (60°, 12 hr.), giving 2 : 11-*diketo*-5 : 14-*dimethyl*-1 : 2 : 9 : 10 : 11 : 18-*hexahydrochrysene*-a, m.p. 312° (decomp.), reduced (Clemmensen) to 5 : 14-*dimethyl*-1 : 2 : 9 : 10 : 11 : 18-*hexahydrochrysene*-a (III), m.p. 140°. Similarly, (II) is converted into 2 : 11-*diketo*-5 : 14-*dimethyl*-1 : 2 : 9 : 10 : 11 : 18-*hexahydrochrysene*-b, m.p. 201—202°, reduced to 5 : 14-*dimethyl*-1 : 2 : 9 : 10 : 11 : 18-*hexahydrochrysene*-b, m.p. 108°. Dehydrogenation (Se, 6 hr., 280—320°) of both this and (III) gives 5 : 14-*dimethylchrysene*, m.p. 218° [*s*-$C_6H_3(NO_3)_3$ *compound*, m.p. 195°; *styphnate*, m.p. 204°; *picrate*, m.p. 171—172°]. *cis*-Diketohexahydrochrysene (*loc. cit.*) gives a *dihydrazone*, decomp. about 120°, which when heated with NaOEt–EtOH (15 hr., 180°) gives *cis*-hexahydrochrysene identical with that obtained by Clemmensen reduction. Similarly the *dihydrazone*, m.p. 360°, of *trans*-diketohexahydrochrysene gives *trans*-hexahydrochrysene. Reduction of $CPhMe{:}CH{\cdot}CO_2Me$ with Al gives $CHPhMe{\cdot}CH_2{\cdot}CO_2Me$ and *Me* β*γ*-*diphenyl*-β*γ*-*dimethyladipate*-a, m.p. 134°, together with the crude isomeride-*b* (IV). The former with hot H_2SO_4–H_2O (3 hr.) gives 2 : 11-*diketo*-9 : 18-*dimethyl*-1 : 2 : 9 : 10 : 11 : 18-*hexahydrochrysene*-a, m.p. 256°, the *dihydrazone* of which with NaOH–EtOH (as above) gives 9 : 18-*dimethyl*-1 : 2 : 9 : 10 : 11 : 18-*hexahydrochrysene*-a, m.p. 144°. Similarly (IV) gives 2 : 11-*diketo*-9 : 18-*dimethyl*-1 : 2 : 9 : 10 : 11 : 18-*hexahydrochrysene*-b, m.p. 229°, the *dihydrazone*, m.p. 232—234° (decomp.), of which is converted into 9 : 18-*dimethyl*-1 : 2 : 9 : 10 : 11 : 18-*hexahydrochrysene*-b, dimorphous, m.p. 105—106°, and 101° (after resolidifying clears at 105°). H. G. M.

Synthesis and resolution of α-*o*-chlorobenzylethylamine [β-*o*-chlorophenyl*iso*propylamine]. I. B. Johns and J. M. Burch (J. Amer. Chem. Soc., 1938, **60**, 919—920).—*o*-$C_6H_4Cl{\cdot}CH_2{\cdot}COCl$ and ZnMeI give o-*chlorobenzyl Me ketone*, b.p. 125—130°/15 mm. (*oxime*, m.p. 120°), converted by $HCO{\cdot}NH_2$ and subsequent hydrolysis into β-o-*chlorophenylisopropylamine*, b.p. 75—80°/8 mm. (*hydrochloride*, m.p. 175—176°; *Bz* derivative, m.p. 135—136°), whence by *d*-tartaric acid is obtained the d-*base*, b.p. 75—77°/6 mm., $[\alpha]_D^{25}$ +13·8°, +11·4° in MeOH, +12·7° in hexane (d-*tartrate*, m.p. 175°, $[\alpha]_D^{24}$ +21·1° in H_2O; *hydrochloride*, m.p. 175—176°, $[\alpha]_D^{25}$ +9° in H_2O, +4·1° in MeOH; *Bz* derivative, m.p. 166°, $[\alpha]_D^{28}$ +97·6° in EtOH), which has the same configuration as *d*-$CH_2Ph{\cdot}CHMe{\cdot}NH_2$, since it is converted thereinto by H_2–Pd in AcOH–EtOH. R. S. C.

Reduction of 2 : 4 : 6-trinitro-*m*-xylene. S. S. Voris and P. E. Spoerri (J. Amer. Chem. Soc., 1938, **60**, 935—936).—Published statements about reduction of 1 : 3 : 2 : 4 : 6-$C_6HMe_2(NO_2)_3$ are confirmed. In addition, an excess of NH_4HS, best in dioxan, gives 71% of 2 : 4 : 1 : 3 : 6-$(NO_2)_2C_6HMe_2{\cdot}NH_2$ (I), m.p. 191° (*hydrochloride*; Ac derivative, m.p. 175°); $TiCl_3$ (equiv. to 1 NO_2) gives 3% of (I) and 51% of 2 : 1 : 3 : 4 : 6-$NO_2{\cdot}C_6HMe_2(NH_2)_2$, m.p. 213° (*dihydrochloride*); H_2–Raney Ni, promoted by $PtCl_4$, in dioxan gives 99% of the triamine (*dihydrochloride*), reduction of the last NO_2 being relatively slow. R. S. C.

Water-soluble derivatives of *p*-aminobenzenesulphonamide [sulphanilamide]. I. H. G. Kolloff (J. Amer. Chem. Soc., 1938, **60**, 950—951).—*p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ and the appropriate amine in alkaline solution give p-*acetamidobenzenesulphon*-4′-, m.p. 253—254°, -3′-, m.p. 274—275°, and -2′-*carboxyanilide*, m.p. 240°, -*di*-β-*hydroxyethylamide*, m.p. 161—162°, and -*anilide*-4′-*sulphonamide*, m.p. 279—280°, p-*acetamidobenzenesulphonylglycine*, m.p. 237·5—238·5°, *Na* p-*acetamidobenzenesulphonanilide*-4′-*sulphonate*, hydrolysed by 4·9N-HCl to the corresponding Ac-free *compounds*, m.p. 202°, 196—197°, 315° (decomp.), 110—111°, — (*hydrochloride*, m.p. 224—225°), 150—151°, and —, respectively. *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ and $NO_2{\cdot}NH{\cdot}CO{\cdot}NH_2$ in warm EtOH give p-*carbamidobenzenesulphonamide*, m.p. 208—209°. R. S. C.

Sulphanilamides.—See B., 1938, 589.

Action of acid chlorides on anilides. C. A. Friedmann and O. G. Backeberg (J.C.S., 1938, 469—470).—$HCO{\cdot}NHPh$ and AcCl at 100° yield diphenylformamidine (I) and a little NHAcPh, whilst with EtCOCl and BzCl, less of (I) and more of the anilide are formed. NHAcPh and AcCl yield a little diphenylacetamidine, which is also formed using $(\cdot CH_2{\cdot}COCl)_2$ (II), EtCOCl, or BzCl, the last two also yielding some propionanilide (III) and NHBzPh, respectively. With AcCl, EtCOCl, or BzCl, (III) yields only traces of basic substance. NHBzPh with AcCl yields small amounts of diphenylbenzamidine (IV), NBzAcPh, and BzCl, whilst EtCOCl affords (III) and BzCl, and (II) yields BzCl and (IV). J. D. R.

Symmetrical acylarylcarbamides. E. N. Abrahart (J.C.S., 1938, 424—426).—$NHBz{\cdot}CO{\cdot}NH_2$

(I) and *o*-$C_6H_4Cl{\cdot}NH_2$ at 175°/2 hr. yield N-*benzoyl*-N′-*o*-*chlorophenylcarbamide*, m.p. 212°; from (I) and the appropriate amine are similarly formed *N*-benzoyl-*N*′-phenyl- [which with NH_2Ph at 220° yields NH_2Bz and $CO(NHPh)_2$], -*o*-tolyl-, and -*p*-chlorophenyl-carbamide. NHPhEt does not react with (I). *p*-$NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2$ with the appropriate NH_2Ar at 165° yields N-p-*nitrobenzoyl*-N′-*phenyl*-, m.p. 232°, -*o*-*tolyl*-, m.p. 219°, and -*p*-*tolyl*-*carbamide*, m.p. 244°, also prepared from $NH_2{\cdot}CO{\cdot}NHAr$ and *p*-$NO_2{\cdot}C_6H_4{\cdot}COCl$ in C_5H_5N. 3 : 2-$OH{\cdot}C_{10}H_6{\cdot}COCl$ (II) with $NHPh{\cdot}CO{\cdot}NH_2$ in C_6H_6 yields N-3-*hydroxy*-2-*naphthoyl*-N′-*phenylcarbamide* (III), m.p. 303—305° (decomp.; shrinks 275—280°), and a resin (which with KOH yields 3 : 2-$OH{\cdot}C_{10}H_6{\cdot}CO_2H$ and with NH_2Ph, 3 : 2-$OH{\cdot}C_{10}H_6{\cdot}CO{\cdot}NHPh$). By the same method are prepared N-3-*hydroxy*-2-*naphthoyl*-N′-*o*-*tolyl*-, darkens and sinters at 310°, -*p*-*tolyl*-, m.p. ~307° (decomp.; blackens and shrinks 290°), -*o*-*anisyl*-, darkens and sinters 270°, -*p*-*anisyl*-, m.p. 240° (sudden heating; chars on slow heating), and -*p*-*chlorophenyl*-*carbamide*, m.p. 240° (decomp.). With $CO(NH_2)_2$, (II) in C_6H_6 gives 3-*hydroxy*-2-*naphthoylcarbamide*, chars 270—275°, which with NH_2Ph (1 mol.) at 170—180°/3 hr. yields 2 : 4-diketo-3 : 4-dihydro-ββ-1 : 3-naphthoxazine, but with NH_2Ph in excess (1 hr.) yields (III).

J. D. R.

Congo-red [laboratory] synthesis. E. R. Kline (J. Chem. Educ., 1938, **15**, 129—131).—Details are given, using C_6H_6 and $C_{10}H_8$ as starting materials. L. S. T.

Hydrazones from thiocyanophenylhydrazine. Z. Horii (J. Pharm. Soc. Japan, 1936, **56**, 53—57; cf. A., 1937, II, 411).—p-*Thiocyanophenylhydrazones* of the following were prepared: $COMe_2$, m.p. 128·5—129°; $COEt_2$, m.p. 72—73°; COMeEt, m.p. 105—106°; COMePr, m.p. 94—95°; $COMePr^{\beta}$, m.p. 97°; COMeBu, m.p. 88—89°; $COMeBu^{\beta}$, m.p. 89—90°; $COMeBu^{\gamma}$, m.p. 88°; $COMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2$, m.p. 63·5—64·5°; Me amyl ketone, m.p. 83—84°; Me *iso*-amyl ketone, m.p. 64—65°; COPhMe, m.p. 109—110°; $C_6H_4X{\cdot}COMe$, X = *p*-Cl, m.p. 143—143·5°, *p*-Br, m.p. 157°, *p*-I, m.p. 169—170°, *p*-Me, m.p. 145°, *p*-OMe, m.p. 146—147°, *o*-OH, m.p. 157·5—158·5°, *o*-OMe, m.p. 111—112°, *p*-NH_2, m.p. 156—156·5°; acetopyrocatechol, m.p. 134—134·5°; resacetophenone, m.p. 193°; resacetophenone Me_2 ether, m.p. 117—118·5°; gallacetophenone, m.p. 192—192·5°; gallacetophenone Me_3 ether, m.p. 113·5—114·5°; 1 : 2-$OH{\cdot}C_{10}H_6{\cdot}COMe$, m.p. 211—212°; $COMe{\cdot}CH{:}CHPh$, m.p. 155—156°; furfurylideneacetone, m.p. 143—143·5°; anisylideneacetone, m.p. 160—162°; *p*-$C_6H_4Me{\cdot}CH{:}CH{\cdot}COMe$, m.p. 190—192°; *o*-, m.p. 160°, *m*-, m.p. 125—125·5°, and *p*-$C_6H_4Cl{\cdot}CHO$, m.p. 149—150°; *m*-$C_6H_4Br{\cdot}CHO$, m.p. 127°; 4 : 3 : 1-$OH{\cdot}C_6H_3Br{\cdot}CHO$, m.p. 127—129°; 3 : 4 : 1-$NO_2{\cdot}C_6H_3(OH){\cdot}CHO$, m.p. 186—187°; 5 : 2 : 1-$NO_2{\cdot}C_6H_3Cl{\cdot}CHO$, m.p. 213—214°; vanillin acetate, m.p. 123—124°; carbomethoxy-, m.p. 121—121·5°, and carbethoxy-vanillin, m.p. 106·5—107·5°; furfuraldehyde, m.p. 124°; methylfurfuraldehyde, m.p. 132°; $AcCO_2H$, m.p. 191—191·5°; lævulic acid, m.p. 156·5°. Ch. Abs. (*c*)

Configuration of isomeric diazocyanides and measurements of their rates of interconversion. R. J. W. Le Fèvre and H. Vine (J.C.S., 1938, 431—438; cf. A., 1937, II, 376).—Measurement of the dipole moments of the isomeric pairs of 4-chloro- (I), 4-bromo- (II), 4-nitro- (III), 2-bromo- (IV), and 2 : 4 : 6-tribromo-benzenediazocyanide (V) (improved preps.) shows that the *cis*-isomerides are the less stable and are those primarily formed, and thus confirms the configurations allotted to the compounds by Hantzsch. The spontaneous isomerisation in C_6H_6, followed by measurements of dielectric constant, shows that the change *cis* to *trans* is a unimol. reaction, and the relative rates of isomerisation are (I) and (II) > (III) and (IV) > (V). J. D. R.

Structure of diazoamino-derivatives. (Mlle.) A. Wohl (Bull. Soc. chim., 1938, [v], **5**, 460—468).—The absorption spectra of NPh:N·NMeR and NR:N·NPhMe (R = *p*-$C_6H_4{\cdot}OMe$ or $C_{10}H_7$) differ slightly. Spectra cannot decide between alternative formulæ for diazoamino-compounds in which the Me above is replaced by H. β-*Naphthyldiazoaminobenzene*, m.p. 150°, and N-*methyl*-p-*anisyldiazoaminobenzenes*, $OMe{\cdot}C_6H_4{\cdot}N{:}N{\cdot}NPhMe$, m.p. 57°, and $NPh{:}N{\cdot}NMe{\cdot}C_6H_4{\cdot}OMe$, m.p. 47°, are prepared. β-$C_{10}H_7{\cdot}N{:}N{\cdot}NHPh$, MeI, and KOH–EtOH give the *triazine*, $NPh{:}N{\cdot}NMe{\cdot}C_{10}H_7$, m.p. 71—72°; the isomeric *triazine*, $C_{10}H_7{\cdot}N{:}N{\cdot}NPhMe$, m.p. 97—98°, is obtained from β-$C_{10}H_7{\cdot}N_2Cl$ and NHPhMe.

R. S. C.

Exchange of hydrogen atoms between nitrophenols and water.—See A., 1938, I, 315.

Manufacture of *o*-aminophenols.—See B., 1938, 487.

Derivatives of picramic acid. Their rearrangements. I. A. Pearl and W. M. Dehn (J. Amer. Chem. Soc., 1938, **60**, 925—927).—With Ac_2O and a drop of H_2SO_4 at 100° picramic acid (I) gives the *N*-Ac derivative (II), new m.p. 204—205° (obtained quantitatively by AcCl in hot C_6H_6 or from the NH_4 salt and warm Ac_2O), and 4 : 6-*dinitro*-1-*methylbenzoxazole* (III), m.p. 193°, considered by Schiff (A., 1886, 612) to be (IV) (below) and converted into (II) by HNO_3, H_2SO_4, or hot dil. alkali. If heated in Ac_2O containing a drop of H_2SO_4 and then kept therein at room temp. overnight, (I) gives (II) and the O-*acetate* (IV), m.p. 160—161°, hydrolysed by hot 5% NaOH, but rearranged into (II) by hot 0·2N-NaOH and converted [as is (II)] into (III) by hot Ac_2O. With BzCl or Bz_2O in hot C_6H_6 (I) gives the *N*-Bz derivative, m.p. 226—227°, converted by Ac_2O and a drop of H_2SO_4 at 100° into a mixture of 4 : 6-*dinitro*-2-*benzamidophenyl acetate*, m.p. 170—171° [converted into (II) by dil. alkali], and 4 : 6-dinitro-1-phenylbenzoxazole, m.p. 220—221°. With hot $ClCO_2Et$ (I) gives a 90—95% yield of the phenylurethane, m.p. 152—153°. The N-*chloroacetyl*, m.p. 150°, N-*dichloroacetyl*, m.p. 118—119°, and N-*PhSO*$_2$, m.p. 202—203° (*acetate*, m.p. 178—179°), derivatives of (I), 3 : 5-*dinitro*-2-*hydroxy*-s-*diphenylthiocarbamide*, m.p. 247—248°, and 4 : 6-*dinitro*-2-*acetamidophenyl benzoate*, m.p. 119·5—120·5°, are also prepared.

R. S. C.

Derivatives of higher ethers of pyrocatechol. G. K. Hughes and F. Lions (J. Proc. Roy. Soc. New South Wales, 1938, **71**, 103—111).—Pyrocatechol Bu^{α}_2 ether (I) and HNO_3 (*d* 1·42) in AcOH give the 4-NO_2- (II), m.p. 56°, nitrated further to the 4 : 5-$(NO_2)_2$-, m.p. 124°, -derivative (whence the 4-*nitro*-5-*piperidino*-compound, m.p. 51°), which with Zn in EtOH–HCl followed by phenanthraquinone (in aq. $NaHSO_3$–NaOAc) yields 2 : 3-*di*-n-*butoxyphenanthraphenazine*, m.p. 190°. (II) and aq. EtOH–Na_2S give 4-*aminopyrocatechol* Bu^{α}_2 *ether* (III), b.p. 157—158°/1·5 mm. [*hydrochloride*, m.p. 173°; *picrate*, m.p. 159°; 5-NO_2-derivative, m.p. 108°; *Ac* derivative, m.p. 97° (5-NO_2-, m.p. 85°, and 5-*Br*-, m.p. 87°, -derivatives)].

(I) and Br–AcOH afford 4-*bromopyrocatechol* Bu^{α}_2 *ether*, b.p. 195—197°/22 mm. [HNO_3 (*d* 1·42) in AcOH yields its 5-NO_2-derivative, m.p. 62°], and the 4 : 5-Br_2-, b.p. 206—208°/23 mm., derivative. (I) (in 70% H_2SO_4) with aq. CH_2O gives 2 : 3 : 6 : 7-*tetra*-n-*butoxy*-9 : 10-*dihydroanthracene*, m.p. 91°, partly debutylated with boiling 40% HNO_3. *o*-$C_6H_4(OH)_2$ and *n*-$C_5H_{11}Cl$ in aq. EtOH–KOH give the di-*n*-amyl ether (IV), b.p. 174—176°/21 mm. [4-NO_2-, m.p. 49°, and 4 : 5-$(NO_2)_2$-, m.p. 117°, -derivatives]. β-(3 : 4-*Di*-n-*butoxyanilino*)*propenyl Me ketone*, b.p. 206—207°/1·5 mm. [from (III) and CH_2Ac_2], and conc. H_2SO_4 at <10°, yield 6 : 7-*di*-n-*butoxy*-2 : 4-*dimethylquinoline*, m.p. 49°, and some 6(or 7)-*hydroxy*-7(or 6)-*butoxy*-derivative, m.p. 180°. (I) and (IV) are dealkylated by $ClSO_3H$ and conc. H_2SO_4. A. T. P.

Ethers of dihydric phenols.—See B., 1938, 486.

Nitro- and amino-derivatives of acylamidoquinol diaryl ethers and azo-dyes derived therefrom.—See B., 1938, 486.

New bismuth iodide derivative of "Aristol." W. Popławski (Arch. Chem. Farm., 1937, **3**, 234—237).—Aristol [3 : 3′-di-iodo-4 : 4′-dihydroxy-2 : 2′-dimethyl-5 : 5′-dipropyldiphenyl (= RH_2)] and BiOI or BiI_3 yield the *salt* $[R_2BiI]_2$, insol. in H_2O and org. solvents. R. T.

Molecular structure in relation to œstrogenic activity. Compounds without a phenanthrene nucleus. E. C. Dodds and W. Lawson (Proc. Roy. Soc., 1938, **125**, B, 222—232).—Investigation of numerous compounds [*e.g.*, 7 : 8-dihydroxyacenaphthenes; CAr_3·OH; OH-derivatives of CH_2Ph_2, $COPh_2$, $CHPh_3$, Ph_2, $(\cdot CH_2Ph)_2$, $CH_2(CH_2Ph)_2$, Ph_2O, and $NHPh_2$; C_6H_4R·OH; hydrocarbons] shows that œstrogenic activity is not dependent on the phenanthrene ring. 4 : 4′-Dihydroxydiphenyl-alkanes and -alkylenes generally show activity; this varies with the length of, and the position of substituents attached to, the C chain, and also with the position of double linkings. Substituents in the aromatic nucleus other than OH generally lessen activity. *p*-$C_6H_4Pr^{\alpha}$·OH is the only *p*-*n*-alkylphenol of the 9 tested to show activity; *p*-OH·C_6H_4·CH:CHMe (anol) is also active and can polymerise to highly active substances, but *p*-OH·C_6H_4·CH_2·CH:CH_2 is inactive. The following show varying degrees of activity (marked when designated *): 7 : 8-*dihydroxy*-7 : 8-*di*-α-*naphthylacenaphthene* * (I), m.p. 142° (from α-$C_{10}H_7$·MgBr and acenaphthenequinone); 7 : 7-*di*-α-*naphthylacenaphthenone*, m.p. 289° [from (I) and conc. HCl in boiling AcOH]; diphenyl-α-naphthylcarbinol (β-isomeride inactive); α-naphthyl-benzoin and -hydrobenzoin; 3 : 3′- and 4 : 4′-dihydroxydiphenylmethane; ββ-di-*p*-hydroxyphenyl-propane, -butane, and -pentane; γγ-di-*p*-hydroxyphenylpentane; αα-di-*p*-hydroxyphenylheptane; α-phenyl-αα-di-*p*-hydroxyphenylethane; ββ-di-(4-hydroxy-3-methylphenyl)-propane and -butane; 4 : 4′-dihydroxytriphenylmethane; 1 : 1-di-*p*-hydroxyphenyl- and -di-(4-hydroxy-3-methylphenyl)-*cyclo*hexane; 4 : 4′-di-, 2 : 3 : 4 : 4′-tetra-, and 2 : 3 : 4 : 3′ : 4′ : 5′-hexa-hydroxybenzophenone; *p*-OH·C_6H_4·$CHPh_2$; 2 : 4-dihydroxytriphenylacetic acid lactone; di-α-naphthyl-*p*-hydroxyphenylmethane *; 4 : 4′-dihydroxydiphenyl (its 3 : 3′-Me_2 derivative shows very slight activity); (*p*-OH·C_6H_4·CH_2·)$_2$; phloridzin; phloretin; αγ-di-*p*-hydroxyphenylpropane; 2 : 4 : 6 : 4′-*tetrahydroxy*-αγ-*diphenylpropane* (+H_2O), m.p. 158—159° (obtained by Clemmensen reduction of phloretin); αε-di-*p*-hydroxyphenylpentane; *p*-OH·C_6H_4·OPh; (*p*-OH·C_6H_4)$_2O$; *p*-*tert*.-amyl- and *p*-*cyclo*hexyl-phenol; *p*-OH·C_6H_4·CH_2·CH_2·OH; stilbene *, which is less active than CHPh:CPh_2* (CPh_2:CPh_2 is inactive); *p*-hydroxy*- and 4 : 4′-dihydroxy-stilbene *; 4 : 4′-dihydroxytolane * (tolane is inactive); αδ-diphenylbutadiene *.

1 : 8-*Di*-α-*naphthoylnaphthalene*, m.p. 227—228°, is obtained by oxidation (CrO_3, AcOH) of (I). *p*-*cyclo*-Pentylphenol is conveniently prepared from PhOH, *cyclo*pentyl bromide, and $ZnCl_2$ (method: Bartlett and Garland, A., 1927, 968). H. B.

Polyhydroxytriphenylmethanes.—See B., 1938, 487.

Phenyl trifluoromethyl sulphides and sulphones.—See B., 1938, 486.

Esters of thio-acids. II. Derivatives of esters of thio-acids of arsenic and antimony and attempted preparation of the "ortho" thio-esters of these elements. R. Klement and A. May (Ber., 1938, **71**, [*B*], 890—894; cf. A., 1935, 1390).—$AsCl_3$ and *p*-NHAc·C_6H_4·SH in C_6H_6 afford *tri*-p-*acetamidophenyl thioarsenite* (I), m.p. 108—111°; *tri*-p-*acetamidophenyl thioantimonite* (II), m.p. 165—168° (decomp.), and *tri*-o-*carboxyphenyl thioarsenite* (III), m.p. 208—210°, are obtained similarly. (I) and (III) are highly toxic. (II) resembles tartar emetic but is less poisonous. Attempts to obtain compounds of As^V or Sb^V by the action of halogen on (*p*-C_6H_4Me·S)$_3$As(Sb) gave (*p*-C_6H_4Me·S)$_2$ and $AsCl_3$ or $SbCl_3$. $SbCl_5$ and *p*-C_6H_4Me·SNa (5 mols.) yield (*p*-C_6H_4Me·S)$_2$ and Sb(S·C_6H_4Me-*p*)$_3$. The prep. of "ortho-" thio-acids of P, As, or Sb appears impossible. $SbCl_3$ and *o*-SH·C_6H_4·CO_2H in anhyd. C_6H_6 yield the *compounds*, $SbCl(S{\cdot}C_6H_4{\cdot}CO_2H)_2$, m.p. 84—86°, and $SbCl_2(S{\cdot}C_6H_4{\cdot}CO_2H)$, m.p. 117—120°. H. W.

Sulphonation by sulphites. II. Simultaneous oxidation of β-naphthol and sodium sulphite. S. V. Bogdanov and V. A. Ivanova (J. Gen. Chem. Russ., 1937, **7**, 2884—2894).—The yield of 2 : 1-OH·$C_{10}H_6$·SO_3H obtained from β-$C_{10}H_7$·OH (I), aq. Na_2SO_3, and CuO is not significantly affected by raising the temp. from 100° to 150°, or by varying the

relative concns. of the substrates, but rises abruptly as the ratio $C_{10}H_7$·ONa : (I) exceeds 3 : 1, and attains 92% when the alkalinity corresponds with 100% Na salt; the yield of by-products [chiefly dinaphthol (II)] falls correspondingly. With MnO_2 in place of CuO the abs. yield is smaller, but increases more rapidly with rising alkalinity; only small amounts of (II) are formed. The reaction ceases before completion in both cases, this being more marked for MnO_2 than for CuO. (I) and CuO alone yield (II), the yield of which falls with rising alkalinity. Aq. Na_2SO_3 and CuO or MnO_2 at 130° yield chiefly Na_2SO_4. Oxidation of Na_2SO_3 by atm. O_2 is greatly retarded in presence of (I). R. T.

Molecular rearrangement of (−)-phenylmethylcarbinyl *dl-p*-toluenesulphinate. C. L. Arcus, M. P. Balfe, and J. Kenyon (J.C.S., 1938, 485—493; cf. A., 1930, 1177).—The mol. rearrangement of (−)- and *dl*-phenylmethylcarbinyl *dl-p*-toluenesulphinate (I) to *dl-p*-tolyl-α-phenylethylsulphone (II) is studied. In the homogeneous state, (II) and a little styrene are formed from (I); in Et_2O–HCl (saturated), a little di-*p*-tolyl disulphoxide (III) and CHPhMeCl are produced, but in Et_2O with 0·7% HCl, 0·1% NH_3, or K_2CO_3, (I) is unchanged. In C_6H_6 at room temp. (II) is formed in 21 days, but at 80° a little (III) is produced. No rearrangement takes place in $COMe_2$ at 56° or in C_5H_5N or MeCN at room temp., but in MeCN at 80°, (III) is formed whilst in $PhNO_2$, (II) is produced. In HCO_2H, (II) is formed together with dl-*phenylmethylcarbinyl formate*, b.p. 88—88·5°/16 mm., and (in presence of HCO_2Na) *p*-C_6H_4Me·SO_2H. In HCO_2H with *p*-C_6H_4Me·SO_2Na, both (II) and (III) are formed. (−)-Phenylmethylcarbinyl *dl-p*-toluenesulphinate, in the homogeneous state and in HCO_2H, yields (II); in HCO_2H with HCO_2Na, (−)+*dl*-phenylmethylcarbinyl formate and (−)+*dl-p*-tolyl-α-phenylethylsulphone (IV), $[\alpha]_{5461}^{18}$ −65·6° in $CHCl_3$, are formed, whilst with HCO_2H–*p*-C_6H_4Me·SO_2Na, (II) and (IV), α_{5461}^{21} −0·47° (*l*, 0·236), are produced. The mechanism of the rearrangement is suggested (cf. *loc. cit.*) as: (*a*) (major reaction; ionic, with racemisation) the sulphinate is solvated to " active sulphinate ", which undergoes reversible ionisation and irreversible racemisation to solvated ions, which recombine irreversibly to yield sulphone, and (*b*) (minor reaction; intramol. with retention of configuration) direct rearrangement to sulphone. This is supported by the observed rapid mutarotation of the (−)-ester in HCO_2H (which can only be ascribed to solvation), and the retention of activity in MeCN, which are parallel with the rapid transformation into sulphone in HCO_2H and the stability in MeCN. J. D. R.

Catalytic properties of rhenium. VII. Dehydrogenation of *cyclo*hexanol over rhenium. E. V. Tur, S. B. Anisimov, and M. S. Platonov (J. Gen. Chem. Russ., 1937, 7, 2895—2898).—*cyclo*-Hexanol yields chiefly *cyclo*hexanone, with traces of PhOH, C_6H_6, and *cyclo*hexene, when passed over disperse Re at 350—400°. The chief product in presence of ReS_2 is PhOH. R. T.

Hydroxymethyl peroxides. I. Tetrahydronaphthyl hydroxymethyl peroxide. K. I. Ivanov, V. K. Savinova, and E. G. Michailova (J. Gen. Chem. Russ., 1938, **8**, 51—55).—1 : 2 : 3 : 4-Tetrahydro-β-naphthyl H peroxide in C_6H_6 and CH_2O (120 hr. at room temp.) yield 1 : 2 : 3 : *4-tetrahydro-β-naphthyl hydroxymethyl peroxide*, m.p. 46·5°, which is decomposed by aq. NaOH, with liberation of H_2. R. T.

Semi-hydrobenzoin change in the dehydration of phenylmethylvinyl glycol and the isomerisation of the corresponding epoxide. Y. Deux (Compt. rend., 1938, **206**, 1017—1019; A., 1937, II, 415).—The chlorohydrin of α-phenyl-β-methyl-$\Delta^{\alpha\gamma}$-butadiene with KOH affords *αβ-oxido-α-phenyl-β-methyl-*Δ^{γ}*-butene* (I), b.p. 80—83°/6 mm., which at 250—280°/6 mm. (on kieselguhr) or with $MgBr_2$–Et_2O gives *α-phenyl-α-methyl-*Δ^{β}*-butenaldehyde* (II), b.p. 105°/16 mm. (*oxime*, m.p. 100—101°), reduced to β-phenyl-β-methylbutyl alcohol (*p-nitrobenzoate*, m.p. 64°), which when dehydrogenated (Cu) gives α-phenyl-α-methylbutaldehyde (cf. A., 1932, 392). (I) with 0·05N-HCl affords α-phenyl-β-methyl-Δ^{γ}-butene-αβ-diol (*di-p-nitrobenzoate*, m.p. 97—98°), which when distilled in a vac. affords (II). J. L. D.

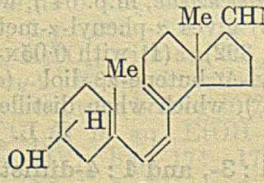
***cis* and *trans*-1 : 2-, 1 : 3-, and 1 : 4-dimethyl-*cyclo*hexanols: dehydration with formic acid.** G. Chiurdoglu (Bull. Soc. chim. Belg., 1938, **47**, 241—259; cf. A., 1936, 201).—1 : 2-Dimethyl- (*cis*-, m.p. 23·2°, b.p. 82·8—82·9°/25 mm.; *trans*-, m.p. 13·2°, b.p. 74°/25 mm.), 1 : 3-dimethyl- (*cis*-, m.p. 27·5°, b.p. 84°/25 mm.; *trans*-, m.p. 14·5°, b.p. 77·5—77·6°/25 mm.), and 1 : 4-dimethyl- (*cis*-, m.p. 24°, b.p. 83·7—83·8°/25 mm.; *trans*-, m.p. 72·5°, b.p. 75·9—76·1°/25 mm.) -*cyclo*hexanol, prepared from MgMeBr and the corresponding 2-methyl-, m.p. −14°, b.p. 165·08°/760 mm. (semicarbazone, decomp. 197°), 3-methyl-, m.p. −73·5°, b.p. 169·58°/760 mm. (semicarbazone, decomp. 191·4°), and 4-methyl-, m.p. −40·6°, b.p. 171·25°/760 mm. (semicarbazone, decomp. 203·5°), -*cyclo*hexanone, are converted (the 1 : 2-derivative most readily) by HCO_2H into 1 : 2-, b.p. 135·5—137·7°/760 mm., 1 : 3-, b.p. 128—128·4°/760 mm., and 1 : 4-, m.p. −59·4°, b.p. 128·7°/760 mm., -dimethyl-Δ^1-*cyclo*hexene, each respective hexene being identical, as shown by physical consts., whether obtained from the *cis*- or the more volatile *trans*-isomeride. The orientation of each pair of stereoisomeric carbinols is determined by the relative speeds of dehydration, being more rapid when H and OH are in the *trans*-position; this is in agreement with von Auwers' rule. Other physical consts., and details of experiments on dehydration velocities, are recorded. A. T. P.

Methylation of triphenylcarbinol. H. H. Hatt (J.C.S., 1938, 483—484).—With MeOH, CPh_3·OH forms an additive *compound*, CPh_3·OH,MeOH, but is not methylated in absence of HCl. In presence of HCl (0·0001—1·0M), the dimorphous CPh_3·OMe, m.p. 82·5—83° (labile) and 96—96·5° (stable), is formed. J. D. R.

Production of an antirachitic provitamin from cholesterol. N. A. Milas and R. Heggie (J. Amer. Chem. Soc., 1938, **60**, 984—985).—Cholesteryl acetate is shown spectroscopically to be converted into 7-dehydrocholesterol in small amounts by methylene-

blue or *p*-benzoquinone (I) + Pd in C_6H_6 in light, by chloranil or (I) + Pd at 120—130°, by succinodehydrogenase, and in better yield (20% in 6 hr.) by (I) at 120—130°. The last-mentioned treatment, followed by irradiation in Et_2O, gives an antirachitically potent material. R. S. C.

Constitution of tachysterol. W. GRUNDMANN (Z. physiol. Chem., 1938, **252**, 151—154).—Ozonisation of tachysterol (I) does not afford CH_2O; (I) does not contain the CH_2 group present in vitamin-D_2 (II). $(:C\cdot CO_2Me)_2$ and (I) readily give a non-cryst. adduct but tachysteryl acetate yields the *compound*, $C_{36}H_{52}O_6$, m.p. 137°, which does not give a cryst. neutral or acid substance when treated with O_3 or $KMnO_4$. Results of previous attempts to determine the constitution of (I), and particularly the observation that the same products are not formed from it and from (II) by



(*A*.)

oxidative degradation, suggest the constitution (*A*) for (I). H. W.

Sugar-cane wax. II. Oxidation of sugar-cane sitosterol. T. MITUI (J. Agric. Chem. Soc. Japan, 1938, **14**, 342—348; cf. A., 1937, III, 368).—Oxidation with CrO_3 gives *trans*-dehydroandrosterone, 3-hydroxy-Δ^5-bisnorcholenic acid, and 3-hydroxy-Δ^5-ætiobilienic acid. As no 3-hydroxy-Δ^5-norcholenic acid is formed, it is concluded the sitosterol contains the side-chain ·CHMe·CH_2·CHMe·CHMePr$^\beta$. J. N. A.

Derivatives of 3-*epi*hydroxy-ætio*allo*cholane and -androstane.—See B., 1938, 589.

Esters of chaulmoogric acid. P. P. HERRERA and L. A. GUEVARA (Univ. Philippines Nat. and Appl. Sci. Bull., 1935, **4**, 332—337; cf. A., 1930, 1579).—The following chaulmoogric esters were prepared by refluxing (3 days) the acid, alcohol, and Et_2O–HCl: iso*amyl*, b.p. 225°/20 mm.; *benzyl*, b.p. 218°/10 mm.; *phenylethylcarbinyl*, b.p. 190°/10 mm.; *phenylbutylcarbinyl*, b.p. 193°/8 mm. CH. ABS. (*c*)

***cyclo*Hexylideneacetic acid.** C. G. LE FÈVRE and R. J. W. LE FÈVRE (J.C.S., 1938, 494—496).—Attempts to resolve *cyclo*hexylideneacetic acid (I) by way of the *brucine*, m.p. 55—57°, $[\alpha]_D^{18}$ ~ −30° in EtOH, *quinine* (+$2H_2O$), m.p. 98—104°, $[\alpha]_{5461}^{18}$ −137° in EtOH, strychnine, m.p. 284—285°, cinchonine, and cinchonidine salts were fruitless. Attempts to resolve (I) and *cyclo*hexanoneoxime with *Aspergillus niger*, *A. versicolor*, and a species of *Penicillium* were unsuccessful. *A. versicolor* attacks the *l*-form of lactic acid (as Na salt in a medium containing $NaNO_3$, KH_2PO_4, KCl, $MgSO_4$, $FeSO_4$, and NH_4OAc) more rapidly than *A. niger* or *Penicillium*, and simultaneous destruction of the two antipodes is not so pronounced as with the other two. J. D. R.

Conversion of phenylglycine into methylaniline.—See B., 1938, 483.

Arylaminopropionic acids.—See B., 1938, 486.

Syntheses starting from hydrogen sulphite derivatives of esters of camphoceanaldehydic acid. J. VÈNE (Compt. rend., 1938, **206**, 844—846).—The H sulphite compounds from Me and Et esters of camphoceanaldehydic acid (cf. A., 1932, 1037) with KCN afford *Me*, m.p. 127°, and *Et* 3-*hydroxycyanomethyl*-2 : 2 : 3-*trimethyl*cyclo*pentane*-1-*carboxylate* (I), m.p. 97°, which with 87% H_2SO_4 give β-carbamyl-β-campholide (II) but with 65—78% acid, β-*cyano*-β-*campholide* (III), m.p. 228°, is formed. (II) with HNO_2 affords β-*carboxy*-β-*campholide*, m.p. 213°, hydrolysed (EtOH–NaOH) to 3-*hydroxycarboxymethyl*-2 : 2 : 3-*trimethyl*cyclo*pentane*-1-*carboxylic acid*, m.p. 198°. (I) with warm conc. KOH or (II) with 20% H_2SO_4 affords *hydroxy*-(3-*carboxy*-1 : 2 : 2-*trimethyl*cyclo*pentyl*)*acetamide* (IV), m.p. 143°, converted by dehydrating agents into (III) which itself is hydrolysed (hot NaOH) to (IV). J. L. D.

Exchange of oxygen between benzil and water. Benzilic acid rearrangement. I. ROBERTS and H. C. UREY (J. Amer. Chem. Soc., 1938, **60**, 880—882).—When Bz_2 (8·75 g.) is heated in MeOH (20 c.c.) and H_2O (1·5 c.c.), containing 0·509% of $H_2{}^{18}O$, slight exchange of O occurs; much exchange occurs if 0·03 c.c. of 50% NaOH is present. This confirms the chemical evidence that rearrangement to OH·CPh_2·CO_2H occurs by rapid, reversible addition of OH′ to give COPh·CPh(OH)·O^-, which slowly rearranges to OH·CPh_2·CO_2^-. R. S. C.

Reaction of alkyl benzoates with sodium alkoxides. A. MAGNANI and S. M. MCELVAIN (J. Amer. Chem. Soc., 1938, **60**, 813—820).—Esters, CH_2R·OBz, and NaO·CH_2R at 175—180° give reversibly PhCHO and R·CHO. Some or all of the following reactions may subsequently occur: (*a*) R·CHO + PhCHO → R·CO_2·CH_2Ph, (*b*) 2PhCHO → CH_2Ph·OBz, (*c*) 2R·CHO → R·CO_2CH_2R, (*d*) PhCHO + CH_2R'·CHO → [OH·CHPh·CHR′·CHO] → CO + OH·CHPh·CH_2R' → CH_2Ph·CO·CH_2R', (*e*) CH_2R'·COPh + ROBz → $CHR'(COPh)_2$, (*f*) CH_2R''·CH_2·OH + CH_2R''·CH_2·ONa → NaOH + CH_2R''·CH_2·CHR″·CH_2·OH. BzOH is obtained by hydrolysis of the ester by H_2O liberated in the secondary reactions. Much ROBz is recovered and some tar is formed. The max. yield (40%) of CH_2Bz_2 is obtained from 4 mols. of EtOBz and 1 of NaOEt, and these proportions were used in all experiments. The following products were isolated in the mol. proportions stated: R = H: BzOH 0·7, MeOH 0·18, CH_2Ph·OBz (I) 0·01, and Me_2O 0·55 (formed by the reaction, MeOBz + NaOMe → NaOBz + Me_2O); R = Me: BzOH 0·55, EtOH 1·8, CH_2Bz_2 0·4, (I) 0·15, CO 0·58, COPhMe a trace; R = Et: BzOH 0·9, Pr$^\alpha$OH 1·57, (I) a trace, CHPhEt·OH 0·2, and its benzoate 0·31, CO 1·07, CHMePr$^\alpha$·CH_2·OH 0·04, and its benzoate 0·24, COPhEt 0·06, and CHPh:CHMe a trace; R = Pr$^\alpha$: BzOH 0·85, Bu$^\alpha$OH 1·27, (I) 0·04, CO 1·03, CHPhPr$^\alpha$·OH 0·34, and its benzoate 0·41, CHEtBu$^\alpha$·CH_2·OH 0·1, and its benzoate 0·25, COPhPr$^\alpha$ 0·07, and CHPh:CHEt a trace; R = Pr$^\beta$: BzOH 1·02, Bu$^\beta$OH 1·42, (I) 0·14, Pr$^\beta CO_2$Bu$^\beta$ 0·31, the benzoate 0·27 and *iso*butyrate 0·02 of CHPhPr$^\beta$·OH 0·19, COPhPr$^\beta$ 0·28, α-phenyl-Δ^α-*iso*butene 0·03 (*dimeride*, m.p. 143—146°), Pr$^\beta$CHO and Pr$^\beta CO_2$H

traces; R = Bu^{γ}: BzOH 0·86, CH_2Bu^{γ}·OH 0·83, (I) 0·14, $Bu^{\gamma}CO_2$·CH_2Ph 0·12, $Bu^{\gamma}CO_2$·CH_2Bu^{γ} 0·8, $Bu^{\gamma}CHO$ 0·12, $Bu^{\gamma}CO_2H$ 0·14, and a *substance*, $C_{18}H_{22}O$, m.p. 103—104°. When CH_2R is Pr^{β}, the products are: BzOH 0·6, $Pr^{\beta}OH$ 1·8, CH_2Bz_2 0·16, COPh·CH_2·COMe 0·08, (I) 0·11, $COMe_2$ trace. The following are incidentally described: β-*methyl*-n-*amyl benzoate*, b.p. 130—132°/9 mm., and α-*naphthylurethane*, m.p. 75—76°; α-*phenylpropyl benzoate*, b.p. 146—147°/3 mm.; β-*ethyl*-n-*hexyl benzoate*, b.p. 119—120°/2 mm., and α-*naphthylurethane*, m.p. 60—61°; p-*phenylphenacyl* α-*methyl*-n-*valerate*, m.p. 64—65°, and α-*ethylhexoate*, m.p. 53—54°; α-*phenyl*-n-*butyl benzoate*, b.p. 145—146°/2 mm., and α-*naphthylurethane*, m.p. 98—99°; α-*phenyl*isobutyl α-*naphthylurethane*, m.p. 116—117°, and *benzoate*, b.p. 148—149°/3 mm. R. S. C.

New anæsthetic. E. Gryszkiewicz-Trochimowski and S. Otolski (Arch. Chem. Farm., 1937, **3**, 215—217).—NEt_2·$[CH_2]_2$·NHEt and OH·CH_2·CH_2Cl yield NN'N'-*triethyl*-N-β-*hydroxyethylethylenediamine* (I), b.p. 120—125°/10 mm., which with *p*-NO_2·C_6H_4·COCl in C_6H_6 gives the p-*nitrobenzoyl ester* of (I) (*hydrochloride*, m.p. 112°), reduced by Sn in HCl to the p-*aminobenzoyl ester* (*mono-*, m.p. 122—124°, and *di-hydrochloride*, m.p. about 200°); the local anæsthetic action of this ester considerably exceeds that of novocaine. R. T.

Homologues of salol. Salicylates of the isomeric amylphenols and amylcresols. H. G. Kolloff and J. O. Page (J. Amer. Chem. Soc., 1938, **60**, 948—949).—*o*-OH·C_6H_4·CO_2H, the appropriate phenol, and $POCl_3$ give 40—50% yields of o-, b.p. 155—157°/0·03 mm., and p-n-*amylphenyl*, b.p. 177—180°/2 mm., 3-, b.p. 141—145°/0·004 mm., and 5-n-*amyl*-o-, b.p. 140—142°/0·06 mm., and 4-n-*amyl*-m-*tolyl*, b.p. 156—160°/0·008 mm., 3-n-, b.p. 150—156°/0·05 mm., and 3-sec.-*amyl*-p-*tolyl*, b.p. 166—168°/0·018 mm., and 4-*chloro*-2-cyclo*hexylphenyl salicylate*, m.p. 99·5—100°, which are hydrolysed at approx. the same rate as salol. 3-sec.-*Amyl*-p-*cresol*, b.p. 127—128°/13 mm. (3 : 5-*dinitrobenzoate*, m.p. 105°), is obtained in 25·2% yield from *n*-C_5H_{11}·OH, *p*-cresol, and $ZnCl_2$. R. S. C.

Trifluoromethylbenzoyl fluorides.—See B., 1938, 488.

Diaroyl peroxides.—See B., 1938, 488.

Benzoyl peroxide and benzylamine. S. Gambarjan, O. Tschaltuikjan, and A. Babajan (Trans. VI Mendeleev Congr. Chem. 1932, 1935, **2**, Pt. I, 1001—1002; cf. de Paolini, A., 1931, 209, 638).—The reaction between Bz_2O_2 (I) and CH_2Ph·NH_2 (II) is: (I) + (II) = BzOH + CH_2Ph·NH·OBz (III); (III) + (II) = CH_2Ph·NHBz + CH_2Ph·NH·OH. Ch. Abs. (*c*)

Iodomethoxyphthalic acid from colchicine. R. Grewe (Ber., 1938, **71**, [*B*], 907—911).—*o*-4-Xylenol Me ether is oxidised ($KMnO_4$, aq. NaOH) to 4-methoxyphthalic acid (yield about 60%), converted into 3-nitro-4-methoxyphthalic anhydride, which is reduced (Pd-sponge in AcOH) to 3-*amino*-4-*methoxyphthalic anhydride*, m.p. 182°; the corresponding *acid*, m.p. 152° (decomp.), gives 3-*iodo*-4-*methoxyphthalic acid*, m.p. 216° (decomp.) (*anhydride*, m.p. 206°). Benzeneazo-*o*-4-xylenol is transformed into its *Me ether*, m.p. 67°, reduced ($Na_2S_2O_4$) to 5-*amino*-4-*methoxy*-o-*xylene*, b.p. 136°/15 mm., m.p. 91°. This yields 5-*iodo*-4-*methoxy*-o-*xylene*, b.p. 147°/15 mm., m.p. 37°, oxidised to 5-*iodo*-4-*methoxyphthalic acid*, m.p. 204° (decomp.) (*anhydride*, m.p. 168°), identical with the acid derived from colchicine (Windaus *et al.*, A., 1915, i, 708). H. W.

***cyclo*Hexane group.** R. Malachowski, J. J. Wasowska, and S. Jóźkiewicz [with J. Adamiczka and G. Zimmerman-Pasternak] (Ber., 1938, **71**, [*B*], 759—767).—No evidence of isomerism such as is required by Sachs' theory is obtained when *cis-* (I) and *trans-* (II) -*cyclo*hexane-1 : 4-dicarboxylic acids are converted into a series of derivatives; the latter can be isolated only in those two steric forms which are required by the plane model. cis-*Hexahydroterephthalyl chloride* (III), b.p. 97—97·5°/0·5 mm., is derived from (I) and $SOCl_2$ at 20° whilst prolonged boiling with $SOCl_2$ is required to convert (II) into trans-*hexahydroterephthalyl chloride* (IV), m.p. 67°. When heated at 190—200°, distilled under 9 mm., and then hydrolysed (III) gives 28% of (I) and 72% of (II) whereas (IV) yields 31% of (I) and 69% of (II). NH_3 transforms (III) into cis-*hexahydroterephthaldiamide*, m.p. 232° (corr.), isomerised when heated at a higher temp. to trans-*hexahydroterephthaldiamide*, m.p. 346° (decomp.), obtained also from (IV) and 25% NH_3. Treatment of the diamides with boiling $SOCl_2$ gives cis-1 : 4-*dicyano*cyclo*hexane* (V), m.p. 65°, hydrolysed by 20% HCl to (I) and by 30% KOH to (II); the trans-*dinitrile*, m.p. 140° (corr.), is hydrolysed by acid or alkali to (II). Hydrogenation (PtO_2 in Ac_2O) of (V) gives the Ac_2 derivative, m.p. 150° (corr.), of cis-1 : 4-*di*(*aminomethyl*)cyclo*hexane*, b.p. 113—115°/8 mm., m.p. −9° [*dihydrochloride* (VI), m.p. 350° (decomp.); *platinichloride*, m.p. 295° (decomp.); Bz_2 derivative, m.p. 219° (corr.)]. trans-1 : 4-*Di*(*aminomethyl*)cyclo*hexane* (VII), b.p. 116—118°/10 mm., m.p. 27° [Ac_2 derivative, m.p. 230° (corr.); *dihydrochloride*, decomp. >380°; *platinichloride*, decomp. >300°; Bz_2 derivative, m.p. 253°], is described. Dry distillation of (VI) yields p-*methylene*cyclo*hexylmethylamine*, b.p. 68—70°/10 mm. [very hygroscopic *hydrochloride*; *platinichloride*, m.p. 198° (decomp.); *Bz* derivative, m.p. 95°], exhaustively methylated to the *compound*, $C_{11}H_{22}NI$, m.p. 208—210° (corr.). Reduction (Bouveault–Blanc) of the isomeric Me_2 hexahydroterephthalates gives a mixture of cis-, b.p. 167°/10 mm., m.p. 43°, and trans-, b.p. 163—165°/10 mm., m.p. 67°, -1 : 4-*di*(*hydroxymethyl*)cyclo*hexane*, separated from one another by crystallisation of the corresponding *dibenzoates*, m.p. 86° and 125°, respectively. The glycols are converted by HBr at 135—140° into cis-, non-cryst., and trans-, m.p. 55°, -1 : 4-*di*(*bromomethyl*)cyclo*hexane*; the latter is converted by *o*-$C_6H_4(CO)_2NK$ into the *diphthalimido*-derivative, m.p. 275° (corr.), hydrolysed to (VII). H. W.

Sodium [dihydronaphthyl]. II. Preparation and properties of dihydronaphthalenedicarboxylic acids. J. F. Walker and N. D. Scott (J. Amer. Chem. Soc., 1938, **60**, 951—955; cf. A., 1937, II, 55).—Passage of CO_2 into Na and $C_{10}H_8$ in Me_2O

or $(CH_2{\cdot}OMe)_2$ at −70° to −80°, or at >−70° for dil. solutions, gives 45—50% of 1 : 4-dihydronaphthalene-1 : 4- (I), m.p. 229—230°, and 28—32% of 1 : 2-*dihydronaphthalene*-1 : 2-*dicarboxylic acid* (II), m.p. 185—190°, converted by $K_3Fe(CN)_6$–KOH into α- and β-$C_{10}H_7{\cdot}CO_2H$, respectively. By the above procedure only half the $C_{10}H_8$ is used, but all is used if the Na and CO_2 are added alternately. In $(CH_2{\cdot}OEt)_2$ 62% of (II) is obtained. With Br–AcOH (I) gives 1 : 4-$C_{10}H_6(CO_2H)_2$, but (II) gives (?) $C_{10}H_8Br_2(CO_2H)_2$, m.p. 227° (decomp.). R. S. C.

Acids derived by oxidation of ovarian follicular hormones.—See B., 1938, 590.

Condensation and polymerisation of αβ-unsaturated aldehydes and acids. II. Condensation of hexa- and tetra-hydrobenzaldehyde with acraldehyde. A. J. Berlin and S. M. Scherlin (J. Gen. Chem. Russ., 1938, **8**, 16—21).—1 : 2 : 3 : 6-Tetrahydrobenzaldehyde and CH_2:CH·CHO with quinol (SO_2 catalyst; 1 hr. at 105°, followed by 1 hr. at 120°) yield 1-β-*formylethyl*-1 : 2 : 3 : 6-*tetrahydrobenzaldehyde*, b.p. 140—142°/14 mm., oxidised ($AgNO_3$ in aq. NaOH) to 1-β-*carboxyethyl*-1 : 2 : 3 : 6-*tetrahydrobenzoic acid*, m.p. 161°. 1-β-*Formylethylhexahydrobenzaldehyde*, b.p. 120—121°/7 mm. (prepared as above), gives the *lactone* of 1-β-*carboxyethylhexahydrobenzyl alcohol*, b.p. 110—112°/0·5 mm., when heated with MeOH–KOMe, and yields 1-β-*carboxyethylhexahydrobenzoic acid*, m.p. 130—131°, when oxidised. R. T.

α-Naphthaldehyde and its derivatives. H. W. Coles and (Miss) M. L. Dodds (J. Amer. Chem. Soc., 1938, **60**, 853—854).—With 30% CH_2O and conc. HCl, followed by conc. H_2SO_4, at 60°, $C_{10}H_8$ gives 67—70% yields of 1-$C_{10}H_7{\cdot}CH_2Cl$ (I), b.p. 291—292°/760 mm., 150°/9 mm. (changes fairly readily to a Cl-free *polymeride*, m.p. about 200°), and a *substance*, m.p. 125°. (I) with $(CH_2)_6N_4$ gives 59—60% of 1-$C_{10}H_7{\cdot}CHO$ (oxime, m.p. 98°; *diphenylsemicarbazone*, m.p. 197°; *semicarbazone*, m.p. 219°; *thiosemicarbazone*, m.p. 217°; *phenyl-*, m.p. 82°, as-*diphenyl-*, m.p. 100·5°, β-*naphthyl-*, m.p. 174—175°, p-*nitro-*, m.p. 237°, 2 : 4-*dinitro-*, m.p. 254°, p-*bromo-*, m.p. 136—137°, and 2 : 5-*dichloro-phenyl-hydrazone*, m.p. 114°; *anil*, m.p. 172°, and o-*tolil*, m.p. 172·5°). *Di*-(β-1-*naphthylvinyl*) *ketone* has m.p. 130°. M.p. are corr. R. S. C.

Mechanism of aromatic side-chain reactions with special reference to the polar effects of substituents. IX. The *ortho*-effect in the reaction of phenacyl bromides with pyridine. J. W. Baker (J.C.S., 1938, 445—448).—o-Methylacetophenone (semicarbazone, m.p. 206°; lit., 203°, 192°) with Br yields o-*methylphenacyl bromide*, b.p. 113·5°/1·7 mm.; similarly, *p-tert.*-butylacetophenone [*semicarbazone*, m.p. 231—232° (decomp.)] yields *p*-tert.-*butylphenacyl bromide*, b.p. 127°/0·5 mm. The kinetics of quaternary salt formation (in 0·025M solution in dry $COMe_2$) from C_5H_5N and $COPh{\cdot}CH_2Br$ (I), *o-* (II) and *p*-methyl- (III), 2 : 4-dimethyl- (IV), *p-tert.*-butyl- (V), *o-* (VI) and *p*-nitro- (VII), and 2 : 4 : 6-trimethyl-phenacyl bromide (VIII) show that the reaction is bimol. and is favoured by electron recession from the side-chain to the nucleus, the val. of the velocity coeff. (*k*) following the order (VII) > (I) > (III) > (V) > (II) > (IV) > (VI) > (VIII). For (VIII), *k* was too small to be measured. The low val. of *k* for (II), (IV), and (VIII) is explained on the basis of the occurrence of resonance between the CO and *o*-Me group, and is supported by the fact that 2 : 4 : 6-$C_6H_2Me_3{\cdot}COMe$ and (VIII) do not react with semicarbazide acetate in EtOH [(IV) similarly yields ω-*semicarbazido*-2 : 4-*dimethylacetophenone*, m.p. 175—176°]. The retarding effect of *o*-NO_2 is ascribed to the electron-repelling effect of the negative O atoms acting directly (through the medium) on the side-chain, since chelation is unlikely. The following are described: o-*nitro-*, decomp. ~260°, o-*methyl-*, m.p. 182°, and 2 : 4 : 6-*trimethyl-phenacylpyridinium bromide*, decomp. ~280°. J. D. R.

Condensation of nitro- and amino-acetophenones with formaldehyde and secondary amines. C. Mannich and M. Dannehl (Arch. Pharm., 1938, **276**, 206—211).—*o-* or *m*-$NO_2{\cdot}C_6H_4{\cdot}COMe$, the hydrochloride of the *sec.* amine, and paraformaldehyde are heated in AcOH until the dark mixture has become homogeneous and miscible with H_2O. Thus are obtained the *hydrochlorides* of m-*nitro*-ω-*dimethylamino-*, m.p. 209° (decomp.) [corresponding *phenylhydrazone*, m.p. 76°, and its *hydrochloride*, m.p. 180° (decomp.)], -ω-*diethylamino-*, m.p. 122°, -ω-*piperidino-*, m.p. 171—172°, o-*nitro*-ω-*dimethylamino-*, m.p. 180° (decomp.), -ω-*diethylamino-*, m.p. 146—147°, and -ω-*piperidino-*, m.p. 183° (decomp.), -*propiophenone*. Addition of NaOH or Na_2CO_3 to an aq. solution of the salts causes an immediate strong odour of amine and a resin separates when the mixture is warmed. Normal reduction of ·NO_2 in slightly acid solution appears impossible. Resins result when condensations between *o-* or *m*-$NH_2{\cdot}C_6H_4{\cdot}COMe$, *o*-$NHAc{\cdot}C_6H_4{\cdot}COMe$, or *o*-$NHBz{\cdot}C_6H_4{\cdot}COMe$, CH_2O, and $NHMe_2$,HCl are attempted. *m*-$NHAc{\cdot}C_6H_4{\cdot}COMe$ gives m-*acetamido*-ω-*dimethylaminopropiophenone hydrochloride* (I), m.p. 194·5° and *m*-$NHBz{\cdot}C_6H_4{\cdot}COMe$ yields m-*benzamido*-ω-*dimethylaminopropiophenone hydrochloride* (II), m.p. 178°; basification of these salts causes liberation of $NHMe_2$. Reduction of (I) by Na–Hg in slightly acid solution yields m-*acetamidophenyl*-β-*dimethylaminoethylcarbinol*, m.p. 123°, which gives a *benzoate hydrochloride*, m.p. 185°, devoid of anæsthetising action. Boiling HCl converts (II) into m-*amino*-ω-*dimethylaminopropiophenone* (*dihydrochloride*, decomp. >180°), reduced to m-*aminophenyl*-β-*dimethylaminoethylcarbinol*, m.p. 74°. The corresponding *o*-compounds could not be obtained in this manner. H. W.

Synthesis of compounds related to the antirachitic vitamins. Condensation of *cyclo*hexylideneacetaldehyde with 4-hydroxy*cyclo*hexanone. J. B. Aldersley and G. N. Burkhardt (J.C.S., 1938, 545).—Ozonolysis of 1-allyl*cyclo*hexanol yields *cyclo*hexylideneacetaldehyde (I) (*semicarbazone*, m.p. 205°) and *cyclo*hexenylacetaldehyde (*semicarbazone*, m.p. 186°). 4-Acetoxy*cyclo*hexanone (*semicarbazone*, m.p. 182—183°) and (I) in aq. NaOH yield α-*cyclo*hexylidene-β-(5-hydroxy-2-keto*cyclo*hexylidene)ethane (*phenylurethane*, m.p. 180°; 2 : 4-*dinitrophenylhydrazone*, m.p. 170—171°). J. D. R.

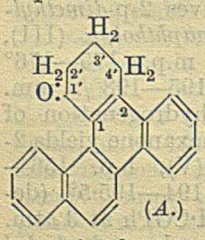
Stereochemistry of cyclanes. I. R. Cornubert. **II. Stereoisomeric monobenzylidene derivatives.** R. Cornubert, M. André, M. de Demo, R. Joly, P. Louis, P. Robinet, and A. Strébel. **III. Stereoisomeric benzylidene-2-methyl*cyclo*pentanones and -hexanones.** R. Cornubert and P. Louis. **IV. Stereoisomeric benzylidene derivatives of 2-benzyl- and 2-*iso*propyl-*cyclo*pentanones. Benzylidene derivatives of 2 : 2-dialkylcyclanones. Alteration of benzylidene derivatives.** R. Cornubert, M. André, M. de Demo, P. Louis, and A. Strébel (Bull. Soc. chim., 1938, [v], **5**, 509—512, 513—520, 520—534, 534—546; cf. A., 1932, 746 and preceding abstracts).—With the possible exception of 2 : 6-dibenzyl*cyclo*hexanone, the no. of isomeric *cyclo*-hexanone and -pentanone derivatives is in accord with a planar structure of the ring. 6-Benzylidene-2-methyl*cyclo*hexanone (I), m.p. 62—63° (*semicarbazone*, m.p. 212°; *oxime*, m.p. 147°), is converted by HCl in *cyclo*hexanol into (or, if prepared in acid solution, is accompanied by) an isomeric *form* (II), b.p. 156—157°/7 mm. (*semicarbazone*, m.p. 183°; *oxime*, m.p. 107°; *oximino-oxime*, m.p. 187°). (I) reacts more readily than does (II) with CO-reagents, Br, O_2, H_2 (Ni), and MgPhI, and is oxidised more readily by $KMnO_4$ to BzOH and α-methyladipic acid [obtained only from (I)]. With MgPhI (1 mol.) (I) gives 2-*benzhydryl*-6-*methyl*cyclo*hexanone*, m.p. 140—141°, but with 1·25 mols. gives also a *stereoisomeride* (III), m.p. 95—103°; with HCl–PhCHO both these products give three *substances*, $C_{27}H_{27}OCl$ (? 6-β-*chloro*-αα*β*-*triphenylethyl*-2-*methyl*cyclo*hexanone*), m.p. 103—109°, 166—167°, and 166—167°, respectively, and in one experiment (III) gave also a small amount of a *tetrahydropyrone* derivative, $C_{34}H_{32}O_2$, m.p. 250—252°. Methylation of Et *cyclo*pentanone-2-carboxylate by MeI gives also Et_2 α-methyladipate; the reaction is influenced by impurities (b.p. >44°) in the MeI. The decarboxylation of Et 2-methyl*cyclo*pentanone-2-carboxylate is modified. The solid form (IV) of 5-benzylidene-2-methyl-*cyclo*pentanone yields the liquid form when heated at 280—290° or kept with HCl in *cyclo*hexanol; Speranski's form of m.p. 124° was not obtained, but his method led to some 2-α-*hydroxybenzyl*-5-*methyl*cyclo*pentanone* (V), m.p. 160—161°, which with hot Ac_2O gives (IV) and (?) an *isomeride*, m.p. 166—168°, of (V). Partial hydrogenation (Co or Ni formate) of 2 : 6-dibenzylidene*cyclo*pentanone gives a *form* (VI), m.p. 129—130°, and its *trimeride* (VII), m.p. 240°, of 2-*benzyl*-5-*benzylidene*cyclo*pentanone*, (VI) being also obtained from 2-benzyl*cyclo*pentanone and PhCHO with NaOMe; use of HCl at −10° in this last condensation gives a *form* (VIII), b.p. 248—250°/18 mm., which is obtained from (VI) by HCl in *cyclo*hexanol. (VII) is obtained from (VI) by irradiation (ultraviolet), or by keeping. (VI) gives a *semicarbazone*, m.p. 207—208°, and an *oxime*, m.p. 108—109°; it is oxidised to BzOH and hydrogenated to 2 : 6-dibenzyl-*cyclo*pentanone (IX), m.p. 39°. (VIII) is reduced to (IX) [in one case, crude (VIII) gave the isomeride, m.p. 58°, of (IX)], gives a *semicarbazone*, m.p. 161°, and an *oxime*, m.p. 174°. (VII) resists hydrogenation and oxidation, and is stable to HCl. The solid form of 5-benzylidene-2-*iso*propyl*cyclo*pentanone (X) (*semicarbazone*, m.p. 206—207°) with HCl gives the liquid form (*semicarbazone*, m.p. 169—170°). 2 : 2-Dimethyl- and 2-methyl-2-*iso*propyl-*cyclo*pentanone and 2-methyl-2-propyl*cyclo*hexanone give each only one benzylidene derivative; 6-benzylidene-2-methyl-2-propyl*cyclo*hexanone gives a *semicarbazone*, m.p. 183—184°, but the C_5-ring compounds give no semicarbazones. In air (or by irradiation) (I) gives an *oxide*, $C_{14}H_{16}O_3$, m.p. 122—123°. (IV) gives a similar *oxide*, m.p. 29—30°. 2-Benzyl-6-benzylidene*cyclo*hexanone gradually acquires a higher and indefinite m.p., and 2-benzyl-6-benzylidene-2-propyl*cyclo*hexanone gives a liquid isomeride, but other similar substances are unchanged. Irradiation of (IV), (VIII), and (X) gives *oxides*, but the liquid isomeride of (X) is unaffected. 2-Benzyl-6-benzylidene*cyclo*hexanone, m.p. 76°, prepared by NaOMe or HCl, gives, when irradiated, a (?) *tetrameride*, m.p. 224°. R. S. C.

Substituted tetrahydronaphthalenes. I. 1-Keto- and 1-hydroxy-2-*p*-dialkylaminobenzyltetrahydronaphthalenes. R. L. Shriner and W. O Teeters (J. Amer. Chem. Soc., 1938, **66**, 936—939).—Addition of 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene (I) to the appropriate dialkylamino-aldehyde in NaOH–EtOH–H_2O and heating at 100° gives the 2-p-*di-methyl*- (II), m.p. 155·5—156·5° (*oxime*, m.p. 207·5—208°), *-ethyl*-, m.p. 95—95·5°, and -n-*propyl-aminobenzylidene* derivatives, m.p. 123—123·5°, hydrogenated in warm EtOH in presence of PtO_2 only to 1-*keto*-2-p-*di-methyl*-, m.p. 112—112·5° (*oxime*, m.p. 166·5—167·5°), *-ethyl*-, m.p. 57·5—58°, and -n-*propyl-aminobenzyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 65·5—66°. Hydrogenation of (II) in warm EtOH in presence of Raney Ni gives 2-p-*dimethyl-aminobenzyl*-1 : 2 : 3 : 4-*tetrahydro*-α-*naphthol*, α- (III), m.p. 100—100·5° [*hydrochloride*, m.p. 175—176° (decomp.)], and β-*form* (IV), b.p. 195—198°/2 mm. (hygroscopic *hydrochloride*). PtO_2-hydrogenation of 2-*p*-dimethylaminobenzylidene*cyclo*hexanone yields 2-p-*dimethylaminobenzyl*cyclo*hexanol* (V), b.p. 156—158°/3 mm. [*hydrochloride*, m.p. 194—195·5° (decomp.)], whilst *p*-$NMe_2{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}COPh$ at 3 atm. gives α-*phenyl*-γ-p-*dimethylaminophenylpropyl alcohol* (VI), b.p. 182—188°/3 mm. (oily *hydrochloride*), and the *p*-chlorobenzylidene derivative of (I) at 3 atm. gives 2-p-*chlorobenzyl*-1 : 2 : 3 : 4-*tetrahydro*-α-*naphthol*, α-, m.p. 124—124·5°, and β-*form*, m.p. 91—92°. M.p. are corr. The CO-amines are very irritant to the rabbit's eye, but not toxic to cats or analgesic in mineral oil to mice. The hydrochlorides of (IV), (V), and (VI) have local anæsthetic action on guinea-pig's skin and rabbit's eye, but that of (III) only on guinea-pig's skin; details are given. R. S. C.

Polyphenylation of *oo'*-ditolyl derivatives. V. 4-Benzhydrylfluorenone. P. G. Sergeev (J. Gen. Chem. Russ., 1938, **8**, 3—6).—2-Benzhydryldiphenyl-2'-carboxylic acid in C_6H_6 is heated with PCl_5 until evolution of HCl ceases, and then with $AlCl_3$, to yield 4-*benzhydrylfluorenone* (I), m.p. 178—179°. 4-*Fluorenylfluorenone*, m.p. 218—219°, is obtained similarly from 2-fluorenyldiphenyl-2'-carboxylic acid. (I) and MgPhBr in Et_2O afford 9-*phenyl*-4-*benzhydrylfluorenol*, m.p. 167—168°, the bromide of which gives intensely coloured solutions when boiled with C_5H_5N. R. T.

Benzanthrones. I. Mechanism of Bally's reaction. F. G. Baddar and F. L. Warren (J.C.S., 1938, 401—404; cf. A., 1937, II, 457).—The mechanism proposed by Bally and Scholl (A., 1911, i, 676) for the synthesis of *meso*benzanthrone from glycerol, H_2SO_4, and anthraquinone (I) is considered to be correct since (I) and α-ethylglycerol in aq. H_2SO_4 with Cu yield anthranol and 1′-*ethyl*meso*benzanthrone* (II), m.p. 106°, the constitution of which is proved as follows. 1-$C_{10}H_7$Et and 99% HNO_3 in AcOH yield 4-*nitro*-1-*ethylnaphthalene*, b.p. 164—165°/3 mm., reduced by $SnCl_2$–HCl in EtOH to 4-ethyl-α-naphthylamine, b.p. 170°/8 mm. (*Ac* derivative, m.p. 151°), converted (diazo-method) into 4-*iodo*-1-*ethylnaphthalene* (III), b.p. 170°/7 mm. *o*-$C_6H_4I{\cdot}CO_2Me$ and (III) with Cu at 180°, followed by hydrolysis, yield o-4′-*ethyl*-1′-*naphthylbenzoic acid*, m.p. 176°, which is converted (Friedel–Crafts; hot 90% H_2SO_4) into (II) and 2′-*ethyl*-3 : 4-*benzfluorenone*, m.p. 139°. Similarly, *o*-1′-naphthylbenzoic acid gives *meso*benzanthrone and benzfluorenone (cf. A., 1918, i, 434). J. D. R.

Polycyclic systems. I. Condensation of chrysene with succinic anhydride. H. Beyer (Ber., 1938, **71**, [*B*], 915—922).—Addition of $AlCl_3$ to $(\cdot CH_2{\cdot}CO)_2O$ (I) and chrysene in C_6H_6 at 35—40° gives β-2-*chrysenoylpropionic acid* (II), m.p. 197—198° (slight decomp.) [*Na* salt; *Me*, m.p. 135—136°, and *Et*, m.p. 105—106° (clear at 107°), esters; *semicarbazone* (III), m.p. 237—239° (decomp.)], in 50—55% yield. At room temp. the yield is about 30—35% whereas at 70—80° more resinous matter is produced whereby the amount and purity of the acid are greatly depressed. Reduction (Clemmensen) of (II) affords


(*A.*)

γ-2-*chrysenylbutyric acid*, m.p. 208—209° (*Me* ester, m.p. 125—126° becoming transparent at 127°), also derived (Wolff–Kishner) from (III). This is converted by the successive action of PCl_5 in C_6H_6 and $AlCl_3$ in $PhNO_2$ into 1′-*keto*-1′ : 2′ : 3′ : 4′-*tetrahydro*-1 : 2-*benzochrysene* (*A*), m.p. 220—221°, which does not give a semicarbazone, oxime, or *p*-nitrophenylhydrazone; it is reduced (Clemmensen) to 1′-*hydroxy*-1′ : 2′ : 3′ : 4′-*tetrahydro*-1 : 2-*benzochrysene*, m.p. 181—182°, which appears indifferent to Ac_2O. In $PhNO_2$ chrysene, (I), and $AlCl_3$ give (?) β-1-*chrysenoylpropionic acid*, m.p. 221—223° (*Me* ester, m.p. 148—149°), reduced to *γ*-1-*chrysenylbutyric acid*, m.p. 213—214° (*Me* ester, m.p. 100—101°). H. W.

Synthesis of linear polynuclear aromatic compounds. C. Marschalk (Bull. Soc. chim., 1938, [v], 5, 306—309).—Condensation of 2 : 3-$C_{10}H_6(CO)_2O$ (I) with dihydroquinizarin (II) (trace of $AlCl_3$) (cf. A., 1936, 1256) gives a hydroxy-ketone probably of the *lin.*-hexacene series. Similar products are obtained from leuco-1 : 4-dihydroxynaphthacenequinone (III) and *o*-$C_6H_4(CO)_2O$ or *o*-$CHO{\cdot}C_6H_4{\cdot}CO_2H$ (condensation in presence of $Na_2S_2O_4$, cyclisation by NaCl–$AlCl_3$). (I) and (III) give a compound, probably derived from *lin.*-heptacene (IV). 1 : 4-Dihydroxyanthraquinone-2 : 3-dicarboxylic anhydride does not condense, but anthraquinone-2 : 3-dicarboxylic anhydride (V) and leucoquinizarin (trace of $AlCl_3$) give a derivative of (IV). From anthracene- and anthraquinone-dicarboxylic anhydrides and (III), products probably derived from *lin.*-octacene are obtained. Pyromellitic anhydride condenses (cf. A., 1911, i, 793) with (II) to a substance sol. in aq. Na_2CO_3 (unlike the above). Quinol and (V) give ($AlCl_3$) 6 : 7-phthaloylquinizarin (?). E. W. W.

Substances with female hormone effect. I. J. Hoch (Bull. Soc. chim., 1938, [v], **5**, 264—276).—In part a more detailed account of work already reported (A., 1937, II, 423). 1-Keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (*loc. cit.*), $CHMeBr{\cdot}CO_2Et$, and Zn in C_6H_6 give *Et* α-3 : 4-*dihydro*-1-*phenanthrylpropionate*, b.p. 207—210°/1 mm., the H_2-derivative of which is hydrolysed and the *acid* cyclised by $SnCl_4$ to the 1-*Me* derivative, m.p. 138° (*oxime*, m.p. 150—151°), of 4 : 5-benzo-6 : 7 : 8 : 9-tetrahydroacenaphthen-2-one (cf. *loc. cit.*) (which is now found to have about 1/60 the activity of folliculin). β-6-Methoxy-1 : 2 : 3 : 4-tetrahydro-1-naphthylethanol (A., 1936, 990), new m.p. 58° (*phenylurethane*, m.p. 75°), in C_6H_6 gives (PBr_3) the corresponding bromide, new b.p. 195—196°/15 mm., which is converted (cf. A., 1936, 990) into *γ*-6-methoxy-1-naphthylbutyric acid, and thence (cf. A., 1936, 76) into 1-keto-7-methoxy-1 : 2 : 3 : 4-tetrahydrophenanthrene (I). With $CH_2Br{\cdot}CO_2Et$ and Zn–Hg (not Zn) in C_6H_6 (I) gives the *Et* ester, b.p. 235—240°/2 mm., of 7-*methoxy*-3 : 4-*dihydro*-, m.p. 170—172° (decomp.), which is hydrogenated to 7-*methoxy*-1 : 2 : 3 : 4-*tetrahydro*-1-*phenanthrylacetic acid*, m.p. 188° (not yet cyclised). With $CHMeBr{\cdot}CO_2Et$, (I) yields the *Et* ester, b.p. 220—235°/2 mm., of α-7-*methoxy*-3 : 4-*dihydro*-, m.p. 180° (decomp.), which is hydrogenated to α-7-*methoxy*-1 : 2 : 3 : 4-*tetrahydro*-1-*phenanthrylpropionic acid*, m.p. 172° (not yet cyclised). E. W. W.

Transition from the androsterone to the progesterone series. A. Butenandt and J. Schmidt-Thomé (Naturwiss., 1938, **26**, 253).—Dehydroandrosterone acetate with KCN–AcOH in EtOH yields the two isomerides, m.p. 195° and 203°, of 17-*cyanoandrostene*-3 : 17-*diol* 3-*acetate*, the mixture of which, dehydrated with $POCl_3$ and C_5H_5N, yields 17-*cyano*-3-*acetoxy*-$\Delta^{5:16}$-*androstadiene*, m.p. 210°, which, with MeMgI at Et_2O, yields $\Delta^{5:16}$-*pregnadien*-3-*ol*-20-*one*, m.p. 178° [*oxime*, m.p. 215° (decomp.)]. J. D. R.

Autocondensation of ethyl acetoneoxalate. A. Heikel (Suomen Kem., 1938, **11**, B, 5—7).—$COMe{\cdot}CH_2{\cdot}CO{\cdot}CO_2Et$ with warm aq. NaOAc gives a compound (I), $C_{12}H_{16}O_8$, m.p. 90—91°, converted by drying in vac. into a substance (II), $C_{12}H_{14}O_7$, m.p. 85°, which with $Ba(OH)_2$ yields 5 : 3 : 1-$OH{\cdot}C_6H_3Me{\cdot}CO_2H$ (cf. Claisen, A., 1890, 364). It is suggested that (II) and (I) are *Et* 6-*hydroxy*-2-*carboxy*-4-*methylbenzoylformate mono*- and *di*-*hydrate*, respectively. F. R. S.

Racemisation of an optically active acid and its methyl ester. C. L. Bickel (J. Amer. Chem. Soc., 1938, **60**, 927—929).—*γ*-Keto-*αγ*-diphenylpropionic acid is resolved by quinine in EtOAc into the *l*- and *d*-acids, m.p. 181°, $[\alpha]_D^{26}$ 148° in MeOH, which are racemised only by hot fairly conc. alkali

or by hot conc. HBr or HI, and not by heat alone. The l-*Me* ester, m.p. 52°, is racemised by very dil. alkali in H_2O or MeOH (50% in 52 hr. by 0·0002N-NaOH–MeOH at 26°; faster by more conc. NaOH) without hydrolysis; 0·38N-NaOH–MeOH also causes hydrolysis (25%). R. S. C.

Derivatives of cyclic β-ketocarboxylic acids.—See B., 1938, 488.

Micro-organisms. LVII. Fumigatin (3-hydroxy-4-methoxy-2 : 5-toluquinone) and spinulosin (3 : 6-dihydroxy-4-methoxy-2 : 5-toluquinone), metabolic products respectively of *Aspergillus fumigatus*, Fresenius, and *Penicillium spinulosum*, Thom. W. K. Anslow and H. Raistrick (Biochem. J., 1938, **32**, 687—696).—*Fumigatin* (I), m.p. 116° (*acetate*, m.p. 95—96°), extracted from the aërated metabolism solution with $CHCl_3$ after acidification (HCl), gives a purple colour with alkali, liberates I from KI, but does not react with *o*-$C_6H_4(NH_2)_2$. (I) and Et_2O–CH_2N_2 yield a *compound*, $C_{10}H_{12}O_4N_2$, m.p. 93° (probably a pyrazole); Me_2SO_4–K_2CO_3–$COMe_2$ afford the *Me*$_1$ *ether*, m.p. 59°, whilst reduction ($Na_2S_2O_4$) gives 3-*hydroxy*-4-*methoxy*-2 : 5-*toluquinol*, m.p. 100—101°, also present in the metabolism solution. The *Ag* salt of (I) with EtI yields 4-methoxy-3-ethoxy-2 : 5-toluquinone, reduced to the *quinol*, m.p. 55—56°. 5-*Nitro*-3-*methoxy*-4-*ethoxytoluene*, m.p. 59° (from 5-nitrocreosol, Et_2SO_4, and K_2CO_3 in PhMe), when reduced (Sn + HCl) yields the NH_2-compound, oxidised ($Na_2Cr_2O_7$, dil. H_2SO_4) to 3-*methoxy*-4-*ethoxy*-2 : 5-*toluquinone*, m.p. 50°, reduced to the *quinol*, m.p. 64° (different from the above quinol). (I) with Ac_2O–conc. H_2SO_4 gives 2 : 3 : 5 : 6-*tetra-acetoxy*-4-*methoxytoluene*, m.p. 192—192·5°, which when hydrolysed (MeOH–H_2SO_4), and the product oxidised (air in alkaline solution), yields 3 : 6-dihydroxy-4-methoxy-2 : 5-toluquinone (spinulosin; A., 1931, 1092). A. Li.

Isomeric dimethoxy-2 : 5-toluquinones and related compounds. W. K. Anslow, J. N. Ashley, and H. Raistrick (J.C.S., 1938, 439—442).—Methylation (Me_2SO_4–K_2CO_3–$COMe_2$) of 3 : 6-dihydroxy-2 : 5-toluquinone yields 3 : 6-*dimethoxy*-2 : 5-*toluquinone*, m.p. 104—105°. 6-Methoxy-2 : 5-toluquinone, m.p. 19—20°, with Ac_2O–H_2SO_4 yields 3 : 4 : 6-*triacetoxy*-2-*methoxytoluene*, m.p. 98—99°, hydrolysed (MeOH–H_2SO_4 in N_2) to 3 : 4 : 6-*trihydroxy*-2-*methoxytoluene*, m.p. 146—147°, which is oxidised ($FeCl_3$) to 4-*hydroxy*-6-*methoxy*-2 : 5-*toluquinone*, m.p. 116°, methylated to 4 : 6-*dimethoxy*-2 : 5-*toluquinone* (I), m.p. 125°. Hydrolysis of 2 : 3 : 6-triacetoxy-4-methoxytoluene with MeOH–H_2SO_4 yields 2 : 3 : 6-trihydroxy-4-methoxytoluene, m.p. 150° (decomp.), which is oxidised ($FeCl_3$) to 6-hydroxy-4-methoxy-2 : 5-toluquinone (II), m.p. 204° (lit. 186°, 183—185°), which with Me_2SO_4–K_2CO_3 yields (I). With Ac_2O–H_2SO_4, (II) does not undergo the Thiele–Winter reaction but yields 6-*acetoxy*-4-*methoxy*-2 : 5-*toluquinone*, m.p. 139°. 5-Nitrohomoveratrole when reduced (Sn–HCl–EtOH) yields 5-aminohomoveratrole, which is oxidised ($Na_2Cr_2O_7$–H_2SO_4) to 3 : 4-*dimethoxy*-2 : 5-*toluquinone*, m.p. 59°, identical with fumigatin Me ether prepared from fumigatin, a metabolic product of *Aspergillus fumigatus*, Fresenius (cf. preceding abstract). J. D. R.

Constitution of compounds formed by the oxidation of quinol in presence of ammonium sulphite or primary amines. (Mlle.) Y. Garreau (Compt. rend., 1938, **206**, 840—842).—The NH_4 salt of 2 : 5-diamino-*p*-benzoquinone-3 : 6-disulphonic acid (I) (the α-acid of A., 1936, 721) with hot H_2SO_4 (*d* 1·83) affords 2 : 5-diamino-*p*-benzoquinone, which indicates that the SO_3H in (I) are in *p*-positions. The β-acid (*loc. cit.*) is 2(or 5)-amino-5(or 2)-hydroxy-*p*-benzoquinone-1-imine-3 : 6-disulphonic acid (II). (I) with $SnCl_2$–HCl or Pt–H_2 affords 2 : 4-*diaminoquinol*-3 : 6-*disulphonic acid*, insol. in H_2O, whilst (II) (NH_4 salt) with Pt–H_2 gives 2 : 4(or 4 : 5)-*diamino*-1 : 5(or 1 : 2)-*dihydroxyquinol*-3 : 6-*disulphonic acid* (+H_2O), easily sol. in H_2O. The α- and β-isomerides of NH_3Bu 2 : 5-dibutylamino-*p*-benzoquinonemonosulphonate (cf. A., 1937, II, 338) are similarly related to one another. J. L. D.

Polymerisation of α-naphthaquinone. C. Marschalk (Bull. Soc. chim., 1938, [v], **5**, 304—306).—α-Naphthaquinone in $PhNO_2$ at 50°, treated slowly with $AlCl_3$, gives a 65% yield of trinaphthobenzene trioxide (trisanhydrohexahydroxytrinaphthobenzene) (A., 1934, 185). E. W. W.

New synthesis of metal salts of hydroxyanthraquinones. I. G. Flumiani and V. Bajić (Monatsh., 1938, **71**, 293—297).—1-Hydroxyanthraquinone when heated (autoclave; at the m.p.) with Cu or CuO gives its *Cu* salt. The reaction does not occur in absence of O_2. Zn and Cd salts are similarly prepared. Similarly 1 : 8-dihydroxyanthraquinone gives a Cu salt (1 Cu : 2 of the anthraquinone), identical with that prepared with $Cu(OAc)_2$–EtOH (Mangini, A., 1932, 164), and *Cu* salts of the following have been prepared: 1 : 2- and 1 : 5-di-, 1 : 2 : 3-, 1 : 2 : 6-, and 1 : 2 : 7-tri-, 1 : 2 : 5 : 8-tetra-, and 1 : 2 : 3 : 5 : 6 : 7-hexahydroxyanthraquinone. No salts (Cu, Zn, or Cd) could be obtained from 2-mono-, 1 : 4-, 2 : 6-, and 2 : 7-di-, or 1 : 2 : 4-tri-hydroxyanthraquinone. H. G. M.

Halogenoaminoflavanthrones and compounds of the anthraquinone series.—See B., 1938, 488.

Structure of lignin. H. Hibbert (Canad. J. Res., 1938, **16**, B, 69—71).—The theories of the structure of lignin advanced by Freudenberg and by Hilpert are considered to be insufficiently supported by experimental evidence. A scheme is advanced in which the basic lignin-building constituent is regarded as arising from the condensation of guaiacol (I) with fructose or one of its derivatives. Lignin is thus a condensation product of (I) with a γ-keto-hydroxypentanol. H. W.

Lignin and related substances. XXX. Formation of formaldehyde from lignin induced by acids. M. J. Hunter, G. F. Wright, and H. Hibbert. **XXXI. Aromatic and non-aromatic portions of lignin.** A. Bell, A. B. Cramer, G. F. Wright, and H. Hibbert (Ber., 1938, **71**, [*B*], 734—745, 746—755).—XXX. Hexoses which contain the groups OH·C(CH_2·OH)·O·, CH(CH_2·OH)·O·, or OH·CH·CH(OH)·O give small amounts of CH_2O and

furfuraldehyde (I) when boiled with dil. acids (HCl; 28% H_2SO_4). The yields depend on the experimental conditions. Under the same conditions, quant. or very good yields of CH_2O are obtained from methylenedioxy-compounds such as piperonal, safrole, or piperonylic acid. Lignin (II) preps. obtained by various known processes of extraction give varying amounts of CH_2O and (I) when boiled with the same acids under the same conditions. A substance containing the CH_2O_2-ring yields little or no CH_2O under the conditions customary for the isolation of lignin. The presence of the CH_2O_2 group in (II) is not therefore confirmed and the results point to the presence of a carbohydrate or its decomp. product chemically united to (II). The yield of CH_2O diminishes as this is more completely removed, *e.g.*, by use of HCO_2H as extracting agent, by methylation, etc.

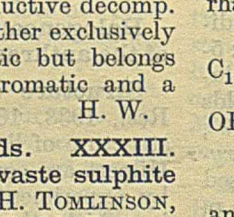
XXXI. Anhyd. HCO_2H is unsuitable for the extraction of wood since it causes deep-seated changes in addition to formylation. The differences between (II) obtained with 100% and 93% HCO_2H are possibly caused by combined carbohydrate. Treatment of glucose, fructose, sucrose, etc. with HCO_2H or AcOH gives (II)-like products in 1—35% yield. They are insol. in H_2O, sol. in dil. alkali. The solubility in org. media is similar to that of the less freely sol. (II). A further analogy exists between "fructose humic acids" (III) and similarly prepared (II) since in each case all the OH groups which can be methylated are acidic in character. The CO content of (III) is considerably > that of (II) with similar Ac or CHO content. More distinct differences are observed in the solubilities of the methylated products. Some of the most highly methylated products of (II) are sol. in light petroleum whereas (III) is transformed by CH_2N_2 into products insol. in all media. Oxidation of (I) does not give veratric acid. Further evidence of the presence of aromatic groups in (II) is found in the formation of EtI in addition to MeI when birch-(I) (obtained by HCO_2H or AcOH) is treated with HI. This does not indicate the presence of OEt but probably arises from a reductive decomp. of (II). It is concluded that (I) is neither exclusively aromatic nor exclusively non-aromatic but belongs to both types and consists of an aromatic and a carbohydrate component. H. W.

Lignin and related compounds. XXXIII. Isolation of acetovanillone from waste sulphite pulp liquor. I. K. Buckland, G. H. Tomlinson, and H. Hibbert (Canad. J. Res., 1938, **16**, B, 54—56).—Waste sulphite pulp liquor when treated with aq. alkali gave vanillin (I), acetovanillone (II), phenolic substances, and a tarry, resinous product. The yield of (II) is about 5·5% of that of the (I) formed or about 0·3% calc. on the basis of the lignin present. H. W.

Lignin and related compounds. XXXIV. Acetovanillone and acetosyringone as degradation products of ligninsulphonic acids. F. Leger and H. Hibbert (J. Amer. Chem. Soc., 1938, **60**, 565—567).—Purified spruce ligninsulphonic acid and hot aq. alkali give 6·4% of vanillin and 0·27% of acetovanillone. Birch ligninsulphonic acid gives 5·8% of vanillin and syringaldehyde and 0·84% of acetosyringone (I) (all yields are calc. on the wt. of lignin used). It is suggested that these products arise by the reactions ·CAr(OH)·CH_2·CHAr· (*A*) → COAr·CH_2·CHAr· → COAr·CH_2·CHAr·OH → COArMe + ArCHO; they are incompatible with Freudenberg's formulæ. The fragment (*A*) is considered to be a degradation product of lignin, which is itself formed from fructose and guaiacol. (I) (*p*-nitrophenylhydrazone, new m.p. 194·5—195·5°) is prepared by rearrangement of 1 : 3 : 4-$C_6H_3(OMe)_2$·OAc by $AlCl_3$ in $PhNO_2$. R. S. C.

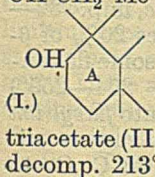
Isolation of guaiacol from waste sulphite liquor. F. Leger and H. Hibbert (Canad. J. Res., 1938, **16**, B, 68).—The acetylvanillone (I) from waste sulphite liquor from soft woods is a degradation product of pure ligninsulphonic acid. The volatile phenolic oil has been identified as guaiacol (II) by its b.p., its *p*-nitrobenzoate and *p*-toluenesulphonate. The ratio of (I) : (II) is approx. 4 : 1. H. W.

Jalap resin and its main constituent, convolvulin. C. Mannich and P. Schumann (Arch. Pharm., 1938, **276**, 211—226).—Convolvulin (I) is a substance of high mol. wt. and colloidal character, insol. in H_2O but freely sol. in H_2O containing less NaOH than corresponds with its small acid val. The nearly neutral solution has a foul taste and strongly attacks the mucous membrane of the throat. It does not diffuse through parchment or Cellophane, is pptd. by salt solutions, and becomes cloudy when warmed. The neutral solution has full purgative action. Excess of NaOH hydrolyses (I) rapidly whereby the solution loses its colloidal character, unpleasant taste, and physiological activity. Alkaline hydrolysis of (I) affords rhamnoconvolvulic acid (II) (74%), tiglic acid (9%), *exogonic acid*, $C_{10}H_{16}O_4$ (III), b.p. 175°/10 mm., $[\alpha]$ ±0° (7%), $Bu^{\beta}CO_2H$ (7·6%), and CHMeEt·CO_2H (1·4%). Votocek's observation that (II) is βλ-dihydroxypalmitic acid linked with two trisaccharide residues each of which can be hydrolysed to 2 mols. of glucose and 1 mol. of rhamnose is confirmed (A., 1929, 541, 543) and the structural unit (*A*) of (I) is formed from it by esterification of three (or four) OH of the sugar residues by the volatile acids and ester-like joining of these larger mols. by a OH of one with a CO_2H of another mol. (III) is monobasic, and contains 1 active H (Zerevitinov) but no OMe. It is not hydrogenated (PtO_2 or Pd–C) at room temp. and pressure. Br in $CHCl_3$ is decolorised with evolution of much HBr. Reduction with Na and EtOH gives highly fluorescent, dark, non-volatile products. Ac_2O and NaOAc give a viscous resin. Reaction does not occur with carbonyl reagents. Oxidation with $KMnO_4$ in alkaline solution yields (?) $EtCO_2H$ and a liquid *acid*, b.p. 170—190°/15 mm. (partial decomp.). The *Ag* salt and *Me* ester, b.p. 128—130°/14 mm., of (III) are described. Conc. HI and red P transform (III) into an *acid*, $C_{10}H_{16}O_3I_2$, m.p. 80—81°. H. W.



(*A*.)

Soya-bean saponins. III. K. TSUDA and S. KITAGAWA (Ber., 1938, 71, [*B*], 790—797; cf. A., 1938, II, 24).—Soya-sapogenol *D* gives a *diformate*, m.p. 231°, *diacetate*, m.p. 192°, and *dibenzoate*, m.p. 240°. It is indifferent towards ketonic reagents and cannot be catalytically hydrogenated. It contains therefore only 2 OH, the remaining O being probably in ethereal union. Soya-sapogenol *B* (I) yields a *triformate*, m.p. 218°, and soya-sapogenol *C* a *diformate*, m.p. 263°, confirming thus the presence of 3 OH and 2 OH, respectively. When titrated with $Pb(OAc)_4$ (I) slowly absorbs 1 O; ketone or aldehyde could not be obtained and half the original substance is isolated from the product. The presence of an α-glycol is therefore unlikely. Oxidation of (I) with CrO_3 in AcOH gives a neutral *substance*, $C_{29}H_{44}O_2$, m.p. 254—256° (*dioxime*, decomp. 266°; *dihydrazone*, decomp. 205°), indicating the presence of a primary OH (oxidised to CO_2H and lost as CO_2) and 2 *sec.* OH. Similar observations have been made with hederagenin



(I.)

Me ester and bromohederagenolactone; the ring A characteristic of hederagenin appears also present in (I). Further confirmation of the presence of an inactive, non-hydrogenatable double linking in (I) is found in the conversion of its triacetate (II) by BzO_2H into an *oxide*, $C_{30}H_{47}O(OAc)_3$, decomp. 213°. Oxidation of (II) by CrO_3–AcOH or by H_2O_2 gives an isomeric *oxide*, $C_{30}H_{47}O(OAc)_3$ (III), m.p. 258°, which does not give a coloration with $C(NO_2)_4$ and could not be acetylated or oximated. When hydrolysed with 0·1N-KOH it gives 3 AcOH and a neutral *deacetyl* derivative, m.p. 254°, which, like (II), is very resistant towards catalytic hydrogenation. It appears probable that (III) is a ketone related to (II) in the same manner as Me ketoacetyldihydro-oleanolate is to Me acetyloleanolate. In confirmation, oxidation of (II) with HNO_3 yields a *triacetyldicarboxylic acid*, $C_{36}H_{56}O_{10}$, decomp. 293° (corresponding *anhydride*, m.p. 283°). H. W.

Constitution of resin phenols and their biogenetic significance. VI. Degradation of pinoresinol dimethyl ether or eudesmin with permanganate and with nitric acid. H. ERDTMAN (Svensk Kem. Tidskr., 1938, 50, 68—72; cf. A., 1937, II, 28, 69).—Dibromopinoresinol Me_2 ether with HNO_3 in AcOH at 10° yields 4-bromo-5-nitroveratrole (80% yield). $KMnO_4$ in $COMe_2$ oxidises pinoresinol Me_2 ether or eudesmin to 1 : 2 : 4-$C_6H_3(OMe)_2$·CO_2H (60%). HNO_3 in AcOH oxidises $CHPh[C_6H_2(OMe)_3$-2 : 4 : 5$]_2$ to PhCHO (75%) and 1 : 2 : 4 : 5-NO_2·$C_6H_2(OMe)_3$ (80%). A. LI.

Yellow pigment from the osage orange (*Maclura pomifera*, Raf.). E. D. WALTER, M. L. WOLFROM, and W. W. HESS (J. Amer. Chem. Soc., 1938, 60, 574—577).—The fruit, previously extracted with light petroleum, yields to Et_2O 5·8% of *osajin*, $C_{24}H_{22}O(CO_2)(OH)_2$, m.p. 189°, 193° (corr.), α 0°, which is an *o*-dihydric phenol, since it reduces Fehling's solution, gives a Ag mirror with hot Tollens' reagent in C_5H_5N, gives a green $FeCl_3$ colour, is sol. in NaOH, and gives a *mono-*, m.p. 159° (green $FeCl_3$ colour), and *di-acetate*, m.p. 152° (no $FeCl_3$ colour). With a little H_2SO_4 or HCl in AcOH it gives a deep orange colour. It gives no CO derivative and with HNO_3 affords only $H_2C_2O_4$. Its absorption spectrum has a single max. at 2750 A. Its behaviour with alkali indicates lactonic structure. It gives a non-reducing *di*-p-*toluenesulphonate*, m.p. 148°, which, since it gives a green $FeCl_3$ colour, probably contains a different lactone structure. R. S. C.

Constituents of pyrethrum flowers. XI. Chrysanthin. W. G. ROSE and H. L. HALLER (J. Org. Chem., 1938, 2, 484—488; cf. A., 1938, II, 151).—Light petroleum extracts of pyrethrum flowers often deposit <0·1% of *chrysanthin*, $C_{17}H_{22}O_5$, m.p. 177—178°, $[\alpha]_D^{20}$ −30·5° in $CHCl_3$, which with P_2O_5 in EtOH gives *dihydrochrysanthin*, m.p. 205—208°, is oxidised by CrO_3–AcOH to *dehydrochrysanthin*, $C_{17}H_{20}O_5$, m.p. 175—177°, gives a small yield of a phenol on KOH-fusion, and with warm 5% NaOH yields AcOH and an *acid*, $C_{15}H_{25}O_6$·OH, m.p. 190—192°. This acid is acetylated by Ac_2O–C_5H_5N, but no acetate was isolated; at 112°/vac. it gives H_2O and an *acid*, $C_{15}H_{24}O_6$, m.p. 210—211°. R. S. C.

Pyroabietic acid. E. E. FLECK and S. PALKIN (J. Amer. Chem. Soc., 1938, 60, 921—925).—Pyroabietic acid, prepared from *l*-abietic acid by Pd–C, is a product of disproportionation (cf. Fieser *et al.*, A., 1938, II, 108); prepared at 225° it contains dehydro- (I), dihydro-, m.p. 129—130°, $[\alpha]_D^{20}$ −3° in abs. EtOH (*Me* ester, an oil), and *tetrahydroabietic acid*, m.p. 183—184°, $[\alpha]_D^{20}$ +6° in abs. EtOH (*Me* ester, m.p. 44—45°), saturated to $C(NO_2)_4$; when prepared at 275° it gives mainly (I), much gas being liberated. R. S. C.

Eschscholtzcanthin from petals of the Californian poppy.—See A., 1938, III, 544.

Preparation and properties of derivatives of 2-aminofuran. H. M. SINGLETON and W. R. EDWARDS, jun. (J. Amer. Chem. Soc., 1938, 60, 540—544).—2-Furoyl chloride and NaN_3 in Et_2O at 0° give 91·6% of the azide, which, when cautiously heated in Ph_2O under N_2 or CO_2, gives 73·4% of 2-*furylcarbimide* (I), b.p. 111—112°/760 mm., 54°/40 mm. This is foul-smelling, lachrymatory, and toxic. Reactions with it are conducted under N_2. The azide and C_6H_6 or distilled (I) and MgPhBr give 2-*benzamidofuran*, m.p. 89—92°, hydrolysed to BzOH, NH_3, and tars; crude (I) yields also a little 2-furoanilide, inseparable from the main product. With MgEtBr (I) gives 2-*propionamidofuran*, m.p. 80·5—81°, b.p. 134°/14 mm., hydrolysed to $EtCO_2H$ and NH_3. 2-Aminofuran could not be isolated. 35% KOH at 50° converts (I) into *K* 2-*furylcarbamate* (81·8% yield), cryst.; $Ba(OH)_2$ gives a worse yield of the *Ba* salt; the K salt with Me_2SO_4–NaOH gives the Me ester, b.p. 115—120°/18 mm. With H_2O at 5° (I) gives (?) furylcarbamic acid, which decomposes spontaneously into s-*di*-2-*furylcarbamide*, m.p. 190° (decomp.). R. S. C.

Conversion of furfuryl alcohol into lævulic acid. F. LEGER and H. HIBBERT (Canad. J. Res., 1938, 16, B, 68—69).—The following scheme is proposed in explanation of the conversion of furfuryl alcohol into

Me lævulate by HCl–MeOH: $\begin{matrix}CH{\cdot}CH\\CH{-}O\end{matrix}\!\!>\!C{\cdot}CH_2{\cdot}OH \longrightarrow$ $\begin{matrix}CH{:}CH\\OH{\cdot}CH{-}O\end{matrix}\!\!>\!CH{\cdot}CH_2{\cdot}OH \longrightarrow$ $\begin{matrix}CH{:}CH\\OH{\cdot}CH{-}O\end{matrix}\!\!>\!C{:}CH_2$ $\longrightarrow$ $\begin{matrix}CH_2{\cdot}CH_2\\CO{-}\!\!-O\end{matrix}\!\!>\!C{:}CH_2$ or $\begin{matrix}CH_2{\cdot}CH\\CO{-}\!\!-O\end{matrix}\!\!>\!CMe \longrightarrow$ $COMe{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$ or $\begin{matrix}CH_2{\cdot}CH_2\\CO{-}\!\!-O\end{matrix}\!\!>\!CMe{\cdot}OH$. The same mechanism explains the production of lævulic acid from hydroxymethylfurfuraldehyde and of γ-ketopimelic acid from furylacrylic acid. H. W.

Furan derivatives. V. I. J. Rinkes (Rec. trav. chim., 1938, **57**, 390—394; cf. A., 1932, 519).—*3-Nitrofuran-2-carboxylic acid*, m.p. 125°, prepared by oxidising the 2-Me derivative with $K_3Fe(CN)_6$–KOAc, is decarboxylated with Cu chromite–C_9H_7N at 150° into *3-nitrofuran*, m.p. 27°. 3-Nitro-2-styrylfuran-5-carboxylic acid, m.p. 237°, similarly yields *3-nitro-2-styrylfuran*, m.p. 135°. 5-Nitrofuran-2-carboxylic acid is isolated from the products of ozonisation of Et 5-nitro-2-furfurylacrylate. A. T. P.

Furoylacetarylamides.—See B., 1938, 490.

Furan-substituted ethanolamines. A. Lespagnol and Van Thienen (Bull. Sci. Pharmacol., 1938, **40**, 49—59).—Furoinoxime is reduced (Zn + NaOH) to *β-hydroxy-αβ-difurylethylamine*, m.p. 104—105° (*hydrochloride*, m.p. 185°). Benzofuroinoxime is reduced (Zn + HCl) to *β-hydroxy-β-phenyl-α-furylethylamine*, m.p. 106—107°. PhCHO and glycine in EtOH–NaOH when treated with furfuraldehyde yield the *furfurylidene* derivative, m.p. 119°, of *β-hydroxy-β-furyl-α-phenylethylamine*, m.p. 123°. A. Li.

2 : 5-Dimesityl- and 2 : 5-di(bromomesityl)-furan. R. E. Lutz, (Miss) E. C. Johnson, and J. L. Wood (J. Amer. Chem. Soc., 1938, **60**, 716—718).—$(C_6H_2Me_3{\cdot}CO{\cdot}CH{:})_2$ (I) is rapidly reduced by Sn–HCl–AcOH to $(C_6H_2Me_3{\cdot}CO{\cdot}CH_2)_2$ (II), also obtained by H_2–Pd–$CaCO_3$. (II) resists further reduction, is unaffected by conc. aq. HCl, gives tars with AcCl, and is converted by Ac_2O–H_2SO_4 into a SO_3H-derivative, m.p. about 230° (decomp.). Long treatment of (I) with Sn–HCl–AcOH affords some *2 : 5-dimesitylfuran*, m.p. 82—83° (corr.) [NO_2-derivative, m.p. 107·5—108° (corr.)], which is obtained from (II) by HCl–Et_2O, 85% H_3PO_4, or, best, HI (*d* 1·7), is stable to Na–EtOH, with 4 Br in CCl_4 gives the *3 : 4-Br*$_2$-derivative, m.p. 146·5—147°, and with Br–$FeBr_3$ in CS_2 gives a *Br*$_5$-derivative. *αδ-Diketo-αδ-di-3-bromomesityl-Δ*$^{\beta}$*-butene*, m.p. 228—230°, obtained in 50% yield from fumaryl chloride, $C_6H_2Me_3Br$, and $AlCl_3$ in CS_2, is reduced by Zn–AcOH to *αδ-diketo-αδ-di-3-bromomesitylbutane*, m.p. 183—184°, which with HI (*d* 1·7) at 182—185°, but not with Ac_2O–H_2SO_4 or HI–AcOH, gives *2 : 5-di-3′-bromomesitylfuran*, m.p. 92—94°. R. S. C.

Hydrogenation of pyrones. R. Mozingo and H. Adkins (J. Amer. Chem. Soc., 1938, **60**, 669—675).—Hydrogenations give least amounts of by-products when reaction is rapid, but the temp. should be as low as possible. Over Cu–Cr_2O_3 at 120—125°/100—200 atm. γ-pyrone gives 50% of *tetrahydropyran-4-ol*, b.p. 119—120°/23 mm. (*3 : 5-dinitrobenzoate*, m.p. 98—99°), and 23% of tetrahydro-γ-pyrone (better obtained with Raney Ni at a lower temp.). *2-Ethylchromone* [prep. from *o*-OH·C_6H_4·COMe (modified prep.), $EtCO_2Et$, and Na in xylene], m.p. 20—20·5°, b.p. 124—126°/2 mm. (*2 : 4-dinitrophenylhydrazone*, m.p. 249—250°), with H_2–Cu–Cr_2O_3 gives *2-ethylchromanone* (I), b.p. 115—116°/2 mm. (*2 : 4-dinitrophenylhydrazone*, m.p. 221—222°), *2-ethylchroman-4-ol* (II), b.p. 137—139°/3 mm., m.p. 78—79° (*3 : 5-dinitrobenzoate*, m.p. 141—142°), 2-ethylchromen-4-ol (not obtained pure; gives *2-ethylbenzpyrylium platinichloride*, m.p. 165—166°), *2-ethylchroman* (III), b.p. 130—131°/26 mm., and *o*-$C_5H_{11}{\cdot}C_6H_4{\cdot}OH$, the relative yields depending greatly on the conditions. By using Raney Ni 30% of (I) or 77% of (II) may be obtained. Ni-hydrogenation of (III) gives 90% of *2-ethylhexahydrochroman*, b.p. 96—97°/18 mm. Hydrogenation of flavone [modified prep. in about 60% yield from EtOBz and *o*-OH·C_6H_4·COMe by way of *o*-OH·C_6H_4·CO·CH_2·COPh, m.p. 119—120° (*2 : 4-dinitrophenylhydrazone*, m.p. 119—120°; *acetate*, m.p. 118—118·5°)] (*2 : 4-dinitrophenylhydrazone*, m.p. 282—283°) is less easy; with Ni at 85° it gives 20% of β-flavan-4-ol (IV), and with Cu–Cr_2O_3 also some flavanone (*2 : 4-dinitrophenylhydrazone*, m.p. 254—255°) and flavan-4-ol (identified by conversion into *flavylium platinichloride*, m.p. 199—200°). Flavanone is smoothly hydrogenated in presence of Cu–Cr_2O_3 to (IV), flavan, and *o*-γ-phenylpropylphenol (*3 : 5-dinitrobenzoate*, m.p. 143—143·5°), yields depending greatly on the conditions. Further hydrogenation of (IV) is smoothly effected with Cu–Cr_2O_3 at 160—170°. *7-Hydroxy-3-phenyl-2-methylchromone*, m.p. 242—243°, with H_2–Cu–Cr_2O_3 at 120—125° gives an oily (?) mixture of alcohols, converted by hydrogenation at 131—138° into *3-phenyl-2-methylchroman-7-ol*, b.p. 172—174°/0·3 mm. (*3 : 5-dinitrobenzoate*, m.p. 169—170°). Flavanol deactivates Cu–Cr_2O_3 and yields only 17% of *3 : 4-dihydroxyflavan*, m.p. 123—124°, and quercetin cannot be hydrogenated with Cu–Cr_2O_3 or Ni, even at 200°. 2-Methylchromone with H_2–Cu–Cr_2O_3 at 150—155° gives 84% of *2-methylchroman-4-ol*, m.p. 87—88°. R. S. C.

Derivatives of coumarin. I. 5- and 6-Methoxy-2-benzylcoumaran-3-one [4- and 5-methoxy-1-benzylbenzfuran-2-one]. R. L. Shriner and R. E. Damschroder (J. Amer. Chem. Soc., 1938, **60**, 894—896).—Hydrogenation (PtO_2; 2—3 atm.) of 4- and 5-methoxy-1-benzylidenebenzfuran-2-one in AcOH gives *4-*, m.p. 76—77° (corr.), and *5-methoxy-1-benzylbenzfuran-2-one*, m.p. 92—93° (corr.), respectively, also obtained less well by boiling with NaOAc–EtOH the condensation product from *p*- and *m*-$C_6H_4(OMe)_2$, respectively, α-bromo-β-phenylpropionyl chloride (prep. from CHPhMe·COCl and Br at 65—70°), b.p. 113—115°/5 mm., and $AlCl_3$ in CS_2. R. S. C.

Vitamin-*E*: structure of β-tocopherol. F. Bergel, A. Jacob, A. R. Todd, and T. S. Work (Nature, 1938, **141**, 646; cf. A., 1938, II, 137).—5-Hydroxy-2 : 4 : 6 : 7-tetramethylcoumaran (I), m.p. 124—125°, has been synthesised starting from ψ-cumoquinol and allyl bromide, and 5-hydroxy-4 : 6 : 7-trimethyl-2-*n*-heptadecylcoumaran (II), m.p.

95—95·5°, isomeric with β-tocopherol (III), from ψ-cumoquinone and Et sodiostearoylacetate followed by partial hydrogenation of the intermediate coumarone. Both (I) and (II) are similar to (III) in absorption spectrum (data given) and reducing properties. (II) distils at 370° without charring, giving a mixture from which a trace of a quinol, m.p. 185—190° (sublimes), is obtained. These results and surface film measurements (cf. following abstract) support the view that (III) is a coumaran derivative. Side-Me determinations of (III) indicate the presence of 6 or 7 Me. The disposition of these is discussed. The structure proposed is supported by the results of oxidation; two oily fatty acids, C_{17-18} and C_{11-12}, are obtained, giving cryst. phenylphenacyl esters.

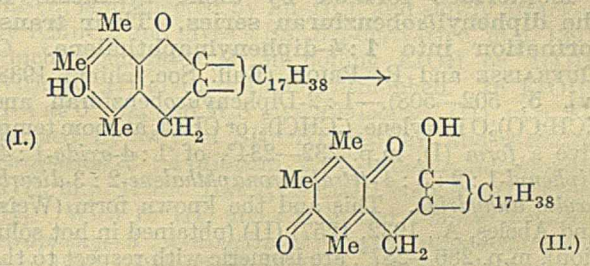
L. S. T.

Vitamin-*E*; structure of β-tocopherol. J. F. Danielli (Nature, 1938, **141**, 646).—β-Tocopherol allophanate (I) and 5-hydroxy-4 : 6 : 7-trimethyl-2-*n*-heptadecylcoumarone (II) both give stable films on 0·01N-HCl; the limiting areas are 30 and 26 sq. A., respectively. Since *p*-hexadecyl*cyclo*hexanol has a limiting area of 30 sq. A., and the lactone of γ-hydroxystearic acid one of 29 sq. A., it is concluded that (I) and (II) are analogous in structure, and that in cross-section β-tocopherol cannot have a ring system > one ring in thickness measured perpendicular to the side-chain. The ring system cannot be analogous to a phenanthrene or sterol skeleton. L. S. T.

Antisterility agents (vitamin-*E*). II. Identity of cumotocopherol and β-tocopherol. W. John. **III. Fission of tocopherols with hydriodic acid.** W. John, E. Dietzel, and P. Gunther (Z. physiol. Chem., 1938, **252**, 201—207, 208—221; cf. A., 1937, III, 497).—II. The identity of cumotocopherol and β-tocopherol (I) is established by their equal physiological activity, by the m.p. and mixed m.p. of the allophanates (sintering 144°, m.p. 145—145·5°, and clear at 145·5—146·5°), by $[\alpha]_D$ (+5·7° to +6·7° in $CHCl_3$), and by the ultra-violet absorption spectra of the allophanates. Analysis of the allophanate and the p-*nitrobenzoate*, m.p. 38—40°, shows (I) to be $C_{28}H_{48}O_2$.

III. Duroquinol, $C_{16}H_{33}Br$, and NaOH in EtOH and N_2 yield the *mono-* (II), m.p. 99·5° (*allophanate*, m.p. 208°), and *di-cetyl ether*, m.p. 90·5°. Similarly are prepared the *mono-*, m.p. 133°, and *di-benzyl*, m.p. 143°, *mono-* (III), m.p. 98°, and *di-dodecyl*, m.p. 83°, and Pr^{β}_1 *ether*, m.p. 90—91°. From ψ-cumoquinol are prepared the *mono-* (IV), m.p. 89° (*allophanate*, m.p. 180°), and *di-cetyl ether*, m.p. 60·5°. Fission of (II) with AcOH–HBr yields duroquinone (V) and $C_{12}H_{25}$·OH, whilst α-tocopherol (VI) and cumotocopherol [= (I)] are only slightly attacked. With HI (*d* 2·0) in Ac_2O–AcOH, (VI) yields 2 : 3 : 5 : 1-$C_6H_2Me_3$·OH (VII), whilst (I) gives *p*-xylenol and a *substance* [*dinitrobenzoate* (probably $C_{16}H_{14}O_6N_2$), m.p. 142°]. Similarly, with HI–Ac_2O–AcOH, (II) or duroquinol yields durenol, whilst (IV) yields (VII). When heated at 350° in N_2, (II) gives duroquinol, and (IV) yields ψ-cumoquinol. Oxidation (AcOH–H_2CrO_4) of (II) yields (V) and palmitic acid. Ultra-violet absorption spectra for most of the above compounds are given. J. D. R.

Constitution of α-tocopherol. W. John (Z. physiol. Chem., 1938, **252**, 222—224).—Oxidation of α-tocopherol (I) with $AgNO_3$ or $FeCl_3$, followed by chromatographic adsorption, yields *α-tocopherylquinone* (II), $C_{29}H_{50}O_3$ (which shows a similar absorption spectrum to duroquinone), reduced to *α-tocopherylquinol* (*triacetate*, m.p. 75°). The oxidation is formulated:



J. D. R.

Coumarins.—See B., 1938, 488.

Anthocyanin pigment in the rind of sugar-cane (Purple mauritius). C. J. D. Rao, D. G. Walawalkar, and B. S. Srikantan (J. Indian Chem. Soc., 1938, **15**, 27—30).—From the aq. extract of this rind is obtained brownish-red *mauritinin chloride*, $+4H_2O$ (violet in Na_2CO_3 or $FeCl_3$–EtOH), hydrolysed to 2 mols. of glucose and *mauritidin sulphate*, $+H_2O$, m.p. >300°, which is converted by HI into a substance believed from colour reactions to be delphinidin. Mauritidin contains 1 OMe and may be ampelopsidin; mauritinin is its diglucoside. R. S. C.

Condensation and polymerisation of αβ-unsaturated aldehydes and acids. I. Condensation of furan with acraldehyde. S. M. Scherlin, A. J. Berlin, T. A. Serebrennikova, and F. E. Rabinovitsch. **III. Polymerisation of acraldehyde and acrylic acid.** S. M. Scherlin, A. J. Berlin, T. A. Serebrennikova, and F. E. Rabinovitsch (J. Gen. Chem. Russ., 1938, **8**, 7—15, 22—34; cf. A., 1938, II, 234).—I. CH_2:CH·CHO (I) and furan with quinol (1 hr. at 100° in an autoclave) yield 2 : 5-*di*-(β-*formylethyl*)*furan*, m.p. 41—42° (*dioxime*, m.p. 132—133°), and β-2-furylpropaldehyde, oxidised by $AgNO_3$ in aq. NaOH to β-2-furylpropionic acid (*Me* ester, b.p. 89°/15 mm.). The reaction is catalysed by SO_2, but not by HCO_2H, AcOH, pyromucic acid, H_2S, or H_2SO_4.

III. (I) in C_6H_6 with quinol, heated at 170° for 5 hr., yields a dimeride, shown to be 3-*formyl*-2 : 3-*dihydro*-1 : 4-*pyran* (II), b.p. 40—40·5°/10 mm., 146°/760 mm., the *semicarbazone*, m.p. 123°, of which is hydrogenated (Pd catalyst) to the *semicarbazone*, m.p. 154°, of 3-formyltetrahydropyran (III). The *oxime*, b.p. 101—102°/10 mm., of (II) similarly yields the *oxime*, b.p. 102—104°/8—9 mm., of (III), from which the corresponding *nitrile*, b.p. 77°/15 mm., is obtained by heating with Ac_2O; this is hydrolysed by HCl in EtOH at 0° to the *Et* ester, b.p. 101—103°/19—20 mm., of tetrahydropyran-3-carboxylic acid. (II) in Et_2O and MgPhBr yield 3-(2 : 3-*dihydro*-1 : 4-*pyranyl*)*phenylcarbinol*, b.p. 166°/20 mm. (II) is oxidised ($AgNO_3$ in aq. NaOH) to 2 : 3-*dihydro*-1 : 4-*pyran*-3-*carboxylic acid* (*Na* salt, $+H_2O$). Acrylic acid, heated in furan or C_6H_6 solution at 160° for 5

hr., yields a dimeride, shown to be *acrylylhydracrylic acid* [*β-carboxyethyl acrylate*], b.p. 136°/10 mm.; this is hydrogenated (Pd catalyst) to *propionylhydracrylic acid* [*β-carboxyethyl propionate*], b.p. 145—146°/10 mm., the Me ester, b.p. 98°/17 mm., of which is identical with the product obtained from EtCOCl and $OH·[CH_2]_2·CO_2Me$. R. T.

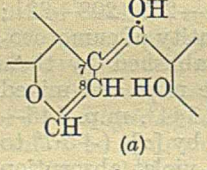
Isomerides formed by diene synthesis in the diphenyl*iso*benzfuran series. Their transformation into 1 : 4-diphenylnaphthalene. C. Dufraisse and R. Priou (Bull. Soc. chim., 1938, [v], 5, 502—508).—1 : 2-Diphenyl*iso*benzfuran and $(CH·CO)_2O$ in xylene, $(CHCl)_2$, or $CHCl_3$ at room temp. give a *form* (I), m.p. 232—234°, of 1 : 4-*oxido*-1 : 4-*diphenyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-2 : 3-*dicarboxylic anhydride*. This and the known form (Weiss and Abeles, A., 1932, 1257) (II) (obtained in hot solution), m.p. 286—287°, are isomeric with respect to the steric arrangement of the rings united at $C_{(2)}$ and $C_{(3)}$. Both forms give the (? same) *acid*, m.p. about 233—234° (decomp.) after sintering at 170°, which in boiling AcOH yields 50% of 1 : 4-$C_{10}H_6Ph_2$ and 25% of 1 : 4 : 2-$C_{10}H_5Ph_2·CO_2H$. The unusually ready decarboxylation is due to substitution by both aryl and OH at the β-C. R. S. C.

Cyclic ketals. I. Products of condensation of glycerol with halogeno- and hydroxy-acetone. V. V. Evlampiev [with V. M. Zoroastrova] (J. Gen. Chem. Russ., 1937, 7, 2941—2944).—Glycerol and $COMe·CH_2X$ in presence of HCl and Na_2SO_4 or $ZnCl_2$ (12—40 hr. at room temp.) yield 2-*methyl*-2-*chloromethyl*-, b.p. 127—128°/14 mm., -2-*bromomethyl*-, b.p. 133—134°/12 mm., or -2-*iodomethyl*-4-*hydroxymethyl*-1 : 3-*dioxa*cyclo*pentane*, b.p. 139—141°/13 mm. Glycerol, $COMe·CH_2·OAc$, HCl, and $ZnCl_2$ or Na_2SO_4 yield similarly 2-*methyl*-4-*hydroxymethyl*-2-*acetoxymethyl*-1 : 3-*dioxa*cyclo*pentane*, b.p. 148·5—149°/11 mm., hydrolysed by aq. $Ca(OH)_2$ to 2-*methyl*-2 : 4-*dihydroxymethyl*-1 : 3-*dioxa*cyclo*pentane*, b.p. 153°/13 mm. R. T.

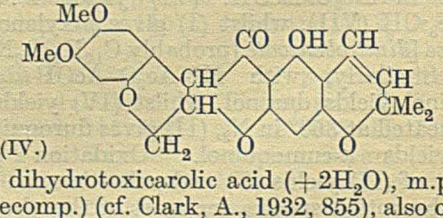
Dioxan sulphotrioxide. Sulphating and sulphonating agent. C. M. Suter, P. B. Evans, and J. M. Kiefer (J. Amer. Chem. Soc., 1938, 60, 538—540).—Dioxan with SO_3 in CCl_4 or $(CH_2Cl)_2$ gives *solids*, $O[CH_2]_2O→SO_3$ and $O_3S←O[CH_2]_2O→SO_3$, the latter with dioxan in CCl_4 yielding the former exothermally. Both products are stable at room temp., decompose in CCl_4 at 75° to give H_2O-sol. products, with H_2O instantly give H_2SO_4 and dioxan, and act as sulphonating and sulphating agents more vigorously than does the SO_3–C_5H_5N compound. With C_6H_6 in CCl_4 at room temp. they give $PhSO_3H$ slowly. *m*-Xylene and PhOMe react very rapidly; $C_{10}H_8$ reacts more rapidly than does C_6H_6, but PhCl is unaffected after 1 day. PhOH gives $PhHSO_4$; NH_2Ph gives $NHPh·SO_3H$. BzOH gives a H_2O-sol. solid, $BzO·SO_3H$, rapidly hydrolysed by hot H_2O. COPhMe also gives a readily hydrolysed product. $Bu^{\alpha}OH$ and $C_{12}H_{25}·OH$ give the pure H sulphates rapidly and quantitatively. C_2H_4 reacts vigorously to yield carbyl sulphate, which precludes S_2O_6 being the active reagent. Olefines react to give $\overset{+}{C}HR·CH_2·\bar{S}O_3$ and then $\begin{matrix}CHR·O·SO_2\\ CH_2——SO_2\end{matrix}>O$. Thus, C_3H_6 gives a product, hydrolysed by hot aq. $Ba(OH)_2$ to *Ba* β-*hydroxypropanesulphonate*, the structure of which is proved by oxidation by CrO_3 to Ba acetonesulphonate, converted by NaOH into NaOAc and $MeSO_3Na$. Δ^{α}-Nonene gives the *acid*, $C_7H_{15}·CH(O·SO_3H)·CH_2·SO_3H$, isolated as *Na* and *Ba* salts; at >50° the Na salt in H_2O yields $NaHSO_4$ and $C_7H_{15}·CH(OH)·CH_2·SO_3Na$. Alkali hydroxydecanesulphonate and higher members of the series have marked detergent properties, the C_{16} and C_{17} compounds being as effective as the sulphates. R. S. C.

Dioxan derivatives.—See B., 1938, 567.

Action of alkali on rotenone and related substances. R. S. Cahn, R. F. Phipers, and J. J. Boam (J.C.S., 1938, 513—536).—Very mild alkali, *e.g.*, K_2CO_3 or a trace of alkali hydroxide in $COMe_2$, alkali acetate in EtOH, alkali hydroxide in C_6H_6–MeOH, or "activated" Al_2O_3 in non-hydroxylic solvents, racemises the two central C: of rotenone (I), toxicarol (II), and related substances by enolisation, followed by fission of the dihydropyranone ring. These reagents with (I) give *mutarotenone*, m.p. 146—148°, $[\alpha]_D$ −83° in C_6H_6, which is a 1 : 1 mol. compound of (I) and *d-epi*rotenone (III); it is isomerised (conc. H_2SO_4–AcOH) to *dl-iso*rotenone, and with I yields *l*-dehydrorotenone. No cryst. derivative of (III) could be prepared, but it is isomerised (H_2SO_4–AcOH) to d-iso*rotenone*, m.p. 182°, $[\alpha]_D$ +75° in C_6H_6 reduced (Pt–H_2) in EtOAc to d-*dihydro*epi*rotenone*, m.p. 127—128°, $[\alpha]_D$ +99° in C_6H_6, and hydrogenated (Pd–$BaSO_4$–H_2 in dioxan) to *d*-rotenonic acid (?), cyclised to d-*dihydrodeguelin* (d-*dihydro*-β-*rotenone*), m.p. 154° (crystallographic measurements). Racemisation of $C_{(7)}$ and $C_{(8)}$ probably occurs through the enol form, type (*a*). Formation of enolic Ac derivatives is also accompanied by racemisation; acetylation of *l-iso*rotenone gives acetyl-*dl-iso*rotenone and of (I) has yielded a new Ac *form*, m.p. 159—160°, into which the known form, m.p. 137°, can be converted. The mechanism of this is discussed.


(*a*)

When ordinary (II) is treated with the reagents which cause racemisation, it is converted into β-*toxicarol* (IV), m.p. 165—167°. The reaction is reversible; (IV) is equilibrated by alcoholic alkali, but (II), being less sol., separates from Et_2O. Removal of (IV) completely by Et_2O or crystallisation (AcOH–C_6H_6) raises the m.p. of (II) to 232—233°. I and NaOAc, followed by Zn–AcOH, convert (IV) into *dehydro*-β-*toxicarol*, m.p. 183—184° (*Ac* derivative, m.p. 196—197°). Reduction (Pt–H_2 in dioxan) of (IV) gives *dihydro*-β-*toxicarol*, m.p. 213—215°, which is converted into *dehydrodihydro*-β-*toxicarol*, m.p. 226—227° (*Ac* derivative, m.p. 175—176°), yielding

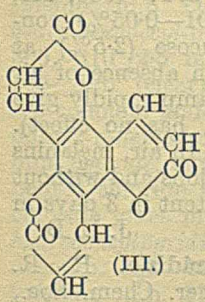

(IV.)

(KOH) dihydrotoxicarolic acid (+2H_2O), m.p. 123—125° (decomp.) (cf. Clark, A., 1932, 855), also obtained from the α-compound. The formula (IV) is assigned.

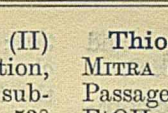
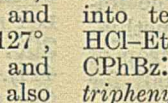
The method of separating the precursor of (II) from *Derris* extract and its subsequent purification, with crystallographic data, are described. The substance is l-α-*toxicarol* (V), m.p. 101—102°, [α] −53° in C_6H_6 +69°, in $COMe_2$ (*monoacetate*, m.p. 158°) (cf. Tattersfield, B., 1937, 728). *Monoacetylsumatrol* has m.p. 217°. The rotation of (V) in MeOH–KOH rises to +350° and falls to 0° [conversion into (II)]. Reduction (PtO_2–H_2) of (V) gives l-*dihydro*-α-*toxicarol*, m.p. 178—180°, $[\alpha]_D$ −57° in C_6H_6 (*Ac* derivative, m.p. 184—186°, $[\alpha]_D$ +64·5° in $COMe_2$). (V) and (II) yield the same *apo*toxicarol. The change of sign of rotation is discussed with reference to the active centres of (V).

Changes in rotation and absorption spectra in the presence of alkali indicate that enolisation is easier in the toxicarol than in the rotenone series. In all cases one form of ring-junction is greatly favoured. A system of nomenclature of the stereoisomerides of (I) is formulated. F. R. S.

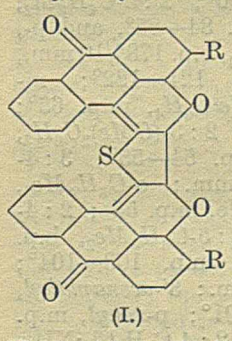
Coumarino-2′-pyrones. E. Späth and P. H. Löwy (Monatsh., 1938, **71**, 365—372).—Umbelliferone is converted by malic acid and conc. H_2SO_4 at 100° into a mixture of coumarino-7 : 6-2′-pyrone (*lin.*-dicoumarin) (I), m.p. 342° (vac.; corr.), and coumarino-7 : 8-2′-pyrone (*ang.*-dicoumarin) (II), m.p. 270° (vac.). 2 : 4-$(OH)_2C_6H_3$·CHO is transformed by $CHCl_3$ and NaOH into resorcinol-2 : 4-dialdehyde, m.p. 127°, converted by anhyd. NaOAc and boiling Ac_2O into (II), which is also obtained from 7-hydroxycoumarin-8-aldehyde, NaOAc, and Ac_2O (cf. Rangaswami *et al.*, A., 1938, II, 27). Successive treatments of (I) with NaOH–Me_2SO_4, KOH–$KMnO_4$, and CH_2N_2 afford Me_2 4 : 6-dimethoxy*iso*phthalate. Similar treatment of (II) gives 2 : 4-dimethoxy-*iso*phthalic acid, identified as the *dianilide*, m.p. 208—209°. Phloroglucinol, malic acid, and conc. H_2SO_4 give *coumarino*-5 : 6-7 : 8-*di*-2′-*pyrone* (III), m.p. 369° (vac.; corr.; decomp.). H. W.


(III.)

Dyes derived from acenaphthenequinone. VI. 2-(4-Methylthionaphthen)acenaphthyleneindigos [3-keto-4-methyl-2-7′-ketodihydroacenaphthylidenedihydrothionaphthens]. S. K. Guha (J. Indian Chem. Soc., 1938, **15**, 20—26; cf. A., 1936, 861).—2 : 1 : 3-CN·C_6H_3Me·N_2Cl, when treated with K xanthate and K_2CO_3 and then with CH_2Cl·CO_2Na, gives 2 : 1 : 3-CN·C_6H_3Me·CH(SH)·CO_2H (Na salt), which, when distilled in steam from acid solution, gives 3-hydroxy-4-methylthionaphthen, m.p. 75—76°. With acenaphthenequinone or its derivatives and HCl–AcOH this gives 3-*keto*-4-*methyl*-2-7′-*keto*-, m.p. 263°, -2-3′-*chloro*-7′-*keto*-, m.p. 270—271° after sintering, -2-3′-*bromo*-7′-*keto*-, m.p. 260°, and -2-7′-*keto*-1′-*methoxy-dihydracenaphthylidenedihydrothionaphthen*, m.p. >305°. The colours, absorption spectra, and dyeing properties of these dyes show that the effect of 4-Me is intermediate between those of 5- and 6-Me in this series. R. S. C.

Thioaldehydes and thioketones. II. S. K. Mitra (J. Indian Chem. Soc., 1938, **15**, 59—64).—Passage of H_2S through a solution of Bz_2 in HCl–EtOH at 14° or in AcOH–aq. HCl gives *tetraphenyl*-2 : 5-*endosulphidothiophen* (I),  , m.p. 195°, which gives the thiophen reaction with isatin–H_2SO_4, is unaffected by Zn–HCl, and slowly attacked by $KMnO_4$, and gives a SS′-Br_4-derivative, m.p. 139°, which regenerates (I) in boiling EtOH or AcOH. With HI (I) gives tetraphenylthiophen. In EtOH–HCl at 0° Bz_2 and H_2S give *dithiobenzil* (II), m.p. 97° (formed by way of SH·CHPh·CSPh), and 3-*ethoxytetraphenyl*-3 : 4-*dihydro*-2 : 5-*endosulphidothiophen* (III), m.p. 126°. Hot HCl–EtOH converts (III) into (II). With Br (II) gives HBr and 4-*bromo*-3-*ethoxytetraphenyl*-3 : 4-*dihydro*-2 : 5-*endosulphidothiophen*, m.p. 178°. OEt·CHPh·COPh and H_2S in HCl–EtOH or –MeOH give (I), (II), and (III); OMe·CHPh·COPh gives similarly in MeOH (I) and 3-*methoxytetraphenyl*-3 : 4-*dihydro*-2 : 5-*endosulphidothiophen*. In MeOH–HCl at 15° Bz_2 and H_2S give (I) and 3-*hydroxytetraphenyl*-3 : 4-*dihydro*-2 : 5-*endo*-*oxidothiophen*,  , m.p. 165°, converted by HI at 127° into tetraphenylthiophen. $(CPhBz{:})_2$ and H_2S in HCl–EtOH give tetraphenylfuran, m.p. 174°. CPhBz:CHBz and H_2S in HCl–EtOH give 2 : 3 : 5-*triphenyl*-2 : 5-*endo*-*oxidothiophen*, m.p. 157°, and 2 : 3 : 5-*triphenylthiophen*, m.p. 198° (formed by way of CSPh·CHPh·CH_2Bz). R. S. C.

Reduction products of hydroxyanthraquinones. XV. Green vat dyes from thiophen and 3-substituted 4-hydroxyanthranols. (The late) A. G. Perkin and N. H. Haddock (J.C.S., 1938, 541—545).—Attempted methylation (Me_2SO_4, Na_2CO_3) of 3 : 4-dihydroxyanthranol in crude $C_6H_3Cl_3$ at 190—200° gives a green *dye* (I) (R = OMe), produced from tetrachlorothiophen in the $C_6H_3Cl_3$. 4-Hydroxy-3-methoxyanthranol and tetrachloro- or tetrabromo-thiophen in boiling $C_{10}H_8$, or 4 : 4′-dihydroxy-3 : 3′-dimethoxydianthrone with Na_2CO_3 and crude $C_6H_3Cl_3$, also yield the same dye, which is oxidised ($AcOH$–H_2CrO_4) to alizarin 2-Me ether. The *Ac* derivative, m.p. 187—189°, of 1-hydroxy-2-methylanthraquinone (II) (improved prep. from 1-amino-2-methylanthraquinone) is reduced ($SnCl_2$–HCl–AcOH) to 4-hydroxy-3-methylanthrone. This, with crude $C_6H_3Cl_3$ and KOAc, yields a green *dye* [(I) R = Me], oxidised ($AcOH$–H_2CrO_4) to (II) and a *substance*, $C_{34}H_{18}O_6S$, m.p. 300—303°.


(I.)

J. D. R.

Preparation of pyrrolidines. G. H. Coleman and G. E. Goheen (J. Amer. Chem. Soc., 1938, **60**, 730).—*N*-Chloro-amines give better yields of pyrrolidines than do *N*-bromo-amines, and dil. is better than conc. H_2SO_4 as reagent. Thus NBu^{α}_2Cl and

n-C_5H_{11}·NMeCl give 73—75% yields of 1-butyl- and 1 : 2-dimethyl-pyrrolidine, respectively. R. S. C.

Catalytic transformations of heterocyclic compounds. VIII. Transformation of furanidin (tetrahydrofuran) into *N*-phenyl-, *N*-*o*-tolyl-, *N*-*p*-tolyl-, and *N*-*cyclo*hexyl-pyrrolidine. J. K. Juriev and G. A. Minkina (J. Gen. Chem. Russ., 1937, 7, 2945—2949).—Tetrahydrofuran and cyclic amines, passed over Al_2O_3 at 400°, yield *N*-phenyl-, N-*o*-*tolyl*-, b.p. 103—104°/9 mm. (*picrate*, m.p. 101·5—102°), *N*-*p*-tolyl-, and *N*-*cyclo*hexyl-pyrrolidine. R. T.

Catalytic transformations of heterocyclic compounds. IX. Synthesis of 1-phenyl-2-methylpyrrole, 1-*o*-tolyl-2-methylpyrrole, and 1-*p*-tolyl-2-methylpyrrole. J. K. Juriev (J. Gen. Chem. Russ., 1938, 8, 116—119).—2-Methylpyrrole is passed over Al_2O_3 catalyst at 475°, in a stream of H_2, together with NH_2Ph or *o*- or *p*-C_6H_4Me·NH_2; the products are 1-*phenyl*-, b.p. 118—119°/14 mm., 1-*o*-*tolyl*-, b.p. 111·5—113°/13 mm., or 1-*p*-*tolyl*-2-*methylpyrrole*, b.p. 119—121°/10 mm. R. T.

Pyrroles derived from acetonylacetone. S. J. Hazlewood, G. K. Hughes, and F. Lions (J. Proc. Roy. Soc. New South Wales, 1938, 71, 92—102).—Acetonylacetone and aromatic amines yield the following 1-substituted derivatives of 2 : 5-dimethylpyrrole : (i) at room temp. in presence of a drop of HCl, followed, if necessary, by heating at 100° for 1 to 2 hr. : *Et* (no HCl), b.p. 102°/79 mm., Ph, m.p. 51—52°; *CH*$_2$*Ph*, m.p. 48°; m-*C*$_6$*H*$_4$*Br*, m.p. 83°; p-*C*$_6$*H*$_4$*Br*, m.p. 74—75°; *m*-CO_2H·C_6H_4, new m.p. 146°; p-*CO*$_2$*H*·*C*$_6$*H*$_4$, m.p. 196—198°; p-*CO*$_2$*Et*·*C*$_6$*H*$_4$, m.p. 87—88°; p-*OMe*·*C*$_6$*H*$_4$, m.p. 65°; p-*OEt*·*C*$_6$*H*$_4$, m.p. 63°; p-*NH*$_2$·*CO*·*C*$_6$*H*$_4$, m.p. 207°; *p*-C_6H_4Me, m.p. 46°; α-, m.p. 121°, and β-*C*$_{10}$*H*$_7$, m.p. 71°; 5′-, m.p. 77°, and 8′-*C*$_9$*H*$_6$*N*, m.p. 143°; o-*xenyl*, m.p. 100°; 1 : 1′-m-, m.p. 106—107° and -p-, m.p. 253° (softens at 245°)-*phenylenebis*; 1 : 1′-(3 : 3′-*dimethyl*-4 : 4′-*diphenylene*)*bis*, m.p. 190°; or method (ii), in boiling EtOH–AcOH for 0·25 to 4 hr. : o-*C*$_6$*H*$_4$*Cl*, b.p. 135°/15 mm.; m-*C*$_6$*H*$_4$*Cl*, m.p. 50°; 2 : 5-*C*$_6$*H*$_3$*Cl*$_2$, b.p. 151—153°/16 mm.; m-, m.p. 84—85°, and p-, m.p. 145°, -*NO*$_2$·*C*$_6$*H*$_4$; m-*OH*·*C*$_6$*H*$_4$, b.p. 178°/10 mm., m.p. 58°; o-*CO*$_2$*H*·*C*$_6$*H*$_4$, m.p. 121—122°; m-*NH*$_2$·*CO*·*C*$_6$*H*$_4$, m.p. 192°; o-*OMe*·*C*$_6$*H*$_4$, m.p. 65°; o-*OEt*·*C*$_6$*H*$_4$, b.p. 140°/10 mm.; 2 : 3-(*OMe*)$_2$*C*$_6$*H*$_3$, m.p. 68°; 3 : 4-(*OMe*)$_2$*C*$_6$*H*$_3$, m.p. 54—55°; 3 : 4-(*OEt*)$_2$*C*$_6$*H*$_3$, b.p. 204—205°/34 mm.; o-*C*$_6$*H*$_4$*Me*-, b.p. 123—125°/22 mm.; *m*-C_6H_4Me, m.p. 55°; 2 : 4-*C*$_6$*H*$_3$*Me*$_2$, b.p. 136°/10 mm.; 2 : 5-*C*$_6$*H*$_3$*Me*$_2$, b.p. 121°/9 mm.; 5 : 2-*NO*$_2$·*C*$_6$*H*$_3$*Me*, m.p. 103—104°; α-*phenylethyl*, b.p. 147—149°/14 mm.; 3′-*acenaphthyl*, m.p. 92°; 3′-*fluorenyl*, m.p. 90—91°; p-*xenyl*, m.p. 65°. $CO(NH_2)_2$, *o*-NO_2·C_6H_4·NH_2, 2 : 4-$C_6H_3Cl_2$·NH_2, 2 : 4 : 6-$C_6H_2Br_3$·NH_2, *o*-NH_2·C_6H_4·CO_2Me (anthranilic acid reacts), *o*-NH_2·C_6H_4·CO·NH_2, and 6-amino-acetoveratrone do not react. A. T. P.

Exchange of hydrogen atoms between pyrrole, indole, or their methyl derivatives and water. III. Exchange of hydrogen atoms between 1-methylpyrrole and water. M. Koizumi and T. Titani (Bull. Chem. Soc. Japan, 1938, 13, 298—304; cf. A., 1938, I, 255).—1-Methylpyrrole is unchanged in dil. D_2O–H_2O at p_H >3. At lower p_H the four nuclear H are all exchanged for D slightly more readily than are those of pyrrole, in accordance with theory. R. S. C.

Exchange of hydrogen atoms between indole and water.—See A., 1938, I, 318.

Reformatsky reaction in the isatin series. F. J. Myers and H. G. Lindwall (J. Amer. Chem. Soc., 1938, 60, 644—645).—Isatin does not undergo the Reformatsky reaction and *O*-methylisatin gives tars and isatin. 1-Ethylisatin (I) with 1 mol. of CH_2Br·CO_2Et and 1 Zn gives 1-ethyloxindole and with 2 equivs. of each reagent gives a 76% yield of *Et* 3-*hydroxy*-1-*ethyloxindolyl*-3-*acetate* (II), m.p. 127—128·5°, converted by hot 50% KOH into 1-*ethyl*-2-*quinoline*-4-*carboxylic acid*, m.p. 205—206° (*Et* ester, m.p. 88·5—89°), also obtained from (*a*) (I) and $CH_2(CO_2H)_2$ in AcOH and (*b*) the *amide* of (I) and 50% KOH; this amide, m.p. 186·5—188·5°, is obtained from (I) by conc. aq. NH_3 at room temp. The 1-Me compounds behave similarly. *Et hydroxy*-1-*methylindolylacetate*, m.p. 100—101·5° (*amide*, 191·5—193·5°), is incidentally described. R. S. C.

Formation of 3-indolylacetic acid by the action of ultra-violet light on tryptophan. A. Berthelot and (Mlle.) G. Amoureux (Compt. rend., 1938, 206, 699—701; cf. A., 1937, III, 374; 1938, III, 444).—Solutions of tryptophan (0·01—0·05%) containing $AcCO_2Na$ (0·5%) and glucose (2·5%) at p_H 6·5—6·8 in quartz vessels and in absence of air when irradiated with a Hg-vapour lamp rapidly give 3-indolylacetic acid (a λ >2900 A. has no effect). At p_H 4·5 the reaction is retarded. In air, melanins are produced. Under aseptic conditions and without O_2, the reaction proceeds to some extent in 3 days in sunlight. J. L. D.

Synthesis of Δ^3-tetrahydropyridine. R. R. Renshaw and R. C. Conn (J. Amer. Chem. Soc., 1938, 60, 745—747).—4-Hydroxypiperidine (I) is obtained from 4-hydroxypyridine by Na–EtOH, but not by catalytic hydrogenation. 4-Bromopiperidine (modified prep.) and solid KOH or 4-iodopiperidine and KOH–EtOH give only (I). The Br-compound and NaOMe or NaOEt give Δ^3-*tetrahydropyridine*, unstable [*hydrochloride*, m.p. 188—189° (corr.); *platini*-, m.p. 187—189° (decomp.; corr.), and *aurichloride*, m.p. 141—142° (decomp.); *dibromide hydrochloride*, m.p. 193° (decomp.; corr.), and *platinichloride*, m.p. 216—217° (decomp.)], and 25% of 4-*methoxypiperidine* (only with NaOMe) [*hydrochloride*, m.p. 137·5—139·5° (corr.); *platinichloride*, m.p. 178—178·5° (decomp.; corr.)]. The former product with MeI–$Ba(OH)_2$ gives 1 : 1-*dimethyl*-Δ^3-*tetrahydropyridinium iodide*, m.p. 274—275° (decomp.; corr.), hydrogenated (PtO_2) to 1 : 1-dimethylpiperidinium iodide. R. S. C.

Preparation of γ-picoline. G. R. Clemo and W. M. Gourlay (J.C.S., 1938, 478—479).—2 : 4-Dimethylpyridine, PhCHO, and Ac_2O give a mixture of 2-*styryl*-4-*methylpyridine* (I), b.p. 160°/1 mm., m.p. 70° (*picrate*, m.p. 258°), and 2 : 4-*distyrylpyridine*, b.p. 250°/1 mm., m.p. 172—173°, separated by distillation.

Oxidation ($KMnO_4$) of (I) yields 4-*methylpyridine*-2-*carboxylic acid*, m.p. 136—137° (*Et* ester, b.p. 105°/1 mm., and its *picrate*, m.p. 126—127°), which when heated above its m.p. affords γ-picoline (*methiodide*, m.p. 149—150°). F. R. S.

Nicotinic acid derivatives. E. Gryszkiewicz-Trochimowski (Arch. Chem. Farm., 1937, 3, 211—214).—The 1-*methochloride*, m.p. 163—165°, *-methobromide*, m.p. 164—166°, and *-methiodide*, m.p. 157—158°, of nicotindiethylamide yield trigonelline when heated with Ag_2O in H_2O. Nicotinoyl chloride and $NHEt{\cdot}[CH_2]_2{\cdot}NEt_2$ in C_6H_6 yield the β-*diethylaminoethyl-ethylamide* of *nicotinic acid*, b.p. 193—194°/10 mm. (*dimethiodide*, m.p. 203—205°). Pyridine-4-carboxydiethylamide yields a 1-*methiodide*, m.p. 138—139°. The above new compounds are physiologically inactive. R. T.

Tautomerism of homologues of pyridine. III. Syntheses in the pyridine series. IV. Syntheses in the pyridine series. Introduction of radicals containing elements other than carbon and hydrogen. A. E. Tschitschibabin (Bull. Soc. chim., 1938, [v], 5, 429—435, 436—442).—III. The substance previously (A., 1936, 1388) termed 2-β-phenylpropylpyridine (I) was really 2-α-*phenylpropylpyridine*. γ-Picoline, $C_{16}H_{33}Cl$, and $NaNH_2$ give 4-n-*heptadecyl*-, m.p. 33°, b.p. 207—210°/2·5 mm. [*picrate*, m.p. 115° (turbid), 185—190° (clear)], and 4-α-n-*hexadecyl*-n-*heptadecyl-pyridine*, m.p. 68°, b.p. 300—310°/2·5 mm. [*picrate*, m.p. 68—70° (turbid), 185—190° (clear); *platinichloride*], the salts of which are colloidal and hydrolyse in H_2O. α-Picoline gives only 2-n-*heptadecylpyridine*, m.p. 23·5°, b.p. 206°/2·5 mm. (*picrate*, m.p. 87°); it does not react with *cyclo*pentyl chloride at room temp., and with *cyclo*hexyl chloride gives much *cyclo*hexene and a little 2-*hexahydrobenzylpyridine*, b.p. 135°/22 mm. (*platinichloride*, decomp. 183—185°). 4-*Hexahydrobenzyl*-, b.p. 266° [*picrate*, m.p. 172°; *platinichloride*, m.p. 243° (decomp.)], and 2-γ-*phenyl*-α-β′-*phenylethylpropyl-pyridine*, b.p. 212°/2·5 mm. (*picrate*, m.p. 102°), and (I), b.p. 140°/0·1 mm. (*picrate*, m.p. 108·5°), are prepared. At high temp. 2-cyclo*pentylmethylpyridine*, b.p. 231° [*picrate*, m.p. 134—135°; *platinichloride*, m.p. 184° (decomp.)], is obtained. 2 mols. of EtBr give 4-*n*-propyl- and 4-α-*ethyl*-n-*propyl-pyridine*, b.p. 200—202° (*picrate*, m.p. 105°).

IV. Condensation of picoline and lepidine with $Cl{\cdot}[CH_2]_2{\cdot}NEt_2$ and $NaNH_2$ gives 2-γ-*diethylaminopropylpyridine*, b.p. 142°/24 mm. [*dipicrate*, m.p. 151°; *platinichloride*, m.p. 206—208° (decomp.)], and 4-γ-*diethylaminopropylquinoline*, b.p. 182°/3·5 mm. [*picrate*, m.p. 138°; *dipicrate*, m.p. 192° (decomp.)]. With α-picoline $(CH_2Cl{\cdot}CH_2)_2O$ loses HCl, but some 2-γ-*ethoxypropylpyridine*, b.p. 230° (*picrate*, m.p. 80—81°), is formed; however, 4-γ-*ethoxypropyl*-, b.p. 242° (*picrate*, m.p. 61—62°), and 4-γ-*ethoxy*-α-β-*ethoxyethylpropylpyridine* (*picrate*) are formed smoothly. β-Collidine gives 3-*ethyl*-4-γ-*ethoxypropylpyridine*, b.p. 265° (*picrate*, m.p. 75°), and a *base* (*picrate*), m.p. 92°. $CH_2Cl{\cdot}CH(OEt)_2$ yields 4-γγ-*diethoxypropylpyridine*, b.p. 153°/12 mm. (*picrate*, m.p. 95°). CH_2Cl_2 and $(CH_2Cl)_2$ do not react with α-picoline, but $CHCl{:}CCl_2$ yields 2-β*γ-dichloroallylpyridine*, an oil, which rapidly polymerises, especially when heated. R. S. C.

Condensation of dihydroresorcinol with benzylideneacetophenone. B. M. Michailov (J. Gen. Chem. Russ., 1937, 7, 2950—2953).—*cyclo*Hexane-2 : 6-dione and CHPh:CHBz in piperidine (18 hr. at 100°) yield 1-(β-*benzoyl*-α-*phenylethyl*)*cyclohexane*-2 : 6-*dione*, m.p. 159—160° [*monoxime*, m.p. 200·5—202·5° (decomp.); *monosemicarbazone*, m.p. 220·5—221·5°], which with NH_2OH,HCl in EtOH (4 hr. at the b.p.) yields the *oxime*, m.p. 216·5—217°, of 5-*keto*-2 : 4-*diphenyl*-5 : 6 : 7 : 8-*tetrahydroquinoline*, which is obtained in two isomeric forms, m.p. 111—112° and 138·5—139·5°, by hydrolysis of the oxime with 25% H_2SO_4 (2 hr. at 100°). R. T.

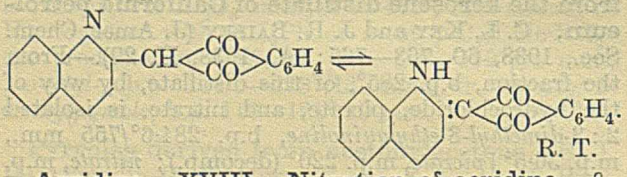
Nitrogen compounds in petroleum distillates. XI. Isolation of 2 : 3-dimethyl-8-ethylquinoline from the kerosene distillate of California petroleum. C. L. Key and J. R. Bailey (J. Amer. Chem. Soc., 1938, 60, 763—765; A., 1938, II, 29).—From the fraction, b.p. 285°, of this distillate, by way of the hydrochloride, picrate, and nitrate, is isolated 2 : 3-*dimethyl*-8-*ethylquinoline*, b.p. 284·6°/755 mm., m.p. 36·5° [*picrate*, m.p. 220° (decomp.); *nitrate*, m.p. 166°; *hydrochloride*, m.p. 212—214° (decomp.); *H sulphate*, m.p. 239—240°; *mercurichloride*, m.p. 212—214°; *chromate*, decomp. about 100°]. This is also obtained from *o*-$C_6H_4Et{\cdot}NH_2$, tiglaldehyde, and HCl at 100°, is oxidised by CrO_3 to 2 : 3-dimethylquinoline-8-carboxylic acid (decarboxylated by soda-lime to 2 : 3-dimethylquinoline), and is converted by CH_2O at 100° into 3-*methyl*-8-*ethyl*-2-ββ′-*dihydroxyisopropylquinoline*, m.p. 94—95° (*picrate*, m.p. 165·5°), which with HNO_3 gives 3-*methyl*-8-*ethylquinoline*-2-*carboxylic acid*, m.p. 84—85°, and thence 3-*methyl*-8-*ethylquinoline*, b.p. 263° (decomp.)/746 mm. (*picrate*) [also obtained in 8% yield from *o*-$C_6H_4Et{\cdot}NH_2$, EtCHO, $CH_2(OMe)_2$, and HCl]. R. S. C.

Quinoline derivatives.—See B., 1938, 486.

Direct introduction of the amino-group into the aromatic and heterocyclic nucleus. III. Action of the alkali amides on quinoline and *iso*quinoline. F. W. Bergstrom (J. Org. Chem., 1938, 2, 411—430; cf. A., 1935, 223).—Quinoline (I) in liquid NH_3 dissolves 1 mol. of $NaNH_2$ with formation of a loose mol. compound; this gradually changes into *o*-$C_6H_4{<}^{CH=CH}_{NNa{\cdot}CH{\cdot}NH_2}$ and *o*-$C_6H_4{<}^{CH(NH_2){\cdot}CH}_{NNa\text{——}CH'}$ so that decreasing amounts of (I) are recovered by treating with NH_4Cl when the solution is kept. 50% of 2- (II) and some 4-aminoquinoline (III) are obtained from (I), an excess of KNH_2, and KNO_3, KNO_2 being also formed; up to about 25% of (II) is obtained when KNO_3 is added to aged solutions of (I) and KNH_2 in NH_3. NH_2-derivatives are obtained only in presence of excess of NH_2'. Other oxidising agents or bases are ineffective. *iso*Quinoline and KNH_2 in NH_3 give a good yield of 1-amino*iso*quinoline (IV) and 80% of H_2; in presence of KNO_3 only 55% of H_2 is formed; a little (IV), but no H_2, is obtained by $NaNH_2$ or <1 mol. of KNH_2 and KNO_3 in NH_3. 2-Phenylquinoline, KNH_2, and KNO_3 give 92% of the 4-NH_2-derivative, smaller yields being obtained even if an

excess of phenylquinoline is used. Interaction of (I) and KNH_2 in presence of Hg gives 1 K as K–Hg; in other reactions nearly 2 K are liberated. The effect of Hg in general varies from case to case. $Ba(NH_2)_2$ and (I) give (II), but no (III). An ionic mechanism is also discussed. R. S. C.

Structure of quinophthalone. A. E. Porai-Koschitz, B. A. Porai-Koschitz, and S. A. Luik (J. Gen. Chem. Russ., 1938, **8**, 120—123).—2-Aminoquinoline in PhCl and *o*-$C_6H_4(CO)_2O$ (1 hr. at 60—80°) yield 2-*quinolylphthalamic acid*, m.p. 187—188°, which when heated at 205—210° for 4 hr. gives N-2-*quinolylphthalimide*, m.p. 237—238°, +EtOH, m.p. 138—139°. N-2-*Pyridylphthalimide*, m.p. 228°, is prepared analogously. These compounds are colourless; it is concluded, on the grounds of their structural similarity to quinophthalone, that this has the structure



R. T.

Acridine. XVIII. Nitration of acridine. β-, 4-, and 2-Nitroacridine. K. Lehmstedt (Ber., 1938, **71**, [*B*], 808—814; cf. A., 1937, ii, 389).—Addition of 98% HNO_3 to acridine in conc. H_2SO_4 at 50—55° and heating of the mixture at 90—95° gives small amounts of 1- and 3-nitroacridone, large quantities of 3-nitroacridine, m.p. 215·5°, small amounts of 1-*nitroacridine*, m.p. 167°, 4- (I), m.p. 154°, and 2- (II), m.p. 125—127°, -nitroacridine. The isolation of (I) can be facilitated owing of its relative resistance to oxidation by CrO_3. (I) is reduced by $SnCl_2$ and conc. HCl to 4-*aminoacridine*, m.p. 165—170° (darkening) (*hydrochloride*, decomp. 286° when brought into a bath preheated at 240°; *picrate*). 4-*Acetamidoacridine*, m.p. 225—226°, gives an orange NO_2-derivative. 3-*Acetamidoacridine*, m.p. 230°, does not give homogeneous products when nitrated. 2 : 4-$(NO_2)_2C_6H_3$·CHO is reduced ($TiCl_3$) to 4 : 2-NO_2·$C_6H_3(NH_2)$·CHO, converted by successive treatments with PhBr, Na_2CO_3, and Cu powder in boiling $PhNO_2$ and conc. H_2SO_4 into (II). H. W.

4-Aminoacridine-1-carboxylic acid. K. Matsumura (J. Amer. Chem. Soc., 1938, **60**, 591—593).—5-*Nitrodiphenylamine*-2 : 2′-*dicarboxylic acid*, m.p. 324—325° (decomp.), prepared from 4 : 2-NO_2·C_6H_3Cl·CO_2H, *o*-NH_2·C_6H_4·CO_2H, K_2CO_3, and Cu in C_5H_{11}·OH at 160°, is converted by PCl_5 into the chloride and thence with or without $AlCl_3$ into 4-*nitroacridone*-1-*carboxylic acid*, m.p. 333° (decomp.) [*chloride*, m.p. 299° (decomp.)]. This is reduced by $SnCl_2$ to 4-*aminoacridone*-1-*carboxylic acid*, m.p. 289—290°, which with HCl–AcOH affords CO_2 and 4-*aminoacridone* (I), m.p. 289—290° (uncorr.), 299—300° (corr.), and with Na–Hg–Na_2CO_3 yields 4-*aminoacridine*-1-*carboxylic acid*, m.p. 273—274° (decomp.; sinters at 268°) (*hydrochloride*, decomp. 245—250°). Aminoacridones are identified by their solubilities and fluorescence. As prepared by Ullmann's method, (I) contains some of the 2-isomeride. R. S. C.

Sulphonation of 2-nitroacridone. K. Matsumura (J. Amer. Chem. Soc., 1938, **60**, 593—595).—2-Nitroacridone and 20% oleum at room temp. give 2-*nitroacridone*-7-*sulphonic acid* (I), m.p. 325—352° [*Na*, *Na*$_2$, and p-C_6H_4Me·NH_2, m.p. 318—320° (decomp.), salts; *amide*, m.p. >360°; *Me* ester, m.p. indefinite], which with PCl_5 in PhMe gives the *chloride* (II), m.p. 289° (decomp.). 4 : 2-NO_2·C_6H_4Cl·CO_2H, *p*-NH_2·C_6H_4·SO_3H, Cu, and K_2CO_3 in H_2O at 115—120° give 5-*nitro*-2-*carboxydiphenylamine*-4′-*sulphonic acid*, m.p. 176—177° (decomp.) [*Na*, +0·5H_2O, m.p. 291—292° (decomp.), and *Ba*, +1·5H_2O, m.p. >360°, salts], which with $POCl_3$ affords (II), hydrolysed by H_2O at 130° to (I), which is further obtained from 5-nitrodiphenylamine-2-carboxylic acid and oleum. Reduction of (I) by $SnCl_2$ gives 2-*aminoacridone*-7-*sulphonic acid* (III), m.p. >360°, converted into the *hydrazino-acid*, m.p. 350° (decomp.), and thence into acridone-3-sulphonic acid. Na–Hg converts (III) into 2-*aminoacridine*-7-*sulphonic acid* (IV), m.p. >360° (*Na* salt), which with CH_2Cl·CO_2H gives 2-*carboxymethylaminoacridine*-7-*sulphonic acid*, m.p. 345—360°. *p*-NH_2·C_6H_4·AsO_3H_2 and CH_2Cl·COCl give p-*chloroacetamidophenylarsinic acid*, m.p. 295—296° (decomp.), which with (IV) yields 7-*sulpho*-2-*acridinylaminoacet*-p-*arsinoanilide*, m.p. 340—360°. R. S. C.

Medicinal products from acridine compounds. IV. Effect of changing substituents in positions 3 and 8, or of changing the amine in the side-chain, on the antimalarial activity. O. J. Magidson, A. M. Grigorovski, and E. P. Galperin (J. Gen. Chem. Russ., 1938, **8**, 56—66).—2 : 4-Dichloro-5-nitrobenzoic acid, *p*-anisidine, and K_2CO_3 and KOAc with Cu catalyst in BuOH are heated at the b.p. for 4 hr., to yield 4-*chloro*-5-*nitro*-N-p-*anisylanthranilic acid*, m.p. 223—224°, which, when heated for 3 hr. at the b.p. with $POCl_3$, affords 5 : 8-*dichloro*-7-*nitro*-3-*methoxyacridine*, m.p. 208—210°. This condenses with NH_2·CHMe·$[CH_2]_3$·NEt_2 (I) or with NH_2·$[CH_2]_3$·NEt_2 in PhOH (4 hr. at 95—100°) to 8-*chloro*-7-*nitro*-5-δ-*diethylamino*-α-*methylbutylamino*-3-*methoxyacridine dihydrochloride*, +2H_2O, m.p. 216—218° (chemotherapeutic index C.I. = 6·6), or 8-*chloro*-7-*nitro*-5-γ-*diethylaminopropylamino*-3-*methoxyacridine*, m.p. 136—138° (*hydrochloride*, m.p. 198—200°). 2 : 4-Dichlorobenzoic acid, heated for 3 hr. under reflux with *p*-C_6H_4Cl·NH_2, K_2CO_3, and Cu in BuOH, gives 4-chloro-*N*-*p*-chlorophenylanthranilic acid, converted by boiling with $POCl_3$ into 3 : 5 : 8-*trichloroacridine*, m.p. 201—203°, which with (I) in PhOH gives 3 : 8-*dichloro*-5-δ-*diethylamino*-α-*methylbutylaminoacridine dihydrochloride*, +2H_2O, m.p. 220°. 5 : 8-Dichloro-3-methoxyacridine (II) and morpholine in PhOH (3·5 hr. at 100°) yield 8-*chloro*-3-*methoxy*-5-N-*morpholinoacridine*, m.p. 222—224° (*hydrochloride*, m.p. 254—255°). γ-Chloropropylphthalimide and morpholine in xylene (7 hr. at the b.p.) give γ-N-*morpholinopropylamine*, b.p. 214—215°, condensed with (II) to give 8-*chloro*-5-γ-N-*morpholinopropylamino*-3-*methoxyacridine*, m.p. 142—144° (*hydrochloride*, +2H_2O, m.p. 250°). 5-Chloro-8-bromo-3-methoxyacridine and (I) give 8-*bromo*-5-δ-*diethylamino*-α-*methylbutylamino*-3-*methoxyacridine*,

$+2H_2O$, m.p. 85—87° [*dihydrochloride*, $+2H_2O$, m.p. 227—229° (C.I. = 7·5)]. $NHMe_2$ and Me γ-bromopropyl ketone at 0° yield *α-dimethylaminopentan-δ-one*, b.p. 168—170°, the *oxime*, b.p. 138—140°/20 mm., m.p. 55—56°, of which is reduced by Na in PhMe–BuOH to *δ-dimethylamino-α-methylbutylamine*, b.p. 167—172°; this condenses with (II) to *8-chloro-5-δ-dimethylamino-α-methylbutylamino-3-methoxyacridine dihydrochloride*, $+3·5H_2O$, m.p. 258—260° (decomp.) (C.I. = 14). 8-Chloro-3-benzoyloxyacridone in PhCl and $POCl_3$ (2 hr. at the b.p.) yield 5 : *8-dichloro-3-benzoyloxyacridine*, m.p. 196—197°, which with (I) gives *8-chloro-5-δ-diethylamino-α-methylbutylamino-3-hydroxyacridine*, an oil [*dioxalate*, $+6H_2O$, m.p. 157—161° (decomp.); C.I. = 3]. The C.I. is lowered by introducing an electronegative substituent into position 7, when 8 is occupied by an electropositive substituent, and also by changing the 3-OMe to OH. The activity is not affected by substituting NMe_2 for NEt_2 in the side-chain, or by substituting Cl for 3-OMe. R. T.

Benzacridones.—See B., 1938, 491.

Compounds of creatinine with alkali hydroxides. A. Bolliger (J. Proc. Roy. Soc. New South Wales, 1938, **71**, 40—44; cf. A., 1938, II, 77).—1 mol. of creatinine and 1·5 mols. of Na, K, or Rb hydroxides in EtOH yield mol. *compounds*: $C_4H_7ON_3$,MOH,H_2O, M = Na, turning yellow at 140° and black at 190°; K, $+2H_2O$, m.p. 89°, and Rb, $+2H_2O$, m.p. 60° (+EtOH, m.p. 35°). The Na and K compounds lose H_2O when heated in a vac. and yield alkali–creatinine *compounds*, readily rehydrated. A. T. P.

Picric acid compounds of creatinine. A. Bolliger (J. Proc. Roy. Soc. New South Wales, 1938, **71**, 60—67).—A mixture of equimol. solutions of creatinine–NaOH and picric acid appears to afford creatinine and Na picrate. Addition to this of 1, 2, 2·5—3·5, and 4—8 mols. of NaOH gives successively four additive *compounds*: $C_4H_7ON_3$,$C_6H_3O_7N_3$,2NaOH,$2H_2O$ (*A*), dehydrated under reduced pressure at 120°; 2*A*,NaOH; *A*,NaOH; and 2*A*,3NaOH, respectively; the last-named is a probable factor in Jaffe's test. A. T. P.

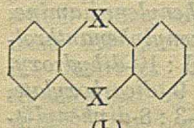
Action of mercuric acetate on peptides, diketopiperazines, and proteins. E. J. Matson, W. O. Teeters, and R. L. Shriner (J. Org. Chem., 1938, **2**, 403—410).—2 : 5-Diketopiperazine (modified prep.) with an excess of $Hg(OAc)_2$ in 0·5% AcOH gives the 1 : 4-$(HgOAc)_2$-derivative, decomp. 390—400° (block), which with an equiv. of HCl gives the $(HgCl)_2$-derivative, m.p. 385—395° (decomp.). With smaller amounts of $Hg(OAc)_2$ mixtures of HgOAc- and $(HgOAc)_2$-derivatives are formed. 2 : 5-Diketo-3 : 6-dimethyldiketopiperazine (modified prep.) gives similarly the 1 : 4-$(HgOAc)_2$-derivative, decomp. 390—400° (block). These Hg compounds are insol., with NaOH give HgO, and with $(NH_4)_2S$ give HgS. Glycylglycine, however, is hydrolysed and oxidised with liberation of Hg. Casein, gelatin, and silk fibroin react only slowly. Casein gives a ppt. containing Hg and casein; gelatin and silk fibroin give mainly Hg. These proteins thus probably do not contain diketopiperazine groups. R. S. C.

Behaviour of peptides when heated in β-naphthol. N. Lichtenstein [with S. Hestrin, E. Dimant, and H. Brzoza] (J. Amer. Chem. Soc., 1938, **60**, 560—563).—When heated in β-$C_{10}H_7$·OH (5 pts.) at 135—150° polypeptides, NH_2·CHR·CO·NH·CHR′·COR″, give $NH<\begin{matrix}CHR'\cdot CO\\CO-CHR\end{matrix}>NH$ and HR″. Thus, dipeptides (6 examples) give only diketopiperazines; tripeptides (6 examples) give diketopiperazines with the free NH_2-acids from the terminal acid unit; a tetrapeptide, *dl*-leucyldiglycyl-*dl*-leucine, gives only the cyclic *dl*-leucylglycine anhydride, because the dipeptide liberated as HR″ undergoes self-condensation. Benzoylation of the free NH_2 prevents the reaction (4 examples), and glycylglycine, which is insol. in β-$C_{10}H_7$·OH, undergoes no change. Edestin and ovalbumin give mainly cryst. products, which, since they are insol. in abs. EtOH, are not simple diketopiperazines. R. S. C.

Nickel catalyst; hydrogenation of 4-amino-5-cyano-2-methylpyrimidine. M. Delépine (Compt. rend., 1938, **206**, 866—869).—During hydrogenation (Raney Ni in NH_3–MeOH) of 4-amino-5-cyano-2-methylpyrimidine to the corresponding 5-NH_2·CH_2 compound, a deposit is formed on the Ni, considered to be a *complex* (I) of Ni and the 5-CHO-derivative (II); (I) is decomposed by boiling aq. AcOH to (II), reconverted into (I) by heating with Ni^{III} salts in aq. NH_3. The mechanism of formation of (I) [(II) and NH_3 yield the 5-NH:CH derivative, converted by NiO into (I); (II) and H_2 give the 5-OH·CH_2 compound] and modifications in procedure [H_2–Ni–H_2O–MeOH–NH_3–$NiCl_2$,$6H_2O$] to prevent complex formation are recorded. A. T. P.

Pyrimidines.—See B., 1938, 489.

Configuration of heterocyclic compounds. VIII. Configuration of anthracene, 9 : 10-dihydroanthracene, phenazine, 9 : 10-dimethyl-9 : 10-dihydrophenazine, thianthren, and selenanthren. (Miss) I. G. M. Campbell, (Mrs.) C. G. Le Fèvre, R. J. W. Le Fèvre, and E. E. Turner (J.C.S., 1938, 404—409).—Theoretical considerations show that a mol. (I) will be least strained when it is folded, provided that the atom or group X prefers a valency angle approximating to the tetrahedral angle. 9 : 10-Dihydroanthracene (X = CH_2) should be folded, and its dipole moment is not 0, but is of the same order as that of dibenzyl. Dipole moments of anthracene, phenazine, thianthren, and selenanthren are also given, whilst that of 9 : 10-dimethyl-9 : 10-dihydrophenazine (X = NMe) could correspond with folding of the mol. about the X–X axis and a certain disposition of the N·Me bonds. The stereoisomerism of anthracene derivatives (Schlenk *et al.*, A., 1928, 1031) is discussed. F. R. S.



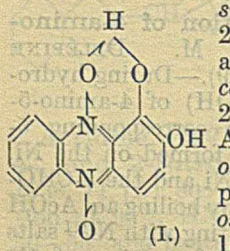
(I.)

Phenazine series. I. Oxidation of phenazine. Z. V. Puschkareva and G. I. Agibalova. **II. Oxidation of monoacetyldihydrophenazine.** Z. P. Puschkareva and I. J. Postovski (J. Gen. Chem. Russ., 1938, **8**, 151—157, 158—163).—I.

Phenazine is oxidised by alkaline $KMnO_4$ to quinoxaline-2 : 3-dicarboxylic acid, and by BzO_2H to *phenazine* 5 : 10-*dioxide*, m.p. 202—203°. *o*-Toluidine when boiled with $NaNH_2$ in $PhNO_2$ yields 1-*methylphenazine* 5-*oxide*, m.p. 142°, whilst *o*-$C_6H_4Me{\cdot}NO_2$ and NH_2Ph give 4-*methylphenazine* 5-*oxide*, m.p. 157—158°.

II. 5-Acetyldihydrophenazine (I) in $CHCl_3$ and $FeCl_3$ give a dark violet co-ordination *compound* of 5-acetyldihydrophenazyl with (I), m.p. 137°. This compound is converted into *bis*-5-*acetyldihydrophenazyl*, m.p. 193—194°, when recrystallised from $C_5H_{11}{\cdot}OH$. R. T.

Phenazine series. VII. Pigment of *Chromobacterium iodinum*; the phenazine di-*N*-oxides. G. R. Clemo and H. McIlwain (J.C.S., 1938, 479—483).—By extraction with H_2O, the *pigment* (I), $C_{12}H_8O_4N_2$, m.p. 236° (decomp.), has been isolated as purple crystals. Reduction (PtO_2–H_2) of (I) gives a

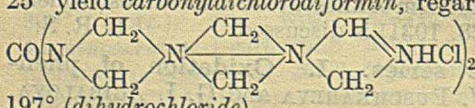


(I.)

substance, $C_{12}H_8O_2N_2$, m.p. 273—274°, converted (Zn) into phenazine. With Ac_2O, (I) affords a *compound*, $C_{12}H_6O_2N_2Ac_2$, m.p. 234°. Phenazine and H_2O_2 in AcOH yield *phenazine di-N-oxide*, m.p. 204°, and 1-hydroxyphenazine similarly gives 1-*hydroxyphenazine di-N-oxide*, m.p. 189—190°. Absorption spectra comparisons indicate that (I) is probably 1 : 2-*dihydroxyphenazine di-N-oxide*. F. R. S.

Di-imidochlorides. I. Synthesis of derivatives of 6 : 6′-diquinolyl and phenanthroline from di-imidochlorides. H. K. S. Rao and T. S. Wheeler (J.C.S., 1938, 476—478).—Dibenzbenzidide-di-imidochloride and Et sodiomalonate give NN′-*bis*-(α-*dicarboxymethylbenzylidene*)*benzidine*, m.p. 189°, cyclised by heating at 200° to *Et* 4 : 4′-*dihydroxy*-2 : 2′-*diphenyl*-6 : 6′-*diquinolyl*-3 : 3′-*dicarboxylate*, m.p. >300° (*acid*, m.p. >300°), which with HCl (sealed tube) affords 4 : 4′-*dihydroxy*-2 : 2′-*diphenyl*-6 : 6′-*diquinolyl*, m.p. >300°. Similar condensation products of the di-imidochlorides derived from *m*- and *p*-$C_6H_4(NH_2)_2$ are NN′-*bis*-(α-*dicarbethoxymethylbenzylidene*)-m-, m.p. 131°, and -p-*phenylenediamine*, m.p. 186°, *Et* 1 : 7-*dihydroxy*-3 : 9-*diphenylphenanthroline*-2 : 8-*dicarboxylate*, m.p. 264°, *Et* 1 : 10-*dihydroxy*-3 : 8-*diphenyl*-ψ-*phenanthroline*-2 : 9-*dicarboxylate*, m.p. 218°, and 1 : 10-*dihydroxy*-3 : 8-*diphenyl*-ψ-*phenanthroline*, m.p. >300°. These compounds have been formulated as OH-compounds, but are probably tautomeric. F. R. S.

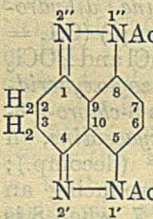
Action of carbonyl chloride on hexamethylenetetramine. M. Dominikiewicz (Arch. Chem. Farm., 1937, 3, 248—254).—$(CH_2)_6N_4$ in $CHCl_3$ and $COCl_2$ at 25° yield *carbonyldichlorodiformin*, regarded as being



m.p. 196—197° (*dihydrochloride*). R. T.

Intermediate forms of oxidation–reduction of flavins.—See B., 1938, III, 527.

Pyrazolo-tetrahydronaphthalenes. V. Veselý and T. Stojanova (Coll. Czech. Chem. Comm., 1938, **10**, 142—147).—5-Acetamido-, 8-nitro-5-acetamido-, and 5 : 8-diacetamido-tetrahydronaphthalenes and N_2O_3 in AcOH give the *N*-nitrosoacetamido-derivatives, converted by boiling C_6H_6 into *pyrazolo*-, m.p. 120—121° (*Ag* salt; *picrate*, m.p. 212—212·5°), 8-

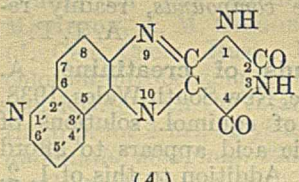


(IV.)

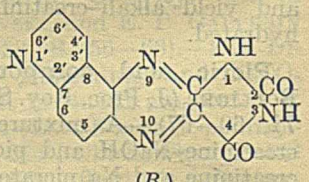
nitropyrazolo-, m.p. 242° [8-NH_2-compound (Fe–AcOH), m.p. 247—248°; 8-*acetamido*-1′-*acetyl* derivative (I), m.p. 221—222°], and *dipyrazolo*- (II), m.p. 253—254° (*Ag* salt; *picrate*, blackens at 275°, m.p. >300°) -*tetrahydronaphthalenes*. (I) gives similarly a nitrosoamine, converted into the 1′-*acetyldipyrazolo*-derivative (III), m.p. >300° [1′ : 1″-Ac_2 derivative (IV), m.p. 268—269°]; (III) or (IV) and EtOH–KOH give (II). A. T. P.

Reaction between disodium phthalocyanine and methyl alcohol. C. E. Dent (J.C.S., 1938, 546—547).—The elimination of Na from Na_2 phthalocyanine rapidly and completely appears to be sp. for MeOH; the reaction can be followed under a microscope with minute quantities. F. R. S.

Pyridinoalloxazines and alloxanaminoquinolylimide. H. Rudy (Ber., 1938, **71**, [*B*], 847—857).—5 : 6-Diaminoquinoline (I) (prep. from 6-nitroquinoline described) condenses with alloxan in boiling AcOH–conc. HCl to a mixture of *pyridino*-3′ : 2′ : 5 : 6-(or



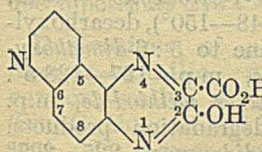
(*A*.)



(*B*.)

2′ : 3′ : 7 : 8-)*alloxazine* (*A* or *B*), gradual decomp. >410°. The isomeric 1 : 3-*dimethylpyridino*-3′ : 2′-5′ : 6′- or -2′ : 3′-7 : 8-*alloxazines*, m.p. 375° and m.p. 264°, respectively (the formulæ cannot at present be allocated to the respective isomerides), are derived from (I) and dimethylalloxan. Use of the $NaHSO_3$ compound of the latter leads exclusively to the form of m.p. 375°; the variety of lower m.p. is obtained in subsidiary amount only in presence of mineral acid or when $ZnCl_2$–AcOH is used as condensing agent. From methylalloxan four isomeric monomethylalloxazines are possible. Their isolation has not been attempted but the crude product of the reaction is readily divisible into two portions, one of which has m.p. 380° whereas the other decomposes slowly between 370° and 450°. The pyridinoalloxazines closely resemble the alloxazines obtained from isocyclic bases. When a free NH is present they give dark yellow salts in dil. alkali; these give an intense green fluorescence in ultra-violet light and are very suitable for detection. The green fluorescence is also observed in daylight with very dil. solutions in alkali, NH_3, or aq. C_5H_5N; in anhyd. C_5H_5N there is no fluorescence. Reduction with Zn and conc. HCl proceeds through a radical-like intermediate phase. Reversible reduction occurs with neutral $Na_2S_2O_4$.

The pyridinoalloxazines are very stable towards alkali. In neutral solution at room temp. (I) and alloxan afford *alloxanaminoquinolylimide*, m.p. 353° (decomp.) (*Na* and *Ag* salts). Its solutions have a greenish-yellow fluorescence in ultra-violet light; this is extinguished by mineral acid or alkali hydroxide. In aq. Na_2CO_3 an intense blue-green fluorescence is visible in daylight. It is converted by the short action of boiling NaOH into (probably) 2-*hydroxypyridino*-3′ : 2′-5 : 6-*quinoxaline*-3-*carboxylic acid*, m.p. 320°, also obtained from (I) and $CO(CO_2H)_2$ in faintly acid solution. Contrary to Kühling, the formation of alloxazines does not occur exclusively from the salts with mineral acids but also from the free base particularly if the temp. is raised. Mineral acids are not essential but helpful since they promote the exclusive formation of alloxazines without other reaction products. H. W.



(*C.*)

***N*-Aralkylmorpholines.** M. T. Leffler and E. H. Volwiler (J. Amer. Chem. Soc., 1938, **60**, 896—899).—1-Benzylmorpholines have local anæsthetic action similar to that of procaine and are less toxic. The 4′-Br-derivative is most effective and its solution can be sterilised. Nitration of $Ph{\cdot}[CH_2]_3{\cdot}Br$ gives *γ*-p-*nitrophenylpropyl bromide*, b.p. 152—156°/2 mm. *o*-$OBu{\cdot}C_6H_4{\cdot}NO_2$, $(CH_2O)_3$, $ZnCl_2$, and HCl in light petroleum at 85° give 3-*nitro*-4-*butoxybenzyl chloride*, b.p. 162—165°/4 mm. o-*Butoxybenzyl chloride*, b.p. 102—103°/4 mm., is prepared from the alcohol and anhyd. HCl at 5—10°, and 3-*bromo*-4-*butoxybenzyl chloride*, b.p. 135—140°/3 mm., from 1 : 3 : 4-$C_6H_3MeBr{\cdot}OBu$ and Cl_2 in light at 170°. Condensation of the aralkyl halide with morpholine or its 2 : 6-Me_2 derivative yields 1-*o*-, b.p. 160—163°/4 mm., and -p-*nitro*-, m.p. 79—80°, -3′-*nitro*-4′-*butoxy*-, b.p. 162—164°/3 mm., -o- (*hydrochloride*, m.p. 216—217°), and -p-*bromo*- (I), b.p. 138—142°/4 mm., m.p. 83—84° [*hydrochloride*, m.p. 280° (block)], -p-*chloro*-, m.p. 68—69° [*hydrochloride*, m.p. 258° (block)], -3′-*bromo*-4′-*butoxy*-, b.p. 185—188°/3 mm. (*hydrochloride*, m.p. 183·5—184·5°), and -o-*butoxy-benzylmorpholine* (*hydrochloride*, m.p. 159·5—160·5°), 1-p-*nitrobenzyl*-, b.p. 163—165°/3 mm., m.p. 66—67°, -*benzyl*-, b.p. 102—104°/3 mm. (*hydrochloride*, m.p. 184—185°), -p-*chlorobenzyl*- (*hydrochloride*, m.p. 189—190°), and -*cinnamyl*-2 : 6-*dimethylmorpholine*, b.p. 140—142°/3 mm., 1-β-p-*nitrophenylethyl*-, b.p. 260°/740 mm., 1-*γ*-p-*nitrophenylpropyl*-, b.p. 175—178°/2 mm., 1-α- (*hydrochloride*, m.p. 211—212°), and -β-*phenylethyl*-, b.p. 107—108°/3 mm. [*hydrochloride*, m.p. 238° (block)], 1-*γ*-*phenylpropyl*-, b.p. 113—115°/2 mm. (*hydrochloride*, m.p. 138—139°), 1-*cinnamyl*-, b.p. 132—134°/3 mm. [*hydrochloride*, m.p. 216° (block)], and 1-α-*naphthylmethyl-morpholine* (*hydrochloride*, m.p. 234—235°). Reduction of the NO_2-compounds by Fe–H_2O affords 1-o-, b.p. 150—152°/4 mm., and -p-*amino*- (II), m.p. 100·5—101·5° (*hydrochloride*, m.p. 188—190°), and 1-3′-*amino*-4′-*butoxy-benzylmorpholine* (*hydrochloride*, m.p. 199·5—200·5°), 1-p-*aminophenylethyl*-, m.p. 80·5—81·5°, and 1-*γ*-p-*aminophenylpropyl-morpholine*, b.p. 156—160°/2 mm. (*hydrochloride*, m.p. 195—196°), and 1-p-*aminobenzyl*-2 : 6-*dimethylmorpholine*, b.p. 160—162°/2 mm. [*hydrochloride*, m.p. 214° (block)]. Passage of Br–air through (I) in H_2O gives 2 : 4 : 6-$C_6H_2Br_3{\cdot}NH_2$, but Br–AcOH yields 1-3′ : 5′-*dibromo*-4′-*aminobenzylmorpholine*, m.p. 62—63° (*hydrochloride*, m.p. 260°). With BuBr at 50—90° (II) gives 1-p-n-*butylaminobenzylmorpholine* (*hydrochloride*, m.p. 180—182°). With H_2SO_4–HNO_3 (I) gives an oily NO_2-derivative, reduced to 1-4′-*bromo*-3′-*aminobenzylmorpholine*, m.p. 102—103°. R. S. C.

Derivatives of 6 : 7-dimethoxybenzoparathiazine. K. J. Baldick and F. Lions (J. Proc. Roy. Soc. New South Wales, 1938, **71**, 112—117).—4 : 5-Dimethoxy-thiophenol and $CH_2Cl{\cdot}CO_2Na$ in 25% aq. NaOH at 50° afford the -*phenylthioglycollic acid* (I), m.p. 106°, which with HNO_3 (*d* 1·42) in AcOH at 20° gives the 2-*NO*$_2$-derivative (II), m.p. 222°, converted by Sn–HCl into 3-*ketodihydro*-6 : 7-*dimethoxybenz*-1 : 4-*thiazine* (III), m.p. 186—187°. (I) and HNO_3 (*d* 1·4) in AcOH at 100° or (II) and 3% H_2O_2 in boiling AcOH give 2-*nitro*-4 : 5-*dimethoxyphenylsulphinylacetic acid*, m.p. 203°, oxidised, as also is (II), with $KMnO_4$ in aq. $MgSO_4$ at 10—15° to the -*sulphonylacetic acid*, m.p. 200°, which with Sn–HCl yields 3-*ketodihydro*-6 : 7-*dimethoxybenzoparasulphazone* [2-*oximino*-3-*keto*-6 : 7-*dimethoxy*-2 : 3-*dihydrobenz*-1 : 4-*thiazine* 1 : 1-*dioxide*] (IV) (+H_2O, removed at 110° in a vac. with P_2O_5), m.p. 233—234° [*NO*-derivative, decomp. 195—200°; 2-(*azo*-α-*naphthalene*-5-*sodium sulphonate*) derivative]. (III) and (IV) do not condense with acenaphthenequinone; (IV) did not react with PhCHO. A. T. P.

Reactions of methylene-blue with metallic salts. II. R. Ralea (Ann. Sci. Univ. Jassy, 1938, **24**, 157—162).—Interaction of $2RCl,CdI_2$ (R = $C_{16}H_{18}N_3S$) with $HgCl_2$ in boiling H_2O gives the *salt*, $2RCl,HgI$, transformed by aq. $K_2S_2O_8$ into the *compound*, $R_2S_2O_8,HgI_2$. Methylene-blue (I) is converted by $K_3Co(CN)_6$ and $K_3Co(NO_2)_6$, respectively, into the *substances* $R_3Co(CN)_6$ and $R_3Co(NO_2)_6$. Excess of $K_2Cd(CN)_4$ and (I) afford the *salt*, $R_2Cd(CN)_4$ whilst NH_4CNS and $2RCl,CdCl_2$ yield the *compound*, $R_2Cd(SCN)_4$. R·CNS and $CdCl_2$ or $CdBr_2$ respectively yield the *substances*, $2RCl,CdCl_2$ (II) and $2RCl,CdBr_2$, which differ somewhat from those derived directly from the components. An excess of boiling aq. KI converts (II) into the substance, $2RI,CdCl_2$, transformed by $HgCl_2$ into the product, $RI,2HgCl_2$, which is unchanged by $K_2S_2O_8$. Treatment of (II) with an equiv. of aq. KI gives the isomeric *salt*, $2RCl,CdI_2$, which with $HgCl_2$ affords a green product, transformed by $K_2S_2O_8$ into the *salt*, $R_2S_2O_8,HgI_2$. The constitution of the additive compounds is uncertain. H. W.

Cytisine. VI. Synthesis of 8-keto-2 : 4-dimethyl-*ψ*-quinolizine, a degradation product of cytisine. E. Späth and F. Galinovsky (Ber., 1938, **71**, [*B*], 721—724; cf. A., 1936, 741).—*Et* 3 : 5-*dimethylpicolinate* (I), b.p. 90—100° (bath)/0·01 mm. (*picrate*, m.p. 111—112°), condenses with Et_2 succinate and EtOH-free NaOEt in C_6H_6 to *Et* β-3 : 5-*dimethyl*-2-*pyridoylpropionate*, m.p. 68—69°, reduced (Clemmensen) to *Et* *γ*-3 : 5-*dimethyl*-2-*pyridylbutyrate*, b.p.

90° (bath)/0·01 mm., which is hydrolysed and then hydrogenated (PtO_2) to *γ*-3 : 5-*dimethyl*-2-*piperidylbutyric acid hydrochloride*, m.p. 194—196° (vac.). This is esterified and then heated at 200°, whereby 8-*keto*-2 : 4-*dimethyloctahydroquinolizine* (II), b.p. 160° (bath)/10 mm., is obtained. Dehydrogenation of (II) by Pd-sponge at 270—280° gives 3 : 5-dimethyl-2-propylpyridine (III) and 8-keto-2 : 4-dimethyl-*ψ*-quinolizine, identical with the degradation product from cytisine. Condensation of (I) with $EtCO_2Et$ and EtOH-free NaOEt in C_6H_6 yields 3 : 5-*dimethyl*-2-*pyridyl Et ketone*, b.p. 120° (bath)/10 mm., m.p. 45—46°, reduced (Zn–Hg and 8N-HCl) to some (III) with a larger proportion of 3 : 5-*dimethyl*-2-*pyridylethylcarbinol*, b.p. 110—120° (bath)/10 mm. (*picrate*, m.p. 116—117°). The latter is transformed by P_2O_5 in boiling PhMe into 3 : 5-*dimethyl*-2-*propenylpyridine*, b.p. 90—100°/10 mm. [*picrate*, m.p. 179—180° (vac.)], hydrogenated (Pd-sponge in AcOH) to (III). H. W.

Syntheses of new antimalarials. III. Lupinine derivatives. I. L. Knunianz and Z. V. Benevolenskaja (J. Gen. Chem. Russ., 1937, **7**, 2930—2933).—8-Amino-6-methoxyquinoline and chlorolupinan (I) (8 hr. at 170—180°) yield 8-*lupinylamino*-6-*methoxyquinoline* (II), b.p. 242—245°/2 mm. (*trihydrochloride*, $+5H_2O$, m.p. 140—142°). (I) and 3-amino-5-methoxy-1-methylbenzthiazole (10 hr. at 180—190°) afford 3-*lupinylamino*-5-*methoxy*-1-*methylbenzthiazole* (III), b.p. 250—260°/3 mm. (*dihydrochloride*, m.p. 216—218°). 5 : 7-Dichloro-3-methoxyacridine in PhOH and aminolupinan (2 hr. at 100°) yield 7-*chloro*-5-*lupinylamino*-3-*methoxyacridine* (IV), m.p. 140° [*dihydrochloride*, $+3H_2O$, m.p. 283° (decomp.)]. (II) and (IV), but not (III), are powerful antimalarials. R. T.

Alkaloid from *Dephinium brownii*, Rydb. R. H. F. Manske (Canad. J. Res., 1938, **16**, B, 57—60).—Extraction of the dried aërial portion of the plant with MeOH leads to the isolation of about 0·5% of a non-cryst. alkaloid (I) which does not give cryst. salts with HCl, H_2SO_4, AcOH, $H_2C_2O_4$, citric acid, $HClO_4$, or H_3PO_4. Hydrolysis of (I) by KOH yields a cryst. *base*, $C_{20}H_{37}O_7N$ or $C_{23}H_{39}O_7N$ (possibly $C_{20}H_{33}O_6N$), m.p. 120—121° after considerable softening, $[\alpha]_D^{22}$ +52·2° in MeOH, in which 3 or 4 OMe are probably present. Mannitol, *o*-$NH_2{\cdot}C_6H_4{\cdot}CO_2H$, and methylsuccinic acid are also identified. H. W.

Electrolytic reduction of morphine and codeine. S. Takagi and T. Ueda (J. Pharm. Soc. Japan, 1936, **56**, 44—53).—Electrolysis with morphine dissolved in 10% HCl in a divided cell as catholyte (Pt cathode) and 10% H_2SO_4 as anolyte (Pd anode) gave an 89% yield of dihydromorphine hydrochloride at a c.d. of 4 amp. per sq. dm. Reduction of codeinephosphoric acid under similar conditions gave a 97% yield of dihydrocodeinephosphoric acid at c.d. 4 amp. per sq. dm. Ch. Abs. (*e*)

Hofmann degradation of domesticine ethers. H. Shishido (Bull. Chem. Soc. Japan, 1938, **13**, 247—252).—The structure of domesticine is confirmed by the identity of the degradation products of its ethers with those of synthetic ethers. Natural *d*-domesticine Me ether gives a *methiodide*, m.p. 105—107°, decomp. 117°, converted by KOH into the *methine* [*de*-N-*Me* base], m.p. 133—134°, the *methiodide*, m.p. 294—295° (decomp.), of which gives the methochloride and thence, by 10% KOH–NMe_3, 3 : 4-*dimethoxy*-6 : 7-*methylenedioxy*-1-*vinylphenanthrene* (I), m.p. 142—143°, and a (?) *polymeride*, m.p. about 250—270° (decomp.). $KMnO_4$ oxidises (I) to 3 : 4-*dimethoxy*-6 : 7-*methylenedioxyphenanthrene*-1-*carboxylic acid*, m.p. 252—253° (*Me* ester, m.p. 148—150°), decarboxylated by Cu in boiling quinoline to 5 : 6-*dimethoxy*-2 : 3-*methylenedioxyphenanthrene*, m.p. 127—128·5°. Synthetic dl-*domesticine Me ether methiodide*, m.p. 230—232°, gives the same degradation products. dl-*Domesticine Et ether methiodide*, m.p. 225—227° (decomp.), gives the *methine* [*de*-N-*Me* base], m.p. 133—134·5°, the *methiodide*, m.p. 290—291° (decomp.), of which affords 3-*methoxy*-4-*ethoxy*-6 : 7-*methylenedioxy*-1-*vinylphenanthrene*, m.p. 114—115·5° [with NMe_3 and a *polymeride*, m.p. 250—260° (decomp.)], 3-*methoxy*-4-*ethoxy*-6 : 7-*methylenedioxyphenanthrene*-1-*carboxylic acid*, m.p. 243—245°, and 6-*methoxy*-5-*ethoxy*-2 : 3-*methylenedioxyphenanthrene*, m.p. 134—135°. The *d*-Et ether affords the same products. dl-iso*Domesticine Et ether methiodide*, m.p. 224—226° (decomp.), affords the *methine* [*de*-N-*Me* base], m.p. 117—118° [*H oxalate*, m.p. 195—197° (decomp.)], the *methiodide*, m.p. 289—290° (decomp.), thereof, 4-*methoxy*-3-*ethoxy*-6 : 7-*methylenedioxy*-1-*vinylphenanthrene*, m.p. 119—120·5° [with NMe_3 and a *polymeride*, m.p. 240—250° (decomp.)], 4-*methoxy*-3-*ethoxy*-6 : 7-*methylenedioxyphenanthrene*-1-*carboxylic acid*, m.p. 235—236·5° [with a neutral *substance*, m.p. 280—282° (decomp.)], and 5-*methoxy*-6-*ethoxy*-2 : 3-*methylenedioxyphenanthrene*, m.p. 126—128°. R. S. C.

Amides of *p*-arsonophenylacetic acid. E. Walton (J.C.S., 1938, 471—472).—*Me* p-*arsonophenylacetate* [*Na* salt ($+H_2O$)], from the corresponding acid, with the appropriate amine gives *phenylacetamide*- (*NH*$_4$ salt), *phenylaceto-methyl*- [*Na* salt ($+H_2O$)], *-dimethyl*- (*Na* salt), *-ethyl*- (*Na* salt), *-n-propyl-amide*- (*Na* and n-*propylamine* salts), and *-piperidide*- (*Na* salt), and *phenylacetanilide*-p-*arsinic acid* (*Na*$_2$ salt). The Na salts show trypanocidal activity. F. R. S.

Constitution and action of aromatic arsinic acids. I. K. Burschkies and M. Rothermundt (Arch. Pharm., 1938, **276**, 226—234).—The therapeutic activity of 4-amino- and 4-amino-2-hydroxyphenylarsinic acid is lessened by the introduction of higher acid residues of the homologous acyl series. The following compounds are prepared from the requisite arsinic acid, 2N-NaOH, and the required acid anhydride : 4-n-*propionamido*-, m.p. 232—233° (decomp.); 4-n-*valeramido*-, m.p. 227—228°; 4-iso*valeramido*-, m.p. 232°, -2-*hydroxyphenylarsinic acid*; 3-*dipropionamido*-, m.p. 182°; 3-iso*butyramido*-, m.p. 194—195°; 3-n-*valeramido*-, m.p. 208—209°; 3-iso*valeramido*-, m.p. 226—227°, -4-*hydroxyphenylarsinic acid*. 4-*Carbethoxyamido*-2-*hydroxyphenylarsinic acid*, m.p. 220—221°, is transformed by conc. H_2SO_4 and HNO_3 (*d* 1·52) at −5° into 3-*nitro*-4-*carbethoxyamido*-2-*hydroxyphenylarsinic acid*, decomp. 240°, reduced by $Na_2S_2O_4$ to 3-*amino*-4-*carbethoxy*-

amido-2-hydroxyphenylarsinic acid, decomp. 170°. 3-*Carbethoxyamido-4-hydroxyphenylarsinic acid* has m.p. 210—211°. 3-Acetamido-4-hydroxyphenylarsinic acid is nitrated [conc. H_2SO_4 and HNO_3 (*d* 1·52) at —10°] to 5-*nitro*-3-*acetamido*-4-*hydroxyphenylarsinic acid*, m.p. 218—220°, reduced to 5-*amino*-3-*acetamido*-4-*hydroxyphenylarsinic acid*. 4-o-*Hydroxybenzylideneamino*-2-*hydroxyphenylarsinic acid* decomposes at 210°. H. W.

Derivatives of *p*-arsanilic acid. VIII. *p*-Arsono-oxanilic and *p*-arsonohexadecanedicarboxylanilic acids and related compounds. (SIR) G. MORGAN and E. WALTON (J.C.S., 1938, 442—444).—*Me* p-*arsono-oxanilate*, from the corresponding acid (*Et* ester, dimorphous), with conc. aq. NH_3 gives *oxanilamide*-p-*arsinic acid* (*Na* salt), and with the appropriate amine yields *oxanilo-methyl-* [*Na* salt (+$2H_2O$)], *-dimethyl-* [*Na* salt (+H_2O)], *-ethyl-* [*Na* salt (+H_2O)], and -n-*propyl-amide-* (*Na* salt), and *-piperidide*-p-*arsinic acid* [*Na* salt (+H_2O)], and *oxanilide*-p-*arsinic acid* [Na_2 salt (+H_2O)]. *p*-Arsono-oxanilic acid forms three NH_2Ph salts, corresponding with acid : base, 1 : 2, 1 : 1, and 2 : 1. The trypanocidal activity of this series is more or less true to type, whilst their toxicity is greater. Hexadecanedicarboxylic acid and $SOCl_2$, followed by Na *p*-arsanilate, give p-*arsonohexadecanedicarboxylanilic acid* (*Na* salt) and *hexadecanedicarboxylanilide*-pp'-*diarsinic acid*. Me hexadecane-αω-dicarboxylate and KOH afford *Me H hexadecane-αω-dicarboxylate*, m.p. 72—74°, which with $SOCl_2$ yields the acid *chloride*, not convertible into the Me ester. The free acid with MeOH and H_2SO_4 (trace) gives crude *Me* p-*arsonohexadecanedicarboxylanilate*. F. R. S.

Arsenicals containing the furan nucleus. III. β-Substituted furan arsenicals. H. W. BECK and C. S. HAMILTON (J. Amer. Chem. Soc., 1938, **60**, 620—621; cf. A., 1936, 217).—3-Chloromercurifuran and $AsCl_3$ (0·33 mol.) in C_6H_6 give 36% of *tri*-3-*furylarsine*, an oil, and 28% of the $HgCl_2$ additive *compound*, m.p. 152—153°, thereof, the latter product being obtained in 70% yield by $AsCl_3$ (1 mol.) in EtOH. *Me* 5-*bromo*-4-*chloromercuri*-2-*furoate* (prep. by way of the *OAc*-derivative, m.p. 198—199°), m.p. 238°, does not react with $AsCl_3$, but with $AsBr_3$ gives 5-*bromo*-2-*carbomethoxy*-4-*furyldibromoarsine* (I), m.p. 95—96°. *Et* 5-*bromo*-4-*acetoxy-*, m.p. 188—189°, and *-4-chloro-mercuri*-2-*furoate*, m.p. 162°, and 5-*bromo*-2-*carbethoxy*-4-*furyldibromoarsine*, m.p. 52—53°, are similarly obtained from Et 5-bromo-2-furoate. The As·C linking of (I) resists $HgCl_2$ or I, but long heating with H_2O gives Me 5-bromo-2-furoate. 3-Furylarsines are more stable than the 2-analogues. R. S. C.

Constitution of organo-magnesium solutions. T. R. BEYER (Kimya Annali, 1937, **2**, No. 14, 16—22; No. 15, 18—34).—I. A review of the literature. —II. A new theory postulates the presence of α- and β-etherates, $(RMgX)_2[OEt_2]_x$, the relative proportions depending on R. The mechanism of the reaction with aldehydes and esters is formulated. The etherates differ from each other in the disposition of valencies. F. R. S.

Reactions between mercury diaryls and selenium tetrabromide. H. M. LEICESTER (J. Amer. Chem. Soc., 1938, **60**, 619—620).—$HgPh_2$, $Hg(C_6H_4Me\text{-}p)_2$, $Hg(C_{10}H_7\text{-}\beta)_2$, and $Hg(C_6H_4Ph)_2$ with $SeBr_4$ (0·33 mol.) give excellent yields of diarylselenides, aryl bromide, and Hg aryl bromide. With more $SeBr_4$ further change occurs thus: $SeBr_4 + 3HgArBr \rightarrow Ar_2Se + ArBr + 3HgBr_2$, a reaction realised separately with HgPhBr. R. S. C.

Reaction of tin and of tin–sodium alloy with mercury- and tin-organic salts, with the object of synthesising highly arylated tin-organic compounds. M. M. NADJ and K. A. KOTSCHESCHKOV (J. Gen. Chem. Russ., 1938, **8**, 42—50).—Compounds of the type SnR_4 and SnR_3Cl are obtained in good yield by the reactions $6HgRCl + 3Sn + 6Na \rightarrow 3SnR_2 + 6NaCl + 6Hg$; $3SnR_2 \rightarrow Sn_2R_6 + Sn$; $Sn_2R_6 \rightarrow SnR_4 + SnR_2$, or $6HgRCl + 3Sn \rightarrow 3SnR_2Cl_2 + 6Hg$; $3SnR_2Cl_2 \rightarrow 2SnR_3Cl + SnCl_4$; $SnCl_4 + Sn \rightarrow 2SnCl_2$ (R = Ph, *p*-C_6H_4Cl, *p*-C_6H_4Me, *p*-$C_6H_4CO_2Et$, and CH_2Ph). The following *compounds* are described: $[Sn(C_6H_4\cdot CO_2Et\text{-}p)_3]_2S$, m.p. 132—133°, $Sn_2(C_6H_4Cl\text{-}p)_6$, m.p. 224—226°, $Sn(CH_2Ph)_3\cdot OH$, m.p. 122—124°. R. T.

Tin-organic compounds of the type $SnAr_2X_2$, containing a carbethoxy-group in the benzene ring. I. T. ESKIN, A. N. NESMEJANOV, and K. A. KOTSCHESCHKOV (J. Gen. Chem. Russ., 1938, **8**, 35—41).—$SnPh_2Cl_2$ in EtOH and H_2S yield *diphenylstannane sulphide*, m.p. 183—184°. The *compounds* SnR_2X_2 (R = *p*-$C_6H_4\cdot CO_2Et$, X = Cl, m.p. 102—103°, X = Br, m.p. 69—69·5°, and X = I, an oil) are prepared by the reaction $HgR_2 + SnX_2 \rightarrow Hg + SnR_2X_2$, and the *compounds* SnR_2S, m.p. 141·5—142·5°, and SnR_2O, not melting at 300°, are hence prepared. SnR_2Cl_2 and MgPhBr in Et_2O give the *compound* $SnPh_2(C_6H_2Ph_2\cdot OH)_2$, m.p. 265—266°. SnR_2I_2 and 8-hydroxyquinoline in EtOH give SnR_2Q_2, m.p. 216—217° (Q = $C_9H_6N\cdot O\cdot$). R. T.

Structure of proteins. Possibility of determining the cyclic form of amino-acid anhydrides by Blanchetière's method. N. I. GAVRILOV and M. A. POLUNINA (Bull. Soc. chim., 1938, [v], **5**, 454—459).—Blanchetière's method removes proline and hydroxyproline, as well as α-NH_2-acids, almost quantitatively. Hydrolysis of gelatin by 2% H_2SO_4 at 180°/10 atm. or by 25% H_2SO_4 gives only 5·34% of diketopiperazine-N; a possible explanation is suggested. R. S. C.

Combination between magnesium and proteins in solution. I, II. W. DUCE (Boll. Soc. ital. Biol. sperim., 1937, **12**, 793—794, 794—795).—I. Measurements of the potential of solutions of varying concn. of gelatin and $Mg(OAc)_2$ indicate that, like Ca (Eversole *et al.*, A., 1934, 253), Mg combines with gelatin at p_H 7·0—7·2 at 20°.

II. Dialysis of aq. gelatin–NaCl–$Mg(OAc)_2$ against aq. NaCl and subsequent determinations of Cl' and $Mg^{\cdot\cdot}$ indicate that, when allowance is made for the Donnan equilibrium, Mg combines with gelatin at p_H 7·0—7·2 at 20°. F. O. H.

Determination of glucosamine in proteins. M. SØRENSEN (Compt. rend. Trav. Lab. Carlsberg, 1938,

22, 487—493).—The protein is hydrolysed with HCl, and the glucosamine condensed with $CH_2Ac{\cdot}OMe$ to form a pyrrole derivative. The red colour produced by the latter with p-$NMe_2{\cdot}C_6H_4{\cdot}CHO$ is compared with controls in a step-photometer. The % of glucosamine in the following proteins are: ovalbumin 1·4, egg-mucoid 13·6, serum-albumin 0·37, and serum-globulin 1·7. J. N. A.

Hydration and denaturation of proteins.—See A., 1938, I, 311.

Semi-micro-determination of carbon and hydrogen. B. Hepner and M. Pojas (Compt. rend. XVII Cong. Chim. Ind., 1937, 397—399).—Ter Meulen and Heslinga's method is made applicable to compounds containing N, S, and halogens by the use of a Pt spiral and a mixed MnO_2 and Pb_3O_4 catalyst at 400° followed by K_2CrO_4 at 200° in the combustion train. The apparatus is described in detail. F. N. W.

Risk of explosion in the use of perchloric acid. E. Kahane (Compt. rend. XVII Cong. Chim. Ind., 1937, 471—475; cf. A., 1938, II, 76).—Precautions to be observed in the use of the $HNO_3 + HClO_4$ and the $HNO_3 + H_2SO_4 + HClO_4$ methods are (i) preliminary attack by HNO_3, and (ii) dilution in an inert medium, *i.e.*, a large excess of $HClO_4$ in the first and sufficient H_2SO_4 in the second method. The first method should not be used for > a few g. of material. L. S. T.

Mercuric selenite as catalyst in the Kjeldahl determination of nitrogen.—See A., 1938, III, 546.

Colorimetric determination of minute amounts of tin in organic matter.—See A., 1938, I, 326.

Thiocyanogen iodide number of hydrocarbons. H. P. Kaufmann and H. Grosse-Oetringhaus (Oel u. Kohle, 1938, **14**, 199—201; cf. A., 1937, II, 359).—CNSI solutions in CCl_4 give better reproducibility and shorter reaction times than those in C_6H_6. Standard 0·2N-CNSI solution is prepared as follows: 900 c.c. of CCl_4 (1 : 1) mixed with 100 c.c. of AcOH and Ac_2O is kept ⩽8 days. 25 g. of $Pb(CNS)_2$ and 2·8 g. of Br are added and the mixture is shaken in diffused light until decolorisation is complete. 13 g. of I are then added and when this has dissolved the solution is filtered. Pure materials must be used; a method of preparing pure $Pb(CNS)_2$ is given. 0·1—0·2 g. of the hydrocarbon to be tested, mixed with 20 c.c. of the CNSI solution, is kept for 15 hr. in the dark; 50 c.c. of 100% aq. KI are then added rapidly and the liberated I is immediately titrated with $Na_2S_2O_3$. A blank is carried out. The CNSI no. gives a measure of unsaturation; practically no substitution occurs. A. B. M.

Identification and determination of volatile alcohols and acids. T. E. Friedemann (J. Biol. Chem., 1938, **123**, 161—184).—Volatile acids are separated by steam-distillation (15—20 min.) with acid Na_2WO_4–$MgSO_4$ followed by redistillation from acid $MgSO_4$–H_2O to remove formic, pyruvic, crotonic, and lactic acids, etc. The distillate is fractionally distilled (Duclaux) from acid $MgSO_4$–H_2O, one half of each fraction being aërated to remove CO_2 and titrated with 0·01N-NaOH. The Et_2O–H_2O distribution const. (K), *i.e.*, % remaining in the aq. phase, is determined with the other half. From the rate of this distillation, K, and the titration vals., the acids are identified and may be determined if ⩾3 are present. The following vals. for K for 1 : 1 H_2O–Et_2O are recorded: AcOH 73·5, $EtCO_2H$ 42·4, $PrCO_2H$ 18·2, crotonic acid 25·6, $Pr^\beta CO_2H$ 16·8. HCO_2H is determined by oxidation with HgO. Alcohols are determined by distillation from Na_2WO_4–$HgSO_4$ followed by redistillation from $Ca(OH)_2$–HgO, thus removing acids, NH_2-compounds, ketones, aldehydes, and phenols. The distillate is oxidised by 2N-H_2SO_4–$K_2Cr_2O_7$ followed by titration and determination of K, whence the alcohols are identified. Results for EtOH in blood and for alcohols and acids in cultures of pathogenic micro-organisms agree with those obtained by the method of Friedemann and Klaas (cf. A., 1936, 1229). EtOH is the only alcohol and AcOH the only volatile acid (not removed by HgO) produced by these organisms in carbohydrate-rich media. E. G. B.

Determination of [ethyl] alcohol [in aqueous solutions]. A. Niini (Suomen Kem., 1938, **11**, A, 45—50).—Comparison of η for an EtOH–H_2O mixture with η for H_2O gives two vals. for the EtOH concn., the correct one being found by (rough) measurement of γ. Corrections are applied to give an accuracy of 0·05%. M. H. M. A.

Determination of ethylene glycol. R. Cuthill and C. Atkins (Analyst, 1938, **63**, 259—261).—$(CH_2{\cdot}OH)_2$ is quantitatively converted into CO_2 and H_2O when treated for 1½ hr. with alkaline $KMnO_4$, then acidified with H_2SO_4, and kept for a further 1 hr. A known amount of $KMnO_4$ is added initially and the excess titrated iodimetrically. E. C. S.

Determination of mono- and di-saccharides with hypoiodide. K. Myrbäck and B. Örtenblad (Svensk Kem. Tidskr., 1938, **50**, 72—77).—Glucose, galactose, arabinose, maltose, and lactose can be determined accurately by adding I followed by NaOH, and titrating the excess of I. Owing to the formation of $NaIO_3$, it is necessary either to use a large excess of I or to add the NaOH very slowly (2—4 min.). A. Li.

Manometric determination of amino-acids. M. F. Mason (Biochem. J., 1938, **32**, 719—724).—α-NH_2-acids are decarboxylated by heating with ninhydrin in H_2O, and the gasometric determination of CO_2 in the Van Slyke apparatus is less liable to error than the colorimetric method. No decarboxylation of peptides (except glutathione) and keto-hydroxy-acids occurs. The method is not satisfactory for alanine, serine, or tryptophan. A. T.

Nephelometric determination of morphine with vanadomolybdic acid. W. Deckert (Z. anal. Chem., 1938, **112**, 241—257).—Of a large no. of alkaloids, only morphine, dilaudide, and heroin have a sensitivity to $HVO_3 + H_2MoO_4$ ⩾ to H_2MoO_4, so that when an acid solution is treated with $(NH_4)_2MoO_4$ and the filtrate treated with NH_4VO_3 the degree of turbidity is a quant. measure of the concn. of these. The *morphine complex* is $V(OH)_5{,}2MoO_3{,}C_{17}H_{19}O_3N$. Details are given of the procedure (cf. A., 1936, 652). F. J. G.