BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

FEBRUARY, 1938.

Review of work in organic chemistry in the U.S.S.R. during the past 20 years. I. F. Bogdanov (J. Appl. Chem. Russ., 1937, **10**, 1784—1804).—A review. R. T.

Mechanism of the reaction of substitution and Walden inversion. II. P. A. Levene, A. Rothen, and M. Kuna (J. Biol. Chem., 1937, **121**, 747—759).—From a comparison of the first and second partial rotations, and the rotation in the visible region, of substances of type $CHRMe{\cdot}CH_2X$ (X = halogen, N_3, SH, OH, NH_2, or SO_3H) with those of the acids $CHRX{\cdot}CO_2H$ as correlated by the two following rules, Levene's "rule of shift" (ascribing identical configurations to α-carboxylic acids of which α changes in the same direction when passing from the undissociated to the ionised state) is now abandoned in favour of the rule that every substitution reaction (including replacement of halogen by N_3) of normal saturated aliphatic compounds is connected with a change of configuration. The configurative relations of substances of type CHRR'X are also discussed, with the same conclusion. Accordingly the configurative relationship of *sec.* carbinols of the corresponding halides, and of α-hydroxy- and α-halogeno-carboxylic acids, as formulated by Clough (A., 1926, 111, 937), by Levene and Mikeska (A., 1927, 1171; 1928, 170), and by Levene and Rothen (A., 1936, 1051; 1937, II, 2, 316) are abandoned in favour of those advocated by Freudenberg (A., 1928, 153, 535; 1935, 849) and by W. Kuhn (A., 1930, 276).

Rotatory dispersion data for (+)-β-thiol-butane and -octane, and for (+)-α-thiol-β-methylbutane and -γ-methylpentane, are tabulated and discussed, as are those for (−)-Na and (−)-Me octane-β-sulphonate and (+)-Na β-methylbutane- and (+)-Me β-methylhexane-α-sulphonate. E. W. W.

Structure of organic compounds. V. N. Ufimtzev (J. Gen. Chem. Russ., 1937, **7**, 1874—1877).—Polemical against Dubrovai (cf. A., 1937, I, 348). R. T.

Catalytic cyclisation of aliphatic compounds. II. Cyclisation and dehydrogenation of hydrocarbons with oxide and sulphide catalysts. B. Moldavski, G. Kamuscher, and M. Kobilskaja. **III. Cyclisation and dehydrogenation of hydrocarbons with different charcoals.** B. Moldavski, F. Bezprozvannaja, G. Kamuscher, and M. Kobilskaja (J. Gen. Chem. Russ., 1937, **7**, 1835—1839, 1840—1847).—II. Dehydrogenation of *cyclo*hexane (I) and cyclisation of *n*-octane (II) are catalysed by the same substances (TiO_2, MoO_2, MoS_2, and ZnO), at 450—550°; SiO_2 and glass are without effect in either reaction.

III. Active C catalyses both dehydrogenation of (I) and cyclisation of (II) and of Bu^{β}_2, at 500—560°. R. T.

Thermal decomposition of dodecane, ββδ-trimethylpentane, and βε-dimethylhexane. Kinetics of decomposition of ethane at reduced pressures.—See A., I, 35.

Mechanism of halogenation of phenols. I. Reaction of benzenesulphondichloroamide with phenol in presence of olefines. M. V. Lichoscherstov and R. A. Archangelskaja (J. Gen. Chem. Russ., 1937, **7**, 1914—1928).—PhOH in CCl_4, $(CHMe{:})_2$ (I), and $PhSO_2{\cdot}NCl_2$ (II) at −15°, followed by extraction with 3% NaOH and distillation of the residual CCl_4 solution, yield two diastereoisomerides, m.p. 83° and 115·8°, of β-*chloro*-γ-*benzenesulphonamido*-n-*butane* (III), yielding, respectively, trans-, m.p. 77°, and cis-2 : 3-*dimethyl*-N-*benzenesulphonylethyleneimine*, m.p. 42°, when treated with NaOH–EtOH at room temp. In addition PhOCl is formed in the original reaction, and this reacts with (I) to give β-*chloro*-γ-*phenoxybutane* (IV), b.p. 120°/20 mm. The entire process is represented: PhOH + (II) → PhOCl + $PhSO_2{\cdot}NHCl$ (V); PhOCl + (I) → (IV); (V) + (I) → (III). The corresponding products obtained with *o*- or *p*-$C_6H_4Cl{\cdot}OH$ in place of PhOH are: (III), β-*chloro*-γ-*o*-, b.p. 145—148°/20 mm., and -*p*-*chlorophenoxybutane*, b.p. 118·5°/5 mm., whilst with $CHEt{:}CH_2$ in place of (I) the products with PhOH are α-*chloro*-β-*phenoxybutane*, b.p. 121·5—122·5°/2 mm., N-*benzenesulphonylethylethyleneimine*, m.p. 76°, and α-*chloro*-β-*benzenesulphonamidobutane*, m.p. 83·5°, and with $CMe_2{:}CH_2$ α-*chloro*-β-*phenoxy*-, b.p. 118—119°/20 mm., and α-*chloro*-β-*benzenesulphonamido*-β-*methylpropane*, m.p. 76°, together with a mixture of chloro*iso*butanes, of which $CH_2Cl{\cdot}CMe{:}CH_2$ is identified. R. T.

Measurement of olefine formation from alkyl bromides. Mechanism of substitution and olefine reactions with alkyl halides. W. Taylor (J.C.S., 1937, 1962—1967; cf. A., 1937, II, 182).—Olefine formation at 25° and 55° from EtBr, $Pr^{\beta}Br$, $Bu^{\gamma}Br$, $CH_2Ph{\cdot}CH_2Br$ (I), and CHPhMeBr has been measured in H_2O, EtOH, and CCl_4 alone, and in solutions in dry EtOH with varying [NaOEt]. Yields of olefine increase in the order primary, *sec.*, *tert.*-bromides and with higher temp. and [NaOEt]. At any temp. [except with (I)] the concn. effect has an upper limit, probably owing to NaOEt mols. being more active in olefine formation than OEt' ions. (I) at 55° alone or in dry EtOH gives no olefine but at [NaOEt] not below 0·05N, it yields about 90% of olefine, probably due to OEt' ions. Yields in solvents

alone show that EtOH (basic) may have considerable effect, H_2O very little effect, and CCl_4 (non-basic) no effect, on olefine formation. Heating of bromides alone at 25° or 55° gives small yields of olefine. Hence possible reagents in olefine formation are OEt′ ions, NaOEt mols., solvents, and the bromides themselves.

Substitution and olefine reactions of alkyl halides $CH_2R{\cdot}CH_2{\cdot}Hal.$ through the agency of (1) anions (*B′*) or (2) unionised mols. (*AB*) are discussed. In case (1) substitution results from electron transfer $B' \rightarrow$ α-C atom, and olefine formation from $B' \rightarrow$ β-H atom. The proportion of olefine formation is therefore determined by basic strength of *B′*, by sizes of positive charges on α-C and β-H, and by polarisability of Hal., since increase of this induces increased positive charge on β-H relative to α-C. In both reactions the transfer α-C → Hal. must occur before completion. Hence substitution will be preferred, since Hal. is more remote from β-H than from α-C. In case (2) substitution results from transfers Hal. → *A* and *B* → α-C, and olefine formation from transfers Hal. → *A* and *B* → β-H. When Hal. is not partly bound by α-H, as in *tert.*-halides, it is freer to react with *A*. *B* therefore acquires more electron-donating power, *i.e.*, becomes a stronger base, and olefine formation is preferred and increases along the series primary, *sec.*-, *tert.*-halides, with increasing [*AB*], and with increasing strength of base. Substitution of I for Br or of Br for Cl will also affect olefine formation through increased polarisability of Hal. and change in reactivities of α-C and β-H. The accelerating effects of H_2O and of ionic base on reaction rates of $CH_2R{\cdot}CH_2{\cdot}Hal.$ in EtOH–H_2O are also explained on this basis. E. G. B.

Kinetics and mechanism of transformations of unsaturated hydrocarbons. VI. Polymerisation of propylene under pressures greater than atmospheric. S. P. Mitzengendler (J. Gen. Chem. Russ., 1937, **7**, 1848—1857).—The process of polymerisation of $CHMe{:}CH_2$ is catalysed by Fe at 480°, but not at 600°, at which temp. catalytically active solid C compounds are formed. At 480° the initial products are dimethyl*cyclo*butane and *n*- or *iso*-hexanes, whilst at 600° a mixture of CH_4, C_2H_4, and C_6H_{10} is obtained. The highest yield of liquid polymerides, b.p. <150°, is obtained at 520°, in a Cu reactor, and at >40 atm. pressure, with ≯50% conversion of $CHMe{:}CH_2$. R. T.

Oxidation velocities of alkenes with peracetic acid.—See A., I, 36.

Thermal reactions of unsaturated hydrocarbons. IV. Cracking of mixtures of propylene with butadiene and *iso*butylene at atmospheric pressure. V. G. Moor and N. V. Strigaleva. **V. Kinetics and mechanism of thermal transformations of di*iso*butylene at atmospheric pressure.** V. G. Moor and L. V. Schilaeva (J. Gen. Chem. Russ., 1937, **7**, 1766—1778, 1779—1786).—IV. $CH_2{:}CHMe$ (I) and $CH_2{:}CMe_2$ react at the same rate to give the same products, whether heated alone or together at 600°, whilst in (I)–$(CH_2{:}CH{\cdot})_2$ (II) mixtures the velocity of transformation of (I) is increased to an extent ∝ concn. of (II).

V. The yields of products of pyrolysis of $CH_2{:}CMe{\cdot}CH_2Bu^{\gamma}$–$CMe_2{:}CHBu^{\gamma}$ mixtures at 490—640° are as would be expected from Rice's theory (A., 1931, 819). R. T.

Velocity of hydrogenation of isomeric hexenes. S. P. Lagerev and S. F. Babak (J. Gen. Chem. Russ., 1937, **7**, 1661—1663).—The velocities of hydrogenation (Pt catalyst) of $CHBu^{\alpha}{:}CH_2$, $CHBu^{\gamma}{:}CH_2$, $CMeEt{:}CHMe$, and $CMe_2{:}CHEt$ are as 33 : 70 : 144 : 240. R. T.

Action of aromatic diazo-compounds on unsaturated compounds. I. A. P. Terentiev. **II. Sensitive reaction for divinyl.** A. P. Terentiev and E. M. Ivanova (J. Gen. Chem. Russ., 1937, **7**, 2026—2027, 2028—2029).—I. Theoretical.

II. *p*-$C_6H_4(NH_2)_2$ is diazotised at < −5°, and 2 ml. of the solution are added to 8 g. of ice and 2 ml. of AcOH, at −15°. The gas under analysis is passed into the mixture, when a deep yellow to red coloration appears in presence of dienes. R. T.

Course of polymerisation of pure olefines. F. Jostes and W. Bartels (Oel u. Kohle, 1937, **13**, 1166—1172).—Heptene (I) does not polymerise when treated with $ZnCl_2$, $SnCl_4$, or H_2SO_4. Treatment of (I) in hexane with $AlCl_3$ gives a mixture from which a definite polymeride could not be isolated. Di- and tri-polymerides of the C_7 to C_{12} olefines are formed by heating them at 80—90° in the presence of P_2O_5. These are strongly branched olefines, the exact structure of which has not yet been determined; it is such as to inhibit further polymerisation under the same experimental conditions. Propylene in the presence of P_2O_5 is polymerised to oils, mainly of b.p. 125—150°, but including also those boiling in the lubricating oil range; di-polymerides could not be isolated from the product. A. B. M.

Isomerisation of allene hydrocarbons by silicates. V. Isomerisation of *tert.*-butylallene. J. M. Slobodin (J. Gen. Chem. Russ., 1937, **7**, 1664—1667).—$CHBu^{\gamma}{:}C{:}CH_2$ is rearranged to $CMe_2{:}C{:}CMe_2$ when passed over floridin at 230°. R. T.

Constitution of lycopene and configuration of 6 : 7-dimethyl-9-*d*-arabityl*iso*alloxazine. P. Karrer (Ber., 1937, **70**, [*B*], 2565—2566; cf. A., 1937, II, 378).—Reply is made to Kuhn and Grundmann (*ibid.*, 438) with regard to the constitution of lycopene and to Kuhn and Weygand (*ibid.*, 233) with respect to the configuration of 6 : 7-dimethyl-9-*d*-arabityl*iso*alloxazine. H. W.

Photochemical oxidation of trichloroethylene to dichloroacetyl chloride by chlorine.—See A., I, 39.

Aliphatic chloro-derivatives. XI. Chlorination of *iso*pentane to dichlorides. M. Davidova, Z. Papkina, and D. Tischtschenko. **XII. Action of chlorine on *n*-pentane.** A. Lemke and D. Tischtschenko (J. Gen. Chem. Russ., 1937, **7**, 1992—1994, 1995—1998).—XI. Chlorination of liquid *iso*pentane at 20°, or of the vapour at 115°, yields βγ-, βδ-, and αδ-dichloro-β-methylbutane.

XII. *n*-Pentane and Cl_2 at 20° afford βγ-, αβ-, αδ-, and probably αε-dichloropentane. R. T.

Elimination of hydrogen bromide from saturated bromohydrins in presence of metallic catalysts. I. Elimination of hydrogen bromide from *iso*butylene bromide in presence of nickel, zinc, aluminium, and copper. N. I. MATUSEVITSCH (J. Gen. Chem. Russ., 1937, **7**, 1909—1913).—An inseparable mixture of products is obtained when $CMe_2Br{\cdot}CH_2Br$ is passed over Ni at 500°, or Zn at 400—500°, pointing to profound structural changes in the mol. In presence of Al at 275—325° gaseous and sooty products are obtained. The chief products with Cu at 420° were iso*butenyl bromide*, b.p. 93·5—94·5°, and some $Bu^{\gamma}Br$. R. T.

Photochemical decomposition of aliphatic alcohols in aqueous solution.—See A., I, 39.

Catalytic dehydration of ethyl alcohol by alumina.—See A., I, 37.

Addition of hypochlorous acid to Δ^{β}-butene-$\alpha\delta$-diol.—See A., I, 36.

Reactions relating to carbohydrates and polysaccharides. LIV. Surface tension constants of the polyethylene glycols and their derivatives. LV. Vapour pressures of the polyethylene glycols and their derivatives. A. F. GALLAUGHER and H. HIBBERT (J. Amer. Chem. Soc., 1937, **59**, 2514—2521, 2521—2525).—LIV. γ and d for mono- to hepta-ethylene glycols are measured over a range of about 100°. The series const. for the total surface energy, 72±1 ergs, is attained with triethylene glycol and closely approaches the val. 73·2 for $(CH_2)_2O$. Therefore, the glycols are probably oriented at the surface in a U-form, with $CH_2{\cdot}O{\cdot}CH_2$ at the surface; the OH group plays little part. The abnormally low val., 68·96, of $(OH{\cdot}CH_2{\cdot}CH_2)_2O$ (I) indicates spatial proximity of the two OH groups. Continuous increase in the Ramsay and Shields const. and in the difference between the calc. and observed vals. of $[P]$ with increasing mol. wt. indicate an abnormal factor, possibly partial orientation at the surface. The observed $[P]$ is low for $(OH{\cdot}CH_2)_2O$ and (I), but thereafter becomes increasingly high; the latter, abnormal deviation may be due to intramol. co-ordination, $\rightarrow H{\cdot}\overset{|}{O}\rightarrow H{\cdot}\overset{|}{O}\rightarrow$. Mol. vols. show large negative anomalies, best explained by zig-zag chains.

LV. V.p. of mono-, di-, tri-, and tetra-ethylene glycol and some allied compounds are determined and the mol. latent heat and Trouton's const. are calc. Certain abnormalities are noted. Initial decomp. temp. are shown to rise with the chain length; replacement of OH by Cl or OMe decreases the stability. R. S. C.

***n*-Propyl esters of pyrophosphorous, hypophosphoric, and pyrophosphoric acids, and the chloride of di-*n*-propylphosphorous acid.** A. E. ARBUSOV and A. I. RAZUMOV (J. Gen. Chem. Russ., 1937, **7**, 1762—1765).—$NaPr^{\alpha}{}_2PO_3$ (I) and Br in light petroleum yield a mixture of $Pr^{\alpha}{}_4P_2O_5$ (II), b.p. 147·5—149°/6 mm., $Pr^{\alpha}{}_4P_2O_6$, b.p. 167—170°/3 mm., and $Pr^{\alpha}{}_4P_2O_7$, b.p. 178—179·5°/4 mm. (II) with H_2O yields $Pr^{\alpha}{}_2HPO_3$. $PCl_2{\cdot}OPr^{\alpha}$ and $NaOPr^{\alpha}$ in Et_2O afford $PCl(OPr^{\alpha})_2$, b.p. 65·5—66·5°/8 mm., which with (I) gives (II). R. T.

Syntheses of glycerophosphatidic acids and of glycerophosphatides. P. E. VERKADE and J. VAN DER LEE (Proc. K. Akad. Wetensch. Amsterdam, 1937, **40**, 858—864).—Theoretical; a review of the literature (cf. A., 1937, II, 439). E. W. W.

Isolation and synthesis of glucose-1-phosphoric acid. C. F. CORI, S. P. COLOWICK, and G. T. CORI (J. Biol. Chem., 1937, **121**, 465—477).—Glucose-1-phosphoric acid (I) (A., 1936, 1533), $[\alpha]_D^{25}$ +118° in H_2O, is obtained free from the 6-ester (II) by treating an extract of rabbit muscle (dialysed to remove $Mg^{\cdot\cdot}$) with glycogen, adenylic acid, and a phosphate buffer of p_H 7, and preparing the *Ba* salt. $C_6H_{11}O_5(PO_4)Ba,3H_2O$, $[\alpha]_D^{25}$ +75·5° in H_2O. Unlike (II), (I) is non-reducing; it is hydrolysed by N-H_2SO_4 at 100°, or by intestinal phosphatase, to glucose and inorg. phosphate. Synthetic (I), from α-1-bromotetra-acetylglucose and Ag_3PO_4, and hydrolysis of the resulting *tris*(*tetra-acetylglucose*-1)-*phosphoric acid*, $[\alpha]_D^{25}$ +122° in MeOH, by 0·2N-MeOH–HCl, at 25° for 16 hr., is identical in properties with natural (I). The velocity coeff. of hydrolysis by 1·25N-HCl at 37° is $1{\cdot}30\times10^{-3}$; apparent dissociation consts. are $pK_1' = 1{\cdot}1$, $pK_2' = 6{\cdot}13$. The accelerating effect of $Mg^{\cdot\cdot}$ on the conversion of (I) into (II) is studied (cf. A., 1937, III, 306). E. W. W.

Thermal decomposition of dimethyl sulphite.—See A., I., 35.

Sulphur studies. XIII. Identification of aliphatic sulphonic acids. P. H. LATIMER and R. W. BOST. **XIV. Derivatives of higher mercaptans.** D. FORE, jun., and R. W. BOST (J. Amer. Chem. Soc., 1937, **59**, 2500—2501, 2557—2558; cf. A., 1937, II, 456).—XIII. The following $NHPh{\cdot}NH_2$ salts are suitable for identifying the acids: *methane*-, m.p. 193·5—194° (decomp.), *ethane*-, m.p. 182·8°, *propane*-α-, m.p. 204·5° (decomp.), *butane*-α-, m.p. 114—115°, *pentane*-α-, m.p. 108—108·2°, *hexane*-α-, m.p. 101—101·6°, *heptane*-α-, m.p. 100—100·5°, and *octane*-α-*sulphonate*, m.p. 90—90·5°. They can be titrated with 0·01N-NaOH. Large depressions of the m.p. are given by sulphonates differing by >1 CH_2, small depressions by those differing by 1 CH_2. 1 : 2 : 4-$C_6H_4Cl(NO_2)_2$, NH_2Ph, p-$C_6H_4Me{\cdot}NH_2$, p-$NO_2{\cdot}C_6H_4{\cdot}CH_2Br$, and p-$C_6H_4Ph{\cdot}CO{\cdot}CH_2Br$ are not suitable for identification of the acids.

XIV. The following are prepared. *Pb* n-*tri*-, m.p. 100° (97°), -*tetra*-, m.p. 104—105° (99°), -*hexa*-, m.p. 106—107° (99°), -*hepta*-, m.p. 108—109° (100°), -*octa*-, m.p. 110—111° (106°), and -*nona-decylmercaptide*, m.p. 112—114° (108°), temp. in parentheses being those of initial darkening. 2 : 4-*Dinitrophenyl* n-*tri*-, m.p. 94—94·5°, -*tetra*-, m.p. 93·5—94°, -*hexa*-, m.p. 95·5—96°, -*hepta*-, m.p. 98·5—99°, -*octa*-, m.p. 97—97·5°, and -*nona-decyl sulphide*, m.p. 99·5—100°. 2 : 4-*Dinitrophenyl* n-*tri*-, m.p. 101·5°, -*hepta*-, m.p. 106·5°, and -*octa-decyl sulphone*, m.p. 107·5°. *Di*-n-*do*-, m.p. 33·5—34°, -*tri*-, m.p. 43·5—44°, -*tetra*-, m.p. 45·5—46°, -hexa-, *hepta*-, m.p. 59·5—60°, -octa-, and -*nona-decyl disulphide*, m.p. 68·5—69°. R. S. C.

Thiocyano-sulphides and -sulphones. A. E. KRETOV and E. M. TOROPOVA (J. Gen. Chem. Russ., 1937, **7**, 2009—2015).—$CH_2Cl{\cdot}CH_2{\cdot}S{\cdot}Et$ (I) in AcOH

and H_2O_2 at 100° yield *Et* β-*chloroethyl sulphone*, b.p. 120—122°/3—4 mm. (I) in EtOH and KCNS (6 hr. at 70°) give *Et* β-*thiocyanoethyl sulphide*, b.p. 105—110°/5 mm., oxidised as above to *Et* β-*thiocyanoethyl sulphone*, m.p. 36—37°. The following compounds are prepared analogously: *Ph* β-*chloroethyl*, m.p. 52°, *Et*, b.p. 160—163°/7 mm., and *Ph* γ-*chloropropyl sulphone*, m.p. 23—24°; *Ph* β-*thiocyanoethyl*, b.p. 143—146°/2 mm., *Et*, b.p. 115—120°/10 mm., and *Ph* γ-*thiocyanopropyl sulphide*, b.p. 176—178°/3 mm.; *Ph* β-*thiocyanoethyl*, m.p. 71·5—72°, *Et*, m.p. 39·5—41°, and *Ph* γ-*thiocyanopropyl sulphone*, m.p. 91°. R. T.

Preparation of esters in presence of aluminium chloride or ferric chloride. A. N. Akopian (J. Gen. Chem. Russ., 1937, **7**, 1687—1689).—Esters are obtained in high yield by adding the acid to a solution of $AlCl_3$ or $FeCl_3$ in the alcohol, and boiling the mixture under reflux. R. T.

Hydrolysis of esters by hydrogen chloride with aluminium chloride at catalyst. E. Ott (Ber., 1937, **70**, [*B*], 2362).—Tetraethylsuccinic esters are indifferent towards boiling KOH–EtOH and are unchanged by HCl at 200°. Addition of $AlCl_3$ to ester and HCl at 200° causes vigorous disengagement of H_2O and alkyl chloride, giving pure tetraethylsuccinic anhydride, b.p. 270°. H. W.

Reaction of *tert.*-butyl chloride with formic acid: *tert.*-butyl formate. W. Taylor (J.C.S., 1937, 1852—1853).—The conclusion of Bateman and Hughes (A., 1937, I, 467) that hydrolysis of $Bu^{\gamma}Cl$ by H_2O in HCO_2H is unimol. is criticised. $Bu^{\gamma}Cl$, HCO_2H, and $(HCO_2)_2Ca$ at room temp. yield *Bu*$^{\gamma}$ *formate*, b.p. 82·5—83·5°/757 mm., which is rapidly hydrolysed by 0·1N-NaOH or by N-HCl. The primary reaction may thus be bimol., $Bu^{\gamma}Cl + HCO_2H \rightleftharpoons HCO_2Bu^{\gamma} + HCl$, independent of small $[H_2O]$. E. W. W.

Electrolysis of mixtures of salts of fatty acids with halides and nitrates. F. Fichter and R. Ruegg (Helv. Chim. Acta, 1937, **20**, 1578—1590; cf. A., 1937, II, 84).—Electrolysis of $EtCO_2H$ and HCl with a Pt anode yields β- and α-chloropropionic acid, but no chlorinated hydrocarbon. Butyrate–chloride mixtures give chlorinated acids and their Pr^{β} esters, C_6H_{14}, and $CHCl_3$. *n*-Hexoate + KCl (or KBr) gives *n*-$C_{10}H_{22}$ with smaller amounts of *n*-amyl hexoate, Δ^{α}-pentene, $CH_2Bu^{\alpha}\cdot OH$, $CHMePr^{\alpha}\cdot OH$, $CHEt_2\cdot OH$, and $CHCl_3$ (or $CHBr_3$). Hexoate and nitrate give *n*-$C_{10}H_{22}$, *n*-$C_5H_{11}\cdot NO_3$, $C_{10}H_{21}\cdot NO_3$, and $C_5H_{10}(NO_3)_2$. The nitrates are considered to be formed by the interaction of an ethylene hydrocarbon with anodically activated HNO_3 (cf. A., 1937, II, 45). F. L. U.

Addition of hydrogen chloride to pentenoic acids. E. Schjänberg (Ber., 1937, **70**, [*B*], 2385—2391).—The course of addition of HCl to the three pentenoic acids is not influenced by the solvent (heptane, Et_2O, PhMe, EtBr, $COMe_2$, BuCl, $CHCl_3$); in the Δ^{α}- (I) and Δ^{β}- (II) -acids Cl occupies the position most distant from $\cdot CO_2H$, but the least distant position in the Δ^{γ}-acid (III). Peroxides do not affect the direction of the addition of HCl to (III), γ-chlorovaleric acid resulting under all conditions. Increase of pressure and rise of temp. increase the yield of Cl-substituted acids, whereas substances such as Bz_2O_2, quinol, and $FeCl_3$ are to be regarded as negative catalysts. Addition is best effected in H_2O, (I) giving a 100% yield exclusively of β-chlorovaleric acid in 2—3 days, whereas (II) and (III) give γ-chlorovaleric acid in 100% yield in 8 days. The behaviour of HCl differs therefore from that of HBr, which depends on solvent and is subject to a peroxide effect. H. W.

Olefinic acids. XVII. Addition of hydrogen bromide to heptenoic and nonenoic acids with terminal double linkings. P. Gaubert, R. P. Linstead, and H. N. Rydon (J.C.S., 1937, 1974—1979; cf. A., 1935, 195).—Orientation of addition of HBr to Δ^{ϵ}-*n*-heptenoic acid (I), Δ^{η}-*n*-nonenoic acid (II), and $CH_2{:}CH\cdot[CH_2]_2\cdot CO_2H$ (III) is in agreement with earlier results for the series $CH_2{:}CH\cdot[CH_2]_n\cdot CO_2H$, *i.e.*, when $n = 1$, 2, 3, 4, or 6 terminal addition occurs in presence of O_2 or peroxides and non-terminal addition in presence of H_2 or antioxidants, whilst in C_6H_{14} anomalous terminal addition occurs even in presence of H_2 or antioxidants. This does not support the view that solvents affect orientation only in so far as they influence the O_2 or peroxide effect. Discrepancy of results in C_6H_{14} with undecenoic acid ($n = 8$) and (III) in results of Kharasch and McNab (A., 1936, 53), who obtained $CHMeBr\cdot[CH_2]_2\cdot CO_2H$, is probably due to difference in technique, purity, or capacity of acids to form catalysts. $CH_2{:}CH\cdot CH_2\cdot CO_2H$ with HBr in absence of solvents or in Et_2O or AcOH yields $CHMeBr\cdot CH_2\cdot CO_2H$, also produced in the presence of peroxides, but in C_6H_{14}, $Br\cdot[CH_2]_3\cdot CO_2H$ is always produced. This disposes of the contention of Smith (A., 1937, II, 438) that peroxides always reverse the usual orientation.

Constitution of the Br-acids from (I) and (II) is confirmed by synthesis or by conversion into the corresponding dibasic acids by malonation and hydrolysis. Thus ζ-bromo-*n*-heptoic acid (IV), new m.p. 29°, obtained from (I) is synthesised from $CH_2Br\cdot[CH_2]_3\cdot CH_2Br$ by conversion into ε-*phenoxy*-n-*amyl bromide*, b.p. 160—165°/11 mm., which by malonation gives $OPh\cdot[CH_2]_5\cdot CH(CO_2Et)_2$, decarboxylated to ζ-phenoxy-*n*-heptoic acid, new m.p. 55°, whence (IV) by action of HBr. β-*Methylsuberic acid* (V), m.p. 83°, obtained by malonation of (I), is synthesised from Et δ-acetyl-*n*-valerate by condensation with $CH_2Br\cdot CO_2Et$ to give a *product* yielding *Et* β-*methyl*-Δ^{α}-n-*hexene*-α*ζ*-*dicarboxylate*, b.p. 160—162°/10 mm., whence the Et ester of (V) by distillation. Condensation of Et ε-bromo-*n*-hexoate with $CHNaAc\cdot CO_2Et$ yields η-ketononoic acid, b.p. 148°/0·8 mm., new m.p. 40°, from which β-*methylsebacic acid*, m.p. 75—76°, obtained by malonation of (II), could not be synthesised by a similar process to (V). θ-*Bromo*-n-*nonoic acid*, from (II) and HBr, has m.p. 37—38°. E. G. B.

Olefinic acids. XVI. Synthesis of Δ^{10}-*n*-undecenoic acid. P. Gaubert, R. P. Linstead, and H. N. Rydon (J.C.S., 1937, 1971—1974).—Δ^{δ}-*n*-Pentenol (I), prepared by action of Na on tetrahydro-

furfuryl chloride, is brominated by PBr_3 in C_5H_5N to the corresponding bromide, which with $CHNa(CO_2Et)_2$ gives Et Δ^{δ}-*n*-pentenylmalonate, hydrolysed to the corresponding *acid* (II), m.p. 87°. (II) is decarboxylated to Δ^{ϵ}-*n*-heptenoic acid (III), b.p. 125°/15 mm., m.p. −6·5° (p-*toluidide*, m.p. 59·6°). Et Δ^{ϵ}-*n*-heptenoate [from (III) with $SOCl_2$ and then EtOH] with Na in EtOH gives Δ^{ζ}-n-*heptenol* (IV), b.p. 105°/20 mm. Under the same treatment as (I), (IV) yields successively Δ^{ζ}-n-*heptenyl bromide*, b.p. 77—81°/20 mm., Δ^{ζ}-n-*heptenylmalonic acid*, m.p. 90—91°, and Δ^{η}-n-*nonenoic acid* (V), b.p. 116—118°/1 mm., m.p. 5° (p-*toluidide*, m.p. 68°). Under the same treatment as (III), (V) yields successively Δ^{θ}-n-*nonenol*, b.p. 135°/20 mm., Δ^{θ}-*n*-*nonenyl bromide*, b.p. 110—115°/15 mm., Δ^{θ}-n-*nonenylmalonic acid*, m.p. 107°, and Δ^{ι}-*n*-undecenoic acid, b.p. 131°/1 mm., m.p. 24—24·5°, identical with the product obtained from castor oil. The constitution of (III) and (V) is proved by their oxidation by $KMnO_4$ in $NaHCO_3$ solution, respectively, to adipic and suberic acids. In KOH solution (V) gives a mixture of pimelic and suberic acids. E. G. B.

Fractional distillation of the fatty acids of phosphatides. W. Diemair and W. Schmidt (Biochem. Z., 1937, **294**, 348—352).—Apparatus for the fractional distillation (separation and determination) in a high vac. of 30—5 and <5 g. of mixed Me esters of the fatty acids (C_{15}—C_{20}) is described. W. McC.

Position of the unsaturated linking in the hexadecenoic acid of certain natural fats. J. M. Spadola and R. W. Riemenschneider (J. Biol. Chem., 1937, **121**, 787—790).—The Me ester of hexadecenoic acid (I) from goat milk, white rat, and egg-yolk fats (cf. A., 1936, 510) is ozonised and hydrolysed, giving azelaic and *n*-heptoic acid; (I) is thus chiefly Δ^{θ}-hexadecenoic acid. E. W. W.

Fat of seeds of *Trichosanthes cucumeroides*.—See A., III, 160.

Synthesis of elastic, factice-like substances from fatty acids. See B., 1938, 196.

Course of hydrogenation in mixtures of mixed glycerides. W. J. Bushell and T. P. Hilditch (J.C.S., 1937, 1767—1774).—By partial hydrogenation (Ni-kieselguhr at 180°) of 1 : 1 binary mixtures of oleodi-palmitin and -stearin, dioleo-palmitin and -stearin, and triolein and determination of the amount of tristearin in the product it is proved that all unsaturated components of a glyceride mixture are reduced concurrently, but that the less saturated components are reduced more rapidly until uniform unsaturation is attained, whereafter the rate of reduction of both components becomes approx. the same. The reported difference in rate of hydrogenation of α- and β-oleyl radicals is disproved. Palmito-oleins are possibly slightly more readily reduced than stearo-oleins. When 3 : 1 mixtures of α-oleodipalmitin or α-palmitodiolein with triolein are half-reduced, no tristearin is formed. This effect of the relative amounts of the components present accounts for the results obtained with natural fats, which contain 75—80% of palmito-olein. R. S. C.

Autoxidation of unsaturated fatty acids. III. W. Franke and D. Terchel (Annalen, 1937, **533**, 46—71; cf. A., 1933, 49).—The rate of absorption of O_2 and the amount absorbed are the same for oleic (I) and ricinoleic (II) acid in bulk and on filter-paper. Both the rate and the amount are, however, larger for linoleic (III) and linolenic acid (IV) on filter-paper. For (I) and (II) in MeOH in presence of 1% of $Co(NO_3)_3$ the ratio of peroxide content to O_2 absorbed decreases rapidly with increasing absorption; the I val. ∝ absorption up to about 25% absorption, but then decreases more slowly. For (III) and (IV) with various accelerators the peroxide content is theoretical up to about 25% absorption and thereafter increasingly less than theoretical; the I val. falls proportionately up to 60% absorption and thereafter more slowly. The peroxides are fairly stable in MeOH; the I val. remains const. The results support the view that peroxides are first formed and then decompose to α-OH-ketones; hydrogenation of the acids oxidised to various stages also supports this view. The individual ethylenic linkings of poly-unsaturated acids autoxidise at different rates and the resultant peroxides have different stabilities. R. S. C.

Acylation of ethyl acetoacetate in presence of magnesium. A. Spassov (Ber., 1937, **70**, [*B*], 2381—2385; cf. A., 1937, II, 439).—Interaction between $CH_2Ac{\cdot}CO_2Et$, acyl chlorides, and Mg occurs readily in C_6H_6 at 80—85°, giving *C*-acyl derivatives in yields closely similar to those obtained from $CHNaAc{\cdot}CO_2Et$. H_2 and HCl are evolved and the change is considered to depend on the direct action of the acid chloride on $OH{\cdot}CMe{:}CH{\cdot}CO_2Et$, in which Mg or the Mg compound functions as a condensing catalyst. In its acidic character the change differs from the Claisen reaction. Interaction between $CH_2Ac{\cdot}CO_2Et$ and AcCl, EtCOCl, $Pr^{\alpha}COCl$, $Pr^{\beta}COCl$, *iso*valeryl chloride, and BzCl are described. *Et* n-*butyrylacetoacetate*, b.p. 109—111°/11 mm. (*Cu* derivative, two forms m.p. 62—63° and 52—53°, respectively), and *Et* iso*butyrylacetoacetate*, b.p. 109·5—111°/13 mm. (*Cu* compound, m.p. 95—96°), appear new. Owing to secondary action of the evolved HCl on $CHAcBz{\cdot}CO_2Et$, the products derived from BzCl include $CH_2Bz{\cdot}CO_2Et$, $CHAc_2{\cdot}CO_2Et$, and $CHAcBz{\cdot}CO_2Et$. H. W.

Labile nature of the halogen atom in organic compounds. XV. Action of hydrazine on bromomalonic esters. H. P. Gallus and A. K. Macbeth (J.C.S., 1937, 1810—1812).—The rate of reaction of $CBr_2(CO_2R)_2$ or $CHBr(CO_2R)_2$ with N_2H_4, and the vol. of N_2 evolved, decrease as the size of R increases (cf. J.C.S., 1922, **121**, 904). That this may in part be due to replacement of Br by OH instead of H is suggested by the isolation of *mesoxal-hydrazide hydrazone*, m.p. 187°, after reaction of N_2H_4 with Bu^{β}, b.p. 138°/10 mm., or iso*amyl dibromo-malonate*, b.p. 142—143°/4 mm. *Bu bromo-*, b.p. 135—136°/10 mm., and *dibromo-malonate*, b.p. 147°/10 mm., Bu^{β}, b.p. 124—126°/12 mm., n-*amyl*, b.p. 144°/4 mm., iso*amyl*, b.p. 146—148°/11 mm., sec.-*octyl*, b.p. 169—170°/4 mm., and cyclo*hexyl bromomalonate*, b.p. 167°/4 mm., are prepared, and 2-, b.p. 176°/6 mm., 3-, b.p. 182°/6 mm., and 4-*methyl*-

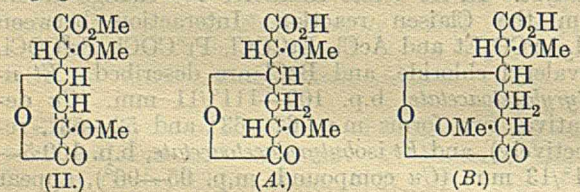
cyclo*hexyl bromomalonate*, b.p. 180—181°/4 mm., are obtained slightly impure. The reactions of these, and of simpler bromo- and dibromomalonates, with N_2H_4 are studied. n-*Octyl*, b.p. 176—177°/6 mm., cyclo*hexyl*, b.p. 173°/10 mm., and 2-, b.p. 172—173°/10 mm., 3-, b.p. 178°/13 mm., and 4-*methyl*cyclo*hexyl malonate*, b.p. 168°/10 mm., are described. E. W. W.

Autoxidation of maleic anhydride–β-elæostearin.—See A., I, 37.

Ethyl acetonedicarboxylate. I. G. Jacini (Gazzetta, 1937, **67**, 715—719).—$(CH_2{\cdot}CO_2Et)_2C{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2$ (I) is hydrolysed by boiling H_2O, giving $(NH{\cdot}CO{\cdot}NH_2)_2$, and in 20% aq. NH_3 at room temp. yields the NH_4 salt, m.p. 144°, of 2 : 6-*dihydroxy*-4-*pyridone semicarbazone*, m.p. 165—167°. When fused and heated at 100—105°, (I) loses EtOH, forming a *substance*, $C_8H_{11}O_4N_3$, m.p. 129°; at 120° a product, m.p. >350°, is formed. These reactions are compared with those of $CO_2Et{\cdot}CH_2{\cdot}CMe{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2$. E. W. W.

Reaction of tartaric acid: Pesez' reaction. C. H. Liberalli (Rev. Quim. Farm., 1935, **1**, 23—24; Chem. Zentr., 1936, i, 4473).—Pesez' method is preferable to the Möhler–Denigès test. Iodides may be removed with HNO_2, but vanadates interfere. J. S. A.

Action of diazomethane on saccharic acid. O. T. Schmidt, H. Zeiser, and H. Dippold (Ber., 1937, **70**, [*B*], 2402—2415).—Saccharic acid (I), like tartaric and trihydroxyglutaric acid, is extensively methylated at the free OH groups, but the production of a double linking appears unique. The action of CH_2N_2, whether obtained from nitrosomethyl-urethane or -carbamide, on (I) gives a 26% yield of the unsaturated *lactone ester* (II), m.p. 87°, $[\alpha]_D^{20}$ +83·1±0·6° in abs. MeOH, which immediately reduces alkaline $KMnO_4$, gives a faint but distinct colour with $C(NO_2)_4$ in EtOH, slowly adds 1 H_2 and 2 Br, but does not give a colour with $FeCl_3$. Hence the double linking lies between C atoms to which OH is not attached. The lactone is opened with greater difficulty than is customary with γ-lactones of the sugar group. Hydrolysis of (II) gives the corresponding unsaturated *lactone acid* (III), m.p. 168°, $[\alpha]_D^{20}$ +72·5°±0·5° in H_2O, in which the relative stability of the lactone ring is pronounced. Hydrogenation of (III) gives the saturated *lactone acid*, m.p. 128—129°, $[\alpha]_D^{20}$ +98·4°±0·4° in H_2O (corresponding free dicarboxylic acid, $[\alpha]_D^{20}$ −21·6°±0·8° in H_2O, and its Na_2 salt, $[\alpha]_D^{20}$ −21·2°±0·4° in H_2O), which appears to be one of the homogeneous forms *A* or *B*. Hydrogenation of (II) gives a syrup apparently hydrolysed to a mixture of *A* and *B*, from which a saturated *acid*, m.p. 144—145°, $[\alpha]_D^{20}$ +84·7°±0·4° in H_2O (initial), is isolated. Ozonisation of (II) gives an aldehyde-ester (not isolated) hydrolysed to $H_2C_2O_4$ in theoretical yield with a simply methylated tetrauronic acid oxidised by Br to *d*-hydroxymethoxysuccinic acid, m.p. 179°, $[\alpha]_D^{20}$ +49·6°±0·6° in H_2O. The further elucidation of the constitution of (II) rests on the application of Hudson's lactone rule. Unexpectedly the yield of (II) obtained from saccharolactonic acid (IV) and CH_2N_2 is > that obtained from the acid; possibly a revision of the structure of (IV) is necessary. Detailed description is given of the non-cryst. products obtained during the methylation of (I); they are more highly methylated and, in part, unsaturated. H. W.


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

Pectin substances. I. Sugar-beet pectins. T. K. Gaponenkov (J. Gen. Chem. Russ., 1937, **7**, 1986—1991).—Sugar-beet protopectin, hydratopectin, araban, pectic acid, and galacturonic acid have been prepared, and certain consts. are recorded for the preps. R. T.

Photochemical decomposition of aliphatic aldehydes in aqueous solutions.—See A., I, 39.

Kinetics of polymeric aldehydes. IX. Gross constants of the dissolution process of solid polyoxymethylenes. K. P. Jung and J. Löbering (Ber., 1937, **70**, [*B*], 2415—2427; cf. A., 1938, II, 4).—The rate of dissolution of solid polyoxymethylenes (I) is either ∝ the actual amount of suspended material or is const. over a portion of its total course. The character of the process is determined by the magnitude of the solubility product of the suspended (I) in relationship to the consts. of the contributing reactions. H. W.

Synthesis of $\Delta^{\beta\zeta}$-octadienal. G. Goethals (Bull. Soc. chim. Belg., 1937, **46**, 409—422).—Me Δ^{β}-pentenoate reduced (Na–MeOH) yields *n*-$C_5H_{11}{\cdot}OH$ and Δ^{γ}-*pentenol*, which with $SOCl_2$ and C_5H_5N in CH_2Cl_2 yields Δ^{γ}-*pentenyl chloride* (I), b.p. 107—107·5°/755 mm., converted (NaI in $COMe_2$) into Δ^{γ}-*pentenyl iodide* (II), b.p. 53·6°/20 mm. The Grignard compound, prepared from a mixture of (I) and (II), is converted by acraldehyde into *pentenylvinylcarbinol*, b.p. 72·5—75·5°/10 mm., which is brominated (PBr_3 and C_5H_5N) in light petroleum to *octadienyl bromide*, b.p. 72—75°/10·5 mm. This, when heated with AgOBz in abs. Et_2O, yields *octadienyl benzoate*, b.p. 122—131°/0·8 mm., hydrolysed (KOH–MeOH) to $\Delta^{\beta\zeta}$-*octadienol*, b.p. 88—90·5°/10 mm., oxidised ($K_2Cr_2O_7$–H_2SO_4) to $\Delta^{\beta\zeta}$-*octadienal*, b.p. 77—79°/10 mm. (*semicarbazone*, m.p. 169·3—170°). J. D. R.

Products formed during the preparation of keten. R. W. Hale (Nature, 1937, **140**, 1017).—Traces of $C_{10}H_8$ have been detected in the $COMe_2$ condensate obtained during the prep. of keten by passing $COMe_2$ over electrolytic Cu heated in a SiO_2 tube. L. S. T.

Photo-oxidation of acetone vapour.—See A., I, 39.

Ketals of hydroxyketones. II. Acetoin ketal. V. V. Evlampiev (J. Gen. Chem. Russ., 1937, **7**, 1579—1580).—$COMe{\cdot}CHMe{\cdot}OAc$, $CH(OEt)_3$, and *p*-$C_6H_4Me{\cdot}SO_3H$ yield the *ketal*, b.p. 88·5—90°/14

mm., of acetoin acetate, converted by heating at 80° with aq. $Ca(OH)_2$ into *acetoin ketal*, b.p. 82·5°/23 mm. R. T.

Configuration of carbohydrates from conductivity measurements in boric acid solution. H. T. Macpherson and E. G. V. Percival (J.C.S., 1937, 1920—1927).—Conductivity measurements in H_3BO_3 solution with α-methylglucopyranoside, 2 : 3 : 6-tri- and 2 : 3 : 4 : 6-tetra-methyl-glucopyranoses and -methylglucopyranosides, and sucrose show that the ring O has no effect on conductivity of H_3BO_3, and that, in the case of glucose, the only OH groups with a positive effect are those at $C_{(1)}$ and $C_{(2)}$, thus confirming Böeseken's configuration (A., 1913, i, 1147) for α- and β-glucose. Depressions of conductivity are shown to be not anomalous by relative viscosities, which run parallel. Initial elevation of conductivity shown by β-glucose may be due to the presence of small amounts of the straight-chain aldehydic form. Contrary to Böeseken and Couvert (A., 1921, i, 497), β-*d*-mannose shows a fall in conductivity during mutarotation in keeping with its accepted *cis*-configuration and confirmed by the initial depression, decreasing during mutarotation, given by 3 : 4 : 6-trimethyl-α-*d*-mannose. α-*l*-Rhamnose shows a rise of conductivity during mutarotation in agreement with *trans*-configuration. The high elevation shown by α-methylmannofuranoside is attributed to proximity of the $C_{(2)}$ and $C_{(3)}$ OH-groups to the side-chain ·CH(OH)·CH_2·OH; γ-methylglucoside, with three OH in proximity, gives a lower elevation, and γ-methylgalactoside a depression. The group ·CH(OH)·CH_2·OH alone has no effect on conductivity, since it is capable of free rotation. α-*l*-Sorbose gives an anomalous high elevation.

Results for OH-compounds in general show no considerable rise in conductivity until four OH are present. H_3BO_3 may react with H_2O in solution to give $\overset{+}{H}[\overset{-}{B}(OH)_4]$, the OH of which may be associated with the H of the org. OH-residue by OH-linkings. Increase in the no. of these decreases the negative charge on the B, thus increasing the tendency to loss of $H^{\cdot}$. The *cis*-OH at $C_{(3)}$ and $C_{(4)}$ in pyranoses have no positive effect on conductivity. *cis-cyclo*Pentane-1 : 2-diol gives an increase and *cis-cyclo*hexane-1 : 2-diol a decrease of conductivity, probably due to the OH being adjacent in the flat five-C ring and not in the strainless six-C ring. E. G. B.

Mechanism of formation of sugars from formaldehyde. S. A. Balezin (J. Gen. Chem. Russ., 1937, **7**, 2099—2115).—Condensation of CH_2O in presence of aq. $Ca(OH)_2$ at 40—45° gives chiefly aldohexoses; in addition HCO_2H, MeOH, and pentoses are formed. The yield of sugars is greater when glucose is present initially. The reaction is conveniently followed dilatometrically; dissolution of the substrates is followed by a rapid fall in vol., followed by a gradual rise, attaining a max. after 105 min. at 45°, and after 3 hr. at 40°, and followed by a second fall in vol., lasting 7—10 min. Formation of sugars takes place during this period, and proceeds to completion only when 6 mols. of CH_2O are present per $Ca^{\cdot\cdot}$. The induction period is greatly shortened by addition of glucose or fructose, but not sucrose. Further incubation after completion of the period of sugar formation leads to decomp. of sugars, causing a further increase in vol. The apparent mol. wt.–time curves have the same shape as the dilatometer curves, whence it is concluded that an intermediate product of higher mol. wt. than hexose is being formed during the induction period, and decomposes to yield hexose in the succeeding period. R. T.

Microanalysis of carbohydrates in vegetable substances.—See A., III, 159.

New preparation of osones. R. Weidenhagen (Z. Wirts. Zuckerind., 1937, **87**, 711—715).—Oxidation of sugars occurs almost homogeneously and leads mainly to osones when a moderate excess of $Cu(OAc)_2$ is used for a short time in EtOH or, preferably, in conc. MeOH. *l*-Sorbosone and *l*-xylosone (I) are thus obtained in at least 60% yield by direct oxidation of the respective sugars. The solutions of (I) have the further advantage that they can be used directly without further purification or isolation of the osone for the addition of HCN in the synthesis of vitamin-*C* (II). This takes place almost quantitatively, and the further operations can be so conducted that (II) is obtained in 42% yield calc. on the dissolved (I). Of this 50% crystallises directly on concn., and further amounts can be obtained from the mother-liquors. The solid material is of 95% purity. *d*-Xylosone is obtained in 60% yield from *d*-xylose. In contrast with sorbose, the yields with the other hexoses attain only 40%; this is reached by galactose, which under other conditions does not yield any osone. H. W.

Conversion of uronic acids into corresponding hexoses. II. Catalytic reduction of the methyl ester of 2 : 3 : 4-trimethyl-α-methyl-*d*-galacturonide. P. A. Levene, R. S. Tipson, and L. C. Kreider. **III. Catalytic reduction and deacetylation of the methyl ester of α-methyl-*d*-galacturonide 2 : 3 : 4-triacetate.** P. A. Levene and C. C. Christman (J. Biol. Chem., 1937, **122**, 199—202, 203—205; cf. A., 1937, II, 484).—II. The Me ester, $[\alpha]_D^{27}$ +166·1° in H_2O, +155·9° in abs. MeOH, +142·7° in $CHCl_3$, +149·3° in $COMe_2$, +166·5° (const.) in N-HCl, of 2 : 3 : 4-trimethyl-α-methyl-*d*-galacturonide with H_2 and Cu chromite in MeOH at 175°/4300 lb. gives a good yield of 2 : 3 : 4-*trimethyl*-α-*methyl*-d-*galactoside*, m.p. about 30°, b.p. about 140° (bath)/0·3 mm., $[\alpha]_D^{25}$ +198·4° in H_2O, $[\alpha]_D^{27}$ +160·8° in abs. MeOH, hydrolysed by N-HCl to 2 : 3 : 4-*trimethyl*-d-*galactose*, m.p. 82—83°, $[\alpha]_D^{27}$ +156° → 119·1° in H_2O in 90 min.

III. Hydrogenation (Cu chromite) of the Me ester of α-methyl-*d*-galacturonide reduces some of the OH, but that of the triacetate of this ester at 175°/3000—4300 lb. in MeOH gives α-methyl-*d*-galactoside. The Me ester of α-methylaldobionide hexa-acetate is probably similarly reduced and deacetylated. Glucosides of uronic acids give no ppt. with boiling $Ba(OH)_2$ solutions. R. S. C.

1 : 5-Anhydride of 2 : 3 : 4 : 6-tetramethylglucose-1 : 2-enediol [2 : 3 : 4 : 6-tetramethyloxyglucal]. M. L. Wolfram and D. R. Husted (J.

Amer. Chem. Soc., 1937, **59**, 2559—2561).—1-Bromo-2 : 3 : 4 : 6-tetramethyl-*d*-glucose (prep. from the acetate and HBr in Ac_2O–AcOH at 0°) with $NHEt_2$ in C_6H_6 gives 1-*diethylamino*-2 : 3 : 4 : 6-*tetramethyl*-d-*glucose*, b.p. 62—65°/10^{-4} mm., m.p. 34°, $[\alpha]_D^{29}$ −2·8° in MeOH, $[\alpha]_D^{25}$ about −8° in saturated aq. H_3BO_3 changing to +64·8° by hydrolysis of the NEt_2 (reduces Fehling's solution only after hydrolysis). With NaOH in dry dioxan–Et_2O it gives 2 : 3 : 4 : 6-tetra-*methyl*-1 : 2-d-*glucoseen* [-*oxyglucal*], b.p. 50—55°/10^{-3} mm., 99·2—99·5°/4 mm., m.p. 12°, $[\alpha]_D^{30}$ +15° in H_2O, +4° in $CHCl_3$, which reduces Fehling's solution only after hydrolysis or when kept, absorbs 2 I under Wijs' conditions, and absorbs 4 I from $NaIO_3$.

R. S. C.

Glycofuranosides and thioglycofuranosides. II. Crystalline α-ethylgalactofuranosides. J. W. Green and E. Pacsu (J. Amer. Chem. Soc., 1937, **59**, 2569—2570).—2% of *α-ethylgalactofuranoside*, m.p. 139—140°, is obtained from the mother-liquors from the β-isomeride (A., 1937, II, 369). The structure follows from the difference of its $[\alpha]_D^{20}$ (+92° in H_2O) from that of the β-compound and from the rate of hydrolysis (k = 0·08) by 0·05N-HCl. R. S. C.

Tagatose and methyltagatoside. (Mme.) Y. Khouvine and Y. Tomoda (Compt. rend., 1937, **205**, 736—738).—*α-d*-Tagatose (I), m.p. 162° (block), $[\alpha]_{578}^{20}$ −3·9° in H_2O, shows mutarotation which is not due to the presence of galactose. (I) in MeOH at 28° with dry HCl affords *methyltagatoside*, m.p. 128° (block), $[\alpha]_{578}^{20}$ +56·8° in MeOH, which has no reducing properties and is hydrolysed by acid, but not by emulsin, to (I). (I) with boiling MeOH containing HCl gives mixtures of substances. J. L. D.

Structure of two sorbose penta-acetates. G. Arragon (Compt. rend., 1937, **205**, 735—736).—Sorbose tetra-acetate with Ac_2O containing H_2SO_4 at −5° affords a *sorbose penta-acetate* (I), m.p. 95°, $[\alpha]_{578}^{20}$ −52·4° in $CHCl_3$; with Ac_2O–$ZnCl_2$ a sorbose penta-acetate (II), identical with that described previously (cf. A., 1933, 811), is formed. Hydrolysis of (I) and (II) affords sorbose (III); methylation of (I), (II), and (III) gives the same methylsorboside. (II) but not (I) shows a strong absorption band at 2700 A. which is characteristic of C:O. (II) with H_2–Raney Ni in MeOH affords, after acetylation, *d*-iditol hexa-acetate; (I) does not react similarly, indicating that it probably has a pyranose structure.

J. L. D.

Synthesis of aldobionides. W. F. Goebel, R. E. Reeves, and R. D. Hotchkiss (J. Amer. Chem. Soc., 1937, **59**, 2745).—The Me ester hepta-acetate of cellobiuronic acid or of the acacia aldobionic acid with HBr–AcOH gives the *Me* ester *hexa-acetate*, m.p. 200°, $[\alpha]_D^{24}$ +99·4° in $CHCl_3$, and m.p. 201—202°, $[\alpha]_D^{23}$ +194·7°, of *α-bromo*-4-β-*glucuronisidoglucose* and 6-β-*glucuronisidoglucose*, respectively. The latter with MeOH–Ag_2O gives 6-β-*glucuronisidomethyl-galactoside Me* ester *hexa-acetate*, m.p. 134°, $[\alpha]_D^{25}$ +86·4°, which is probably an α- and not, as expected, a β-glucoside. R. S. C.

Mol. wt. of araban. T. K. Gaponenkov (J. Gen. Chem. Russ., 1937, **7**, 1729—1732).—The mean mol. wt. as determined by the osmotic pressure, cryoscopic, terminal group, and viscosity methods is 6328, 2522, 4970, and 1102. The terminal group method is the most trustworthy; the high results given by the osmotic pressure method are ascribed to presence of low mol. wt. fragments in the sample, and the low results given by the other two methods are due to hydration of the araban mols., and to the non-applicability to araban of the Staudinger η coeff. for cellulose. R. T.

Polysaccharides. XXVI. Xylan. R. A. S. Bywater, W. N. Haworth, E. L. Hirst, and S. Peat (J.C.S., 1937, 1983—1988; cf. A., 1937, II, 277).—Earlier work has shown that xylan (I) consists of linked chains of xylopyranose units terminated at one end by arabofuranose units. By treatment of (I) with 0·005N-HNO_3 partial removal of arabinose occurs, as shown by methylation and hydrolysis of the product (xylan *A*) (II) to a mixture of trimethylpentoses consisting of trimethylarabofuranose and trimethylxylopyranose. With 0·2% $H_2C_2O_4$, however, (I) yields as arabinose-free xylan (III) which on methylation and fractionation gives a *product* (IV), $[\alpha]_D^{21}$ −91·2° in $CHCl_3$ [methylated (I) has $[\alpha]_D^{20}$ −98·3°], with viscosity < and reducing power > that of methylated (I). Hydrolysis of (IV) and fractionation gives a 7% yield of trimethylmethylxylopyranoside, corresponding with a chain length in (I) of 18—19 xylose units, in agreement with earlier work. (I), (II), and (III) have the same chain length. (I) probably consists of primary chains, arabinose–$(xylose)_{16-17}$–xylose, linked through the free xylose reducing group and an OH (possibly at $C_{(3)}$ of a xylose residue) in a second chain. This link is relatively stable to alkaline methylating agents and does not involve the arabofuranose unit since this functions as an end group. This linked chain structure is common to most polysaccharides. E. G. B.

Reactions relating to carbohydrates and polysaccharides. LIII. Structure of the dextran synthesised by the action of *Leuconostoc mesenteroides* on sucrose. F. L. Fowler, I. K. Buckland, F. Brauns, and H. Hibbert (Canad. J. Res., 1937, **15**, **B**, 486—497).—Dextran (I) (*tribenzoate*, $[\alpha]_D$ +193·7° in $CHCl_2$·$CHCl_2$; *triacetate*; *Me*$_3$ derivative (II), $[\alpha]_D^{21}$ +202·2° in $CHCl_2$·$CHCl_2$) is hydrolysed by dil. H_2SO_4 to glucose. Hydrolysis of (II) with MeOH–HCl gives 2 : 3-dimethyl-, 2 : 3 : 4-trimethyl-, and 2 : 3 : 4 : 6-tetramethyl-methylglucoside in the ratio 1 : 3 : 1. (I) is thus probably a polymeride of a pentaglucopyranose anhydride. One of the glucopyranose units is attached as a side-chain, the remaining four being most probably connected by linear linkings. Three of the linkings between glucopyranose units are of the 1 : 6 type; the remaining two are 1 : 4 or 1 : 6. The antigenic properties shown by (I) probably result from the presence of glucose side-chains. D. E. W.

Comparative study of solutions of amylose, amylophosphoric acid, and cellulose.—See A., I, 79.

Plant colloids. XLV. Alkali-lability as a characteristic of starch substances. M. Samec (Kolloid-Beih., 1937, **47**, 91—99; cf. A., 1937, II,

370).—Examination of the suitability of "alkali-lability" (alteration of reducing power after treatment with alkali) for characterising different starches and starch products shows a general, but not invariable, parallelism between the reducing power of the original and the "alkali-labile" substance, amounting to a const. ratio in the dextrin group. There is no relation between alkali-lability and I consumption. F. L. U.

Highly polymerised compounds. CLXXXII. [Lieser's micellary theory of cellulose.] H. STAUDINGER (Ber., 1937, **70**, [*B*], 2514—2517).—In reply to Lieser (A., 1937, II, 179) it is considered that in the present condition of the investigation of cellulose (I) the conception of micelle should be confined to the solid state; the colloidal particles in dil. solutions of (I) and its derivatives are macromols. The cryst. portions of solid (I) are crystallites which have a mol. lattice. Such a crystallite can be regarded as a micelle according to Nägeli's definition. H. W.

Highly polymerised compounds. CLXXXI. Solutions of cellulose. H. STAUDINGER and G. DAUMILLER (Ber., 1937, **70**, [*B*], 2508—2513).—The vals. of $K_m \times 10^4$ are 4·2, about 5·5, 5·0, 8·0, 8·0, 18—21, and 20, respectively, for cellulose (I) in NEt_4·OH, NaOH, and LiOH, Schweitzer's reagent, Cu–$(CH_2{\cdot}NH_2)_2$ solution, $Ca(CNS)_2$, H_3PO_4, and H_2SO_4 at 20°. The differences are much more marked than those observed with homopolar complex compounds in different homopolar media. This is ascribed to the fact that (I) is present as alkoxide in alkali solutions, as oxonium salt in acids, and as Cu complex in solutions of Cu salts. It is further obvious that (I) is present similarly in all these solvents, since the simple relationships between the sp. viscosity of the polymeric-homologous celluloses in different media are inexplicable if the condition is sometimes micellary and at other times mol. H. W.

Highly polymerised compounds. CLXXX. Degree of polymerisation of cellulose in different varieties of wood. H. STAUDINGER, E. DREHER, and I. JURISCH (Ber., 1937, **70**, [*B*], 2502—2507).—The proportion of cellulose (I) and cellopolyoses (II) [(I) + hemicelluloses] in finely divided poplar, pine, silver fir, spruce, and beech is determined by extraction with EtOH, C_6H_6, and Et_2O for 15 hr., desiccation at about 50°/vac., and treatment of the residue with Schweitzer's solution in absence of light and air. From this solution (II) are pptd. by Na K tartrate and, after re-pptn., have degree of polymerisation 900—1200, according to the variety of the wood. They are therefore somewhat more complex than sulphite- and soda-cellulose. Treatment of wood with 40% NaOH gives only incomplete rupture of the linkings between (II) and the other constituents of the wood. Treatment of wood with $Ca(HSO_3)_2$ or NaOH gives (II) which are sol. in Schweitzer's reagent and have degree of polymerisation 500—1000, mainly dependent on the nature of the bleaching process. Treatment of wood with dil. HNO_3 gives moderately complex (I), but the products obtained by use of HCl in dioxan and, particularly, of H_2O and EtOH at 185° are greatly degraded. Cl_2–H_2O and other oxidising agents degrade (I), which, however, is little affected by 0·25% ClO_2. Treatment of wood sawdust with 0·25% ClO_2 and C_5H_5N for 1—2 days causes removal of lignin to such an extent that the residual (II) are more or less completely sol. in Schweitzer's reagent; the process is more rapid with aged than with fresh sawdust. Determinations of the viscosity of (II) obtained in this manner show their degree of polymerisation to be similar to that of the fibre celluloses. H. W.

Flax cellulose. J. DĄBROVSKI and L. MARCHLEWSKI (Bull. Acad. Polonaise, 1937, **A**, 201—216).—Flax and cotton cellulose behave identically when hydrolysed to glucose by acid, methylated, acetylated, or converted into hydrocellulose (cf. Marchlewski *et al.*, A., 1935, 913). The Ac derivatives of the two celluloses are similar in [α], η, and Cu no., which vary according to the method of prep.; small η is correlated with large Cu no. The Me and Ac derivatives show continuous absorption in the ultra-violet; the hydrocelluloses show slight selective absorption in NaOH, increasing with time of contact. Hydrolysis of both celluloses gives solutions the [α] of which, originally high, decreases until about in accord with the amount of sucrose determined by Bertrand's method. R. S. C.

Beech wood (*Fagus silvatica*). E. SCHMIDT, W. JANDEBEUR, M. HECKER, E. COFFARI, and E. J. STOETZER [with K. MEINEL] (Ber., 1937, **70**, [*B*], 2345—2360).—The successive action of ClO_2 and C_5H_5N on beech wood transforms the lignin into sol. compounds and leaves the skeleton substance (I), about 77% of the wood, which consists of cellulose (II), xylan acetate, and the freely sol. polymeric carbohydrates. Treatment of (I) with 0·04—0·2% NaOH leaves an insol. product (III) consisting of (II) and deacetylated xylan (IV). (II) is obtained by the action of 5% NaOH containing NaCl on (III). It contains 0·282% CO_2H, in agreement with observation on native cotton cellulose and native *B*-cellulose (from sucrose and *B. xylinum*). It also contains 0·197% OMe, and since 0·199% OMe is equiv. to 0·282% CO_2H, it follows that each chain of (II) contains 96 C_6 individual links. The composition of (III) is invariable and independent of the age and origin of the investigated wood. (III) constitutes about 57% of the wood and contains 78·4% of (II) and 21·6% of (IV) corresponding with the ratio $(C_6H_{10}O_5)_3 : (C_5H_8O_4)_1$. (III) contains 0·661% CO_2H, which corresponds with 2·04% of CO_2H in (IV), which therefore contains 16 C_5 individual links in its chain. In isolated (IV) 1·88% of CO_2H is observed, so that the material is not completely stable towards 5% NaOH, though stable to the 0·2% solution. (III) of every age and from every source contains 0·466% of OMe, which is stable towards NaOH, and hence is in ether-like union. This corresponds with the presence of 1·44% of OMe in (IV), whereas 1·35% is found in the isolated material. 0·466% OMe and 0·661% CO_2H are equimol. The criteria of native composition are observed in (II) and (III) only when the wood is healthy. Wood badly damaged by frost contained >0·282% CO_2H and had the composition $(C_6H_{10}O_5)_{2\cdot86}(C_5H_8O_4)_1$. Xylan, with 2·04% CO_2H,

appears to be the carrier of the ester-like Ac group of beech wood, and since the integral relationship, xylose anhydride : Ac = 1 : 1, is established, the expression $(C_6H_{10}O_5)_3,(C_5H_7O_4Ac)$ is obtained for (I), This appears characteristic of all cell walls of beech. H. W.

Highly polymerised compounds. Determination of the viscosity of cellulose nitrates. H. Staudinger and M. Sorkin (Ber., 1937, **70**, [*B*], 2518).—A mathematical extension of published work (A., 1937, II, 447). H. W.

Additive complexes of hydrogen peroxide with organic compounds. J. H. Křepelka and R. Buksa (Chem. Listy, 1937, **31**, 447—455).—Crystal hydrate H_2O may be replaced by H_2O_2, by dissolving the substance in H_2O_2 at low temp., and pptg. with EtOH–Et_2O. The following *complexes* are described: $(CH_2)_6N_4,1{\cdot}5H_2O_2$, $CH_2(CO{\cdot}NH{\cdot}NH_2)_2,H_2O_2$, HCO_2Na,H_2O_2, $CHMeCl{\cdot}CO_2Na,H_2O_2$, quinine,$H_2SO_4$,$2{\cdot}5H_2O_2$,$H_2O$, quinine,$2HCl$,$1{\cdot}5H_2O_2$,$H_2O$, $NH_2{\cdot}CH_2{\cdot}CO_2H$,$1{\cdot}5H_2O$. The stability of these compounds varies approx. parallel with their basicity. R. T.

Methylation of glucosamine. W. O. Cutler, W. N. Haworth, and S. Peat (J.C.S., 1937, 1979—1983).—Reduction of the activity of NH_2 by substitution is necessary to avoid decomp. of glucosamine (I) during methylation. *CHPh*:, m.p. 156° (decomp.), and *o*-hydroxy- and *p*-methoxy-benzylidene derivatives of (I) cannot be methylated in aq. alkaline solution owing to decomp. to (I) and PhCHO etc. The penta-acetate (II) of (I) with Me_2SO_4 in NaOH yields N-*acetyltrimethyl*-β-*methylglucosaminide* (III), m.p. 195°, $[\alpha]_D^{21}$ +19·6° in $CHCl_3$, $[\alpha]_D^{16}$ −29·0° in H_2O, $[\alpha]_D^{20}$ −13·1° in dry MeOH, obtained in better yield from acetobromoglucosamine hydrobromide by conversion into the β-methylglucoside, and acetylation to N-*acetyltriacetyl*-β-*methylglucosaminide*, m.p. 159°, $[\alpha]_D^{17}$ −21·0° in MeOH, followed by methylation. (III) is converted by 5% HCl into *trimethylglucosamine hydrochloride*, decomp. 210°, $[\alpha]_D^{16}$ +56·8° in MeOH, mutarotating in H_2O, $[\alpha]_D^{19}$ +49·2° → +99·4°. With 2% HCl in MeOH, (III) yields N-*acetyltrimethyl*-α-*methylglucosaminide* (IV), m.p. 150°, $[\alpha]_D^{18}$ +120·0° in $CHCl_3$, $[\alpha]_D^{20}$ +104·3° in H_2O, $[\alpha]_D^{21}$ +135·0° in dry MeOH. With boiling 7% HCl in MeOH, (III) and (IV) both give *trimethyl*-α-*methylglucosaminide hydrochloride* (V), decomp. 237°, $[\alpha]_D^{20}$ +129·6° in H_2O, $[\alpha]_D^{22}$ +113·6° in MeOH, which with $NaHCO_3$ gives the free *amine*, $[\alpha]_D^{22}$ +169·8° in dry MeOH, from which (V) is regenerated by boiling with 2% HCl in MeOH. The α-configuration of (V) and (VI) is shown by their acetylation to (IV). E. G. B.

Action of sodium glycocholate on fatty acids and soaps. I. Dissolving action of glycocholate. K. Holwerda (Biochem. Z., 1937, **294**, 372—389; cf. Verzár and Kúthy, A., 1929, 1194).—The amount of saturated fatty acid (I) brought into aq. solution (PO_4 buffer) by a fixed amount of Na glycocholate (II) at p_H 6·0—6·2 and 18—20° [octoic acid (III) at 37°] decreases greatly as the C chain of (I) lengthens, the approx. max. no. of mols. of (II) required for dissolving 1 mol. of (I) being: (III) <0·35, decoic <0·75, undecoic <2·2, lauric <2·5, myristic <7, palmitic <10. The length of the chain directly affects the stability and composition of the association product, increasing length of chain tending to increase this stability and consequently to increase the amount of (I) held in solution. Opposed to this tendency, however, is the more powerful indirect effect of decreasing solubility of (I) in H_2O (or H_2O + buffer) as length of chain increases. W. McC.

Crystalline anhydrous and monohydrated *dl*-glutamic acid. M. S. Dunn and M. P. Stoddard (J. Biol. Chem., 1937, **121**, 521—529).—Na *d*-glutamate and NH_4Cl at 230—235° give a product (containing *dl*-pyroglutamide and *dl*-2-pyrrolidonecarboxylic acid), which with boiling 6N-HCl gives *dl*-glutamic acid (I). Crystallographic data are given for the monohydrate of (I), distinguishable microscopically from the anhyd. form; the existence of the two forms may explain previous discrepancies in solubility data (A., 1934, 139). E. W. W.

Oxidation of cysteine in non-aqueous media. "Sulphenic acid" as primary oxidation product. G. Toennies (J. Biol. Chem., 1938, **122**, 27—47).—$Bu^{\beta}OH$ is the best medium for the demonstration of the "sulphenic acid" among the S-containing products which are pptd. from cysteine perchlorate solutions by the action of $H_2S_2O_8$. The "sulphenic acid" is present in variable amounts. P. G. M.

Reactions of semimercaptals with amino-compounds. M. P. Schubert (J. Biol. Chem., 1937, **121**, 539—548; cf. A., 1936, 824).—The OH of $OH{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CO{\cdot}NHPh$ (I) reacts with NH_2-compounds to form aminomethyl thioethers. With 2 : 4 : 1-$(NO_2)_2C_6H_3{\cdot}NH{\cdot}NH_2$ in AcOH, 2 : 4-*dinitrophenylhydrazinomethylthiolacetanilide*, m.p. 125—127°, is formed. $NHPh{\cdot}NH_2$, (I), EtOH, and aq. KOAc yield *phenylhydrazinobismethylthiolacetanilide*, $NHPh{\cdot}N(CH_2{\cdot}S{\cdot}CH_2{\cdot}CO{\cdot}NHPh)_2$, m.p. 120—122°. With $C_5H_{11}N$ in EtOH, *piperidinomethylthiolacetanilide*, m.p. 60—61° (*hydrochloride*, m.p. 180—182°), is formed, and with glycine, *carboxymethylaminobismethylthiolacetanilide*, m.p. 109°. *o*-$NH_2{\cdot}C_6H_4{\cdot}CO_2H$ yields o-*carboxyphenylaminomethylthiolacetanilide*, m.p. 146—148°. These compounds behave as if dissociated in EtOH; thus they react readily with I, and all, like $SH{\cdot}CH_2{\cdot}CO{\cdot}NHPh$ itself, with $HgCl_2$ in OH, give the *compound* $Hg[S{\cdot}CH_2{\cdot}CO{\cdot}NHPh]_2,HgCl_2$. The reported formation of an additive compound of cysteine and $AcCO_2H$ is not confirmed. In C_5H_5N a *compound* (II) (*Zn* derivative, $C_6H_7O_4NSZn,3H_2O$) is obtained of composition varying between that of $CO_2H{\cdot}CMe(OH){\cdot}S{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$ and $CO_2H{\cdot}CMe<\begin{matrix}NH\\S{\cdot}CH_2\end{matrix}>CH{\cdot}CO_2H$ (III), which with C_5H_5N yields the C_5H_5N salt, m.p. 100—101°, of (III). The reported prep. of an Ac_2 derivative is not confirmed. In Ac_2O–AcOH–C_5H_5N, (II) gives the *Ac* derivative (IV), m.p. 225—226°, of (III), with the C_5H_5N salt, m.p. 160—162°, and the *anhydride*, m.p. 134—136°, of (IV). *o*-$C_6H_4Me{\cdot}NH_2$ gives the o-*toluidide* of (IV). α-$C_{10}H_7{\cdot}NCO$ and (II) form the *compound* $C_{17}H_{16}O_5N_2S$. $AcCO_2H$ and $SH{\cdot}CH_2{\cdot}CO_2H$ give S-*carboxymethyl*-α-*thiol-lactic acid*, m.p. 112—113°;

this with α-$C_{10}H_7$·NCO yields *α-thiolacetic acid* S-*carboxy-α′-naphthylamide*. The compound of $SH·CH_2·CO_2H$ and BzCHO (A., 1936, 55) with AcOH–NaOAc yields the *compound* $CHBz<^{O·CO}_{S}>CH_2$, m.p. 93—94°. E. W. W.

Isomeric amylcarbamides and derived barbitals. J. S. Buck and A. M. Hjort (J. Amer. Chem. Soc., 1937, **59**, 2567—2569).—The following are prepared. tert.-*Butyl-acetamide*, m.p. 134°, and -*malonic acid*, m.p. 156°; dl-sec.-*amyl*-, m.p. 144°, α-*ethyl*-n-*propyl*-, m.p. 193°, dl-sec.-iso*amyl*-, m.p. 200°, and -β-*methyl*-n-*butyl-carbamide*, m.p. 125°; dl-sec.-iso*amyl*-, m.p. 216°, β-*methyl*-iso-, m.p. >285°, and -n-*butyl-amine hydrochloride*, m.p. 180°; 5 : 5-*diethyl*-1-n-, m.p. 36°, -iso-, m.p. 78°, -sec.-, m.p. 35°, -sec.-iso-, m.p. 132°, and -tert.-*amyl*-, m.p. 75°, -1-α-*ethyl*-n-*propyl*-, m.p. 85°, -β-*methyl*-n-*butyl*-, m.p. 76°, and -β-*methyl*iso*butyl-barbituric acid*, m.p. 112°. The min. hypnotic and lethal doses of the carbamides and barbiturates are listed. R. S. C.

Phosphine and arsine derivatives of silver and aurous halides.—See A., I, 65.

Compounds of platinum with unsaturated hydrocarbons of the ethylene series.—See A., I, 43.

Two reactions for detection of *cyclo*pentadiene. A. P. Terentiev and M. I. Ivanova (J. Gen. Chem. Russ., 1937, **7**, 2087—2091).—The gas is passed into a solution of 30 g. of $Hg(NO_3)_2$ in 100 ml. of dil. HNO_3; a turbidity is obtained in presence of <0·25 mg. *cyclo*pentadiene (I). Aromatic hydrocarbons, $CMe_2{:}CH_2$, $(CHMe{:})_2$, and $(CH_2{:}CH·)_2$ do not interfere, but C_2H_2 gives a similar reaction. Alternatively, the gas is passed into 0·25% *p*-benzoquinone in EtOH, and a few drops of 10% KOH are added; a blue coloration appears in presence of <5 mg. of (I). C_2H_2 does not interfere. R. T.

Cracking of di*cyclo*pentyl in presence of anhydrous aluminium chloride. J. K. Juriev, R. J. Levina, and M. I. Spektor (J. Gen. Chem. Russ., 1937, **7**, 1581—1586).—The products obtained by heating di*cyclo*pentyl with $AlCl_3$ at 170—290° contain *cyclo*hexane about 35, *cyclo*pentane 46, and paraffin hydrocarbons 18·5%. R. T.

Contact transformations of δ-*cyclo*hexyl-Δ^{α}-butine. R. J. Levina and A. I. Ivanov (J. Gen. Chem. Russ., 1937, **7**, 1866—1867).—δ-*cyclo*Hexyl-Δ^{α}-butene and Br in Et_2O give αβ-*dibromo*-δ-*cyclohexylbutane*, b.p. 155°/13 mm., converted by heating with $NaNH_2$ at 160° into δ-*cyclo*hexyl-Δ^{α}-butine. This yields PhBu$^{\alpha}$ and butyl*cyclo*hexane when heated with Pt on C. R. T.

1 : 4-Bisdiphenylmethylene*cyclo*hexane. Stabilisation of linkings in rings. G. Wittig and H. Pook (Ber., 1937, **70**, [*B*], 2485—2491).—1 : 4-*Bisdiphenylmethylene*cyclo*hexane* (I) is much more stable towards heat and alkali metals than is its acyclic analogue ααζζ-tetraphenyl-$\Delta^{\alpha\epsilon}$-hexadiene, the linking becoming stabilised by being involved in a ring. Terephthalic acid, purified through the Et_2 ester, is smoothly hydrogenated to a mixture of the *cyclo*hexane-1 : 4-dicarboxylic acids when the suspension of its K salt in H_2O is hydrogenated under pressure in presence of a Ni–Co–Cu catalyst at 320°. Me_2 *trans-cyclo*hexane-1 : 4-dicarboxylate in Et_2O is transformed by LiPh into trans-1 : 4-*dihydroxydiphenylmethyl*cyclo*hexane* (II), m.p. 252—253·4°. cis-1 : 4-*Dihydroxydiphenylmethyl*cyclo*hexane* (III), m.p. 195—196°, is derived similarly from the corresponding *cis*-ester. (II) is converted by boiling MeOH containing a little H_2SO_4 into trans-1 : 4-*dimethoxydiphenylmethyl*cyclo*hexane*, m.p. 3053—07°, converted by K–Na followed by MeOH and H_2O into trans-1 : 4-*dibenzhydryl*cyclo*hexane* (IV), m.p. 248—250°; analogous methods do not lead to the isolation of cis-1 : 4-*dimethoxydiphenylmethyl*cyclo*hexane*, m.p. 174—176°, which is obtained from (III) and K phenyl*iso*propyl and is transformed by K–Na into cis-1 : 4-*dibenzhydryl*cyclo*hexane*, m.p. 224—225°. (II) or (III) with HCl in boiling AcOH affords (I), m.p. 258—260°. This is converted by K–Na in dioxan into (IV) in 70% yields, with unidentified hydrocarbon fractions, m.p. 146—147° (V), and m.p. 104·3—106°, respectively. For purposes of comparison Me_2 αα′-dimethyladipate (mixture of isomerides) is converted by LiPh into a mixture, m.p. 219—223°, of the stereoisomeric αζ-*dihydroxy*-ααζζ-*tetraphenyl*-βε-*dimethylhexanes*, which is dehydrated to ααζζ-*tetraphenyl*-βε-*dimethyl*-$\Delta^{\alpha\epsilon}$-*hexadiene*, m.p. 145—146° [not identical with (V)]. This is converted by K–Na in Et_2O followed by EtOH into $CPh_2{:}CMe_2$ or followed by CO_2 into *γγ-diphenyl*-β-*methyl*-Δ^{β}-*butenoic acid*, m.p. 119—121°. H. W.

Oxidation of hydrocarbons in the vapour phase. I. Aromatic hydrocarbons. II. Hydroaromatic hydrocarbons. J. K. Chowdhury and M. A. Saboor (J. Indian Chem. Soc., 1937, **14**, 633—637, 638—643).—I. Oxidation of $C_{10}H_8$ using as catalyst V_2O_5, Sn vanadate, Mn vanadate, Sn and V oxides, and Ni and Al oxides, gives phthalic (I) and maleic (II) anhydrides with small amounts of 1 : 4-naphthaquinone, BzOH, and $C_{10}H_7$·OH; the greatest activity is shown by mixed Sn and V oxides, and Sn vanadate. Phenanthrene is similarly oxidised to (I), with small quantities of (II), naphthalic anhydride, benzoquinone, and phenanthrol. The mechanism of the oxidation is suggested.

II. *cyclo*Hexane is oxidised to MeCHO, acraldehyde, AcOH, $AcCO_2H$, and some peroxides; temp. and flow of air influence the nature and yield of the products. Similar oxidation decahydronaphthalene gives (I) and (II), $CH_2(CO_2H)_2$, naphthaquinone, and CH_2O. F. R. S.

Alkylation with a hydrogenating catalyst. V. I. Komarewsky (J. Amer. Chem. Soc., 1937, **59**, 2715—2716).—Passage of C_2H_4 and C_6H_6 over Ni–Al at 350° gives PhMe (5%), $C_{10}H_8$ + Ph_2 (2%), and some H_2, CH_4, and C_2H_6; C_6H_6 alone gives only a little Ph_2 and traces of H_2; the alkylation is thus due to formation of PhEt, which is known to decompose under the experimental conditions. C_2H_4 and *cyclo*hexane (I) over Ni–Al at 300° give PhMe (5%), CH_4, H_2, and C_2H_6; since (I) alone gives C_6H_6, the alkylation is preceded by dehydrogenation.

C_2H_4 alone gives C, H_2, CH_4, and C_2H_6. Olefines are not formed in any of the reactions. R. S. C.

Contact isomerisation of ethylenic hydrocarbons. R. J. Levina (J. Gen. Chem. Russ., 1937, **7**, 1587—1593).—Allylbenzene and *o*-, *m*-, and *p*-allyltoluene yield the corresponding propenyl derivatives when passed over floridin at 220—225°. Under such conditions, $(CH_2{:}CMe{\cdot}CH_2{\cdot})_2$ gives $(CMe_2{:}CH{\cdot})_2$, and diallyl gives $(CHMe{:}CH{\cdot})_2$. R. T.

Liquid-phase reactions at high pressures. II. Polymerisation of ethylenes. R. H. Sapiro, R. P. Linstead, and D. M. Newitt (J.C.S., 1937, 1784—1790).—Substances, $Ar{\cdot}CR{:}CH_2$, but not $Ar{\cdot}CR{:}CHR$, are readily polymerised at 100—150°/5000—10,000 atm. in absence of catalysts. The behaviour of $CPhMe{:}CH_2$ is studied in detail at 2000—10,000 atm.: at 100° up to 85% of polymeride (I) of mean mol. wt. 5400—5800 is formed, with very little lower polymeride; raising the temp. decreases both the yield and mol. wt. of the high polymeride and gives increasing amounts of lower polymerides; (I) is partly depolymerised at 125°. The unsaturated dimeride cannot be polymerised. Two modes of polymerisation are thus proved, viz., formation of (I) (main reaction at 100°) and of lower polymerides (significant at 125°). Dry HCl favours formation of lower polymerides, but not of (I); Bz_2O_2 diminishes formation of both. $ZnCl_2$ causes absence of (I) and formation of 90% of lower polymerides. Pouring (I) in C_6H_6 into MeOH ppts. it as fibres, but it is mainly hemicolloidal. At 100—150°/5000—10,000 atm. $CPhMe{:}CH_2$ gives only traces of dimeride, and $CH_2Ph{\cdot}CH_2{\cdot}CH{:}CH_2$ is almost unchanged. $CMe_2{:}CHMe$ gives no polymeride. $CPh_2{:}CH_2$ gives 35% of saturated (Br) *dimeride*, m.p. 100—105°. At 125°/5000 atm. α-$C_{10}H_7{\cdot}CMe{:}CH_2$ gives 1·9% of penta- to hexa-meride, but at 10,000 atm. affords 58% of (? amorphous) *polymeride*, sublimes at about 320° (decomp.) in a sealed tube, readily hydrolysed; 0·25% of dry HCl does not accelerate this reaction. R. S. C.

Effect of oxygen and reduced nickel on the catalytic action of hydrogen bromide on the isomerisation of *iso*stilbene to stilbene. Y. Urushibara and O. Simamura (Bull. Chem. Soc. Japan, 1937, **12**, 507—509).—A direct influence on the isomerisation of *iso*stilbene to stilbene is not exerted by O_2 or reduced Ni, but they co-operate with HBr, which is inactive by itself, in accelerating the change. It appears probable that in the presence of O_2 or Ni an active catalyst is formed from HBr. H. W.

Dissociation of hexa-*p*-alkylphenylethanes. M. F. Roy and C. S. Marvel (J. Amer. Chem. Soc., 1937, **59**, 2622—2625; cf. A., 1937, II, 373).—The % dissociation of compounds, $C_2(C_6H_4R\text{-}p)_6$, is found by the magnetic method to be R = Et 3·5, Pr^{α} 4·2, Pr^{β} 4·5, Bu^{α} 4·9, CHMeEt 5·9, and Bu^{β} 6·7. The increase in dissociation with increasing mol. wt. and branching of the chain is contrary to electronic ideas of Ingold. R. S. C.

Photosensitive nitro-compounds. N. N. Voroschcov and V. V. Kozlov (Prom. Org. Chim., 1937, **4**, 399—406).—The work of the authors (1921—1937) is reviewed. R. T.

Mechanism of M. I. Konovalov's reaction. I. A. I. Titov (J. Gen. Chem. Russ., 1937, **7**, 1695—1703).—PhMe and NO_2 yield mixtures of $CHPh(NO_2)_2$, $CH_2Ph{\cdot}NO_2$, $C_6H_4Me{\cdot}NO_2$, and BzOH, the yields and relative proportions of the products varying according to the temp. and duration of the reaction, and to the $[NO_2]$. Analogous results are obtained with PhMe and HNO_3 (*d* 1·4). The mechanism of the reaction is discussed. R. T.

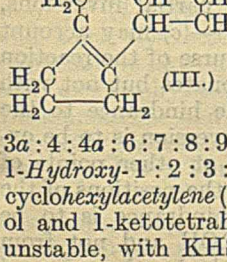
Isomerisation in cracking of hydrindene with aluminium chloride. M. B. Turova-Pollak and F. I. Podolskaja (J. Gen. Chem. Russ., 1937, **7**, 1738—1741).—Hydrindene yields *cyclo*pentane derivatives and methyldi*cyclo*pentane when heated with $AlCl_3$ at 170—230°. R. T.

Cyclisation of dieneynes. IV. *trans*-1 : 2-Dialkyloctahydronaphthalene derivatives. G. A. Nesty and C. S. Marvel. **V. Hydrophenanthrenes.** P. S. Pinkney, G. A. Nesty, D. E. Pearson, and C. S. Marvel. **Fused ring systems from dieneynes. VI. Limitations of the cyclisation reaction.** P. S. Pinkney and C. S. Marvel (J. Amer. Chem. Soc., 1937, **59**, 2662—2665, 2666—2668, 2669—2672; cf. A., 1936, 313).—IV. Syntheses of *trans*-1 : 2-dialkyloctahydronaphthalenes are described, the *trans*-structure being inferred from the resistance of the products to dehydrogenation. Addition of MgEtBr and then of $COPr^{\alpha}_2$ to 1-acetylenyl*cyclo*hexan-1-ol gives α-1-*hydroxy*cyclo*hexyl*-γ-n-*propyl*-Δ^1-*hexinen*-γ-*ol* (I), m.p. 65—67°, dehydrated by $KHSO_4$ at 190—200° to α-Δ^1-cyclo*hexenyl*-γ-n-*propyl*-n-*hex*-Δ^{γ}-*en*-Δ^{α}-*inene*, b.p. 98—100°/2 mm. (oxidises in air). This is hydrogenated (PtO_2; 3 atm.) in EtOH to α-cyclo*hexyl*-γ-n-*propyl*-n-*hexane*, b.p. 83—85°/2 mm., and is cyclised by HCO_2H to 1-*keto*-4-*ethyl*-3-n-*propyl*-1 : 2 : 5 : 6 : 7 : 8 : 9 : 10-*octahydronaphthalene*, b.p. 107—108°/2 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 168—169°), converted by Zn–Hg–HCl into 1-*ethyl*-2-n-*propyl*-3 : 4 : 5 : 6 : 7 : 8 : 9 : 10-*octahydronaphthalene* (II), b.p. 89—90°/2 mm., obtained also in poor yield from (I) by Zn–Hg–HCl. PtO_2-hydrogenation of (II) gives 1-*ethyl*-2-n-*propyldecahydronaphthalene*, b.p. 79—89°/2 mm. Similar reactions starting from $COBu^{\alpha}_2$ give α-1-*hydroxy*cyclo*hexyl*-γ-n-*butyl*-Δ^{α}-*heptinen*-γ-*ol*, m.p. 71·5—72·5°, α-Δ^1-cyclo*hexenyl*-γ-n-*butyl*-n-*hept*-Δ^{γ}-*en*-Δ^{α}-*inene*, b.p. 112—113°/2 mm., α-cyclo*hexyl*-γ-n-*butyl*-n-*heptane*, b.p. 95—96°/2 mm., 1-*keto*-4-n-*propyl*-3-n-*butyl*-1 : 2 : 5 : 6 : 7 : 8 : 9 : 10-*octahydronaphthalene* (III), b.p. 128—131°/2 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 156—157°), 1-n-*propyl*-2-n-*butyl*-3 : 4 : 5 : 6 : 7 : 8 : 9 : 10-*octahydronaphthalene* (IV), b.p. 109—110°/2 mm., and 1-n-*propyl*-2-n-*butyldecahydronaphthalene*, b.p. 98—100°/2 mm. The position of the ethylenic linking in the $C_{10}H_{16}$ derivatives is determined by ozonisation of (III) in CCl_4 to $Bu^{\alpha}CO_2H$ and 2-n-*butyryl*cyclo*hexane*-1-*carboxylic acid*, b.p. 165—170°/2 mm. With Se at 365—390° (II) and (III) give blue liquids, containing Se, showing none of the ultra-violet absorption bands of $C_{10}H_8$ derivatives, but showing bands at

260, 267, and 273 mμ., characteristic of compounds having fused C_6H_6 and alicyclic rings.

V. Phenanthrene derivatives are obtained, but not always in good yield, and sometimes cyclisation fails. Di-Δ^1-*cyclo*hexenylacetylene (I), b.p. 105—110°/1·5 mm., m.p. < room temp., is obtained in 88% yield from di-1-hydroxy*cyclo*hexylacetylene (II) by $KHSO_4$ at 200—205°. With Zn–Hg–HCl (II) or (much less readily) (I) gives $\Delta^{11:12}$-dodecahydrophenanthrene, which gives with Se at 300—335° *trans-as*-octahydrophenanthrene, b.p. 94—95°/1·5 mm. The H_8-compound is oxidised to *o*-$C_6H_4(CO_2H)_2$ and absence of αα-pentamethylenehomophthalic acid indicates absence of the spirane. 1-Phenylacetylenyl*cyclo*hexanol (prep. from CPh:C·MgBr and *cyclo*hexanone in 66% yield) with PCl_5 gives 75% of phenyl-Δ^1-*cyclo*hexenylacetylene, b.p. 117—118·5°/1·5 mm., which with HCO_2H or AcOH gives CH_2Ph Δ^1-*cyclo*hexenyl ketone (semicarbazone, new m.p. 170—171°) and no cyclic product. The ketone with H_2–Raney Ni gives αβ-di*cyclo*hexylethyl alcohol; similar reduction of 9-keto-$\Delta^{11:12}$-dodecahydrophenanthrene gives *tetradecahydrophenanthr*-9-*ol*, b.p. 122—125°/1·5 mm. With H_2–PtO_2–Pt-black at 40—50 lb. in AcOH (II) gives αβ-di-1-hydroxy*cyclo*hexylethylene, m.p. 154—155°, but in HBr–EtOH gives αβ-*di*cyclo*hexylethane*, m.p. 128—129°.

VI. The following reactions and those previously reported indicate the following necessities for ring formation from compounds containing C:C·C:C. At least one terminal C must carry a H; substitution must be sufficient to repress the rate of polymerisation; the C:C may not be part of an aromatic ring; one, but not both, of the unsaturated linkings may be conjugated with an aromatic ring. *cyclo*Pentanone and $(:C\cdot MgBr)_2$ in Et_2O give 77% of *di*-1-*hydroxy*-cyclo*pentylacetylene* (I), m.p. 107—108°, and traces of 1-*acetylenyl*cyclo*pentanol* (II), m.p. 20°, b.p. 65—65·5°/16 mm.; $(:C\cdot MgI)_2$ gives only 42% of (II) and much *cyclo*pentylidene*cyclo*pentanone. With $KHSO_4$ (I) gives *di*-Δ^1-cyclo*pentenylacetylene*, m.p. 58·5—60°, hydrogenated to αβ-*di*cyclo*pentylethane*, b.p. 109—110°/17 mm. With Zn–Hg–HCl (I) or (II) gives a little 1 : 2 : 3 : 3*a* : 4 : 5 : 6 : 7 : 8 : 8*b*-*decahydro*-as-*indacene* (III), b.p. 107—108°/17 mm., reduced by H_2–Raney Ni to *dodecahydro*-as-*indacene*, b.p. 106—108°/18 mm. Only tars are obtained from (I) and (II) by H_2SO_4 and AcOH or HCO_2H. 1-Hydroxy*cyclo*-pentyl-1′-hydroxy*cyclo*hexyl-acetylene and Zn–Hg–HCl give 3*a* : 4 : 4*a* : 6 : 7 : 8 : 9 : 9*b*-octahydro-α-naphthindane. 1-*Hydroxy*-1 : 2 : 3 : 4-*tetrahydronaphthyl*-1′-*hydroxy*-cyclo*hexylacetylene* (prep. from 1-acetylenyl*cyclo*hexanol and 1-ketotetrahydronaphthalene), m.p. 85—95°, unstable, with $KHSO_4$ gives Δ^1-cyclo*hexenyl*-3 : 4-*dihydro*-1-*naphthylacetylene*, b.p. 170—172°/2 mm., which gives tars with acidic cyclising agents, but with Zn–Hg affords 1 : 2 : 2*a* : 3 : 4 : 5 : 6 : 6*a* : 7 : 8-*decahydrochrysene*, b.p. 140—144°/1·5 mm., not converted into chrysene by Se. *Di*-3 : 4-*dihydro*-1-*naphthylacetylene*, m.p. 120—121°, obtained directly from



(III.)

$(:C\cdot MgBr)_2$ and the ketone, could not be cyclised. $COBu^{\beta}\cdot CH_2Ph$ leads to δη-*dibenzylidene*-ακ-*dimethyl*-Δ^{ϵ}-*noninene*, b.p. 179—180°/2 mm., which could not be cyclised. R. S. C.

Oxidation of anthracene and methylanthracene by chromic acid and by dilute nitric acid. M. A. Iljinski and E. S. Pokrovskaja (Compt. rend. Acad. Sci. U.R.S.S., 1937, **17**, 111—115).—Variations in vals. obtained when anthracene (I) is determined in presence of methylanthracene (II) by CrO_3 oxidation are caused by variations in concn. of solvent AcOH. In conc. AcOH, some methylanthraquinone (III) is formed, and there is considerable destruction of the anthracene nucleus. In aq. AcOH suspension, anthraquinone and (III) are, however, extremely stable. In dil. HNO_3, (I) and (II) give only impure products. E. W. W.

Homologues of para-anthracene: polymerides of 9-methyl- and 9-ethyl-anthracene. A. Willemart (Compt. rend., 1937, **205**, 993—994).—9-Methyl- and 9-ethyl-anthracene in Et_2O yield, on irradiation with the light of a Hg-vapour lamp, *polymerides* of high m.p., which when heated to the m.p. regenerate the original hydrocarbons. 9 : 10-Dimethyl-, 9-methyl-10-ethyl-, and 9-phenyl-anthracene do not polymerise. J. D. R.

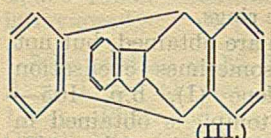
Alkyl derivatives of anthracene. E. Martin (Ann. Off. nat. Combust. Liq., 1937, **12**, 97—147).—The chemical and physical properties of the 9 : 10-dialkyl-, 9 : 10-dialkyl-9 : 10-dihydro-, and 9 : 9 : 10 : 10-tetra-alkyl-anthracenes and anthracene (I) are compared. Hydrogenation (Ni) of 9 : 10-di*iso*butyl-9 : 10-dihydroanthracene (II) gives 9 : 10-*diiso*butyl-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 9 : 10-*decahydroanthracene*, m.p. 86—87°. 9 : 9 : 10 : 10-Tetra*iso*butyldihydroanthracene is not hydrogenated at room temp. but higher temp. gives paraffins, alkyl-benzenes and -naphthalenes. (I) and 9 : 10-dihydroanthracene form 1 : 2 : 3 : 4 : 9 : 10-hexabromo-1 : 2 : 3 : 4 : 9 : 10-hexahydroanthracene. 9 : 10-Di*iso*butylanthracene and (II) give 1 : 2 : 3 : 4-tetrabromo-9 : 10-di*iso*butyl-1 : 2 : 3 : 4-tetracene. The 9 : 9 : 10 : 10-tetra-alkyl-9 : 10-dihydroanthracenes do not react with Br in the dry state or in CCl_4. The 9 : 10-dialkylanthracenes are oxidised by HNO_3–H_2SO_4 in the same manner as (I) and give anthraquinone. 9 : 9 : 10 : 10-Tetra-*iso*butyl-9 : 10-dihydroanthracenes, however, are nitrated; *e.g.*, 9 : 9 : 10 : 10-dihydroanthracene gives a 2 : 7-$(NO_2)_2$-derivative, m.p. 232—233°, identified by oxidation to 2 : 7-dinitroanthraquinone. Reduction gives 2 : 7-*diamino*-9 : 9 : 10 : 10-*tetra*iso*butyl*-9 : 10-*dihydroanthracene*, m.p. 158—160°. 9 : 10-Di-*iso*butyl-9 : 10-disodioanthracene (III) with CO_2 gives 9 : 10-*diiso*butylanthracene-9 : 10-*dicarboxylic acid*, m.p. 255—257° (decomp.). (III) with H_2O leads to rearrangement to 9 : 9-*diiso*butyl-10 : 10-*dihydroanthracene*, m.p. 97—98°, also produced from (II) and $AlCl_3$ in the cold. On dehydrogenation with Br or benzoquinone this *gem*-dialkyl compound yields 9 : 10-di*iso*butylanthracene. The ultra-violet absorption spectrum of this hydrocarbon resembles those of 9 : 9-diethyl-10 : 10-dihydroanthracene and CH_2Ph_2. D. J. B.

Dissociable anthracene oxides. Influence of *meso*-aliphatic groups. A. Willemart (Compt. rend., 1937, **205**, 866—867; cf. A., 1937, II, 93).—9-Methyl-, 9 : 10-diethyl-, 9-10-dimethyl-, and 9-*methyl*-10-*ethyl*-*anthracene*, m.p. 144° (prepared from 9-methylanthrone and MgEtI), when insolated in CS_2 absorb 2 O per mol.; the photo-oxides decompose when gradually heated but do not liberate O_2. Rapid heating liberates a little O_2. J. L. D.

Reduction and hydrogenation of compounds of the 1 : 2-benzanthracene series. L. F. Fieser and E. B. Hirschberg (J. Amer. Chem. Soc., 1937, **59**, 2502—2509).—1 : 2-Benzanthracene (prep. in 61% yield from α-$C_{10}H_7$·CO·C_6H_4Me-*o*; Zn is a catalyst) with H_2–PtO_2 in EtOH containing a little $FeCl_2$ and HCl gives the 5 : 6 : 7 : 8-*H*$_4$-derivative, m.p. 88·5—89·5° [*picrate*, m.p. 156·5—157·5°; $C_6H_3(NO_2)_3$ *compound*, m.p. 159·5—160·5°], but with Na–*iso*-C_5H_{11}·OH gives the 1′ : 2′ : 3′ : 4′ : 9 : 10-*H*$_6$-compound, m.p. 69·3—69·9° [no picrate or $C_6H_3(NO_2)_2$ compound], also obtained from 1′ : 2′ : 3′ : 4′-tetrahydro-1 : 2-benzanthracene by Na in xylene, followed by EtOH, or from 1′ : 2′ : 3′ : 4′-tetrahydro-1 : 2-benzanthranyl 10-acetate (I) by Zn dust, aq. NH_3, and PhMe. Catalytic hydrogenation of 10-methyl-1 : 2-benzanthracene (II) gives similarly the 5 : 6 : 7 : 8-*H*$_4$-derivative, m.p. 73·9—74·4° (*picrate*, m.p. 186—187°; gives a cryst. *quinone*, forming a *quinoxaline* derivative, m.p. 162—164°). 1′ : 2′ : 3′ : 4′-Tetrahydro-1 : 2-benzanthr-10-one and MgMeCl give 10-*methyl*-1′ : 2′ : 3′ : 4′-*tetrahydro*-1 : 2-*benzanthracene*, m.p. 117·3—117·8° (*picrate*, m.p. 161—162°), which by the Na–xylene–EtOH process gives 10-*methyl*-1′ : 2′ : 3′ : 4′ : 9 : 10-*hexahydro*-1 : 2-*benzanthracene*, an oil, unstable in air (oxidised to 1′ : 2′ : 3′ : 4′-tetrahydro-1 : 2-benzanthraquinone), also obtained from (II) by Na–C_5H_{11}·OH or from the 9 : 10-H_2-compound [prepared from (II) by the Na–xylene–EtOH process], m.p. 94·4—94·9° (*picrate*, m.p. 112·5—113·5°; oxidised to 1 : 2-benzanthraquinone), by H_2–PtO_2 in EtOH–$FeCl_3$. Hydrogenation of 1 : 2-benzanthranyl 10-acetate (III) in AcOH gives 5 : 6 : 7 : 8-*tetrahydro*-1 : 2-*benzanthranyl acetate*, m.p. 159—159·5°, oxidised by CrO_3 to 10-*acetoxy*-5 : 6 : 7 : 8-*tetrahydro*-1 : 2-*benz*-3 : 4-*anthraquinone*, m.p. 232—233° (*quinoxaline* derivative, m.p. 276—278°). Prolonged hydrogenation of (III) gives 1′ : 2′ : 3′ : 4′ : 5 : 6 : 7 : 8-*octahydro*-1 : 2-*benzanthranyl acetate*, m.p. 129·3—129·6°, also obtained by hydrogenation of (I). The hydrocarbons are usually better purified by way of the $C_6H_3(NO_2)_3$ compounds than of the picrates; they are best recovered from either by chromatographic absorption. 1 : 2-*cyclo*Pentano-5 : 10-aceanthrene is carcinogenic. Injection of (II) into mice gives tumours much more rapidly than does painting; the difference due to method of administration is less marked with other compounds. R. S. C.

Long life of excited organic molecules, exemplified by the rubrene oxidation.—See A., I, 40.

Indene group. I. Diene synthesis of anthraindane. E. Mameli (Gazzetta, 1937, **67**, 669—681).—Anthracene (I) and excess of indene (II) combine at 200—211° in CO_2 to a 94—96% yield of 9 : 10-*anthra*-2′ : 3′-*indane* [endo-2′ : 3′-*indano*-9 : 10-*anthracene*] (III), m.p. 118° (98° ex C_6H_6), which is stable, in C_6H_6 or EtOH, to light or heat, is insol. in cold H_2SO_4, stable to Br or to dil. $KMnO_4$–Na_2CO_3, and, unlike (II), does not react with $Et_2C_2O_4$–NaOEt or with PhCHO. CrO_3–H_2SO_4 oxidises (III) to anthraquinone and a substance, m.p. 202°. At 200—300°, (III) decomposes into (I) and (II). In fluorescence it resembles fluorene. C_6H_6, $C_{10}H_8$, or phenanthrene does not combine with (II). The structure of (I) is discussed. E. W. W.


(III.)

Walden inversion. W. Hückel [with, in part, E. Kammenz, A. Gross, W. Tappe, E. Tiedermann, and G. Becker] (Annalen, 1937, **533**, 1—45).—Walden inversion can be studied with compounds containing two asymmetric C, as the occurrence or absence of inversion depends on the energy difference between the complex of reactants and the stereoisomeric products and is thus independent of a second asymmetric centre. Further examples are provided that acylation with *p*-C_6H_4Me·SO_2Cl and C_5H_5N or hydrolysis of acetates does not cause inversion, but that production of acetates from *p*-toluenesulphonates by KOAc in EtOH, but less so in AcOH, involves inversion. The nature of the alcohol obtained by alkaline reduction or hydrogenation in acid of a cyclic ketone is correlated with the nature of the amine obtained from the corresponding oxime; existing data on these points and on the steric outcome of the reaction of an amine with HNO_2 are summarised and extended. In particular, new data are provided on the reaction of HNO_2 with amines of the decahydronaphthalene and hydrindane series and such regularities as exist are stressed. The possibility that *sec.* amines and HNO_2 give aliphatic diazo-compounds is refuted and it is concluded that reaction occurs by way of RN_2^+, which breaks down to N_2 and R^+. The outcome of the reaction may be (*a*) loss of H^+ from R^+ to yield an olefine, this being effected either by spontaneous decomp. or under the influence of a negative ion, (*b*) union of R^+ and OH^- to give ROH, or (*c*) union of R^+ and H_2O to give a complex $[\rangle C{\cdot}OH_2]^+$, which loses H^+ to give ROH. These mechanisms can be applied to any reaction involving positive C ions. Simultaneous occurrence of (*b*) and (*c*) may account for partial inversions, or the alternative mechanisms (*a*)—(*c*) may account for the effect of solvent on the course of the reaction (evident with the *p*-toluenesulphonates but not with the amines). If R^+ offers steric hindrance to the approach of OH^- or H_2O, then inversion is to be expected, since reaction will occur at other points of the mol. involving disturbance of the positions of the substituents (existence of such hindrance is to be judged from the reactivity of ROH and not from models). Such hindrance should, in the case of amines and HNO_2, lead to formation of relatively large amounts of olefines, but other factors, *e.g.*, ring size, also affect the amount. These conceptions are often, but not always, borne out by experience with amines. *p*-Toluenesulphonates and KOAc in

EtOH react by Bergmann's "negative mechanism" (approach of the reactant from the side of the C remote from the charge), but in AcOH the author's mechanism must also play a part.

Reactions marked * below involve inversion. *cyclo*-Pentylamine and HNO_2 give equal amounts of olefine and alcohol, but with *cyclo*hexylamine the ratio of these two products is 1 : 5. With HNO_2 *trans*-decahydro-α-naphthylamine-I, m.p. −18°, gives * 70% of $\Delta^{1:9}$- and *trans*-$\Delta^{1:2}$-octahydronaphthalene and 30% of *trans*-decahydro-α-naphthol (I), m.p. 63° (with some of the isomeride, m.p. 49°, obtained without inversion). *trans*-Decahydro-α-naphthylamine-II, m.p. −1°, gives the related (I) and only traces of hydrocarbon. Similarly in glacial or dil. AcOH the *trans*-β-amine-II, new m.p. 15° (*Bz* derivative, m.p. 176—177°; *hydrochloride*, decomp. 245—250°), gives quantitatively the alcohol (II), m.p. 75°, but the *trans*-β-amine-I, m.p. −47° (*hydrochloride*, decomp. 238°), gives 70% of *trans*-Δ^2-octahydronaphthalene and (II) * with a little of the alcohol, m.p. 53°, formed without inversion. Results in the *cis*-series differ. Thus, *cis*-decahydro-α-naphthylamine-I, m.p. −18°, gives only the related alcohol, m.p. 93°; about 7% of the same alcohol *, but 68% of cis-*decahydro-α-naphthol*-II, m.p. 55°, b.p. 118°/12 mm. (*phthalate*, m.p. 142°), and 25% of *cis*-$\Delta^{1:2}$-(with a little $\Delta^{1:9}$-)octahydronaphthalene are obtained from the *cis*-α-amine-II. *cis*-Decahydro-β-naphthylamine-I, m.p. 14° (hydrochloride, decomp. 270°), gives about 63% of the alcohol *, m.p. 18—31°, about 7% of the alcohol, m.p. 105°, and 30% of a mixture of *cis*-Δ^1- and -Δ^2-octahydronaphthalene (under various conditions the speed, but not the course, of the reaction, varied), but the *cis*-β-amine-II (*hydrochloride*, decomp. 255—260°) gives * only the alcohol, m.p. 105°. The configuration of the 9-hydroxydecahydronaphthalenes is supported by cryoscopic data. α-Hydrindanylamine-I (NH_2 in C_5 ring), m.p. −2°, gives 30% of *hexahydroindene* (unstable *nitrosochloride*, m.p. 102—106°; *nitrolpiperidide*, m.p. 170°) and 70% of alcohol, mainly the liquid *cis*-α-hydrindanol-II * (II) (phthalate, m.p. 140°). The liquid *cis*-α-hydrindanylamine-II (IV) (polymorphic benzoate, new m.p. 135°) gives 35% of a mixture of $\Delta^{1:9}$- (cryst. *nitrosochloride*) and $\Delta^{1:2}$-hexahydroindene, about 52% of (III), and 13% of α-hydrindanol *, m.p. 18°. β-Hydrindanylamine-I (Bz derivative, m.p. 144°) gives the β-alcohol-II *, m.p. 10° (4 parts), the β-alcohol-I, m.p. 5° (1 part), and some hydrocarbon. *trans*- and *cis*-Decahydronaphthalene have m.p. −33° and −45°, respectively, and other physical data are also given. *trans*-β-Decaloneoxime and Na–EtOH give mainly the amine, m.p. 15° (gives *Me* trans-*decahydro*-β-*naphthylcarbamate*, m.p. 109°), but hydrogenation (Pt-black) of the ketone in EtOH–NH_3 gives mainly the amine-I (benzoate, m.p. 177°). The *H phthalate* of *cis*-decahydro-β-naphthol, m.p. 105°, has m.p. 116°, and the *p*-toluenesulphonate gives *forms*, m.p. 44° and 76° (corr.) (stable). *cis*-α-Hydrindanols (OH in C_5 ring) with Na in decahydronaphthalene (V) give an equilibrium mixture containing about equal amounts of the two forms. However, *cis*-hydrindan-5-ol with Na in (V) and reduction of the ketone with Na–EtOH give mainly *cis*-hydrindan-5-ol, m.p. 20°, with a little of the isomeride, m.p. 43°; catalytic hydrogenation of the ketone gives only the second-mentioned alcohol. Hydrogenation (Pt-black) of α-hydrindoneoxime (OH in C_5 ring) in AcOH gives mainly the amine (Bz derivative, m.p. 180°), but also fair amounts of its isomeride. *cis*-5-Hydrindanylamine-I (Bz derivative, m.p. 166°) has m.p. −19°. Hydrogenation (Pt-black) of *cis*-α-hydrindanoneoxime gives entirely the *cis*-amine-I, but with Na–EtOH 60—70% of (IV) is formed. *l*-Menthol *p*-toluenesulphonate and KOAc in abs. EtOH give a little *d*-neomenthyl acetate and Et ether with much Δ^3-menthene; the ether and menthene are also obtained by heating in abs. EtOH alone or with $CaCO_3$. The *p*-toluenesulphonate, m.p. 66°, of *trans*-decahydro-β-naphthol, m.p. 75°, with KOAc in abs. EtOH gives * much Δ^2-octahydronaphthalene with decahydro-β-naphthyl Et ether and the acetate of the isomeric alcohol, m.p. 53°; the sulphinate of the alcohol, m.p. 53°, is similarly inverted in EtOH. In AcOH only 15% of inversion occurs with the sulphonate, m.p. 66°; considerable amounts of octahydronaphthalene are also formed.

R. S. C.

Alkanolamines. III. Reactions of chloronitrobenzenes with ethanolamines. M. Meltsner, L. Greenstein, G. Gross, and M. Cohen (J. Amer. Chem. Soc., 1937, **59**, 2660—2661; cf. Kremer, A., 1937, II, 455).—*o*-$C_6H_4Cl{\cdot}NO_2$ and $NH(CH_2{\cdot}CH_2{\cdot}OH)_2$ at 175—180° give $(o\text{-}C_6H_4Cl{\cdot}N{:})_2$ (I), *o*-$C_6H_4Cl{\cdot}NH_2$, and (?) N-o-*aminophenylmorpholine*, m.p. 200°. Addition of NaOH increases the yield of (I). *o*-$C_6H_4Cl{\cdot}NO_2$ and $NH_2{\cdot}[CH_2]_2{\cdot}OH$ in H_2O at 175° give *o*-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}[CH_2]_2{\cdot}OH$.

R. S. C.

Derivatives of glucamine and galactamine. H. P. den Otter (Rec. trav. chim., 1937, **56**, 1196—1202).—Glucose anilide when reduced (Pd–H_2 or Al–Hg) yields NH_2Ph and no glucamine. The following are prepared by interaction of glucamine and the appropriate chloro- (or dichloro-)nitrohydrocarbon: N-2 : 4-*dinitrophenyl*-, m.p. 151—152°, N-2 : 4 : 6-*trinitrophenyl*-, m.p. 183°, N-2 : 4-*dinitronaphthyl*-, m.p. 189°, and N-3-*chloro*-4 : 6-*dinitrophenyl-glucamine*, m.p. 181°. Similarly, from galactamine the following are prepared: N-2 : 4-*dinitrophenyl*-, m.p. 190°, N-2 : 4 : 6-*trinitrophenyl*-, m.p. 197°, N-3-*chloro*-4 : 6-*dinitrophenyl*-, m.p. 201°, and N-2 : 4-*dinitronaphthyl-galactamine*, m.p. 181°.

J. D. R.

Chemical and textile-chemical studies of new textile assistants and dyes. II. F. Seidel and A. Brösamle (Ber., 1937, **70**, [*B*], 2497—2500).—The products obtained by the alkylation of aromatic mono- and di-amines by octadecyl bromide (cf. B., 1937, 116) and C_5H_5N contain octadecylpyridinium bromide as constituent of the complex since when treated with picric acid they slowly give *octadecylpyridinium picrate*, m.p. 57—61°, in almost quant. yield. They have therefore the structures:

$[NH{\cdot}C_{18}H_{37}{\cdot}C_6H_4{\cdot}NH{\cdot}C_{18}H_{37},$
$2HBr,4C_5H_5N(Br)(C_{18}H_{37}),5H_2O]$,

$[C_5H_5N(C_{18}H_{37})(SO_3{\cdot}C_6H_4{\cdot}NH_2),$
$2C_5H_5N(Br)(C_{18}H_{37}),2C_6H_6,3H_2O]$,

$[(\cdot C_6H_4\cdot NH\cdot C_{18}H_{37})_2,2HBr,$
$4C_5H_5N(Br)(C_{18}H_{37}),3H_2O]$,
$[NH_2\cdot C_{10}H_6\cdot SO_3]^-[(C_5H_5N(C_{18}H_{37})]^+$. The compound from aminoazobenzene gives *octadecylpyridinium nitrate*, m.p. 75—78° and after re-solidification, m.p. 238°, with dil. HNO_3 and hence is $[NPh{:}N\cdot C_6H_4\cdot N(C_{18}H_{37})_2,C_5H_5N(Br)(C_{18}H_{37},2HBr,3H_2O]$. H. W.

Emeraldin sols.—See A., I, 79.

Manufacture of substituted 3-aminopyrenes.—See B., 1937, 1314.

Preparation of unsymmetrical fluorophenylthioureas.—See B., 1937, 1314.

Decomposition reactions of aromatic diazo-compounds. II. Reactions of benzenediazonium chloride. III. Non-ionic reactions of diazobenzene hydroxide. W. A. Waters (J.C.S., 1937, 2007—2014, 2014—2016; cf. A., 1937, II, 97).—The decomp. of solid PhN_2Cl under $COMe_2$, C_6H_{14}, and CCl_4 yields HCl and PhCl; under EtI, some PhI is also formed. Decomp. in $COMe_2$ with $CaCO_3$ yields C_6H_6 and $CH_2Cl\cdot COMe$, and under these conditions Pb, Bi, Sn, Ni, Fe, Cu, and Ag are attacked to yield the metallic chlorides; Hg gives some HgPhCl, and Sb some $CPh_3\cdot SbCl_2$. It is suggested that the salt $PhN_2{}^+Cl^-$ first undergoes rearrangement to NPh:NCl, which then decomposes spontaneously with the formation of neutral Ph and Cl radicals and N_2, or by a bimol. collision with the reagent. Dichloramine-*T* in dry $COMe_2$, C_6H_6, or CCl_4 reacts with Hg, which supports the possibility of reaction by fission of the covalent :N·Cl linking to give transient Cl atoms.

III. Decomp. of $PhN_2\cdot OH$ in CS_2 yields $(PhS)_2$, and in *cyclo*hexane, C_6H_6 and unidentified products. In absence of any other org. substance, Na benzenediazotate in H_2O decomposes to form a trace of C_6H_6. It is suggested that $PhN_2\cdot OH$ decomposes to neutral Ph and OH radicals, and N_2, and the known oxidising reactions of $PhN_2\cdot OH$ are discussed in connexion with this view. J. D. R.

Problem of racemate and racemic mixture. The optical antipodes of *cis*-β-decahydronaphthol. W. Hückel and C. Kühn (Ber., 1937, **70**, [*B*], 2479—2484; cf. A., 1935, 80).—It is shown by the prep. of the pure optical antipodes that *cis*-2-decahydronaphthol, m.p. 18°, is a *dl*-mixture whilst the substance, m.p. 31°, is a racemic compound. *r-cis*-2-Decahydronaphthylamine is resolved into its optical antipodes by *d*-camphorsulphonic acid in EtOH. (+)-cis-2-*Decahydronaphthylamine*, m.p. 30·5°, gives a d-*camphorsulphonate*, $[\alpha]_D^{20\cdot5}$ +31·45° in EtOH, a *hydrochloride*, $[\alpha]_D^{20\cdot5}$ −15·49° in H_2O, a *Bz* derivative, m.p. 205°, $[\alpha]_D^{20\cdot5}$ +1·72° in $CHCl_3$, an *α-bromo-π-camphorsulphonate*, $[\alpha]_D^{20}$ +73·4° in EtOH, and an *Ac* compound, m.p. 173°, $[\alpha]_D^{21}$ +21·44° in EtOH. (−)-cis-2-*Decahydronaphthylamine*, m.p. 30·5°, affords a *camphorsulphonate*, $[\alpha]_D^{18\cdot5}$ +15·14° in EtOH, a *hydrochloride*, $[\alpha]_D^{20\cdot5}$ −15·53° in H_2O, a *Bz* derivative, m.p. 205°, $[\alpha]_D^{21\cdot5}$ −1·68° in $CHCl_3$, an *α-bromo-π-camphorsulphonate*, $[\alpha]_D^{19}$ +61·5° in EtOH, and an *Ac* derivative, m.p. 173°, $[\alpha]_D^{23}$ −21·35° in EtOH. The (+)-amine is transformed by HNO_2 into octahydronaphthalene, b.p. 84°/16 mm., 188°/760 mm., α_D^{22} +23·6°, and (+)-cis-2-*decahydronaphthol*-II, m.p. 38°, $[\alpha]_D^{21}$ +12·42° in EtOH, $[\alpha]_D^{21}$ +3·94° in C_6H_6, $[\alpha]_D^{22\cdot5}$ +4·24° in *cyclo*hexane (*H phthalate*, m.p. 146°, $[\alpha]_D^{20\cdot8}$ −17·80° in abs. EtOH, and its *Me* ester, m.p. 50°, $[\alpha]_D^{20}$ −10·22° in EtOH; the corresponding optically inactive *compound* has m.p. 61° and is therefore a racemate). (−)-cis-2-*Decahydronaphthol*-II has m.p. 38°, $[\alpha]_D^{22\cdot5}$ −12·41° in EtOH; it gives a *H phthalate*, m.p. 146°, $[\alpha]_D^{20}$ +17·47° in EtOH, and its *Me* ester, m.p. 50°, $[\alpha]_D^{18}$ +10·1° in EtOH (which is accompanied by a *compound*, m.p. 58°, $[\alpha]_D^{20}$ −1·66° in EtOH). H. W.

Nitration of phenols by nitrous fumes. (Signa.) L. Monti (Gazzetta, 1937, **67**, 628—633).—Phenols are readily mononitrated by nitrous fumes when dissolved in light petroleum (b.p. 40—70°). From PhOH, *o*- remains in solution whilst *p*-$NO_2\cdot C_6H_4\cdot OH$ separates as an oil. *o*-Cresol yields, in solution, 3-nitro- and, as an oil, 5-nitro-*o*-cresol; with C_6H_6 or AcOH as solvent, 3 : 5-dinitro-*o*-cresol is formed. *p*-Cresol yields, in petroleum, 3-nitro- and, in C_6H_6, 3 : 5-dinitro-*p*-cresol. *m*-Cresol in either solvent gives 2-, 4-, and 6-nitro-*m*-cresol. Thymol in petroleum yields *p*- and, in solution, *o*-nitrothymol; both are also obtained in C_6H_6. E. W. W.

Aromatic compounds of fluorine. XXIII. Attempted preparation of difluorinated phenols. G. Schiemann and M. Seyhan (Ber., 1937, **70**, [*B*], 2396—2401).—*o*-$C_6H_4F\cdot OMe$ is nitrated to 2-fluoro-4-nitroanisole, m.p. 104·6°, reduced by Fe powder and conc. HCl at 100° to 2-fluoro-*p*-anisidine, m.p. 82·6°, which is diazotised and transformed into 3-*fluoro*-4-*methoxybenzenediazonium borofluoride*, decomp. 98°, dry decomp. of which affords 2 : 4-*difluoroanisole*, b.p. 52°/17 mm.; this is smoothly transformed by $AlCl_3$ in anhyd. C_6H_6 into 2 : 4-*difluorophenol* (I), b.p. 52—53°/19 mm., m.p. 22·4° (*Na* salt, m.p. 76°). The following processes are less suitable. *o*-$NH_2\cdot C_6H_4\cdot OEt$ is transformed through the diazonium borofluoride into *o*-$C_6H_4F\cdot OEt$ in 36% yield. This with HNO_3 (*d* 1·5) and AcOH at 0° gives 2-fluoro-4-nitrophenetole, m.p. 78—80° (yield 28%), which is reduced by $SnCl_2$ and HCl to 2-*fluoro*-p-*phenetidine*, m.p. 239° (yield 55%). This gives only 17% yield of 3-*fluoro*-4-*ethoxybenzenediazonium borofluoride*, from which 2 : 4-difluorophenetole was obtained in very small yield. 2 : 4-$C_6H_3F_2\cdot NO_2$ is converted into (I). *p*-Cresol is converted by HNO_3 (*d* 1·5) in AcOH at 0° into 2 : 6-dinitro-*p*-cresol, m.p. 80—81° (61% yield), the *Na* derivative of which with Me_2SO_4 and PhMe at 120—140° gives 2 : 6-*dinitro*-4-*methylanisole*, m.p. 122°; this is reduced to 2 : 6-diamino-4-methylanisole [*dihydrochloride*, m.p. 241° (decomp.)], which gives a *tetrazonium borofluoride*, yielding a small amount of oil when decomposed. H. W.

Reaction between titanium tetrachloride and phenols. II. Reaction with chloro- and nitrophenols. G. P. Lutschinski (J. Gen. Chem. Russ., 1937, **7**, 2044—2047).—$TiCl_4$ and *p*-$C_6H_4Cl\cdot OH$ afford *di*-p-*chlorophenoxytitanium dichloride*. *Di*-o- and -p-*nitrophenoxytitanium dichloride* and m-*nitrophenoxytitanium trichloride* are obtained similarly from $TiCl_4$ and *o*-, *p*-, and *m*-$NO_2\cdot C_6H_4\cdot OH$. R. T.

2 : 4-Dibromo-*m*-anisidine and its derivatives. E. Bureš and S. Ježek (Chem. Listy, 1937, **31**, 464—470).—*Acet*-m-*anisidide*, m.p. 76°, in AcOH and Br yield 2 : 4-*dibromo*-3-*acetamidoanisole*, m.p. 150·5°, hydrolysed by KOH in EtOH to 2 : 4-*dibromo*-m-*anisidine* (I), m.p. 65° [*Bz*, m.p. 141°, and *Me* derivative, b.p. 159°; *hydrochloride*, m.p. 184—186° (decomp.); *sulphate*, m.p. 155° (decomp.)]. 3-*Chloro*-, m.p. 82°, and 3-*iodo*-2 : 4-*dibromoanisole*, m.p. 90°, were obtained from (I) by the Sandmeyer reaction. R. T.

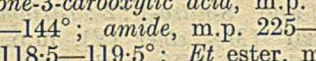
2 : 6-Dibromo-3-aminophenetole, 2 : 4-dibromo-3-aminophenetole, and their derivatives. E. Bureš and Z. Mansfeld (Chem. Listy, 1937, **31**, 480—489).—*m*-Phenetidine and Br at room temp. yield 2 : 6-*dibromo*-3-*aminophenetole*, m.p. 47° [*hydrochloride*, m.p. 180—190° (decomp.); *sulphate*; *Ac*, m.p. 93°, Ac_2, m.p. 100°, *Bz*, m.p. 147°, and *Et* derivative, m.p. 71°], converted by the Sandmeyer reaction into 3-*chloro*-, m.p. 62°, 3-*iodo*-, m.p. 95°, or 3-*cyano*-2 : 6-*dibromo*-, m.p. 112°, or 2 : 3 : 6-*tribromo*-*phenetole*, m.p. 87°. *Acet*-m-*phenetidide*, m.p. 96—97°, in EtOH and Br yield 2 : 4-*dibromo*-3-*acetamidophenetole*, m.p. 156·5°, hydrolysed by aq. NaOH to 2 : 4-*dibromo*-3-*aminophenetole*, m.p. 54° (*hydrochloride*, decomp. at 200°; *sulphate*; Ac_2, m.p. 106°, *Bz*, m.p. 108°, and *Et* derivative, m.p. 62°), from which 3-*chloro*-, m.p. 56°, 3-*iodo*-, m.p. 86°, or 3-*cyano*-2 : 4-*dibromo*-, m.p. 97°, or 2 : 3 : 4-*tribromo*-*phenetole*, m.p. 77°, are obtained by the Sandmeyer reaction. R. T.

β-Arylaminoacrylic esters. I. Anisidinoacrylic ester and its reactions. M. V. Rubtzov (J. Gen. Chem. Russ., 1937, **7**, 1885—1895).—$ONa{\cdot}CH{:}CH{\cdot}CO_2Et$ and *p*-anisidine in aq. AcOH yield *Et* trans-β-p-*anisidinoacrylate* (I), m.p. 120—121° (N-*Ac* derivative, m.p. 117—118·5°), whilst in aq. EtOH–AcOH the product is Et_2 p-*anisidino*-ββ′-*diacrylate* (II), m.p. 97—98° [Br_5-derivative, m.p. 195° (decomp.)], also obtained by heating (I) in vac. at 100°. The cis-*isomeride* (III), m.p. 57—57·5°, of (I) is prepared by boiling a $CHCl_3$ solution of (I) for 20 min., and adding the resulting solution to light petroleum. (III) when heated at 100° yields successively an intermediate compound, m.p. 99—101°, (I), and (II). The N-*Me* derivative, m.p. 37·5—39°, of (I) gives p-$OMe{\cdot}C_6H_4{\cdot}NHMe$, but not the expected quinoline derivative, when heated with $SOCl_2$. (II) when boiled with 10% in MeOH affords 1-p-*anisyl*-4-*pyridone*-3-*carboxylic acid*, m.p. 252° (*chloride*, m.p. 142·5—144°; *amide*, m.p. 225—226°; *diethylamide*, m.p. 118·5—119·5°; *Et* ester, m.p. 88—88·5°) from which 1-p-*anisyl*-4-*pyridone*, m.p. 110—111°, is obtained by distillation alone or from Zn dust. R. T.

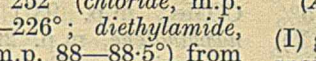
Coupling of organic radicals by the action of Grignard reagents on heavy metal salts. II. Coupling of dissimilar radicals. J. H. Gardner, L. Joseph, and F. Gollub (J. Amer. Chem. Soc., 1937, **59**, 2583—2584; cf. A., 1930, 76).—1 mol. each of MgPhBr and p-$OMe{\cdot}C_6H_4{\cdot}MgBr$ with AgBr give 22—46·8% of Ph_2, 1·7—3·6% of $(4\text{-}OH{\cdot}C_6H_4)_2$, and 4·7—8·2% of the " mixed " product, p-$C_6H_4Ph{\cdot}OH$. R. S. C.

Synthesis of 3-substituted derivatives of methylcholanthrene. L. F. Fieser and B. Riegel (J. Amer. Chem. Soc., 1937, **59**, 2561—2565).—The prep. of 1 : 6-$NHAc{\cdot}C_{10}H_6{\cdot}OMe$ is modified. 6 : 1-$OMe{\cdot}C_{10}H_6{\cdot}MgI$ and 7-cyano-4-methylhydrindene (I) in Et_2O–C_6H_6 give 7-6′-*methoxy*-1′-*naphthoyl*-4-*methylhydrindene*, m.p. 87·5—89° (softens at 82°), b.p. 260—265°/3 mm., converted by Zn at 400—405° into 3-*methoxy*-20-*methylcholanthrene*, dimorphic, m.p. 166—167·5° (softens at 161°) or mostly at 161° (*picrate*, m.p. 182·5°), which with HBr–AcOH gives 3-hydroxy-20-methylcholanthrene, m.p. 220·5—222° or 218—220° [*picrate*, m.p. 201—201·5° (decomp.)]. The conversion of $\beta\text{-}C_{10}H_7{\cdot}NH_2$ into its Ac derivative and thence into 1 : 6 : $2\text{-}C_{10}H_5Br_2{\cdot}NHAc$, m.p. 214·5—216°, 1 : 6 : $2\text{-}C_{10}H_5Br_2{\cdot}NH_2{,}HCl$, m.p. 120—121°, and 1 : $6\text{-}C_{10}H_6Br_2$ (II), m.p. 56—57°, b.p. 175°/15 mm., is detailed. Grignard reactions with (II) attack either both Br or preferentially the Br in position 6. Thus condensation with (I) yields 7-5′-*bromo*-2′-*naphthoyl*-4-*methylhydrindene*, m.p. 102·5—105°, b.p. 246°/2 mm., converted at 270° into 4′-*bromo*-7-*methyl*-8 : 9-*dimethylene*-1 : 2-*benzanthracene*, m.p. 246·5—248° (no picrate). $2\text{-}C_{10}H_7{\cdot}NO_2$ and Br in $CHCl_3$ give 5 : $2\text{-}C_{10}H_6Br{\cdot}NO_2$ and some x-*bromo*-2-*nitronaphthalene*, m.p. 98—102°. 5 : $2\text{-}C_{10}H_6Br{\cdot}NH_2$ gives 6-*chloro*-1-*bromonaphthalene*, m.p. 41—41·5° (no picrate), which with Mg and a little $MgBu^aBr$ gives the Grignard reagent; this with (I) affords 7-6′-*chloro*-1′-*naphthoyl*-4-*methylhydrindene*, m.p. 92—94°, b.p. 300°/20 mm., and thence at 400° 3-*chloro*-20-*methylcholanthrene*, m.p. 197—198·8° {$[C_6H_3(NO_2)_3]_2$ *compound*, m.p. 165·5—166·5°}, converted by CuCN in C_5H_5N at 200—220° into the 3-*CN*-derivative, m.p. 243—251°. R. S. C.

***iso*Eugenol and its polymerides. II, III.** E. Puxeddu and (Signa.) A. Rattu (Gazzetta, 1937, **67**, 647—654, 654—659; cf. A., 1937, II, 58).—II. *iso*Eugenol Pr^a ether and KNO_2–AcOH give, in addition to dioximinodihydro*iso*eugenol Pr^a ether peroxide (I) (*loc. cit.*), new m.p. 85°, iso*eugenol* Pr^a *ether nitrosite*, $C_{13}H_{18}O_5N_2$, m.p. 127° (also obtained by Malagnini's method; A., 1895, i, 35), and a *substance*, m.p. 99·5°. *iso*Eugenol Et ether similarly gives a *nitrosite*, m.p. 105°. Reduction of (I) by Zn–AcOH yields 3-*methoxy*-4-*propoxyphenyl Me diketone* α-*dioxime* (*A*), m.p. 139°, converted when heated into the β-*dioxime* (*B*), m.p. 178°. With HNO_3 (76%)



(*A*.)



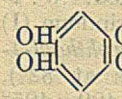
(*B*.)

(I) gives a NO_2-derivative, m.p. 112°, and the corresponding Et ether (II) a NO_2-derivative, m.p. 102°. The *Br*-derivatives of (I) and of (II) have m.p. 94° and 115°, respectively.

III. Either ordinary or Schimmel's cryst. *iso*eugenol, m.p. 32°, when treated with various polymerising agents gives the same cryst. polymeride (III), with an amorphous *polymeride*, also obtained when (III) is distilled at 20 mm. E. W. W.

[Similarity of] *o*-divinylbenzene and naphthalene. K. Fries and H. Bestian (Annalen, 1937, **533**, 72—92).—4 : 5-*Divinylpyrocatechol* (I) resembles 2 : $3\text{-}C_{10}H_6(OH)_2$ in not forming a quinone with Ag_2O in Et_2O, which indicates fixation of the ethylenic linkings as shown. 3 : $4\text{-}(OMe)_2C_6H_3{\cdot}[CH_2]_2{\cdot}CO_2H$

affords readily 3 : 4-$(OMe)_2C_6H_3\cdot[CH_2]_2\cdot NH_2$, b.p. 153°/12 mm., by way of the acid *chloride*, b.p. 152°/1 mm., m.p. 48°, *azide*, m.p. 52° (decomp.), and iso*carbimide*, m.p. 174°/16 mm., 142°/0·8 mm. (corresponding *s*-carbamide, m.p. 149°), and thence 6 : 7-dimethoxy-1-methyl-3 : 4-dihydro*iso*quinoline, which is best reduced to the 1 : 2 : 3 : 4-H_4-compound by H_2 in the presence of Ni–Cu–Co in EtOH at 80°/>1 atm. The H_4-base affords 6 : 7-dimethoxy-1 : 2-dimethyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline (II), which cannot be converted into $(OMe)_2C_6H_2(CH{:}CH_2)_2$ owing to polymerisation. Hofmann degradation of the methiodide (III) of (II) gives a substance, which is hydrogenated to a mixture of *isomerides*, $C_{14}H_{23}O_2N$, b.p. 110—114°/0·2 mm., the cryst., mixed *methiodides* from which with Ag_2O afford *dimethoxyethylstyrene*, b.p. 90°/0·2 mm., hydrogenated to 4 : 5-*dimethoxy*-1 : 2-*diethylbenzene*, b.p. 85°/0·2 mm. With HI–red P–AcOH at 145° (II) gives 6 : 7-*dihydroxy*-1 : 2-*dimethyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline, b.p. 128°/0·5 mm., m.p. 70° (Ac_2 derivative, m.p. 65°), which with Ag_2O gives 4 : 5-*diethyl*-o-*benzoquinone*, m.p. 76—86°. With HBr (III) gives 6 : 7-*dihydroxy*-1 : 2-*dimethyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline *methobromide*, m.p. 227° (decomp.), the Ac_2 derivative, m.p. 257° (decomp.), of which is converted by Ag_2O into a mixture of *isomerides*, $C_{16}H_{21}O_4N$, b.p. 160—165°/0·4 mm.; the mixed *methiodides*, m.p. 225° (sinter at 178°), therefrom, when distilled with Ag_2O and sand, give 4 : 5-*diacetoxy*-1 : 2-*divinylbenzene*, m.p. 87° [*tetrabromide*, m.p. about 180° (decomp.)], converted by aq. alkali into (I), which polymerises readily and was not isolated. Hydrogenation of 3-$NO_2\cdot C_6H_4\cdot CH{:}CH\cdot CO_2H$ (improved prep.; 75% yield), m.p. 199°, gives only β-m-*aminophenylpropionic acid*; this is best obtained from the Na salt by H_2–Ni–Cu–Co in H_2O at 50°/1 atm. and is isolated as *Bz* derivative, m.p. 149°, which affords successively the *chloride*, m.p. 80—90° (decomp.) (*amide*, m.p. 154°), *azide*, m.p. 71·5° (decomp.) (*s-carbamide*, m.p. 219°), and β-m-*benzamidodiphenylethylamine* (IV), m.p. 111° [*hydrochloride*, m.p. 247° (decomp.); N-*Bz* derivative, m.p. 176°], and thence by 50% H_2SO_4 β-m-*aminophenylethylamine*, b.p. 156—157°/21 mm. [*picrate*, m.p. 204°; *dihydrochloride*, m.p. 308° (decomp.); Ac_2 derivative, m.p. 134°]. The *Ac* derivative, m.p. 144°, of (IV) with P_2O_5 in boiling PhCl gives 75% of 6-*benzamido*-1-*methyl*-3 : 4-*dihydro*isoquinoline (V), m.p. 179° [*phosphate*, m.p. 239°; *nitrate*, m.p. 202° (decomp.); *dihydrochloride*, m.p. 309° (decomp.)], hydrolysed by KOH to 6-*amino*-1-*methyl*-3 : 4-*dihydro*isoquinoline, m.p. 131° [*picrate*, m.p. 216° (decomp.); *dihydrochloride*, m.p. 297° (decomp.)]. Hydrogenation (Ni–Cu–Co in EtOH at 100°/>1 atm. or PtO_2) of (V) gives 6-*benzamido*-1-*methyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline, an oil [*hydrochloride*, m.p. 314° (decomp.); N-*Bz* derivative, m.p. 220°], which with CH_2O–HCO_2H gives 6-*benzamido*-1 : 2-*dimethyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline (VI), m.p. 115° [*hydrochloride*, m.p. 225° (decomp.)], and thence the free 6-NH_2-compound, b.p. 124°/0·9 mm., m.p. 70° [*picrate*, m.p. 185° (decomp.); *dihydrochloride*, a hygroscopic glass]. The *methiodide*, m.p. 209°, of (VI) with KOH–MeOH gives a mixture of *isomerides*, $C_{12}H_{18}N_2$, b.p. 115—125°/high vac. (hygroscopic *dihydrochloride*; oily *Bz* derivative), the *Ac* derivatives, b.p. 185—195°/0·9 mm., from which give an oily mixed *methiodide*. With KOH–MeOH this salt gives 3 : 4-*divinylaniline*, b.p. 100°/0·4 mm., which affords a (?) polymerised cryst. *hydrochloride* (no m.p.), is reduced to 3 : 4-*diethylaniline*, b.p. 146°/13 mm., and with $SO_3H\cdot C_6H_4\cdot N_2Cl$ gives an abnormal insol. grey product. R. S. C.


(I.)

Naphthalene series. I. Preparation of polyhydroxy-derivatives of naphthalene. S. N. Chakravarti and V. Pasupati (J.C.S., 1937, 1859—1862).—Nitration of 2 : 6-$C_{10}H_6(OMe)_2$ (I) with HNO_3–AcOH yields 1-*nitro*-, m.p. 189°, and with HNO_3–AcOH–H_2SO_4 1 : 5-*dinitro*-2 : 6-*dimethoxynaphthalene*, m.p. 265°, which are reduced ($SnCl_2$–EtOH) to 1-*amino*- [*hydrochloride*, m.p. 270° (decomp.)] and 1 : 5-*diamino*-, m.p. 192°, -2 : 6-*dimethoxynaphthalene* [*hydrochloride*, m.p. 265° (decomp.)], respectively. Similarly, 1-*amino*-, m.p. 83°, and 1 : 8-*diamino*-, m.p. 115°, -2 : 7-*dimethoxynaphthalene*, are prepared by nitration and reduction of 2 : 7-$C_{10}H_6(OMe)_2$. The Grignard reagent from 1 : 2-$C_{10}H_6Br\cdot OMe$ when treated successively with dry O_2 and BzCl–NaOH yields 2-*methoxy*-1-*naphthyl benzoate*, m.p. 110°. Bromination (Br–AcOH) of 2 : 6-$C_{10}H_6(OH)_2$ yields 1 : 5-*dibromo*-2 : 6-*dihydroxynaphthalene*, m.p. 233° [*Me*$_2$ *ether*, by Me_2SO_4–NaOH, m.p. 257°, also formed by bromination (Br–AcOH) of (I)]. Oxidation ($K_2Cr_2O_7$–H_2SO_4) of 1-amino-7-methoxy-2-naphthol hydrochloride yields 7-*methoxy*-1 : 2-*naphthaquinone*, m.p. 183°, reduced (SO_2–EtOH) to 1 : 2-*dihydroxy*-7-*methoxynaphthalene*, m.p. 127° (*picrate*, m.p. 156°; *diacetate*, m.p. 122°). Similarly, reduction (SO_2–H_2O) of 6- (II) and 7-hydroxy-1 : 2-naphthaquinone (III) yields 1 : 2 : 6-, m.p. 188° (*triacetate*, m.p. 262°), and 1 : 2 : 7-*trihydroxynaphthalene*, m.p. 197° (*triacetate*, m.p. 181—182°), respectively, which are methylated (MeI–K_2CO_3 in $COMe_2$) to 1 : 2 : 6-, m.p. 55° (*picrate*, m.p. 98°), and 1 : 2 : 7-*trimethoxynaphthalene*, an oil (*picrate*, m.p. 115°). Nitration (HNO_3–AcOH) of (II) and (III) yields 5-*nitro*-6-*hydroxy*-, m.p. 205°, and 8-*nitro*-7-*hydroxy*-, (IV), m.p. 210° (decomp.), -1 : 2-*naphthaquinone*, respectively, which are reduced by SO_2 to 5-*nitro*-1 : 2 : 6- (*Me*$_3$ *ether*, by MeI–K_2CO_3 in $COMe_2$, m.p. 93°) and 8-*nitro*-1 : 2 : 7-*trihydroxynaphthalene*, m.p. 220° [*Me*$_3$ *ether* (V), m.p. 98°], respectively. Reduction of (IV) with $SnCl_2$ gives 8-*amino*-1 : 2 : 7-*trihydroxynaphthalene* [*hydrochloride*, m.p. 270—275° (decomp.)], whilst similar reduction of (V) yields 8-*amino*-1 : 2 : 7-*trimethoxynaphthalene* [*hydrochloride*, m.p. 255° (decomp.)], converted by diazotisation and treatment with aq. KI into 8-*iodo*-1 : 2 : 7-*trimethoxynaphthalene*, m.p. 72°. J. D. R.

Condensation of 4 : 4′-dihydroxydiphenylmethane with formaldehyde. I. P. Losev, K. A. Andrianov, and O. J. Fedotova (J. Gen. Chem. Russ., 1937, **7**, 1828—1834).—$CH_2(C_6H_4\cdot OH\text{-}p)_2$ is best prepared by the method of Voroshcov and Iuruigina (A., 1931, 937). It does not undergo polymerisation when heated at 180° in presence of HCl,

NaOH, or aq. NH_3. It condenses with CH_2O in aq. EtOH–HCl, at the b.p., to give resinous products, from which 2 : 2′-*dihydroxy*-5 : 5′-*di*-(p-*hydroxybenzyl*)-*diphenylmethane*, m.p. 85—88°, was isolated. R. T.

Dehydro-2 : 2′-dihydroxy-1 : 1′-dinaphthylmethane. E. A. Shearing and S. Smiles (J.C.S., 1937, 1931—1936).—The literature on the structure of dehydro-2 : 2′-dihydroxy-1 : 1′-dinaphthylmethane (I) is reviewed critically. It is concluded that the conversion of (I) and similar substances into the dehydro-derivatives involves the removal of both mobile H atoms of the C_{10} nuclei, and that the CH_2 group is not directly concerned as is required by the structure assigned to (I) by Kohn and Ostersetzer (A., 1918, i, 501). The structure suggested by Pummerer and Cherbuliez (A., 1915, i, 417) is shown to be correct. When treated with Ac_2O or Ac_2O–AcCl, (I) is unchanged; with AcI in Ac_2O it yields 2 : 2′-diacetoxy-1 : 1′-dinaphthylmethane, and with *p*-$C_6H_4Me{\cdot}SO_2K$ in aq. H_2SO_4, a *product*, $C_{28}H_{22}O_4S$, m.p. 139—140° (decomp.). Nitration (HNO_3–Ac_2O) of (I) yields 4(?)-*nitrodehydro*-2 : 2′-*dihydroxy*-1 : 1′-*dinaphthylmethane*, m.p. 166° [*phenylhydrazone*, m.p. 191° (decomp.)], whilst with MeMgI in C_6H_6 (I) gives the compound, m.p. 135°, recorded by Kohn and Ostersetzer (*loc. cit.*). Addition of Br to (I) in AcOH yields *dehydro*-2 : 2′-*dihydroxy*-1 : 1′-*dinaphthylmethane* 3 : 4-*dibromide*, m.p. 148°, which is converted by C_5H_5N into 3-bromo-2 : 2′-dihydroxy-1 : 1′-dinaphthylmethane. Interaction of CH_2O and 6 : 2-$C_{10}H_6Br{\cdot}OH$ in AcOH–HCl yields 6 : 6′-*dibromo*-2 : 2′-*dihydroxy*-1 : 1′-*dinaphthylmethane*, m.p. 242° (decomp.) [*diacetate* (II), m.p. 287°; *Na* derivative], oxidised by HOCl to the *dehydro*-derivative, m.p. 209° (*phenylhydrazone*, m.p. 200°), which with AcI–Ac_2O yields (II). Similarly from 3 : 2-$C_{10}H_6Br{\cdot}OH$, 3 : 3′-*dibromo*-2 : 2′-*dihydroxy*-1 : 1′-*dinaphthylmethane* (III), m.p. 207°, is formed, oxidised (HOCl) to the *dehydro*-derivative, m.p. 232°, which does not form a phenylhydrazone. 2-Hydroxy-2′-methoxy-1 : 1′-dinaphthylmethane (IV) treated with NaOCl in EtOH–NaOH yields 1′-*chloro*-, m.p. 147°, and with Br and AcOH–NaOAc, 1′-*bromo*-, m.p. 155°, -2′-*keto*-2-*methoxy*-1′ : 2′-*dihydro*-1 : 1′-*dinaphthylmethane*, both of which when treated with AcOH–Zn regenerate (IV). Interaction of the Na salt of 2 : 2′-dihydroxy-1 : 1′-dinaphthylmethane and Ac_2O yields 2-*hydroxy*-2′-*acetoxy*-1 : 1′-*dinaphthylmethane*, m.p. 195°, which with Br in AcOH–NaOAc yields 1′-*bromo*-2′-*keto*-2-*acetoxy*-1′ : 2′-*dihydro*-1 : 1′-*dinaphthylmethane*, m.p. 127° (decomp.). Oxidation (NaOCl–NaOH) of 2 : 2′-dihydroxy-3 : 5 : 6 : 3′ : 5′ : 6′-hexamethyldiphenylmethane (V) yields a *dehydro*-derivative, m.p. 137°, and of 1-(2′-hydroxy-3′ : 5′-dimethylbenzyl)-2-naphthol, a *dehydro*-derivative, m.p. 107° (*phenylhydrazone*, m.p. 167°). The following covalent *Na* derivatives are described: of (V), m.p. about 175°, of 6-bromo-2 : 2′-dihydroxy-1 : 1′-dinaphthylmethane, m.p. about 215°, and of phenyl-2 : 2′-dihydroxy-1 : 1′-dinaphthylmethane. Di-(2-hydroxy-3 : 5-dimethylphenyl)methane does not form a Na derivative. J. D. R.

Dissociable organic oxides. Hydrogenation of photo-oxides. C. Dufraisse and J. Houpillart (Compt. rend., 1937, **205**, 740—743; cf. A., 1936, 1499).—The photo-oxides of tetraphenylnaphthacene (rubrene), *meso*-diphenylanthracene, and anthracene with H_2–Raney Ni afford 5 : 12-*dihydroxy*-5 : 6 : 11 : 12-*tetraphenyl*-5 : 12-*dihydronaphthacene*, m.p. 308—309° (cf. A., 1931, 1052), 9 : 10-dihydroxy-9 : 10-diphenyl-9 : 10-dihydroanthracene (cf. A., 1937, II, 332), and 9 : 10-*dihydroxy*-9 : 10-*dihydroanthracene*, m.p. 195° (cf. A., 1935, 487), respectively. Naphthacene is more difficult to reduce, but its reduction product is easily reduced further. Anthraquinone with H_2–Raney Ni and alkali absorbs 6 H but only tetrahydroanthraquinone can be isolated as the diquinol is instantaneously oxidised in air. J. L. D.

Derivatives of thiophloroglucinol. C. M. Suter and G. A. Harrington (J. Amer. Chem. Soc., 1937, **59**, 2575—2578).—1 : 3 : 5-$C_6H_3(SO_3Na)_3$ (modified prep.) and NaOH at 240—250°, best in Ni, give 77% of Na 3 : 5-dihydroxybenzenesulphonate, $+2H_2O$ [not converted into *s*-$C_6H_3(OH)_3$ by NaOH; the Ac_2 derivative, hygroscopic, gives an intractable chloride], the Bz_2 derivative whereof affords *resorcinol*-5-*sulphonyl chloride dibenzoate*, m.p. 105°, reduced by Zn in boiling AcOH (not at 50°) to 5-*thiolresorcinol dibenzoate*, m.p. 110° (corresponding *disulphide*, m.p. 146°). This thiol with EtOH and a trace of NaOEt gives 5-*thiolresorcinol*, m.p. 88—89°, sublimes at 140°/1 mm., and with the alkyl halide and a trace of NaOEt in EtOH affords 5-*methyl*-, m.p. 78—78·5°, -*ethyl*-, m.p. 71—72°, -n-*propyl*-, m.p. 67—68°, -n-*butyl*-, m.p. 66°, -n-*amyl*-, m.p. 66°, and -n-*hexyl*-*thiolresorcinol*, b.p. 250°/1 mm. The PhOH coeffs. towards *S. aureus* and *E. typhi* of the alkylthiols are recorded; in general they increase with increasing mol. wt. of the alkyl substituent. R. S. C.

Synthesis of a derivative of hydroxyquinol. M. Meyer (Compt. rend., 1937, **205**, 920—922).—Prolonged interaction of OEt·$CNa(CO_2Et)_2$ (1 mol.) with mesityl oxide (1 mol.) in PhMe–EtOH at room temp. and then at 50° affords an additive compound which is immediately cyclised and with HCl affords 2-*ethoxy*-2-*carbethoxy*-3 : 3-*dimethylcyclohexane*-1 : 5-*dione*, b.p. 126°/2 mm. [*monosemicarbazone*, m.p. 236° (block)], hydrolysed (large excess of NaOH) and simultaneously decarboxylated to 2-*ethoxy*-3 : 3-*dimethyl*-3 : 4-*dihydroresorcinol*, m.p. 85·5°. J. L. D.

Simultaneous dehydrogenation and dehydration with mixed catalysts. M. P. Masina (J. Gen. Chem. Russ., 1937, **7**, 2128—2136).—Zelinski's Ni–Al_2O_3 catalyst activates both dehydrogenation and dehydration of *cyclo*hexanol and of methyl*cyclo*hexanol, at 260—380°. The intensity of dehydrogenation and polymerisation reactions rises with increasing Ni content of the catalyst. A Cr_2O_3–Cu–Al_2O_3 catalyst acted similarly to the above. R. T.

Molecular structure and rate of reaction. W. Hückel, H. Havekoss, K. Kumetat, D. Ullmann, and W. Doll (Annalen, 1937, **533**, 128—171).—Further observations of the rate of hydrolysis of the H succinates and H phthalates of the alcohols of the decahydronaphthalene and hydrindene series confirm the view (A., 1935, 41) that the simple reaction

kinetic considerations on which the Arrhenius equation is based have not the same theoretical importance with solutions as with gases. Configurative decisions based on physical data are not so significant with diastereoisomeric alcohols as with hydrocarbons. Further it is found that the good agreement between the methods of Vavon and Skita for the elucidation of configuration is not general. In dubtful cases the degree of association of the alcohol is not more useful than the rate of hydrolysis with which it is connected. The thermal stability of the toluenesulphonates is invariably parallel to the conditions of formation of diastereoisomeric alcohols. Those isomerides which are formed preferentially by catalytic hydrogenation in acid solution give toluenesulphonates which are unstable and decompose on long keeping or completely when boiled for about 1 hr. in MeOH into, among other products, unsaturated hydrocarbons. The esters of isomeric alcohols endure prolonged boiling with alcohol without giving appreciable quantities of hydrocarbons. Adopting Skita's arrangement, it appears that a substituent in the *cis*-vicinity to a strongly negative group tends to displace it, possibly with previous ionisation. Observations on models of the compounds under consideration are complicated by the mobility of the six-membered ring present in them. In consequence two substituents in the *cis*-position can be remote from one another by an angle between the *cis*-valencies not exceeding 72° and *trans*-substituents can approach to an angle of 48°. Herein lies a possible explanation of the unusual behaviour of α-alcohols with *cis*-union of rings. The Arrhenius formula $k = \alpha e^{-q/RT}$ cannot be strictly applied. The rate of reaction of sterically unhindered alcohols in the case of succinates and phthalides approximates closely to that of the corresponding esters of *cyclo*hexanol. The vals. $k_{40} = 1$ and $k_{60} = 0{\cdot}1$ are readily recognised data for "normal" rates of succinates and phthalates. The view that the action consts. of alcohols with β-OH exceed those with α-OH and that the protection of the OH by the vicinal ring is thus directly evidenced could not be confirmed. In general the action consts. of esters reacting at the "normal" rate lie between 2 and 5×10^7 for succinates and phthalates. It is not universally true that high energy of activation causes a "steric hindrance" or, otherwise expressed, a particularly small rate of reaction, since many of the compounds with calc. relatively high energy react at the "normal" rate. Pronounced diminution of the rate is observed with only a few alcohols. High energy of activation and high action const. are frequently found simultaneously and their influences may compensate one another so that normal rates of reaction result. It is not possible to give general rules for the incidence of steric hindrance or for the relationship between energy of activation and action const. Among abnormal cases examples of simultaneous high energy of activation and high action const. are relatively frequent. H succinates are more rapidly hydrolysed than the corresponding H phthalates solely by reason of the greater energy of activation of the latter. These also are not hydrolysed at the same rates by NaOH and KOH; with the succinates this is not the case. The foaming power of the alkali phthalate solutions indicates their presence partly as colloids and the proportion is probably not the same for the Na and K salts.

trans-1-Decahydronaphthol (I), m.p. 49°, is remarkable for its very small rate of reaction, possibly owing to very marked steric hindrance. In the decahydronaphthalene series apart from (I) the 1-alcohols have universally smaller rates of reaction than the 2-compounds. This is true of the α-hydroxyhydrindanes with OH in the six-membered ring, whereas those with OH in the five-membered ring behave "normally." The hydrindan-β-ols and decahydronaphth-β-ols are normal. *iso*Camphanol-II, m.p. 84°, although a primary alcohol, is exactly similar to the "normal" phthalates of the decahydronaphthols, whereas the isomeric *iso*camphanol-I, m.p. 101°, has so small a rate of reaction that it is comparable with *iso*borneol. *cyclo*Hexyl H succinate but not the H phthalate resembles the corresponding compounds of the dicyclic alcohols. In comparison with *cyclo*hexanol the rate of reaction of *o*-methyl*cyclo*hexanol is greatly diminished even when Me is in the *trans*-position. In respect of the Arrhenius formula the rate of reaction of *cis*-2-methyl*cyclo*hexanol is more dependent on the temp. at low than at high temp. whereas with the *trans*-compound the conditions are reversed. The experimental technique of the hydrolysis is described in detail. Many cryoscopic measurements and some determinations of heats of combustion are recorded.

Catalytic hydrogenation of *cis*-1-ketodecahydronaphthalene gives almost exclusively *cis*-decahydronaphth-1-ol, m.p. 93°, whilst similar treatment of *ar*-tetrahydronaphth-1-ol affords a complex mixture. *cis*-Decahydronaphth-1-ol-II, m.p. 55° (*H succinate*, m.p. 53—54°; *phenylurethane*, m.p. 80—81°; p-*nitrobenzoate*, m.p. 85—86°; p-*toluenesulphonate*, m.p. 89—90°), is therefore obtained from the corresponding amine. *cis*-Decahydronaphth-1-ol, m.p. 93°, gives a very unstable p-*toluenesulphonate*. The *H phthalate*, m.p. 107—108°, of *trans*decahydronaphth-2-ol, m.p. 53°, is described. The *p*-nitrobenzoate, m.p. 56°, of 4-hydroxy-*cis*-hydrindane is reduced (PtO_2 in EtOH containing HCl) to the p-*aminobenzoate*, m.p. 179—181°, which is hydrolysed to the non-cryst. alcohol, b.p. 104°/12 mm. (*phenylurethane*, m.p. 82—83°; *H succinate*, m.p. 37°; p-*toluenesulphonate*, m.p. 53—54°). Similarly, the p-*nitrobenzoate*, m.p. 72°, of *cis*-α-hydrindanol is reduced to the p-*aminobenzoate*, which is hydrolysed to the alcohol, which gives a *H succinate*, dimorphous, m.p. 63° or 56—58°, and a very unstable p-*toluenesulphonate*, m.p. 54°. The non-cryst. α-hydrindanol-II gives a p-*aminobenzoate*, m.p. 83—84°, p-*benzamidobenzoate*, m.p. 146—147°, *H succinate*, m.p. 47°, and p-*toluenesulphonate*, m.p. 32—33°. The *H succinates* of the following decahydronaphthols are described (m.p. of alcohol first): *trans*-α-I, 49°, m.p. 107°; *trans*-α-II, 63°, m.p 85°; *cis*-α-I, 93°, m.p. 66°; *cis*-α-II, 55°, m.p. 53—54°; *trans*-β-I, 53°, m.p. 64°; *trans*-β-II, 75°, m.p. 81°; *cis*-β-I, 105°, m.p. 81°, and *cis*-β-II, 18—31°, m.p. 54°; of the following hydrindanols; 4-hydroxy-*cis*-I, 16/31, m.p. 47°; 4-hydroxy-*cis*-II, liquid, m.p. 37°; 5-hydroxy-*cis*-I, 43°, m.p. 81·5°; 5-hydroxy-*cis*-II, 20°, m.p. 47°; β-*cis*-I, 5°, m.p. 71°; β-*trans*-, 21°, m.p.

58°; β-*indanyl*, cyclo*hexyl*, and *Pr*$^{\beta}$ *H succinate* have m.p. 113°, 43°, and 51°, respectively. H. W.

Dehydration of 1-β-phenylethyl-3-methylcyclohexan-1-ol. D. PERLMAN and M.T. BOGERT (J. Amer. Chem. Soc., 1937, **59**, 2534—2536).—Dehydration of 1-β-*phenylethyl*-3-*methyl*cyclo*hexan*-1-*ol*, m.p. about 25—26°, b.p. 145—146°/3—4 mm. [*phenylurethane*, m.p. 102—103° (corr.)], by 85% H_2SO_4 is accompanied by ring-closure and gives mainly 2-methyl-1:2:3:4:9:10:13:14-octahydrophenanthrene with some of the spiran $CH_2<\begin{matrix}CH_2\\C_6H_4\end{matrix}>C<\begin{matrix}CH_2\cdot CHMe\\CH_2—CH_2\end{matrix}>CH_2$. Neither product was isolated pure, but dehydrogenation by Se gives 2-methylphenanthrene and oxidation by CrO_3, followed by H_2O_2, gives some α-m-*tolylhomophthalic acid*, m.p. 140—142° (decomp.). The spiran is present mostly in the low-boiling portion of the crude product. R. S. C.

Introduction of the triphenylmethyl group. IV. By-products formed during reactions with triphenylmethyl chloride. E. FUNAKUBO and T. MATSUI (Ber., 1937, **70**, [*B*], 2437—2446).—The by-product obtained by the action of CPh_3Cl on *iso*chavibetol and *iso*eugenol in C_5H_5N is CPh_3·OEt (cf. A., 1936, 1388). Reaction is never complete and the small amount of residual CPh_3Cl is not quantitatively transformed by H_2O into CPh_3·OH. CPh_3·OEt can arise from CPh_3Cl and EtOH or from CPh_3·OH and EtOH in presence of HCl but not in its absence. Reasons are advanced for the small and very variable yield of CPh_3·OEt. The "product," m.p. 81°, of van Alphen (A., 1927, 660) is probably CPh_3·OEt (cf. Schorigin, A., 1928, 59). H. W.

Condensations by sodium. IX. Preparation and properties of trixenyl- and trimethyltrixenyl-carbinols and their derivatives. A. A. MORTON and W. S. EMERSON (J. Amer. Chem. Soc., 1937, **59**, 1947—1949).—*p*-C_6H_4PhCl, Et_2CO_3, and Na powder in C_6H_6 (cf. A., 1932, 157) give 39% of $(p\text{-}C_6H_4Ph)_3C$·OH (I), reduced ($SnCl_2$, AcOH–conc. HCl) to tri-*p*-diphenylylmethane (II), which with Br in CS_2 and sunlight affords the *tetrabromide*, $(p\text{-}C_6H_4Ph)_3CBr_4$, m.p. 170—171° [hydrolysed by aq. alkali to (I)]. (II) with HNO_3 (*d* 1·6), conc. H_2SO_4, and 30% oleum gives a $(NO_2)_9$-derivative, m.p. 278—279° (decomp.). (II) could not be oxidised (CrO_3, AcOH). 4-Bromo-4′-methyldiphenyl, Et_2CO_3, and Na similarly afford 23% of *tri*-(4′-*methyl*-p-*diphenylyl*)-*carbinol*, m.p. 221—221·5° (*chloride*, m.p. 204—205°), reduced (method: Schmidlin and Garcia-Banús, A., 1913, i, 34) to *tri*-(4′-*methyl*-p-*diphenylyl*)*methane*, m.p. 174—174·5° (*tetrabromide*, m.p. 99—103°). The above compounds show more intense colour reactions than the corresponding compounds of the CPh_3 series. H. B.

Dehydration of *r*-α-phenyl-β-*o*-, -*m*-, and -*p*-tolyl-αβ-butylene glycols ("α"-forms). R. ROGER and A. M. ROBERTS (J.C.S., 1937, 1753—1761).—α-*Phenyl*-β-o- (I), m.p. 76—79°, -β-m- (II), m.p. 101—102°, and -β-p-*tolyl*-αβ-*butylene glycol* ("α"-*form*) (III), m.p. 100—101°, obtained from COEt·CHPh·OH and the Mg derivatives of *o*-, *m*-, and *p*-C_6H_4MeBr, are dehydrated by dil. H_2SO_4, molten $H_2C_2O_4$, or Et_2O–HCl, by semihydrobenzoin transformation, to α-*phenyl*-α-o- (IV), b.p. 176—178°/20 mm. (*semicarbazone*, m.p. 168—169°), -α-m- (V), b.p. 175—177°/18 mm. (*semicarbazone*, m.p. 164—165°; 2:4-*dinitrophenylhydrazone*, m.p. 169·5—170·5°), and -α-p-*tolylbutaldehyde* (VI), b.p. 170—173°/17 mm. (*semicarbazone*, m.p. 154—155°; 2:4-*dinitrophenylhydrazone*, m.p. 162—163°). With KOH–EtOH, (V) and (VI) give respectively α-*phenyl*-α-m-, b.p. 143—144°/17 mm., and -α-p-*tolylpropane*, b.p. 154—156°/23 mm.; (VI) is oxidised by CrO_3–AcOH to *p*-C_6H_4MeBz and *p*-$C_6H_4Bz\cdot CO_2H$.

Dehydration by conc. H_2SO_4 is more complex, causing semipinacolinic transformation of (I) and (II), with the unexpected migration of Et, and respective formation of r-o- (VII), m.p. 39·5°, and r-m-*tolyl* α-*phenylpropyl ketone* (VIII), m.p. 82—83° (2:4-*dinitrophenylhydrazone*, m.p. 130—131° [accompanied by a *compound* (IX), m.p. 97—98°, containing S]. Synthetically, (VII) and (VIII) are prepared from CHPhEt·CN and *o*- and *p*-C_6H_4MeBr (Mg); (VIII) is not affected by boiling KOH–EtOH. Conc. H_2SO_4 converts (III), however, into α-p-*tolylbutyrophenone* (X), m.p. 54—55° (*semicarbazone*, m.p. 160—161°; 2:4-*dinitrophenylhydrazone*, m.p. 145·5—146·5°), with *phenyl*-p-*tolylmethyl Et ketone* (XI) (*semicarbazone*, m.p. 202·5—203·5°). Formation of (X) may be either by semihydrobenzoin migration of H or by vinyl dehydration; that of (XI) by semipinacolinic migration of *p*-C_6H_4Me. A mixture of (X) and (XI) on oxidation (CrO_3–AcOH) gives an *acid*, $C_{17}H_{16}O_3$, m.p. 138—139°, which may be derived from either. Synthetically, (X) is prepared from *p*-$C_6H_4Me\cdot COEt$, reduced by Na–EtOH to *p*-$C_6H_4Me\cdot CHEt\cdot OH$, new b.p. 110°/21 mm. (and by Na–Hg to s-p-*tolylethylpinacol*, m.p. 101—102°), converted through α-*chloro*-α-p-*tolylpropane*, b.p. 94—95°/15 mm., into $[Hg(CN)_2]$ α-p-*tolylbutyronitrile*, which with MgPhBr gives (X); (XI) is prepared from *p*-$C_6H_4Me\cdot CHPh\cdot CN$ and MgEtBr.

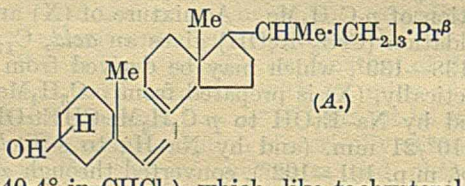
Conc. H_2SO_4 converts (IV) into (VII); (V) gives, not (VIII), but r-α-m-*tolylbutyrophenone* (?) (XII) (*semicarbazone*, m.p. 134—135°), with (IX); (VI) gives a mixture of (X) and (XI). Attempted prep. of (XII) from *m*-$C_6H_4Me\cdot CHEt\cdot OH$ through α-*chloro*-α-m-*tolylpropane*, b.p. 104—106°/21 mm., gives $[Hg(CN)_2]$ only m-*propenyltoluene* (?), b.p. 87—88°/25 mm. *m*-$C_6H_4Me\cdot CHPh\cdot CN$ and MgEtBr give r-*phenyl*-m-*tolylmethyl Et ketone* (?) (*semicarbazone*, m.p. 161°).

From the migration of Et (above) it is concluded that the conversion of alkylhydrobenzoins by H_2SO_4 into alkyldeoxybenzoins (A., 1921, i, 565; 1923, i, 333) is the result of semipinacolinic migration of alkyl, and not of vinyl dehydration. Results with (I) suggest that in saturation capacity *o*-C_6H_4Me > Ph (cf. A., 1937, II, 190). In dehydrations by conc. H_2SO_4, aldehydes cannot always be regarded as intermediate products. E. W. W.

Photochemical dehydrogenation of 7-dehydrocholesterol and the pyrolysis of the product. Y. URUSHIBARA and T. ANDO (Bull. Chem. Soc. Japan, 1937, **12**, 495—498).—7-Dehydrocholesterol [3:5-*dinitrobenzoate*, m.p. 212—212·5° (corr.; decomp.)] is dehydrogenated by prolonged insolation in EtOH–

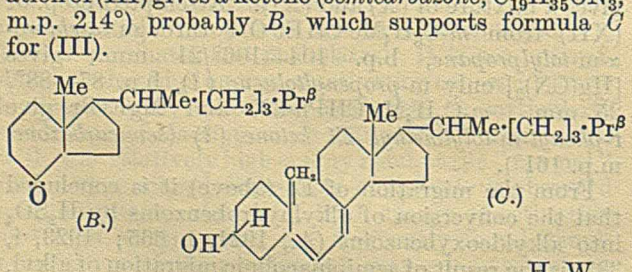
C_6H_6 containing eosin to the "*pinacol*," $C_{54}H_{86}O_2$, m.p. 185·5—186° (corr.; decomp.), $[\alpha]_D^{18}$ −171° in C_5H_5N, also +1H_2O, m.p. 184—185° (corr.; decomp.). This when heated at 185°/0·25 mm. and then distilled affords 10-*demethylcholestatrien*-3-*ol*, $C_{26}H_{40}O$, m.p. 76°, almost inactive optically [3 : 5-*dinitrobenzoate*, m.p. 210·5—211° (corr.), $[\alpha]_D^{17}$ −3·8° in $CHCl_3$]. Similar dehydrogenation of 7-dehydrocholesteryl benzoate gives a *product*, $C_{68}H_{94}O_4$, m.p. 183—183·5° (corr.; decomp.), $[\alpha]_D^{17}$ −114° in $CHCl_3$. H. W.

Substances obtained by irradiation of 7-dehydrocholesterol. A. WINDAUS, M. DEPPE, and W. WUNDERLICH (Annalen, 1937, **533**, 118—127).—Irradiation of 7-dehydrocholesterol (I) with ultra-violet light of >280 mμ. gives *lumisterol*-3, $C_{27}H_{44}O$, m.p. 87—88° (from $COMe_2$) or m.p. 63—64° (from MeOH), $[\alpha]_D^{18}$ +197° in $CHCl_3$ (*dinitrobenzoate*, m.p. 131°, $[\alpha]_D^{20}$ +20° in $CHCl_3$; *acetate*, m.p. 131—132°, $[\alpha]_D^{13}$ +142° in $CHCl_3$), which very closely resembles lumisterol (II) except in that it does not give an isolable compound with vitamin-D_3 whereas the compound from (II) and vitamin-D_2 is very characteristic. Constitutionally it probably differs from (II) only in the steric arrangement of groups at $C_{(10)}$. Irradiation of (I) with the ultra-violet light from Mg leads to non-cryst. *tachysterol*-3 (probably *A*), $[\alpha]_D^{21}$ −11·5° in benzine (*methyldinitrobenzoate*, m.p. 137°,



(*A*.)

$[\alpha]_D^{16}$ +40·4° in $CHCl_3$), which, like tachysterol, combines with citraconic anhydride giving an adduct resolved into its components by heat. Vitamin-D_3 (III) is isolated as the 3 : 5-dinitrobenzoate, m.p. 128°, or (from Et_2O), m.p. 140°. The *anisate*, m.p. 114°, $[\alpha]_D^{21}$ +127° in $CHCl_3$, and p-*nitrobenzoate*, m.p. 127°, $[\alpha]_D^{21}$ +114° in $CHCl_3$, are described. Ozonisation of (III) gives a ketone (*semicarbazone*, $C_{19}H_{35}ON_3$, m.p. 214°) probably *B*, which supports formula *C* for (III).



H. W.

Sterols. XXIV. Sitostenone and stigmastenone. R. E. MARKER and E. L. WITTLE. **XXV. *allo*Stigmasterols and *allo*sitosterols.** R. E. MARKER and T. S. OAKWOOD. **XXVI. Sitosteryl and stigmasteryl chloride and related compounds.** R. E. MARKER and E. J. LAWSON **XXVII. *epi*Sitosterol and *epi*stigmasterol.** R. E. MARKER, E. J. LAWSON, E. L. WITTLE, and T. S. OAKWOOD (J. Amer. Chem. Soc., 1937, **59**, 2704—2708, 2708—2710, 2711—2713, 2714—2715; cf. A., 1938, II, 12).—XXIV. The identity of tallol-sitosterol, termed simply sitosterol (I), with 22-dihydrostigmasterol is confirmed. With pptd. Cu at 150—200°/2 mm. (I) gives sitostenone, hydrogenated (PtO_2; 3 atm.) in Et_2O to 24-*ethyl*epi*coprostanol* (II), m.p. 137° (*acetate*, m.p. 94°), also obtained similarly from stigmastenone and oxidised by CrO_3 to 24-*ethylcoprostanone* (III), m.p. 114°. With $Al(OPr^\beta)_3$ this ketone gives 24-*ethylcoprostan*-β-*ol*, m.p. 127° (*acetate*, m.p. 89°) [and some (II)], which is epimerised to (II) by Na in xylene. With Br and a drop of HBr in AcOH (III) gives the 4-*Br*-derivative, m.p. 149°, converted by C_5H_5N into sitostenone, which is reduced by Na–C_5H_{11}·OH to sitostanol, identical with stigmastanol (IV) (acetate, m.p. 136°). Stigmasterol and Na–C_5H_{11}·OH give 5 : 6-dihydrostigmasterol [*acetate*, m.p. 122° (*dibromide*)] and a (?) *hydrocarbon*, m.p. 72°; the 5 : 6-H_2-compound gives (IV) when hydrogenated.

XXV. epiallo- (V) and allo-*Sitosterol* (VI) and allo*stigmasterol* (VII) are prepared. All are readily dehydrated and *epiallo*stigmasterol (VIII) is too unstable for isolation in a pure state. Stigmastenone with $Al(OPr^\beta)_3$ gives (VI), m.p. 137° (*digitonide*), the *acetate*, m.p. 132°, of which gives (II) when hydrogenated and hydrolysed; the mother-liquors afford a mixture of (VIII) and its dehydration product, also reduced to (II). Sitostenone gives similarly (VI), m.p. 158° (*digitonide*), and (V), m.p. 138°, the *acetates*, m.p. 88° and 92°, respectively, of which are hydrogenated to (II).

XXVI. PCl_5 and (I) give *sitosteryl chloride*, m.p. 86° (*dibromide*, m.p. 96°), hydrolysed by KOAc–AcOH to sitosteryl acetate and hydrogenated (PtO_2) in Et_2O to α-*sitostyl* [α-*stigmastyl*] *chloride*, m.p. 107°, which is also obtained by hydrogenation of *stigmasteryl chloride* (prep. by PCl_5), m.p. 83° (*dibromide*, m.p. 182°), from *epi*stigmastanol by PCl_5, and from stigmastanol by $SOCl_2$. β-*Sitostyl* [β-*stigmastyl*] *chloride*, m.p. 118°, is obtained from stigmastanol or sitostanol and PCl_5 or from *epi*stigmastanol and $SOCl_2$, and is hydrolysed to stigmastanol. The α-chloride is hydrolysed by KOAc in $BuCO_2H$ to *epi*stigmastanol and with Na–C_5H_{11}·OH gives *stigmastane* [*sitostane*], m.p. 84°.

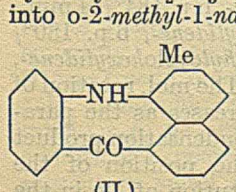
XXVII. The Grignard reagent from sitosteryl chloride with dil. H_2SO_4 gives (I) and epi*sitosterol*, m.p. 135° (*acetate*, m.p. 66°), hydrogenated to *epi*stigmastanol. Stigmasteryl chloride similarly affords epi*stigmasterol*, m.p. 151° (*acetate*, m.p. 98°), reduced to *epi*stigmastanol. Both new *epi*-compounds are readily dehydrated. R. S. C.

Vitamin-*E*. Tocopherols from various sources. O. H. EMERSON, G. A. EMERSON, A. MOHAMMAD, and H. M. EVANS (J. Biol. Chem., 1937, **122**, 99—107).—α-Tocopherol is isolated from cottonseed oil, lettuce leaves, and palm oil. Its absorption spectrum is revised. Two additional tocopherols have been isolated, β-tocopherol as allophanate, $C_{31}H_{52}O_4N_2$ or $C_{30}H_{50}O_4N_2$, m.p. 144—146°, $[\alpha]_D^{25}$ +5·7° in C_6H_6, from wheat-germ oil, and *γ-tocopherol* as *allophanate* (isomeric with the β-compound), m.p. 138—140°, $[\alpha]_D^{20}$ +3·4° in C_6H_6, from cottonseed oil and probably also from palm oil. β- and γ-Tocopherol are half to one third as active biologically as α-tocopherol. R. S. C.

Action of metals on acid chlorides. G. A. VARVOGLIS (Ber., 1937, **70**, [*B*], 2391—2396).—The action of Zn on BzCl in Et_2O gives unchanged Zn, and mainly EtOBz with EtCl, BzOH, $CH_2Ph{\cdot}OH$, and $ZnCl_2$. After removal of these substances a small quantity of viscous residue (I) remains in which benzil or *iso*benzil could not be detected. The initial change is between the acid chloride or a mol. compound of it with Et_2O and Zn and leads to $ZnCl_2$; the Bz residues do not unite to benzil but are involved in a complex manner in the formation of (I). The $ZnCl_2$ thus produced accelerates the change between BzCl and Et_2O to EtCl and EtOBz, which occurs also in absence of $ZnCl_2$. A third reaction is the reduction of BzCl to $CH_2Ph{\cdot}OH$. The liberation of H is proved by the formation of quinol dibenzoate (II) and chloroquinol dibenzoate (III) from Zn and BzCl in Et_2O cobtaining *p*-benzoquinone (IV). In *iso*amyl ether and dioxan, respectively, the main products are *iso*amyl benzoate or glycol dibenzoate, respectively; the latter is not produced in presence of (IV), its place being taken by (II) and (III). In C_6H_6, CS_2, or CCl_4 the only change is a slight conversion of the chloride into the acid. In C_6H_6 containing (IV) there is a considerable production of (III) and particularly of (II); the change is probably due to a catalytic action of $ZnCl_2$ formed in small amount on C_6H_6 and BzCl in the sense of a Friedel–Crafts reaction. (The presence of $COPh_2$ could not be detected.) A similar change is observed in anisole. Fe powder behaves similarly to Zn. AcCl resembles BzCl but gives a greater proportion of (I). H. W.

Bromo-derivatives of novocaine. III. L. FREJKA and L. ČRŽMÁŘ (Chem. Listy, 1937, **31**, 460—464).—3-Bromoacet-*p*-toluidide in 2·5% aq. $MgSO_4$ and $KMnO_4$ at 70° yield 3-*bromo*-4-*acetamidobenzoic acid*, m.p. 228—229°, hydrolysed by conc. H_2SO_4 to 3-*bromo*-4-*aminobenzoic acid*, m.p. 218—219° (*Et* ester, m.p. 90—91°; *Pr*$^{\alpha}$ ester, m.p. 58—59°), which with $OH{\cdot}CH_2{\cdot}CH_2Cl$ gives β-*chloroethyl* 3-*bromo*-4-*aminobenzoate*, m.p. 100°. This yields β-*diethylaminoethyl* 3-*bromo*-4-*aminobenzoate* (I), m.p. m.p. 157—158°, with $NHEt_2$ at 105—110° (10 hr.). (I) is also obtained by gradual addition of Br in Et_2O to an aq. solution of novocaine in sunlight. R. T.

o-2-Methyl-1-naphthylaminobenzoic acid. W. KNAPP (Monatsh., 1937, **71**, 122—127).—2 : 1-$C_{10}H_6MeBr$ and *o*-$NH_2{\cdot}C_6H_4{\cdot}CO_2H$ are transformed by anhyd. K_2CO_3 and Cu powder in boiling $PhNO_2$ into o-2-*methyl*-1-*naphthylaminobenzoic acid* (I), m.p. 215—216° (incipient decomp.), converted by P_2O_5 in boiling PhMe into *phenyl* 2-*methyl*-8-*naphthyl ketone* o : 1-*imine* (II), m.p. 196—197°, and a *methylbenzacridone*, m.p. 337—339°. At somewhat above its m.p. (I) is converted into *phenyl*-2-*methyl*-1-*naphthylamine*, m.p. 121—122°. H. W.



(II.)

Effects of oxygen and peroxides on the rate of addition of bromine to cinnamic acid in carbon tetrachloride. Y. URUSHIBARA and M. TAKEBAYASHI (Bull. Chem. Soc. Japan, 1937, **12**, 499—506).—The effect of O_2 on the addition of Br to $CHPh{:}CH{\cdot}CO_2H$ in CCl_4 has been established. In presence or absence of O_2 the reaction between Br and $CHPh{:}CH{\cdot}CO_2H$ in CCl_4 is not affected by HBr. Bz_2O_2 accelerates the addition. In all cases, in a vac. or in presence of O_2, Bz_2O_2, or HBr the product which separates is cinnamic acid dibromide, m.p. 198°. The experiments are performed in the dark at room temp. H. W.

Some derivatives of diphenylamine and a new synthesis of *N*-arylanthranilic acids and of acridones. (MISS) M. M. JAMISON and E. E. TURNER (J.C.S., 1937, 1954—1959).—Application of the method of Chapman (A., 1929, 550) yields the following: N-o-*chloro*-, m.p. 59—60°, N-2 : 4-*dichloro*-, m.p. 81°, and N-p-*bromo*-*phenylbenzimino*-p-*chlorophenyl ether*, m.p. 83—84°, and N-2 : 4-*dichlorophenylbenzimino*-2 : 4 : 6-*trichlorophenyl ether*, m.p. 86—88°. When heated these give N-*benzoyl*-2 : 4-*dichloro*-, m.p. 115°, -2 : 4 : 4′-*trichloro*-, m.p. 117—118°, -4-*chloro*-4′-*bromo*-, m.p. 149°, and -2 : 4 : 6 : 2′ : 4′-*pentachloro*-*diphenylamine*, m.p. 160°, respectively, which are hydrolysed to 2 : 4′-*dichloro*- (I), m.p. 42°, 2 : 4 : 4′-*trichloro*- (II), m.p. 67—68°, 4-*chloro*-4′-*bromo*-, m.p. 91·5°, and 2 : 4 : 6 : 2′ : 4′-*pentachloro*-*diphenylamine*, m.p. 94°, respectively. Interaction of 1 : 2 : 4-$OH{\cdot}C_6H_3Cl_2$ and N-*p*-chlorophenyl-*p*-toluanilideiminochloride (from *p*-tolu-*p*-chloroanilide and PCl_5) yields N-*p*-chlorophenyl-*p*-toluimino-2 : 4-dichlorophenyl ether, a glass, which when heated gives N-p-*toluoyl*-2 : 4 : 4′-*trichlorodiphenylamine*, m.p. 157°. Similarly, benz-*p*-chloroanilideiminochloride (III) and *l*-menthyl salicylate give N-p-*chlorophenylbenzimino*-2′-(*carbo*-*l*-*menthoxy*)*phenyl ether*, a glass; this when heated yields *N*-benzoyl-4-chloro-2′-(carbo-*l*-menthoxy)diphenylamine, which immediately decomposes at the formation temp. into *l*-menthene, BzOH, and 3-chloroacridone (IV). Nitrosation (Fischer, A., 1878, 313) of *p*-chlorodiphenylamine and of (I) yields respectively, N-*nitroso*-p-*chloro*-, m.p. 88°, and N-*nitroso*-2 : 4′-*dichloro*-*diphenylamine*, m.p. 66—67°, which are reduced (Zn–aq. EtOH–AcOH) to N-*phenyl*-N-p-*chlorophenyl*-, b.p. 174°/2 mm., and 2 : 4′-*dichloro*-NN-*diphenylhydrazine* (V), b.p. 241°/8 mm., respectively. (V) with 4-chlorophthalic anhydride yields N-2-*chlorophenyl*-N-4′-*chlorophenyl*-N′N′-4-*chlorophthalylhydrazine*, m.p. 142—142·5°. 2 : 4 : 4′-*Trichlorodiphenylcarbamyl chloride*, m.p. 117—118°, is obtained from (II) and $COCl_2$ at 150—200°. Me salicylate (VI) and (III) with NaOEt give N-p-*chlorophenylbenzimino*-o-*carbomethoxyphenyl ether*, m.p. 130—131°, which at 300° is converted into *Me* N-*benzoyl*-4-*chlorodiphenylamine*-2′-*carboxylate*, m.p. 139—140°; this is decomposed at 320° into MeOBz and (IV), and hydrolysed by NaOH in aq. EtOH to N-*benzoyl*-4-*chlorodiphenylamine*-2′-*carboxylic acid*, m.p. 191—192° [also decomposed by heat to BzOH and (IV)], and by conc. aq. NaOH to 4-chlorodiphenylamine-2′-carboxylic acid [also converted into (IV)]. Benz-2 : 4-dichloroanilideiminochloride and (VI) yield N-2 : 4-*dichlorophenylbenzimino*-o-*carbomethoxyphenyl ether*, m.p. 85—87° converted at 280° into *Me* N-*benzoyl*-2 : 4-*dichlorodiphenylamine*-2′-*carboxylate*, m.p. 114—116°, which is hydrolysed successively to

N-benzoyl-2 : 4-dichlorodiphenylamine-2'-carboxylic acid, m.p. 177°, and to 2 : 4'-dichlorodiphenylamine-2'-carboxylic acid. Similar reactions yield 4-m-*xylylbenzimino-2'-carbomethoxyphenyl ether*, m.p. 87—88° [isomerised at 275° to *Me N-benzoyl-2 : 4-dimethyldiphenylamine-2'-carboxylate*, m.p. 132—133° (no acridone formed at 350°), which is hydrolysed to *N-benzoyl-2 : 4-dimethyldiphenylamine-2'-carboxylic acid*, m.p. 192—193° (gives 1 : 3-dimethylacridone at 300°)], and *N-phenylbenzimino-o-carbomethoxyphenyl ether*, m.p. 110—111°, isomerised at 275° to *Me N-benzoyldiphenylamine-2-carboxylate*, m.p. 132—133°, which is partly hydrolysed to *N-benzoyl-N-phenylanthranilic acid*, m.p. 186°. From Me 3 : 5-dibromosalicylate and benz-*p*-bromoanilideiminochloride is obtained *N-p-bromophenylbenzimino-4' : 6'-dibromo-2'-carbomethoxyphenyl ether*, m.p. 105°, converted at 270° into *Me N-benzoyl-4 : 6 : 4'-tribromodiphehylamine-2-carboxylate*, m.p. 138—139°, successively hydrolysed to *N-benzoyl-4 : 6 : 4'-tribromodiphenylamine-2-carboxylic acid*, m.p. 217—218°, and 4 : 6 : 4'-*tribromodiphenylamine-2-carboxylic acid*, m.p. 222°, which with $POCl_3$ in boiling xylene yields 1 : 3 : 7-*tribromoacridone*, m.p. >300°. *N-p-Methoxyphenylbenzimino-p-chloro-o-carbomethoxyphenyl ether*, m.p. 105—106° (from Me 5-chlorosalicylate and benz-*p*-anisidideiminochloride), by the same series of reactions gives *Me N-benzoyl-4-chloro-4'-methoxydiphenylamine-2-carboxylate*, m.p. 164°, and *N-benzoyl-4-chloro-4'-methoxydiphenylamine-2-carboxylic acid* (softens and loses $0{\cdot}5C_6H_6$ at 120—125°; no sharp m.p.; converted at 300° into 3-*chloro-7-methoxyacridone*, m.p. >300°). *N-p-Chlorophenylbenzimino-p-carbomethoxyphenyl ether*, m.p. 78—79° (from benz-*p*-chloroanilideiminochloride and *p*-$OH{\cdot}C_6H_4{\cdot}CO_2Me$), similarly gives *Me N-benzoyl-4-chlorodiphenylamine-4'-carboxylate*, m.p. 140—141°, hydrolysed to *N-benzoyl-4-chlorodiphenylamine-4'-carboxylic acid*, m.p. 223—224°. J. D. R.

Configuration of cyclic 1 : 1-hydroxycarboxylic acids. J. Böeseken and (Mlle.) F. J. van Buuren (Rec. trav. chim., 1937, **56**, 1211—1218).—Measurements of the increase in the conductivity of H_3BO_3 solutions caused by the addition of 1-hydroxy*cyclo*heptane-, -hexane-, -pentane-, -butane-, and -propane-1-carboxylic acid shows that with rings of 4 C atoms, the relative positions of the OH and CO_2H are the same as in the open-chain hydroxy-carboxylic acids. In rings of 3 or 4 C, the angle between the OH and the CO_2H is increased by distortion, and the increase in the conductivity of H_3BO_3 solutions is very much diminished. Hydroxy*cyclo*butanecarboxylic acid readily forms a lactide, even in H_2O, and conductivity measurements in presence of this acid are only approx. J. D. R.

Use of "sodium phenoxide–methyl salicylate" as a catalyst in exchange esterification. K. N. Kinzerskaja (J. Appl. Chem. Russ., 1937, **10**, 1889—1893).—Benzyl salicylate is obtained in 73% yield, and the cinnamate in 40% yield, by adding NaOPh to 1 : 1 $CH_2Ph{\cdot}OH$–*o*-$OH{\cdot}C_6H_4{\cdot}CO_2Me$ or –$CHPh{:}CH{\cdot}CO_2Me$ mixtures, distilling off the MeOH liberated, and heating the product at 160—170°/50—80 mm., when excess of $CH_2Ph{\cdot}OH$ distils off. R. T.

α-Bromo-β-methoxy-β-phenylpropionic acids. E. J. van Loon and H. E. Carter (J. Amer. Chem. Soc., 1937, **59**, 2555—2557).—Contrary to Schrauth and Geller (A., 1922, i, 1125) pure $CHPh{:}CH{\cdot}CO_2H$ and $Hg(OAc)_2$ in MeOH give β-*methoxy-β-phenylanhydro-α-hydroxymercuripropionic acid*, decomp. 210—211°, but more prolonged contact gives a *compound* (I), decomp. 210—212°, possibly the mixed acid, $OAc{\cdot}[Hg{\cdot}CH(CHPh{\cdot}OMe){\cdot}CO_2]_x{\cdot}H$, insol. in $CHCl_3$. The Hg compounds absorb 2 Br, but give mixtures under all conditions. The best method is to add Br to (I) in aq. KBr, which leads to much α-bromo-β-methoxy-β-phenylpropionic acid, m.p. 139—140° (lit. 126—127°), and a little of the form, m.p. 165—170° (182—183°), readily separated by way of the Na salts. R. S. C.

Configuration and mobility of *cyclo*hexene. J. Böeseken and W. J. F. de Rijck van der Gracht (Rec. trav. chim., 1937, **56**, 1203—1210).—Butadiene and maleic anhydride in C_6H_6 yield Δ^1-*cyclo*hexene-4 : 5-dicarboxylic anhydride, which is hydrolysed (H_2O) to the acid (I); similarly from isoprene, 1-*methyl*-Δ^1-cyclo*hexene*-4 : 5-*dicarboxylic anhydride*, m.p. 63—64° [*acid* (II), m.p. 147—148°], is prepared, and from βγ-dimethyl-$\Delta^{\alpha\gamma}$-butadiene, 1 : 2-*dimethyl*-Δ^1-cyclo*hexene*-4 : 5-*dicarboxylic anhydride*, m.p. 78—79° [*acid* (III), m.p. 204°]. (II), which contains an asymmetric C, is resolved through its *strychnine* salt, m.p. 167°, into two *isomerides*, both m.p. 147—148°, $[\alpha]_D^{20}$ ±16·5° in EtOH, but (I) and (III) cannot be resolved, indicating that the mobilities of these acids are too great to allow the existence of stable isomerides. J. D. R.

Condensation of acetone with phenylpyruvic acid. P. Cordier (Compt. rend., 1937, **205**, 918—920; cf. A., 1912, i, 770).—Prolonged interaction of $CH_2Ph{\cdot}CO{\cdot}CO_2Na$ (1 mol.) with $COMe_2$ (5 mols.) and K_2CO_3 (1 mol.) (KOH gives a smaller yield) at room temp. affords *α-hydroxy-γ-keto-α-benzylvaleric acid*, m.p. 105°, which with HCl–AcOH affords an unsaturated *acid*, m.p. 93°. J. L. D.

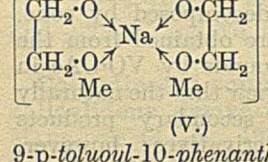
Condensation of ethyl tartrate with cyclic ketones and the molecular rotation of the resulting compounds. Y. Tsuzuki (Bull. Chem. Soc. Japan, 1937, **12**, 487—492).—Et_2 *d*-tartrate is readily condensed with the appropriate cyclic ketone by P_2O_5 at 80—90° to the following Et_2 *d*-dioxysuccinates: -cyclo*pentylidene*-, b.p. 170—171°/12 mm., $[\alpha]_D^{20}$ —40·55; -cyclo*hexylidene*-, b.p. 178°/12 mm., $[\alpha]_D^{20}$ —35·37°; -o-*methyl*cyclo*hexylidene*-, b.p. 184°/14 mm., $[\alpha]_D^{20}$ —21·81°; -m-*methyl*cyclo*hexylidene*-, b.p. 180°/14 mm., $[\alpha]_D^{20}$ —35·42°; -p-*methyl*cyclo*hexylidene*-, b.p. 188°/14 mm., $[\alpha]_D^{20}$ —30·49°. The mol. rotation of these homologous compounds decreases as the parachor of the ketone residue in the condensation product increases but the influence of the position of the substituent is noticed; the substitution of Me in the *o*-position is the most effective and that of the *m*-position is nearly ineffective. H. W.

Preparation of 1 : 2-dicarboxyl chlorides by the action of chlorine on thioanhydrides. E. Ott, A. Langenohl, and W. Zerweck (Ber., 1937, **70**, [*B*], 2360—2362).—The frequent failure of PCl_5 to convert acid anhydrides into 1 : 2-dicarboxyl

chlorides is attributed to the slight difference in the affinity of P towards Cl and O. Interaction between Cl_2 and the thioanhydride is more successful since the affinity of Cl for S is sufficient to overcome the union of S and the two C and to remove S as S_2Cl_2 leaving the dichloride. Thus *o*-$C_6H_4(COCl)_2$ is obtained in good yield by passing dry Cl_2 through thiophthalic anhydride at 245°. Similarly, pyromellitic anhydride and Na_2S afford *thiopyromellitic anhydride*, m.p. 239°, transformed by Cl_2 at 245° into pyromellityl chloride in 96% yield; this could not be isomerised by $AlCl_3$ at 150°. H. W.

Chemiluminescence of phthalhydrazide derivatives. C. N. Zellner and G. Dougherty (J. Amer. Chem. Soc., 1937, **59**, 2580—2583).—The luminescence of 3- and 4-amidophthalhydrazides during oxidation is measured by a photronic cell and galvanometer. The intensity varies greatly according to the substituent and its position. The rate of oxidation (measured by the evolution of N_2) also varies, but bears no relation to the intensity of luminescence, except for compounds substituted in the heterocyclic ring. Luminescence depends on transference of energy from a decomposing enolic or dienolic mol. to unchanged diketonic mols. 3-*Acet-*, m.p. 160°, 3-, m.p. 269°, and 4-*benz-amidophthalhydrazide*, m.p. 273—274°, were prepared from the substituted Et phthalates or phthalic anhydride. $NHMe{\cdot}NH_2$ and $NHAc{\cdot}C_6H_3(CO)_2O$ give α-, m.p. 302° (*Ac* derivative, m.p. 198—199°), and β-3-, m.p. 273—274°, and α-, m.p. 329°, and β-4-*acetamido*-N-*methylphthalhydrazide* (impure), m.p. about 260°. $(NHMe)_2$ and 4 : 1 : 2-$OH{\cdot}C_6H_3(CO_2H)_2$ give 4-*hydroxy*-NN′-*dimethylphthalhydrazide*, m.p. about 290°. o-*Methylaminobenzhydrazide* has m.p. 146—147°. Impure 3-hydroxy- and -chloro-phthalhydrazides were also prepared. M.p. are corr. R. S. C.

Addition of alkali metals to phenanthrene. A. Jeanes and R. Adams (J. Amer. Chem. Soc., 1937, **59**, 2608—2622).—Contrary to Schlenck and Bergmann (A., 1928, 1031), Li adds to phenanthrene (I) in the 9 : 10-positions; reaction is best in $(CH_2{\cdot}OMe)_2$ and treatment with CO_2 gives trans-9 : 10-*dihydrophenanthrene*-9 : 10-*dicarboxylic acid* (II), m.p. 235—242° (decomp.). The product obtained by EtOH from the Li_2 compound is 9 : 10-dihydrophenanthrene; it yields 1 : 2 : 3 : 4-tetrahydrophenanthrene, when hydrogenated, by rearrangement of the 1 : 4 : 9 : 10-H_4-compound initially formed. In $(CH_2{\cdot}OMe)_2$ K reacts readily with (I), Na less rapidly but also smoothly. Carbonation yields (II), but, unless the (I) was freed from fluorene, some fluorene-9-carboxylic acid, dimorphic, m.p. 226° or 232° (decomp.) (*Me* ester, m.p. 67—68°), is formed, particularly under conditions expected to favour reaction of an impurity present in small amount. The last-mentioned acid is the product termed 9 : 9′ : 10 : 10′-tetrahydro-9 : 9′-diphenanthryl-10 : 10′-dicarboxylic acid by Schlenck. Smooth dehydrogenation of (II) cannot be effected; $K_3Fe(CN)_6$ causes also loss of CO_2 and gives phenanthrene-9-carboxylic acid; CrO_3 gives phenanthrenequinone. Methylation of (II) gives the Me_2 ester, m.p. 128°; heating with Ac_2O affords cis-9 : 10-*dihydrophenanthrene*-9 : 10-*dicarboxylic anhydride* (III), m.p. 193·5°, and a little *phenanthrene*-9 : 10-*dicarboxylic anhydride* (IV), m.p. 322°; heating alone gives a little (IV) and much cis-9 : 10-*dihydrophenanthrene*-9 : 10-*dicarboxylic acid*, double m.p. 196° and 232° (Me_2 ester, m.p. 119°). This *cis*-acid is unstable; it dissolves in NaOH to an orange solution (containing either the enolic or dienolic form), which soon becomes colourless and then yields the *trans*-acid (II), which is also obtained from the *cis*-acid in hot AcOH; at 230—240° alone or with CrO_3 in cold AcOH it loses H_2 and gives (IV); it is obtained from the anhydride (III). The anhydride (IV) is extremely stable; analogies are discussed and the stability is considered to be due to proximity of the two CO_2H of the corresponding acid owing to (*a*) alteration of the valency angles by the α-substituents (the two Ph rings) and (*b*) the shortening of 9 : 10-C:C linking by the unusually aliphatic nature of this linking. The acid corresponding with (IV) cannot be prepared; dissolution in hot NaOH (cold NaOH is without effect), followed by acidification, regenerates the anhydride, but $NaOH–Me_2SO_4$ gives Me_2 *phenanthrene*-9 : 10-*dicarboxylate*, m.p. 131°; $MeOH–H_2SO_4$ is without effect on (III). Reaction of alkali metals with (I) is believed to produce equilibrium with the 9-ion and 9 : 10-di-ion, probably in solvated form, the existence of which is indicated by temporary disappearance of the colour on too rapid addition of CO_2; some of the solvent $(CH_2{\cdot}OMe)_2$ is removed from the reaction sphere, probably as the solvate (V), formation of which would account for the advantage of using $(CH_2{\cdot}OMe)_2$ as solvent. The anhydride (IV) undergoes reactions of *o*-$C_6H_4(CO)_2O$. Thus with PhMe and $AlCl_3$ it gives 9-p-*toluoyl*-10-*phenanthroic acid*, m.p. 236° (softens at 231°), and *ditolylphenanphthalein*, m.p. 247°. With C_6H_6 and $AlCl_3$ it gives 9-*benzoyl*-10-*phenanthroic acid*, m.p. 232°, converted with difficulty (10—15%) by P_2O_5 at 220—260° into 1 : 2 : 3 : 4-dibenzanthraquinone and by BzCl in $C_6H_3Cl_3$ into a *keto-lactone*, $C_{22}H_{14}O_3$, m.p. 228°, reconverted into the parent acid by KOH. With *o*-$C_6H_4(NH_2)_2$ (IV) gives the *product*, $C_{22}H_{12}ON_2$, m.p. 279°; (III) gives the *product*, $C_{22}H_{14}ON_2$, m.p. 274°. R. S. C.



(V.)

Synthesis of conjugated bile acids. IV. Bodi and Mueller procedure. F. Cortese (J. Amer. Chem. Soc., 1937, **59**, 2532—2534; cf. A., 1937, II, 342).—Prep. of Et and Me cholate, Et deoxycholate, cholyl- and deoxycholyl-hydrazide and -azide, Na tauro- and taurodeoxy-cholate, and glyco- and deoxyglyco-cholic acid and their Na salts in good yields is described. R. S. C.

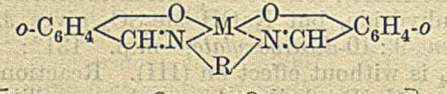
Preparation of esters of dihydronaphthalenedicarboxylic acids.—See B., 1937, 1314.

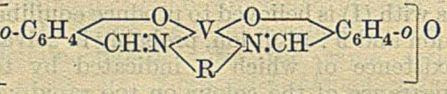
Manufacture of polycyclic aromatic aldehydes and carboxylic acids.—See B., 1937, 1315.

Preparation of *m*-dimethylaminobenzaldehyde. I. A. C. Bottomley, W. Cocker, and (Miss) P. Nanney (J.C.S., 1937, 1891—1892).—Interaction of *m*-$CHO{\cdot}C_6H_4{\cdot}NH_2$ and $CH(OEt)_3$ in

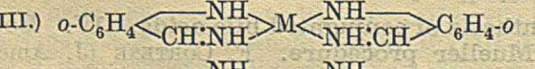
5% HCl–EtOH yields *m*-$(OEt)_2CH{\cdot}C_6H_4{\cdot}NH_2$, methylated (MeI–$Na_2CO_3$) to *m-dimethylaminobenzaldehyde methiodide*, m.p. 185—186° (decomp.), which, when heated at 150—160°/10—15 mm., is converted into *m-dimethylaminobenzaldehyde*, b.p. 137·5—138°/9 mm. [*oxime*, m.p. 75—76°; *semicarbazone*, m.p. 218—222° (slow heating) or 228—229° (instantaneous); *picrate*, m.p. 147—147·5°]. J. D. R.

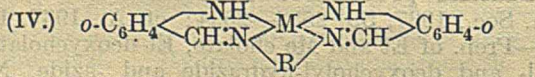
Internal complex salts of the aldimine and azo-series. P. Pfeiffer, T. Hesse, H. Pfitzner, W. Scholl, and H. Thielert with, in part, Lübbe (J. pr. Chem., 1937, [ii], **149**, 217—296).—Metal-organic complexes of many new types are described. They exhibit the colours and solubility in org. solvents characteristic of the class. Substances of type (I) (M = Cu, Ni, or Zn) are obtained from the metal acetate and (*a*) *o*-hydroxy-aldehyde and diamine or (*b*) the preformed di-*o*-hydroxyarylidenediamine; they are in general stable to 2N-NaOH and -H_2SO_4 at room temp. Substances of type (II) are obtained

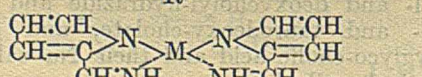
(I.) 

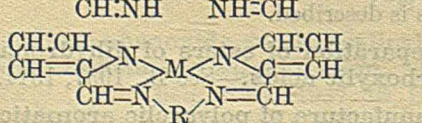
(II.) 

from VO·OAc and the Schiff's base in hot C_5H_5N or EtOH; O in these compounds can be replaced by 2 Cl or 2 OAc, which are ionic; except for compounds derived from *o*-$OH{\cdot}C_6H_4{\cdot}COMe$, they are very stable, some even being only slowly decomposed by conc. H_2SO_4. The VO compounds are obtained from the corresponding Fe or Mg compounds by VO·OAc in C_5H_5N, which confirms Treibs' view that the naturally occurring VO-porphyrins are secondary products derived from the Fe or Mg derivatives; however, $Cu(OAc)_2$ gives the Cu compounds from the VO derivatives, and the reverse replacement does not occur. Schiff's bases and $UO_2(OAc)_2$ give good yields of UO_2-complexes [(I) M = UO_2], which are not stable, being decomposed by cold acid or warm alkali. Cu and Ni salts with *o*-aminoarylideneamines give very readily substances of types (III) and (IV) (M = Cu or Ni); pyrrole-2-methyleneimine or amines give similarly substances (V) and (VI) (M = Cu or Ni);

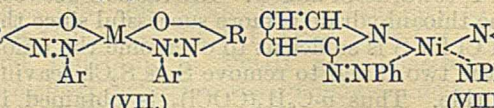
(III.) 

(IV.) 

(V.) 

(VI.) 

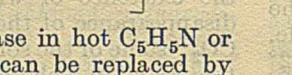
these resemble (I) in properties. Hydroxyazo-compounds readily form substances (VII) (M = Ni or Cu). The *Cu* compound [(VII) R = $OH{\cdot}C_6H_3$; Ar = Ph] from benzeneazoresorcinol is so stable to alkali that it is convertible into a *Me_2 ether* and *Bz_2* derivative, +0·5C_5H_5N, which with dil. HCl give 2:4-$OH{\cdot}C_6H_3(OH){\cdot}N{:}NPh$ and 2-*hydroxy*-4-*benzoyloxy*-



(VII.) (VIII.)

azobenzene, m.p. 139°, respectively; the Ni compounds of this series are less stable. A Cu compound (VII) containing SO_3H in R is also obtained. 2-Pyrroleazobenzene, m.p. 62°, gives the *Ni* compound (VIII). No internal complexes are formed from *m*- or *p*-compounds, and some *o*-compounds do not react; in certain cases complexes formed are not of the type mentioned.

Aldimines and ketimines described below are prepared from the aldehyde and base in EtOH or the hydrochloride of the base and NaOAc in EtOH. Salicylald-*o*-hydroxyphenylimine, m.p. 181°, gives the *Cu* derivative (IX),  , m.p. about 390°, anhyd., +$PhNO_2$, +C_5H_5N, and +NH_3,0·5H_2O, but salicylald-*m*-, m.p. 130°, and -*p*-hydroxyphenylimine, m.p. 135°, give only the "bimol." *Cu* derivative (X); the Cu derivative, anhyd. and +2MeOH,

(X.) 

of the *p*-compound is stable to 1% KOH, but not to mineral acid, and with BzCl and 0·2N-KOH gives *p*-$NHBz{\cdot}C_6H_4{\cdot}OBz$. The analogous *Cu* derivative, +C_6H_6 and anhyd., from resorcylaldphenylimine, m.p. 131°, is much less stable to alkali. $NH_2{\cdot}CHMe{\cdot}CH_2{\cdot}NH_2$,2HCl, *m*-$OH{\cdot}C_6H_4{\cdot}CHO$, $Cu(OAc)_2$, and NaOAc in aq. EtOH give the *Cu* derivative, +1·5H_2O, of type (I) (R = $\cdot CH_2{\cdot}CHMe\cdot$). Other *Cu* derivatives of type (I) are obtained from *disalicylald*-4-*chloro*-, -4-*nitro*-, and -4-*carboxy*-1:2-*phenylenedi-imide*, m.p. indef., and disalicylaldnaphthylene-1:8-di-imide; the Cu derivative of *o*-$OH{\cdot}C_6H_4{\cdot}CHO$ (XI) with $(NH_2{\cdot}CHPh)_2$ and NaOAc in EtOH gives a *Cu* derivative {(I) R = $[CHPh]_2$}, anhyd. and +$CHCl_3$, whilst 4:1:8-$SO_3H{\cdot}C_{10}H_5(NH_2)_2$ affords the *Ba*, *Pb*, and unstable *NH_4* salts of a similar *Cu* derivative. *Ni* derivatives are obtained analogous to (IX) and (X) (*p*-compound only prepared), and the methods indicated above afford *Ni* derivatives (I), in which R = $\cdot CHMe{\cdot}CH_2\cdot$ (XII), 4:1:2-$C_6H_3Cl<$, 4:1:2-$NO_2{\cdot}C_6H_3<$, and 1:8-$C_{10}H_6<$; that in which R = $[CHPh]_2$ is obtained anhyd. and +$CHCl_3$. The Ni derivative of (XI) and 1:3:4-$CO_2H{\cdot}C_6H_3(NH_2)_2$ in EtOH yield a *Ni* derivative [(I) R = 4:1:2-$CO_2H{\cdot}C_6H_3<$] [*C_5H_5N* (loses 0·5C_5H_5N at 140°), *NH_4*, +2·5H_2O, and *coniine* salts; *l-menthyl* ester, +C_5H_5N and 0·5C_5H_5N; no resolution occurs], which with $NH_2{\cdot}CHMe{\cdot}CH_2{\cdot}NH_2$ exchanges the basic component to give (XII). A *Zn* derivative {(I) R = $[CH_2]_2$}, anhyd., +C_5H_5N, and +0·5$(CH_2{\cdot}NH_2)_2$, is obtained from (XI), $Zn(OAc)_2$, NaOAc, and $(CH_2{\cdot}NH_2)_2$,2HCl. (XI) and the appropriate diamine give *UO_2* derivatives (I), in which R = $[CH_2]_2$, anhyd., +MeOH, and +C_5H_5N (mol. wt. determined in acridine), stable to cold

KOH, but not to hot KOH or cold, conc. H_2SO_4, and ·CHMe·CH_2·, anhyd., +EtOH, and +C_5H_5N. *Di-salicylaldtrimethylenedi-imide*, m.p. 163°, gives a UO_2 derivative (I), anhyd. and +MeOH; its *VO* derivative [(II) R = *o*-C_6H_4], anhyd., +MeOH, +AcOH, and +C_5H_5N (mol. wt. determined in acridine), is very stable to H_2SO_4 and yields the corresponding *dichloride* and *diacetate*. *Di-2-hydroxy-1-naphthald-ethylenedi-imide*, m.p. 311°, gives a UO_2, anhyd. and +MeOH, and *VO* derivative [as (II); R = $[CH_2]_2$, but 1 : 2-CH·$C_{10}H_6$·O instead of CH·C_6H_4·O]. *Di-2-hydroxy-1-naphthald-αβ-diphenylethylenedi-imide*, m.p. 223°, give UO_2 and *VO*, anhyd. and +PhMe, derivatives. *Di-2-hydroxy-1-naphthald-o-phenylenedi-imide*, m.p. 163°, gives UO_2, anhyd. and +MeOH, and *VO* derivatives. Di-*o*-hydroxyacetophenone-ethylenedi-imide gives UO_2, anhyd., +EtOH, and +C_5H_5N, and *VO* derivatives, and similar UO_2 and *VO* derivatives, anhyd., are obtained from *di*-o-*hydroxyacetophenone-o-phenylene-* (XIII) and *-αβ-diphenylethylene-di-imide* (XIV), m.p. 221°, respectively. UO_2 derivatives could not be prepared from *disalicylald-tetramethylene-*, m.p. 91°, *-pentamethylene-*, m.p. 64°, or -m-*phenylene-di-imide*, m.p. 109°, *disalicylald-benzidide*, m.p. 256°, or *-stilbene-4 : 4′-di-imide*, m.p. 266°, (XIV), *diresorcylald-*, m.p. indef., or *diresacetophenone-ethylenedi-imide*; most of these and (XIII) failed to yield also VO derivatives. The appropriate Schiff's bases yield *VO* derivatives (II), in which R = $[CH_2]_2$, anhyd., +$CHCl_3$, and +C_5H_5N (mol. wt. determined in $CHCl_3$ and acridine), ·CHMe·CH_2·, anhyd., +MeOH, and +C_5H_5N, and $[CHPh]_2$; the *VO* derivative, anhyd. and +C_5H_5N, from diresorcylaldethylenedi-imide is decomposed by cold 10% KOH, but with Ac_2O gives the Ac_2 derivative. The following are prepared: Na_2 NN′-*disalicylald-stilbene-4 : 4′-di-imide-2 : 2′-disulphonate*, anhyd. and +EtOH; 2 : 2′-*dihydroxydiphenylene-5 : 5′-*, m.p. 246°, and *-3 : 3′-diamine*, unstable; *disalicylald-2 : 2′-dihydroxy-diphenylene-5 : 5′-*, m.p. 241°, and *-3 : 3′-di-imide*, m.p. 232°, neither of which gives a Cu complex. The prep. of αβ-diphenylethylenediamine from $(·CPh:N·OH)_2$ is improved.

o-NH_2·C_6H_4·CHO (XV), m.p. 40°, with $CuSO_4$ or $NiSO_4$ in aq. NH_3 gives the *Cu* and *Ni* complexes (III). The *Ni* and *Cu* complexes [(IV); R = *o*-C_6H_4] are similarly obtained from the crude oily Schiff's base from (XV) and *o*-$C_6H_4(NH_2)_2$; the *Ni* derivative {(IV); R = $[CH_2]_2$} is also prepared from a crude condensation product, but the *Cu* analogue is prepared from *di*-o-*aminobenzaldethylenedi-imide* (prep. at room temp. without a condensing agent), m.p. 178° (Ac_2 derivative, m.p. 200°). *Di*-o-*aminobenzald-p-phenylene-*, m.p. 215° (decomp.), and *-diphenylene-4 : 4′-di-imide*, m.p. 273—274°, are prepared by use of dil. NaOH; neither gives a Cu complex.

The *Cu* and *Ni* complexes (V) are obtained from pyrrole-2-aldehyde and $CuSO_4$ or $NiSO_4$ in aq. NH_3. The *Cu* and *Ni* complexes [(VI); R = *o*-C_6H_4] were similarly obtained from the aldehyde and *o*-$C_6H_4(NH_2)_2$ in H_2O, but the *Cu* and *Ni* derivatives {(VI); R = $[CH_2]_2$} are prepared from *di(pyrrole-2-ald)ethylenedi-imide*, m.p. about 175° (decomp.). *Di(pyrrole-2-ald)-diphenylene-4 : 4′-di-imide*, m.p. about 270° (decomp.), gives a *Cu* derivative [(VI); R = ·C_6H_4·C_6H_4·], but *di(pyrrole-2-ald)-p-phenylenedi-imide*, m.p. 210—212° (decomp.), gives no complex salts.

Benzeneazo-*p*-cresol, m.p. 104°, gives a *Cu* derivative $\left[\text{(VII)};\ Ar = Ph,\ R = 4\text{-}C_6H_3Me\langle^{(O\text{-}1)}_{(N\text{-}2)}\right]$, but *m*- (prep. from the OMe-compound by $AlBr_3$) and *p*-hydroxyazobenzene do not react with $CuSO_4$. *o*-OH·C_6H_4·N:NPh, m.p. 79—80°, and benzeneazo-resorcinol, m.p. 170°, give *Ni* derivatives of type (VII). Benzeneazo-2-naphthol-4-sulphonic acid gives a *Ni* $\left[\text{(VII)};\ Ar = Ph,\ R = 4\text{-}SO_3H\text{·}C_{10}H_5\langle^{(O\text{-}2)}_{(N\text{-}1)}\right]$, +6$H_2O$, +6$NH_3$, and +3$(CH_2·NH_2)_2$, and *Cu* derivative, anhyd. and +6·5H_2O [*di(ethylenediamine)*, +3H_2O, *Cu*, +2NH_3, K_2, and *Ba* salts]. 2 : 2′-Dihydroxyazobenzene gives a *Cu* derivative [(VII) Ar = *o*-C_6H_4·OH], anhyd. and +NH_3,0·5H_2O. 2 : 1-OH·$C_{10}H_6$·N:NPh gives a *Co* derivative (XVI).

Benzeneazo-β-naphthylamine and $[CoCl(NH_3)_5]Cl_2$ in NH_3–EtOH–H_2O give the Co^{III} complex (XVII), but attempts to obtain Cu derivatives by $CuSO_4$–NH_3

$$\left[{}^{2}_{1}\rangle C_{10}H_6\langle^{O}_{N:NPh}\rangle\right]_3Co \qquad \left({}^{2}_{1}\rangle C_{10}H_6\langle^{NH}_{N:NPh}\rangle\right)_3Co$$

(XVI) (XVII)

from 6-amino-3 : 4′-dimethylazobenzene and benzeneazo-2-naphthylamine-4-sulphonic acid resulted in oxidation to the dimethyltriazole, 4 : 1 : 2-$C_6H_3Me\langle^{N}_{N}\rangle N\text{·}C_6H_4Me\text{-}p$, m.p. 125—126°, and the *phenylnaphthatriazole* derivative,

1 : 2-$C_{10}H_6\langle^{N}_{N}\rangle N\text{·}C_6H_4\text{·}SO_3H$, cryst. (*Cu*^{II}, anhyd. and +3NH_3, and Na_2 salts) (cf. Crippa, A., 1929, 181).

R. S. C.

Co-ordinated copper and nickel compounds of salicylidene derivatives. L. Hunter and J. A. Marriott (J.C.S., 1937, 2000—2003).—By interaction of the appropriate salicylidene derivative (2 mols.) with the metal acetate (1 mol.) in hot EtOH, or by interaction of salicylaldehyde (2 mols.), metal acetate (1 mol.) and amine or hydrazine derivative (2 mols.) in hot EtOH, the following derivatives of the type $\left[{}^{C_6H_4\text{·}O}_{CH:N-R}\right]_2M$ (where R is Ar, NHAr, or NH·CO·NH_2) are formed: Cu^{II} *salicylidene-o-*, m.p. 243—246° (decomp.), -m-, m.p. 188° (decomp.), -p-*toluidine*, m.p. 211—213° (decomp.), -α-, m.p. 259° (decomp.), -β-*naphthylamine*, m.p. 194—196° (decomp.), -m-, m.p. 210—212° (decomp.), -p-*chloroaniline*, m.p. 240°, -p-*bromoaniline*, m.p. 250—251°, -m-, m.p. 272° (decomp.), -p-*nitroaniline*, m.p. 313° (decomp.), -o-, m.p. 222° (decomp.), -p-*anisidine*, m.p. 179° (decomp.), *-hydrazone*, decomp. 270—275°, *-phenylhydrazone*, m.p. 174°, -p-*nitrophenylhydrazone*, m.p. 221° (decomp.), and Cu^{II} *salicylaldimine*, m.p. 195° (decomp.); *Ni salicylidene-aniline*, m.p 248° (decomp.), -o-, m.p. 293° (decomp.), -m-, m.p. 260° (decomp.), -p-*toluidine*, m.p. 274° (decomp.), -α-, m.p. 311° (decomp.), -β-*naphthylamine*, m.p. 220° (decomp.), -o-*anisidine*, m.p. 319° (decomp.); *nickel-salicylaldimine*, m.p. 335° (decomp.), *-salicylaldazine*, stable at 360°, *-disalicylidenebenzidine*, m.p. >360°; *Ni salicylidene-hydrazone*, decomp. 313°, *-phenyl-*

hydrazone, decomp. about 230°, and *-semicarbazone*, decomp. 302°. None of the Cu derivatives offers any advantage over that of salicylaldoxime for the determination of Cu. J. D. R.

Addition of ketens to hydrocarbons. E. H. Farmer and M. O. Farooq (Chem. and Ind., 1937, 1079—1080).—CPh_2:CO appears to react successfully with all simple conjugated dienic hydrocarbons, whether cyclic or open-chain, since it gives homogeneous cryst. additive products with *cyclo*pentadiene, *cyclo*hexene (I), *cyclo*hexadiene (II), βγ-dimethylbutadiene, and piperylene. It does not appear to react with CMe_2:CMe_2. The H_2-derivative of the additive product from (II) is identical with the additive product (III) from (I) so that in these cases addition cannot involve the formation of a six-C ring. Further the product of the hydrolytic fission of (III) does not correspond with the diphenyl*cyclo*hexylacetic acid of Ziegler and Schnell (A., 1924, i, 850) so that Staudinger's simple explanation of the change, $CH_2{\cdot}CH_2{\cdot}CH{\cdot}CPh_2$ / $CH_2{\cdot}CH_2{\cdot}CH{\cdot}CO$ → $C_6H_{11}{\cdot}CPh_2{\cdot}CO_2H$, is inadequate. The behaviour of the various additive products towards hot alkali is not uniform but, where fission occurs at all, more than one product results. H. W.

Action of ω-bromoacetophenone on dimagnesium acetylenyl dibromide. S. A. Zaboev (J. Gen. Chem. Russ., 1937, **7**, 1858—1859).—(:C·MgBr)$_2$ and COPh·CH_2Br in Et_2O yield *αζ-dibromo-βε-diphenyl-Δ$^\gamma$-hexine-βε-diol*, m.p. 121—123°. R. T.

Lability of the dimethylamino-group in some dimethylaminoketones. (Miss) A. Jacob and J. Madinaveitia (J.C.S., 1937, 1929—1931).—Treatment of $CH_2Bz{\cdot}NMe_2$ (I) with MeI–KOH–MeOH yields BzOH and NMe_3, both of which are formed from $CH_2Bz{\cdot}NMe_3I$ and MeOH–KOH. Similarly, treatment of $Bz{\cdot}[CH_2]_2{\cdot}NMe_2$ (II) with MeI–KOH–MeOH, or of $Bz{\cdot}[CH_2]_2{\cdot}NMe_3I$ with KOH–MeOH, yields NMe_3 and a *substance*, $C_{18}H_{16}O_2$, m.p. 172° (probably dibenzoyl*cyclo*butane). From $CH_2Ac{\cdot}NMe_2$ (III) by treatment with MeI–KOH–MeOH, $NMe_4{\cdot}OH$ is formed. (I) with $NHPh{\cdot}NH_2$ in aq. AcOH yields the phenylosazone of BzCHO, also obtained from $CH_2Bz{\cdot}NH_2$,HCl and $NHPh{\cdot}NH_2$. Similar treatment of (II) and (III) yields 1 : 3-diphenyl- and 1-phenyl-3-methyl-pyrazoline, respectively. With N_2H_4, (I) gives a *substance*, $C_{16}H_{16}N_6$, m.p. 206°, and (II) yields a *substance*, C_6H_6N, m.p. 141°. J. D. R.

Constitution of Liebermann's benzanthrone. E. Ghigi (Ber., 1937, **70**, [*B*], 2469—2478).—Liebermann's compound is identified as 2 : 3-dimethylbenzanthrone (I). Its amended prep. by the action of conc. H_2SO_4 on *ms-iso*amyloxanthranol is described. Alkaline oxidation of (I) does not proceed satisfactorily and the compound is therefore reduced by Zn and conc. HCl in AcOH to 9-*hydroxy*-2 : 3-*dimethyl*-1 : 9-*trimethylenephenanthrene*, m.p. 176°. This is oxidised by $KMnO_4$ in presence of NaOH to 3 : 4-*dimethyldiphenyl*-5 : 2′-*dicarboxylic*-6-*glyoxylic acid* (II), m.p. 260—262° (decomp.) after changing at 250°, which is converted by $KMnO_4$ in acid solution into 3 : 4-*dimethyldiphenyl*-5 : 6 : 2′-*tricarboxylic acid* (III), m.p. 239—240°. This is decarboxylated in boiling quinoline containing Cu to 3 : 4-dimethyldiphenyl (IV), b.p. 281—283°, characterised by its oxidation to diphenyl-3 : 4-dicarboxylic acid, m.p. 201—202° (anhydride, m.p. 140—141° when rapidly heated); a *dimethyldiphenyldicarboxylic anhydride*, m.p. 190—191°, is obtained as by-product and is transformed by conc. H_2SO_4 at 150—160° into a sulphonated fluorenonecarboxylic acid. Oxidation of (II) in acid solution gives 4-*methyldiphenyl*-3 : 5 : 6 : 2′-*tetracarboxylic acid*, m.p. 335° after incipient blackening at 300°, decarboxylated to 4-methyldiphenyl, m.p. 47—48°. Treatment of (II) or (III) with conc. H_2SO_4 at 150—160° yields 2 : 3-*dimethylfluorenone*-1 : 5-*dicarboxylic acid*, m.p. 320° after softening at 290°. Distillation of (II) with $Ca(OH)_2$ affords a *dimethylfluorene*, m.p. 107—108° [with a small proportion of (IV)], which is oxidised to a *methylfluorenonecarboxylic acid*, m.p. 291—292°, and a *dimethylfluorenone*, m.p. 101—102°. H. W.

Compounds of the benzanthrone series.—See B., 1937, 1315.

Condensation of aldol with dimedon. I. Kasuya (J. Amer. Chem. Soc., 1937, **59**, 2742).—Dimedon and aldol give the *product* (I), $C_{20}H_{30}O_5$, m.p. 146—148°, and crotonaldehyde gives the *product* (II), $C_{20}H_{28}O_4$ +0·5EtOH, m.p. 185—186°. Fricke's substance, m.p. 170—172° (A., 1922, i, 300), supposed to be (I), was probably impure (II), since his conditions allow dehydration of aldol. R. S. C.

Acylation of diazomethane. II. Reaction of diazomethane with *O*-acetylmandelyl chloride and some transformations of the product. W. Bradley and J. K. Eaton (J.C.S., 1937, 1913—1915).—Acetylmandelyl chloride with CH_2N_2 in Et_2O yields *α-acetoxybenzyl chloromethyl ketone*, m.p. 57° (hydrolysed by NaOAc to AcBz, which is also formed by spontaneous decomp. on long keeping), and hydrolysed by aq. H_2SO_4 to benzylglyoxal (*dioxime*, m.p. 163°). J. D. R.

Reaction between hydrazoic acid and benzil. M. A. Spielman and F. L. Austin (J. Amer. Chem. Soc., 1937, **59**, 2658—2660).—Bz_2, NH_3, and H_2SO_4 in $CHCl_3$ give mainly NHBz·CO·NHPh, some $(CO{\cdot}NHPh)_2$, and small amounts of BzOH, NH_2Ph, 5-amino-, 5-anilino-, and 5-benzamido-1-phenyltetrazole. Benzil-γ-dioxime is unaffected by HN_3–H_2SO_4 and is thus not an intermediate. NHBz·CO·NHPh is also unattacked and is thus not the forerunner of the tetrazoles, which are formed by an independent, but obscure, mechanism. HN_3 is stable in H_2SO_4–$CHCl_3$ and >NH is thus not the effective reagent. R. S. C.

Preparation of diphenacyl. T. Ajello (Gazzetta, 1937, **67**, 708—710).—$(CH_2Bz)_2$ (I) is prepared cheaply from CH_2BzBr in 95% EtOH, which with aq. KOH gives a 95% yield of $CHBzBr{\cdot}CH_2Bz$, converted by Mg and EtOH into (I). E. W. W.

3-*epi*Hydroxyætio*allo*cholyl *iso*hexyl ketone. M. I. Uschakov, P. F. Epifanski, and A. D. Tschinaeva (J. Gen. Chem. Russ., 1937, **7**, 1825—1827).—Oxidation according to Ruzicka (A., 1934, 1221) of *epi*cholestanyl acetate yields, apart from androsterone

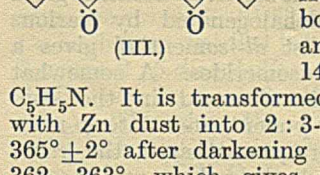
acetate, 3-epi*hydroxyætio*allo*cholyl* iso*hexyl ketone*, m.p. 175—177° (*acetate*, m.p. 135—136°), the *semicarbazone*, m.p. 223—227° (decomp.), of which separates when the neutral fraction of the oxidation products is allowed to react with semicarbazide during 20 days. R. T.

Dehydroandrosterone oxide. M. I. Uschakov and A. I. Lutenberg (J. Gen. Chem. Russ., 1937, **7**, 1821—1824).—Dehydroandrosterone (I) and BzO_2H in $CHCl_3$ yield the 5 : 6-*oxide* of (I), m.p. 227·5°, converted by dil. H_2SO_4 into androstane-3 : 5 : 6-triol-17-one. This is oxidised (CrO_3 in AcOH) to androstan-5-ol-3 : 6 : 17-trione, a $CHCl_3$ solution of which is treated with dry HCl at 0°, to yield Δ^4-androstene-3 : 6 : 17-trione. R. T.

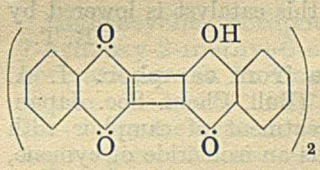
Polyphenyl derivatives of *oo'*-ditolyl. III. Condensation of phenol with phenanthrenequinone. IV. Transformations of di-*p*-hydroxyphenylphenanthrone. P. G. Sergeev (J. Gen. Chem. Russ., 1937, **7**, 1645—1653, 1654—1660).—III. Bachmann's work on the prep. and rearrangement of 9 : 10-dianisyldihydrophenanthrenediol (A., 1932, 745) is confirmed. 9 : 9-Di-*p*-anisylphenanthrone (I) and KOH in EtOH at 150° (4 hr.) yield 2-(*di*-p-*anisylmethyl*)*diphenyl*-2'-*carboxylic acid*, m.p. 136—137°, which regenerates (I) when heated at the m.p. (I) is also synthesised from $\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>C(OH)\cdot CO_2Me$ and *p*-$OMe\cdot C_6H_4MgBr$, or from 9 : 9-dichlorophenanthrone and anisole. Phenanthrenequinone and PhOH in HCl–EtOH at room temp. (3 hr.) yield 9 : 9-*di*-(p-*hydroxyphenyl*)*phenanthrone* (II), m.p. 255—256° (+H_2O, m.p. 244—246°; Ac_2 derivative, m.p. 216—217°), from which (I) is prepared by methylation, and its Et_2 analogue, m.p. 139—140°, by ethylation.

IV. (II) and Zn in boiling 20% NaOH yield 10-*hydroxy*-9 : 9-*di*-p-*hydroxyphenyl*-9 : 10-*dihydrophenanthrene* (III), m.p. 204—205° (+C_6H_6, m.p. 132—135°; *Me*$_2$ *ether*, m.p. 171—172°; Ac_2 ester, +MeOH, m.p. 248—249°), which is oxidised by AgOH to 2-(*hydroxydi*-p-*hydroxyphenylmethyl*)*diphenyl*-2'-*carboxylic acid*. (III) gives 9 : 10-*di*-p-*hydroxyphenylphenanthrene* (IV), m.p. 302—303° (Ac_2 ester, m.p. 282°), when treated with HBr in AcOH at room temp. (IV) is also prepared by distilling (I) from Zn dust. R. T.

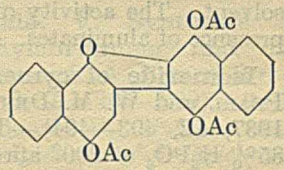
Processes of polymerisation. Condensation of 1 : 4-naphthaquinone to 2 : 3-dinaphthylenediquinone by pyridine in two stages. E. Rosenhauer, F. Braun, R. Pummerer, and G. Riegelbauer (Ber., 1937, **70**, [*B*], 2281—2295).—Passage of air through a boiling solution of β-naphthaquinone in EtOH containing AcOH and quinoline followed by oxidation of the quinhydrone with PbO_2 in $C_6H_3Cl_3$ gives 1 : 1'-dinaphthyl-3 : 4-3' : 4'-diquinone, m.p. 288—290° (also +1$PhNO_2$). Similarly air transforms α-naphthaquinone (I) in AcOH containing C_5H_5N at 40—45° into a quinhydrone, oxidised to 2 : 2'-dinaphthyl-1 : 4-1' : 4'-diquinone (II), decomp. 274—275° (block), which with 1 : 4 : 1' : 4'-tetrahydroxy-2 : 2'-dinaphthyl yields a black-violet *quinhydrone*, decomp. >200° after darkening, of unexplained structure. 1 : 4 : 1' : 4'-*Tetra-acetoxy*-2 : 2'-*dinaphthyl* has m.p. 227°. 2 : 3-2' : 3'-*Dinaphthylene*-1 : 4-1' : 4'-*diquinone* (III), m.p. >400°, is obtained by treating (I) with boiling C_5H_5N, with C_5H_5N in AcOH at 100° followed by boiling $PhNO_2$, with AcOH and C_5H_5N in $PhNO_2$ at 145°, or from (II) and boiling C_5H_5N. It is transformed by cautious distillation with Zn dust into 2 : 3-2' : 3'-*dinaphthylene*, m.p. 365°±2° after darkening at 310° and softening at 362—363°, which gives a very unstable *picrate*, $(C_{20}H_{12})_3[C_6H_2(NO_2)_3\cdot OH]_2$, m.p. >260°. Addition of Zn dust to a solution of (IV) in boiling C_5H_5N containing Ac_2O and a little AcOH gives 1 : 4 : 1' : 4'-*tetra-acetoxy*-2 : 3-2' : 3'-*dinaphthylene*, m.p. 278—280° (decomp.). Reduction of (III) with Zn dust–AcOH, Sn–HCl, or H_2SO_3 is slow and incomplete whereas alkaline $SnCl_2$ or $Na_2S_2O_4$ and NaOH readily give 1 : 4 : 1' : 4'-*tetrahydroxy*-2 : 3-2' : 3'-*dinaphthylene* (IV), decomp. >250°. Crude (III), particularly if prepared by means of C_5H_5N–AcOH, contains the



(III.)



(V.)



(VI.)

anhydro-quinhydrone of *dinaphthylenediquinone* (V), m.p. about 382° (block; decomp.), more conveniently obtained from (IV); its Ac_2 derivative has m.p. 285° (decomp.) when placed on block preheated to 280°. Reductive acetylation transforms (V) into (probably) the corresponding *hexa-acetate*, decomp. >300°, re-converted by 50% H_2SO_4 into (V). During the alkaline reduction of (III) a mixture of sparingly sol. K salts separates, better obtained by treatment of (III) with KOH alone in presence or absence of air. This is converted by mineral but not by org. acids into a red *compound*, $C_{20}H_{10}O_4$, m.p. 296°±2° on Cu block preheated to 270°, transformed by reductive acetylation into the corresponding *dihydrotriacetate* (VI), decomp. 293° after darkening. 3 : 3'-Dihydroxy-2 : 2'-dinaphthyl-1 : 4-1' : 4'-diquinone, m.p. 272—275°, is formed as by-product of the fission with alkali. H. W.

Preparation of 2-aminoanthraquinone from 2-chloroanthraquinone. N. N. Voroschcov and V. P. Schkitin (J. Gen. Chem. Russ., 1937, **7**, 2080—2086).—2-Aminoanthraquinone is obtained in 96% yield, and 98·5—99·5% pure, from 2-chloroanthraquinone and 25% aq. NH_3 (5 hr. at 210°) in presence of $KClO_3$ and Cu^{II}; under the conditions of Groggins and Stirton (A., 1933, 277, 396) considerable contamination with Fe salts arising from corrosion of the autoclave takes place. Groggins' finding that impure products are obtained in presence of Cu^{II} salts is not confirmed. R. T.

Configurations of some *p*-menthane derivatives. G. H. Keats (J.C.S., 1937, 2003—2007).—Electrolytic reduction of *l*-menthone gives *trans*-p-

menthane (I), and *dl-iso*menthone yields the *cis*-isomeride, the configurations of the *p*-menthanes being based on a comparison of their physical properties with application of the Auwers–Skita rule. Hence *l*-menthol belongs to the *trans*- and *dl-iso*menthol to the *cis*-*p*-menthane series. *l*-Menthol gives the bromide, which is dehalogenated by various methods to give (I), whilst *dl-iso*menthol gives a mixture of *cis*- and *trans*-isomerides. A somewhat analogous isomerisation is observed in the conversion of the 8-hydroxy-*p*-menthanes into *p*-menthane, through the 8-chloro-*p*-menthanes, the *trans*-carbinol yielding the *trans*-hydrocarbon, and the *cis*-carbinol a mixture of *cis*- and *trans*-isomerides.

F. R. S.

Dehydrogenation of borneol. B. N. Rutovski, I. P. Losev, and A. A. Berlin (Prom. Org. Chim., 1937, **4**, 410—416).—Borneol when dehydrogenated with dispersed Ni catalyst in PhMe (1 hr. at 210°, followed by 3 hr. at 220°) gives 92·5% camphor, in 91% yield. Better results are obtained with a continuous liquid-phase process, using 72 : 28 Al–Ni catalyst at 235—240°, and a 2 : 3 vaseline oil–PhMe solvent. The activity of this catalyst is lowered by presence of aluminates. R. T.

Isomeride of cymene from camphor. I. A. Pearl and W. M. Dehn (Bull. Chem. Soc. Japan, 1937, **12**, 493—494).—Treatment of camphor with 85% H_3PO_4 at 200° affords an isomeride of cymene, b.p. 180—182°, $[\alpha]_D$ +6·94°, probably 1-methyl-4-*iso*propenyl-$\Delta^{2:4}$-*cyclo*hexadiene. H. W.

Stereochemistry of pinocampheols. T. Kuwata (J. Amer. Chem. Soc., 1937, **59**, 2509—2511).—*d*-α-Pinene and $KMnO_4$ in 90% aq. $COMe_2$ give 1-*hydroxypinocamphone*, m.p. 35·5—36·5°, $[\alpha]_D^{25}$ —18·56° in EtOH [*semicarbazone*, m.p. 230° (decomp.)], reduced by Na–EtOH to 1-cis-*pinocampheol*, m.p. 55—56°, b.p. 84—87°/3 mm. (*acetate*, b.p. 82—84°/3 mm.; *naphthylurethane*, m.p. 87·5—88°), which with CrO_3 gives d-*pinocamphone*, b.p. 61—64°/3 mm. (*semicarbazone*, m.p. 228°), converted by Na–EtOH into d-*pinocampheol*, b.p. 103—105°/13 mm., m.p. 65—66° (*phenylurethane*, m.p. 74—75°). *dl*-Pinene leads similarly to dl-*hydroxypinocamphone*, m.p. 38·5—39° [*semicarbazone*, m.p. 213—214° (decomp.); *acetate*, b.p. 104—108°/4 mm.], dl-cis-*pinocampheol*, b.p. 90—95°/3 mm., 214—217°/762 mm. (*phenylurethane*, an oil), dl-*pinocamphone*, b.p. 60—63°/3 mm. (*semicarbazone*, m.p. 207—209°), and dl-*pinocampheol*, b.p. 82—84°/5 mm. (*phenylurethane*, m.p. 95—96°). R. S. C.

***N*-Substituted diamides of camphoric acid.**—See B., 1938, 105.

Action of chloroacetic acid on Willstätter lignin and wood. N. I. Nikitin and T. I. Rudneva (J. Appl. Chem. Russ., 1937, **10**, 1915—1920).—Willstätter lignin dissolves in $CH_2Cl{\cdot}CO_2H$ (I) (2—3 hr. at 100—120°), to yield a chloroacetate (75% esterification), pptd. from the solution by Et_2O, and from which lignin is regenerated by the action of NH_3 in EtOH. Two thirds of the lignin content of pine sawdust is extracted by (I), the ester so obtained is hydrolysed as above, and carbohydrates are removed by hydrolysis with 5% H_2SO_4, when the final product is identical with lignin. R. T.

Hydrogenation of uropterin. W. Koschara (Z. physiol. Chem., 1937, **250**, 161—174).—Uropterin (I) (xanthopterin; A., 1936, 882) is reversibly reduced by H_2S and org. SH groups, the mechanism differing from that of reduction by $Na_2S_2O_4$ or Na_2SO_3 which does not occur in aq. Na_2CO_3. Data from hydrogenation followed by autoxidation indicate the composition $C_{13}H_{11}O_4N_{11}$ instead of $C_{19}H_{18}O_6N_{16}$ for (I), which contains 13·2—14·8% of NH_2-N. F. O. H.

Quassin. II. Neoquassin. E. P. Clark (J. Amer. Chem. Soc., 1937, **59**, 2511—2514; cf. A., 1937, II, 297).—Neoquassin (I) (best purified by 2·5% KOH–EtOH) is shown by its reactions to be closely related to quassin (II). With dil. HCl (I) gives semidemethoxyquassin, but with HCl–EtOH gives *ethoxyneoquassin*, $C_{24}H_{34}O_6$, m.p. 180°, obtained similarly, together with some (I), from (II). CrO_3 oxidised (I) to *iso*quassin (III). Ac_2O–NaOAc converts (I) into anhydroquassin, but oxidises (III) to dehydroquassin, m.p. 256—263°. R. S. C.

Rottlerin. K. S. Narang, J. N. Ray, and B. S. Roy (Current Sci., 1937, **6**, 156, and J.C.S., 1937, 1862—1865).—Rottlerin, new formula, $C_{27}H_{26}O_7$, with $KHCO_3$, K_2CO_3, and Me_2SO_4 in $COMe_2$ gives a *Me*$_4$ *ether*, m.p. 144°, which (*a*) gives no Ac derivative, (*b*) with alkaline H_2O_2 gives a *substance*, $C_{31}H_{36}O_8$, m.p. 128° (decomp.), converted by catalytic hydrogenation into *tetrahydrorottlerin Me*$_4$ *ether*, m.p. 108°, also obtained by methylation of tetrahydrorottlerin (I) (*Ac*$_4$ derivative, m.p. 178°), and (*c*) with $NaNO_2$–AcOH yields a *substance*, (?) $C_{19}H_{21}O_6N$, which is catalytically hydrogenated to a *substance*, $C_{19}H_{23}O_6N$, m.p. 162°, and with alkali gives PhCHO. With EtOH–HCl (I) gives an Et_2O-sol. *substance*, m.p. 274—278°, and an Et_2O-insol. *substance*, $C_{20}H_{22}O_4$, m.p. 171°. R. S. C.

Structure of gossypol. A. M. Zamischlaeva and S. S. Krivitsch (J. Gen. Chem. Russ., 1937, **7**, 1969—1971).—The infra-red absorption spectra (λ 1—10 μ.) of gossypol in CCl_4 and Et_2O are indicative of the presence of CH_2, Me, CO, C:C, and OH groups. R. T.

***Amanita* toxins. IV.** F. Lynen and U. Wieland (Annalen, 1937, **533**, 93—117; cf. A., 1932, 785; 1933, 746; 1935, 267).—Extraction of the fresh material with MeOH and treatment of the solution with $Pb(OAc)_2$ appear to show that in addition to the thermostable *Amanita* toxin another poisonous constituent exists in the crude extract; this is destroyed by pptn. with heavy metals or by heat. From its solution the toxin is salted out by $(NH_4)_2SO_4$. Extraction of the dry material with EtOH and adsorption by Al_2O_3 leads to the separation of a rapidly acting *toxin* II from the known toxin, now named toxin I. Better separation is effected by fractional extraction of the aq. solution of the solid with Bu^{t}OH, whereby the first portions (*A*) contain 90% of toxin-II and 50% of toxin I, the second portions (*B*) contain almost only toxin I as active material, whilst the third portions and the aq. extract contain little active matter. Toxin I is pptd. quantitatively by $Hg(OAc)_2$

but loss of activity occurs when the ppt. is treated with H_2S; improved results are not obtained by decomp. with Zn or Ca and salting out of the aq. solutions. It cannot be fractionated by phosphotungstic acid. The most active samples of toxin I contain S. It gives a positive Hopkins–Cole and a negative Ehrlich reaction. The Keller coloration is dark green. The biuret and ninhydrin tests are negative. (II) is a complex substance the hydrolysate of which gives the ninhydrin reaction, indicating the presence of embedded NH_2-acids. Previous to hydrolysis toxin I in EtOH neutralises alkali and gives a *K* and *Ba* salt insol. in EtOH. Treatment of *A* in H_2O–EtOH–Bu$^{\alpha}$OH with Al_2O_3 leads to the separation of toxin II and *toxin* III which is slow in physiological action and is characterised by its *platinichloride*. Toxin II is obtained cryst. and is designated *phalloidine*. It has m.p. 280—282° (decomp.) when rapidly heated. It is probably $C_{30}H_{43}O_9N_7S$ and retains $5H_2O$ with unusual tenacity. It gives a cryst. Ac_2 derivative, m.p. 203—205° (decomp.), and a non-cryst. *Bz* compound. It is neutral in solution, does not give sparingly sol. compounds with the usual alkaloidal precipitants, but affords a powdery ppt. with phosphotungstic acid in H_2SO_4. CO_2H and $\cdot NH_2$ are absent. It contains 2 OH. It is hydrolysed to NH_2-acids, among which alanine has been identified. A modified titration of the hydrolysate according to Willstätter–Waldschmidt-Leitz and a Van Slyke determination establish the presence of 3 ·NH·CO·. The toxins appear to be distantly related to the ergot alkaloids. H. W.

Catalytic transformation of heterocyclic compounds. VII. Conversion of tetrahydrofuran (furanidin) into pyrrolidine and thiophen. J. K. Juriev and M. N. Prokina (J. Gen. Chem. Russ., 1937, **7**, 1868—1873).—Tetrahydrofuran gives pyrrolidine or thiophen in high yields when passed over Al_2O_3 in a stream of NH_3 or H_2S at 400°. R. T.

Aromatic character of the furan nucleus. Preparation and properties of simple 3-aminofurans. B. H. Stevenson and J. R. Johnson (J. Amer. Chem. Soc., 1937, **59**, 2525—2532).—Reactions of 3-amino- and -hydroxy-furans indicate that the furan ring has little aromatic character. Et 2-methyl-3-furoate and N_2H_4,H_2O at 115—125° give a 90—93% yield of the *azide* (I), m.p. about 25°, and thence by H_2O quantitatively or by way of the *carbimide* (II), b.p. 40°/13 mm., *s-di-2-methyl-3-furylcarbamide* (III), m.p. 220—222°. With HCO_2H in H_2 or CH_4 (I) gives *3-formamido-2-methylfuran*, m.p. 65·5—67°, converted best (80% yield) by rapid distillation in steam–CH_4 or, less well, by solid NaOH at 130—140° into *3-amino-2-methylfuran*, b.p. 51—52°/4 mm., very unstable in air. The amine is also obtained impure in poor yield by distilling (III) or the crude *urethane* from (II) with NaOH. With BzCl–C_5H_5N it gives the known Bz derivative, with $CHCl_3$–KOH it gives the carbylamine reaction, with hot H_2SO_4 under CH_4 an 89% yield of NH_3, and with HNO_2 a diazo-solution, which with β-$C_{10}H_7$·OH gives an *azo-dye*, m.p. 122—122·5°, but it does not undergo other diazo-reactions. CH_2Br·COMe, CH_2Ac·CO_2Et, and Na in C_6H_6 give 63% of CH_2Ac·CHAc·CO_2Et, b.p. 131—133°/17—18 mm., converted in 74% yield by aq. H_2SO_4–EtOH into Et 2 : 5-dimethyl-3-furoate, b.p. 96—100°/16 mm., which yields the *hydrazide*, m.p. 136—137°, and thence the *azide* (IV), m.p. 24—25°. With HCO_2H (IV) gives *3-formamido-2 : 5-dimethylfuran*, b.p. 152—154°/11 mm., m.p. 80·5—81·5°, which, when heated with Cu or, better, distilled in steam from aq. alkali, yields *3-amino-2 : 5-dimethylfuran*, b.p. 55—56°/4 mm. (*Bz* derivative, m.p. 152—152·4°, sublimes at 140°/2 mm.). This gives the carbylamine reaction and reacts with PhCHO in aq. EtOH at —10° without elimination of H_2O to give a *substance* (? *3-phenylhydroxymethylimino-2 : 5-dimethylfuran* or *2-phenyl-5 : 5′-dimethylfurano-2′ : 3′ : 5 : 4-tetrahydro-oxazole*), m.p. 113—115°. The amine is hydrolysed by $Ba(OH)_2$ to AcOH and OH·CHMe·COMe by way of the NH-form, the ring-ketone, and CH_2Ac·CO·CHMe·OH; with HNO_2 it gives a diazo-solution, which with β-$C_{10}H_7$·OH gives an *azo-dye*, m.p. 108—110°, but gives no other diazonium reactions. Attempts to prepare 2-aminofuran from the carbimide gave only traces of impure base. M.p. are corr. R. S. C.

Heterocyclic compounds. V. Synthesis of 7-hydroxy-2-methyl-6-ethylchromone and its derivatives. R. D. Desai and S. A. Hamid (Proc. Indian Acad. Sci., 1937, **6**, **A**, 287—290).—2 : 4-Dihydroxy-5-ethylacetophenone (I), NaOAc, and Ac_2O give *7-acetoxy-3-acetyl-2-methyl-6-ethylchromone*, m.p. 138°, hydrolysed to the *7-OH*-compound, m.p. 193° (*Me ether*, m.p. 158°), which with Na_2CO_3 affords *7-hydroxy-2-methyl-6-ethylchromone* (II), m.p. 204° (*Me ether*, m.p. 90°; *Ac* derivative, m.p. 99°). Hydrolysis of (II) with NaOH yields (I), but its Me ether similarly forms *2-hydroxy-4-methoxy-5-ethylbenzoic acid*, m.p. 192° (*OMe*-derivative, m.p. 126°), also obtained by methylation of 2 : 4-*dihydroxy-5-ethylbenzoic acid*, m.p. 188°, prepared from 4-ethylresorcinol and $KHCO_3$. F. R. S.

Indigoid vat dyes containing fluorine.—See B., 1938, 42.

Phenoxthionine. II. Extension of the Ferrario reaction. C. M. Suter and F. O. Green (J. Amer. Chem. Soc., 1937, **59**, 2578—2580; cf. A., 1936, 861).—The appropriate Ph aryl ether, S (1 mol.), and $AlCl_3$ (0·5 mol.) at 100° give 4-, b.p. 186—187° (*dioxide*, m.p. 141—142°), 3- (? 1-), m.p. 83—84° (*dioxide*, m.p. 138—139°), and *2-methyl-*, m.p. 38—39° (*dioxide*, m.p. 134—135°), 4-, b.p. 192—193°/7 mm. (*dioxide*, m.p. 148—149°), 3- (? 1-), m.p. 59—60° (*dioxide*, m.p. 152—153°), and *2-chloro-phenoxthionine*, m.p. 88—89° (*dioxide*, m.p. 158—159°). 2-Bromophenoxthionine, PhOH, and Cu in PhOH at 185—195° give *2-phenoxyphenoxthionine*, m.p. 81—82°, b.p. 230—235°/7 mm. (*dioxide*, m.p. 112—113°), which with S and $AlCl_3$ at 40° gives H_2S slowly and at 40° gives HCl. *p*-C_6H_4Br·OPh and *o*-OMe·C_6H_4·OPh give no phenoxthionine. Chlorination of phenoxthionine gives a (? 1-)*Cl*-derivative, m.p. 81—82° (*dioxide*, m.p. 178—179°). *Ph* o-, b.p. 152—153°/15 mm., m.p. 39—40°, m-, b.p. 168—169°/30 mm., and *p-chlorophenyl ether*, b.p. 161—162°/19 mm., are prepared. R. S. C.

Pyrrole derivatives. III. I. J. Rinkes (Rec. trav. chim., 1837, **56**, 1224—1228).—Interaction of $NH_2{\cdot}CH_2{\cdot}CHO$ and $Et_2C_2O_4$ in aq. KOH yields 3-*carbethoxypyrrole*-2-*carboxylic acid*, m.p. 146—147°, converted by $Cu(CrO_2)_2$ in boiling quinoline into 3-*carbethoxypyrrole*, m.p. 48—49°, hydrolysed (KOH) to *pyrrole*-3-*carboxylic* acid, m.p. 147—148° (*Me* ester, m.p. 87°). J. D. R.

***N*-Phenylpyrroles from phenacyl-lævulic acid.** M. G. Holdsworth and F. Lions (J. Proc. Roy. Soc. New South Wales, 1937, **70**, 431—436).—Phenacyl-lævulic acid (I), when boiled with NaOH and the product acidified, yields 3-*phenyl*-Δ^2-cyclo*penten*-1-*one*-2-*acetic acid*, m.p. 138° (*phenylhydrazone*, m.p. 180—181°; *semicarbazone*, m.p. 224—225°), reduced (Na–Hg) to the cyclo*pentane acid*, m.p. 132° (*phenylhydrazone*, m.p. 165°; *semicarbazone*, m.p. 198—199°). Condensation of (I) with arylamines at 100° (in EtOH if necessary) yields 1-aryl-2-phenylpyrrole-5-β-propionic acids: 1-*phenyl*-, m.p. 175° (*Et* ester, m.p. 102—103°; *hydrazide*, m.p. 142°); 1-o-*chloro*-, m.p. 170°, -*bromo*-, m.p. 191°, -*methoxy*-, m.p. 162°, -*ethoxy*-, m.p. 149°, -*xenyl*-, m.p. 73°, and -*carboxyphenyl*-, m.p. 191°; 1-α-*naphthyl*-, m.p. 130°, 1-8′-*quinolyl*-, m.p. 182°. A. Li.

Purification of piperidine. E. S. Cook (J. Amer. Chem. Soc., 1937, **59**, 2661).—Piperidine, prepared by catalytic hydrogenation, is purer than that prepared by electrolytic reduction, but also gives "diothane" of low activity (cf. A., 1937, II, 466, 467). R. S. C.

Diaminomethane and its derivatives. II. 2-Aminopiperidine and the reduction products of 2-aminopyridine. A. V. Kirsanov and J. N. Ivaschtschenko (J. Gen. Chem. Russ., 1937, **7**, 2092—2098).—2-Aminopyridine (I) in EtOH and Na yield piperidine, cadaverine, and NH_3; 2-aminopiperidine is not obtained, and is shown on theoretical grounds to be so unstable as not to be able to exist under the conditions of the experiment. Hydrogenation of (I) (PtO_2) in Ac_2O yields 2-*acetamido*-1-*acetpiperidide*, m.p. 122—123°. 2-*Diphenylaminopiperidine*, m.p. 131—133°, is prepared analogously. R. T.

Conductivities of metallic complexes.—See A., I, 83.

2-Ketoquinuclidine and a new synthesis of quinuclidine. G. R. Clemo and T. P. Metcalfe (J.C.S., 1937, 1989—1990).—*Et piperidine*-1-*acetate*-4-*carboxylate*, b.p. 134—136°/1 mm., obtained from Et piperidine-4-carboxylate and $CH_2Cl{\cdot}CO_2Et$, undergoes the Dieckmann reaction to form 2-*ketoquinuclidine*, m.p. 138° [*methiodide*, m.p. 310° (decomp.); *picrate*, m.p. 210°], which is reduced (Wolff or Clemmensen) to quinuclidine. F. R. S.

Hydrogenation of some *N*-substituted 2-pyridones with Raney nickel. J. A. Gautier (Compt. rend., 1937, **205**, 614—616; cf. A., 1937, II, 75).—Many 2-pyridones in EtOH with H_2–Raney Ni at room temp. and pressure absorb 4 H at a const. rate to give the corresponding piperidones in theoretical yield. The following are prepared: N-β-*hydroxyethyl*-, m.p. 39—40° (*aurichloride*, m.p. 169°; *picrate*, m.p. 71°; *phenylcarbamate*, m.p. 118°), -γ-*propoxypropyl*- (I), b.p. 193°/13 mm., and -γ-iso*amyloxypropyl*-2-*piperidone* (II), b.p. 208°/14 mm. (I) and (II) are feebly basic and are decomposed by acid chlorides. J. L. D.

4-Hydroxypyridinebetaine. A. Kirpal and F. Poisel (Ber., 1937, **70**, [*B*], 2367—2369).—4-Hydroxypyridine and $CH_2Cl{\cdot}CO_2H$ in boiling, slightly alkaline solution give 4-*hydroxypyridinebetaine*, $OH{\cdot}C\langle\begin{matrix}CH{\cdot}CH\\CH{:}CH\end{matrix}\rangle N\langle\begin{matrix}CH_2\\O\end{matrix}\rangle CO$, decomp. 270° [*hydrochloride*; *Na* (+2·5H_2O), m.p. 122°, and *Ag* (+1H_2O), decomp. 252°, salts]. Its constitution follows from its conversion into 4-*methoxypyridinebetaine*, m.p. 182° (decomp.), and thence by conc. aq. NH_3 at room temp. into 4-*aminopyridinebetaine*, decomp. 315°, also derived from 4-aminopyridine and $CH_2Cl{\cdot}CO_2H$. H. W.

Manufacture of 4 : 6-diamino-2-alkylpyridines.—See B., 1938, 39.

Derivatives of 3-diazo-2-phenylindole. I. F. Angelico and S. Capuano. **II.** S. Capuano (Gazzetta, 1937, **67**, 633—637, 710—714).—I. 3-Amino-2-phenylindole (I) (new prep. from oximinophenylindole, NH_3, and H_2S) with $NaNO_2$ gives, in addition to 3-diazo-2-phenylindole (II) (A., 1905, i, 940), 3-*azo*-2-*phenylindole* (?), $C_{28}H_{20}N_4$ (III), red, m.p. 263° (decomp.). The product from (II) and 25% H_2SO_4, previously regarded (*loc. cit.*) as (III), is probably *hydrazophenylindole* (IV), m.p. 271° (decomp.), reddish-yellow.

II. The constitutions suggested above for (III) and (IV) are confirmed. With NH_2OH,HCl, N_2H_4,HCl, or $NHPh{\cdot}NH_2$ in EtOH, (II) evolves N_2 and yields (IV) and (I), which are also obtained by reduction of (III) (aq. NH_3–H_2S). Oxidation of (IV) by N_2O_4 or of (I) by amyl nitrite gives (III). With boiling HCl, (II) yields (IV) and another substance. E. W. W.

Formation of the compound between tungstic acid and 8-hydroxyquinoline.—See A., I, 93.

Quinoline derivatives. III. (Signa.) L. Monti (Gazzetta, 1937, **67**, 624—628; cf. A., 1932, 1261).—2-Hydroxy-4 : 8-dimethylquinoline and $OH{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}CH_2Cl$ in conc. H_2SO_4 yield the N-*chloroacetyl* derivative, m.p. 260—262° (decomp.), of 2-*hydroxy*-4 : 8-*dimethyl*-3-*quinolylmethylamine* [*hydrochloride*; *picrate*, m.p. 263—264° (decomp.)]. 4-Hydroxy-2 : 8-dimethylquinoline similarly gives the N-*chloroacetyl* derivative, m.p. 252—254° (decomp.), of 4-*hydroxy*-2 : 8-*dimethyl*-3-*quinolylmethylamine*, no. m.p. <280° (*picrate*, decomp. 180—190°). E. W. W.

Quinoline compounds as bases of medicinal compounds. VI. Antimalarial compounds with the side-chain in position 4. O. J. Magidson and M. V. Rubtzov (J. Gen. Chem. Russ., 1937, **7**, 1896—1908).—6-Methoxyquinoline and BzO_2H in $CHCl_3$ (18 hr. at 0—2°) yield 6-*methoxyquinoline* N-*oxide*, m.p. 108—109° (+2H_2O, m.p. 88—89°; *hydrochloride*, m.p. 193—194°; *picrate*, m.p. 173·5—174·5°), which with SO_2Cl_2 at 60° gives a mixture of di- and trichloro-6-methoxyquinoline, whilst with $POCl_3$ the product consists of 2- (I) and 4-chloro-6-methoxy-

quinoline (II). NH_2·CHMe·$[CH_2]_3$·NEt_2 and (II) when heated at 165—170° (6·5 hr.) yield 4-(δ-*diethylamino*-α-*methylbutyl*)*amino*-6-*methoxyquinoline* (III), m.p. 127—127·5° (*picrate*, m.p. 182—183·5°), whilst under similar conditions (I) gives a mixture of 2-(δ-*diethylamino*-α-*methylbutyl*)*amino*-6-*methoxyquinoline*, b.p. 180°/2 mm. (*hydrochloride*, m.p. 98—101°; *picrate*, m.p. 153·5—155°), and α-*diethylamino*-δ-*di*-(6-*methoxy*-2-*quinolyl*)*aminopentane*, m.p. 77·5—78·5° (*picrate*, m.p. 187·5—188·5°). The following compounds were prepared analogously to (III): 4- (IV), m.p. 90—90·5° (*picrate*, m.p. 198—199°), and 2-(δ-*diethylaminobutyl*)*amino*-, b.p. 187—192° (*picrate*, m.p. 182·5—183·5°; *dihydrochloride*, m.p. 187—188°); 4- (V), an oil (*picrate*, m.p. 210—212°, and its *acetate*, m.p. 205—207°), and 2-(γ-*diethylamino*-β-*hydroxypropyl*)-*amino*-6-*methoxyquinoline*, m.p. 65—66° (*hydrochloride*, m.p. 99—102°; *picrate*, m.p. 190·5—192°). The 2-NH_2-quinoline derivatives had no antimalarial action; the activity of the 4-NH_2-compounds rises in the order (IV) < (III) < (V). R. T.

Thalleioquinine reaction. III. (SIGNA.) L. MONTI (Gazzetta, 1937, **67**, 621—624; cf. A., 1936, 613).—8-Hydroxy-7-methylquinoline (I) and OH·CH_2·NHBz in conc. H_2SO_4 yield *benz*-8-*hydroxy*-7-*methyl*-5-*quinolylmethylamide*, m.p. 175—176°. With CH_2O in 15% NaOH, (I) gives 8-*hydroxy*-7-*methylquinolylmethyl alcohol*, decomp. 150—160°. Since these products fail to give the thalleioquinine reaction, unlike the product (II) from 6-hydroxyquinoline, it is concluded that (II) is not substituted in position 7, but is *benz*-6-*hydroxy*-5-*quinolylmethylamide* (cf. A., 1932, 1261—1262). E. W. W.

Catalytic condensation of acetylene with aromatic amines. N. KOZLOV (J. Gen. Chem. Russ., 1937, **7**, 1860—1865).—NH_2Ph in $COMe_2$ and C_2H_2 in presence of $HgCl_2$ (7 hr. at room temp.) yield 2-methyl- and 2 : 4-dimethyl-quinoline. The products obtained similarly from *o*-, *m*-, and *p*-toluidine are respectively 2 : 8-di- and 2 : 4 : 8-tri-, 2 : 4 : 5-tri-, and 2 : 6-di- and 2 : 4 : 6-*tri-methylquinoline*, m.p. 38° (*hydrochloride*, m.p. >240°; *picrate*, m.p. 203°). NPh:CHMe is an intermediate product in the above condensations. R. T.

6 : 9-Diamino-2-ethoxyacridine methanesulphonate.—See B., 1938, 105.

Formation of tetrahydrophenanthroline as a by-product in the Skraup synthesis of *p*-phenanthroline. J. P. WIBAUT, C. W. F. SPIERS, and J. L. OUWELTJES (Rec. trav. chim., 1937, **56**, 1218—1223).—*p*-$C_6H_4(NH_2)_2$, glycerol, and H_3AsO_4 yield *p*-phenanthroline and the H_4-compound, m.p. 151·2—151·6°, described by Matsumura (A., 1935, 631) (Bz_1 derivative, m.p. 180·7—181°; Ac_1 derivative, m.p. 121°), which is probably 1 : 2 : 3 : 4-tetrahydrophenanthroline. J. D. R.

Yellow and colourless modifications of benzylidene- and *N*-3-methylbenzylidene-hydantoin. (MISSES) D. A. HAHN and M. M. ENDICOTT (J. Amer. Chem. Soc., 1937, **59**, 2741—2742).—The substances named exist each in yellow and colourless forms, otherwise similar, which are interconvertible. The yellow form is stable in acid, the colourless in alkaline, solution; they may thus be lactam and lactim forms, respectively. R. S. C.

Additive products of antipyrine and pyramidone. G. LA PAROLA (Gazzetta, 1937, **67**, 645—647).—Antipyrine (I) with maleic anhydride (II) in moist air gives the (1 : 1) *maleate*, m.p. 115°. Pyramidone (III) when heated with (II) forms the (1 : 1) *maleate*, m.p. 123—124°. With picric acid these yield the picrates of (I) and (III). E. W. W.

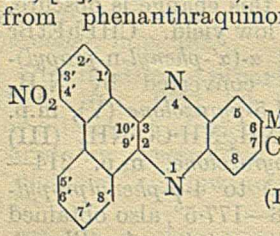
Rearrangement of some β-allyloxycrotonic esters. W. M. LAUER and (MISS) E. I. KILBURN (J. Amer. Chem. Soc., 1937, **59**, 2586—2588).—Rearrangement of *Et* β-*cinnamyloxycrotonate* (I) by NH_4Cl at 110° gives *Et* α-(α′-*phenylallyl*)*acetoacetate* (II), different from the *Et* α-*cinnamylacetoacetate* (III), b.p. 156—158°/0·5—1 mm., obtained from CHPh:CH·CH_2Br, NaOEt, and CH_2Ac·CO_2Et. Thus *C*-alkylation does not occur by way of the *O*-ether. *Et* β-*allyloxycrotonate* [from a mixture (IV) of Et β-chloro-crotonate and *-iso*crotonate, $NaNH_2$, and CH_2:CH·CH_2·OH], m.p. 7—11°, gives Et α-allylacetoacetate (identified by conversion into the pyrazolone), but the mechanism of this change is obscure. Prep. of (I) from (IV) gives a low yield. CHPhEtBr and CHNaAc·CO_2Et give *Et* α-(α′-*phenyl*-n-*propyl*)-*acetoacetate*, b.p. 127—129°, converted by N_2H_4 into 4-α-*phenylpropyl*-3-*methyl*-5-*pyrazolone* (V), m.p. 193—194°. With N_2H_4 or NH_2·NH·CO·NH_2 (III) gives 4-*cinnamyl*-3-*methyl*-5-*pyrazolone*, m.p. 214—219°, hydrogenated (H_2–PtO_2) to 4-γ-*phenylpropyl*-3-*methyl*-5-*pyrazolone*, m.p. 176—177·5°, also obtained from Et α-γ′-phenylpropylacetoacetate. 4-α-*Phenylallyl*-3-*methyl*-5-*pyrazolone*, m.p. 180—182°, is obtained from (II) and N_2H_4 or from (I), N_2H_4, and a little HCl, and, when reduced, gives (V). R. S. C.

Derivatives of piperazine. XIII. Analogues of ephedrine containing the *N*-phenylpiperazine nucleus. B. L. HAMPTON and C. B. POLLARD (J. Amer. Chem. Soc., 1937, **59**, 2570—2572; cf. A., 1938, II, 30).—*N*-Phenyl-*N*′-phenacylpiperazine gives *N*-phenylpiperazine and COPhMe with Al–Hg in H_2O or N_2H_4 at 185—195°, but with H_2–Pd–C in dil. HCl gives an 85% and with NaOEt–EtOH at 185—195° gives an 80% yield of *N*-*phenyl*-*N*′-β-*hydroxy*-β-*phenylethylpiperazine* (I), m.p. 110—111° [*dihydrochloride*, m.p. 210—212°; *Bz* derivative, an oil (*dihydrochloride*, m.p. 228—230°)]. With N_2H_4, NaOEt, and EtOH mixtures of (I) and N-*phenyl*-N′-β-*phenylethylpiperazine*, m.p. 77—78° (*dihydrochloride*, m.p. 220—222°), are obtained. N-*Phenyl*-N′-β-*hydroxy*-β-p-*tolylethylpiperazine*, m.p. 127—128° [*dihydrochloride*, m.p. 199—201°; *Bz* derivative, an oil (*dihydrochloride*, m.p. 219—221°)], is similarly obtained. R. S. C.

Cyanine dye series. IX. 4 : 4′-Pyridocyanines and 4-pyrido-4′-cyanines. R. H. SPRAGUE and L. G. S. BROOKER (J. Amer. Chem. Soc., 1937, **59**, 2697—2699; cf. A., 1937, II, 124).—4-Iodopyridine meth- and eth-iodide could not be obtained. PhSH and 4-chloropyridine give 4-*phenylthiolpyridine*, b.p. 128—129°/3 mm., the *methiodide*, m.p. 174—176°, (decomp.), of which with γ-picoline metho-*p*-toluenesulphonate and NEt_3 in $Pr^{\alpha}OH$ leads to 1 : 1′-*dimethyl*-

4 : 4′-*pyridocyanine* [*bis*-1-*methyl*-4-*pyridinemethinecyanine*] *perchlorate* (I), m.p. 263—265° (decomp.) [corresponding *picrate*, m.p. 231—232° (decomp.)], also obtained similarly from 4-*chloropyridine methiodide*, m.p. 161—163° (decomp.). 4-*Phenylthiolpyridine ethiodide*, m.p. 178—180° (decomp.), gives similarly 1 : 1′-*diethyl*-4 : 4′-*pyridocyanine* [*bis*-1-*ethyl*-4-*pyridinemethinecyanine*] *perchlorate* (II), m.p. 196—198° (decomp.), not obtained from 4-chloropyridine ethiodide. By either method lepidine methiodide gives 1 : 1′-*dimethyl*-4-*pyridino*-4′-*cyanine* [1-*methyl*-4-*pyridine*-1′-*methyl*-4′-*quinolinemethinecyanine*] *perchlorate* (III), m.p. 220—221° (decomp.), and by the thiol method the analogous *diethyl-perchlorate* (IV), m.p. 172—174° (decomp.). The dyes are strong photographic sensitisers with absorption max. in MeOH as follows: (I) 5025 A., (II) 5050 A., (III) 5285 A. (secondary max. 5050 A.), and (IV) 5300 A. (secondary max. 5450 A.), and only (IV) causes fogging. R. S. C.

Dyes derived from phenanthraquinone. D. Prasad, S. C. Sen, and P. C. Dutta (Ber., 1937, **70**, [*B*], 2363—2365).—Deeply coloured dyes derived from phenanthraquinone are described. 4-Nitrophenanthraquinone and 6-chloro-3 : 4-diaminotoluene in hot AcOH yield 7-*chloro*-4′-*nitro*-6-*methyl*-9′ : 10′-2 : 3-*phenanthrenoquinoxaline* (I), m.p. 227°. The corresponding -2′-*nitro*-, m.p. >300°, -4′ : 5′-*dinitro*-, m.p. 268°, -2′ : 7′-*dinitro*-, m.p. >300°, -2′-*bromo*-, m.p. 242°, -??-*dibromo*-, m.p. >300°, -2′-*hydroxy*-, m.p. 245°, -2′-*amino*-, m.p. 291°, and -4′-*amino*-, m.p. 134°, -derivatives are prepared analogously. Treatment of (I) with Cu powder and boiling NH_2Ph affords 4′-*nitro*-7-*anilino*-6-*methyl*-9′ : 10′-2 : 3-*phenanthrenoquinoxaline*, m.p. 178°. Analogous methods lead to the production of the corresponding 2′-*nitro*-, m.p. 242°, 4′ : 5′-*dinitro*-, m.p. 136°, 2′ : 7′-*dinitro*-, m.p. 205°, 2-*amino*-, m.p. 253°, and -2-*hydroxy*-, m.p. 202°, -compounds. 2′ : 7-*Dianilino*-6-*methyl*-9′ : 10′-2 : 3-*phenanthrenoquinoxaline* has m.p. 157°. H. W.


(I.)

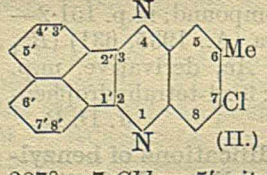
Symmetry of certain types of benztriazoles. W. M. Lauer, W. F. Filbert, and G. E. Ullyott (J. Amer. Chem. Soc., 1937, **59**, 2584—2586).—2-p-*Hydroxyphenyl*-6- (I), m.p. 242—243°, and -5-*methylbenztriazole* 1-*oxide* (II), m.p. 265—266° (decomp.), differ, but with $SnCl_2$ give the same 2-*p*-hydroxyphenyl-5- (or -6-)methylbenztriazole, demonstrating the equivalence of positions 5 and 6 of benztriazoles. 3 : 1 : 4-NO_2·C_6H_3Me·NH_2 (III) is converted into 2-nitro-4′-hydroxy-4-methylazobenzene, m.p. 156—157°, which with $Na_2S_2O_4$ yields (I). With $H_2S_2O_8$ (III) gives 3 : 1 : 4-NO_2·C_6H_3Me·NO, oxidised by HNO_3 to 1 : 3 : 4-$C_6H_3Me(NO_2)_2$, which with NH_3–EtOH gives 4 : 1 : 3-NO_2·C_6H_3Me·NH_2; under clearly defined conditions this affords 2-nitro-4′-hydroxy-5-methylazobenzene, m.p. 129—130°, and thence (II) using $Na_2S_2O_4$. M.p. are corr. R. S. C.

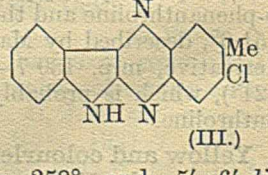
Triazines. I. Reactions of *iso*cyanuric esters with organo-magnesium compounds. H. Sobotka and (Miss) E. Bloch (J. Amer. Chem. Soc., 1937, **59**, 2606—2608).—Me_3 cyanurate (prep. by CH_2N_2), m.p. 174°, with MgRBr in Et_2O gives 2-*hydroxy*-4 : 6-*diketo*-2-*phenyl*-1 : 3 : 5-*trimethyl*- (I), m.p. 158—159° (decomp.), -1 : 3 : 5-*trimethyl*-2-*ethyl*-, m.p. 112—113°, and -1 : 3 : 5-*trimethyl*-2-n-*propyl*-1 : 3 : 5-*triazine* (II), m.p. 129°. These products form *tribromides*, m.p. 196°, 128°, and 151°, respectively, formulated as $[NMe<^{CO\cdot NMe}_{CO\cdot NMe}>NR]^+Br_3^-$, and (II) gives an analogous *tri-iodide*, m.p. 112—115°. In C_6H_6 some (I) with CPh_3·OH is obtained. No reaction occurs between (I) and MgPhBr. R. S. C.

γ-Triazines. XXXVI. Aminothiol*iso*butyltriazine and the corresponding aminohydroxy-derivative. V. Galea and A. Ostrogovich (Gazzetta, 1937, **67**, 664—668; cf. A., 1930, 368; 1935, 1255).—K thiol*iso*valerate, from $Bu^{\beta}COCl$ and KSH, and cyanoguanidine yield 4-*amino*-6-*thiol*-2-iso*butyl*-1 : 3 : 5-*triazine*, m.p. 269—270° (decomp.) [*hydrochloride* (+H_2O); *picrate*, m.p. 174—175° (decomp.)], the *Ag* salt, m.p. 150° (decomp.), of which forms a complex *salt* (explodes when heated) with $AgNO_3$; it is converted by KOH–H_2O_2 into 4-*amino*-6-*hydroxy*-2-iso*butyl*-1 : 3 : 5-*triazine*, m.p. 263—264° (decomp.) [*Ag* salt; *hydrochloride*; *sulphate*; *picrate*, m.p. 217—218° (decomp.)]. E. W. W.

Syntheses in the pyrazolinoquinoline series. A. Kocwa (Bull. Acad. Polonaise, 1937, **A**, 232—238).—α-$C_{10}H_7$·NH_2,HCl, 1-phenyl-3-methylpyrazolone, and $POCl_3$ at 260—270° give 5-α-*naphthylimino*-1-*phenyl*-3-*methyl*-4 : 5-*dihydropyrazole* (I), m.p. 146—147° (*hydrochloride*, m.p. 206°; *picrate*, m.p. 184°), the *methiodide*, m.p. 220°, of which with NaOH gives 5-α-naphthyliminoantipyrine, m.p. 161—162°. With PhNCO at 270° or PhNCS at 230—235° (I) gives 4-*anilino*-7 : 8-*benzo*-1′-*phenyl*-3′-*methylpyrazolino*-5′ : 4′-2 : 3-*quinoline*, m.p. 198° [*hydrochloride*, m.p. 205°; *NO*-derivative, m.p. 184—185° (decomp.)], which is hydrolysed by 50% KOH–EtOH at 200—220° to 4-*hydroxy*-7 : 8-*benzo*-1′-*phenyl*-3′-*methylpyrazolino*-5′ : 4′-2 : 3-*quinoline*, m.p. 281—282°, also obtained by hydrolysis of 4-α-*naphthylamino*-7 : 8-*benzo*-1′-*phenyl*-3′-*methylpyrazolino*-5′ : 4′-2 : 3-*quinoline*, m.p. 225° [obtained from (I) and α-$C_{10}H_7$·CNO at 230°]. R. S. C.

Dyes derived from acenaphthenequinone and isatin. D. Prasad and P. C. Dutta (Ber., 1937, **70**, [*B*], 2365—2366).—Acenaphthenequinone and 6-chloro-3 : 4-diaminotoluene (I) afford 7-*chloro*-6-*methyl* 1′ : 2′-2 : 3-*acenaphthylenoquinoxaline* (II), m.p.


(II.)


(III.)

287°. 7-*Chloro*-5′-*nitro*-, m.p. 258°, and -5′ : 6′-*dinitro*-, m.p. 290°, -6-*methyl*-1′ : 2′-2 : 3-*acenaphthylenoquinoxaline* are described. 7-*Chloro*-6-*methyl*-2′ : 3′-2 : 3-*indoloquinoxaline*, m.p. >300° (III), is derived from (I) and isatin and is converted by Cu powder and boiling NH_2Ph into 7-*anilino*-6-*methyl*-2′ : 3′-

2 : 3-*indoloquinoxaline*, m.p. 260°. 7-*Anilino*-6-*methyl*-1′ : 2′-2 : 3-*acenaphthylenoquinoxaline* has m.p. 243°. H. W.

Constitution of the purine nucleosides. V. Adenine thiomethylpentoside. R. Falconer and J. M. Gulland (J.C.S., 1937, 1912—1913).—The ultra-violet absorption spectra of adenine thiomethylpentoside in aq., acid, and alkaline solutions closely resemble those of adenosine and 9-methyladenine in similar conditions and are unlike those of 7-methyladenine ; hence, the thio-sugar is attached to position 9. F. R. S.

Ammoniacal absorption spectrum of stercobilin and urobilin and its relationship to the constitution of bilirubinoid pigments. L. Heilmeyer, H. Geiger, and R. Schultze (Biochem. Z., 1937, **294**, 90—94).—The absorption spectrum of stercobilin hydrochloride (obtained from hæmolytic jaundice stool) in 1% aq. NH_3 is compared with that of bilirubin (I) in $CHCl_3$; both solutions show a broad band about 450 mμ. Comparison of the absorption spectra of (I), mesobilirubin, and xanthobilirubic acid in EtOH and stercobilin in aq. NH_3 and their mol. extinction coeffs. suggests that in the stercobilin mol. there is a double linking attached to one pyrrolidine nucleus. C. C. N. V.

Preparation of 1-methylbenzoxazole. M. A. Phillips (J.S.C.I., 1937, **56**, 474T).—1-Methylbenzoxazole is obtained in 74% yield from *o*-NH_2·C_6H_4·OH and Ac_2O; the method used presents advantages over that of Beilenson (A., 1937, II, 392). (Cf. Newbery and Phillips, A., 1928, 311.)

***iso*Oxazole and pyrazole groups. I.** C. Musante (Gazzetta, 1937, **67**, 682—690).—CMe:C·CO_2Et and CHPh:N·OH (I) at 120—130° yield 4-*benzylidene*-3-*methyl*-5-iso*oxazolone*, m.p. 145°, also obtained from (I) and $CH_2Ac·CO_2Et$ ($ZnCl_2$). Similarly 4-*anisylidene*-3-*methyl*-5-iso*oxazolone*, m.p. 175°, is obtained by either method. CPh:C·CO_2Et (II) and CHPh:N·NHPh at 170—180° give Et 1 : 3 : 5-triphenylpyrazole-4-carboxylate (A., 1929, 196); the 1 : 5-diphenyl-3-*p*-nitrophenyl compound, new m.p. 177° (cf. *loc. cit.*), is obtained similarly. $CH_2Bz·CO_2Et$ and CHEt:N·NHPh (III) yield ($ZnCl_2$) the *Et* ester, m.p. 119°, of 1 : 5-*diphenyl*-3-*ethylpyrazole*-4-*carboxylic acid*, m.p. 192°. From (II) and (III) at 140°, a *substance*, $C_{33}H_{28}O_2N_4$ (2 : 2′-*propylidene*-1 : 5 : 1′ : 5′-*tetraphenylbis*-3 : 3′-*pyrazolone*?), m.p. 192—194°, is obtained, hydrolysed to EtCHO and 1 : 5-diphenyl-3-pyrazolone. E. W. W.

Oximinopyrroles. VIII. Action of acids. T. Ajello (Gazzetta, 1937, **67**, 728—738; cf. A., 1937, II, 524).—Oximinotriphenylpyrrole and H_2SO_4 in EtOH at the b.p. give 3-*benzoyl*-4 : 5-*diphenyl*iso*oxazole*, m.p. 158° (or 168°?) [p-*nitrophenylhydrazone*, m.p. 140—141°; *semicarbazone*, m.p. 227°; *oxime*, m.p. 162° (*Bz* derivative, m.p. 122°)], and a yellow *substance*, m.p. 242°. Oximinodiphenylpyrrole yields 3-*benzoyl*-5-*phenyl*iso*oxazole*, m.p. 89—90° [*semicarbazone*, m.p. 182°; *oxime*, m.p. 115° (*Bz* derivative, m.p. 140°); p-*nitrophenylhydrazone*, m.p. 180°; *hydrazone*, m.p. 200°], and a yellow *substance*, m.p. 235°. Oximinophenylmethylpyrrole yields 3-*acetyl*-5-*phenyl*iso*oxazole*, m.p. 105° (p-*nitrophenylhydrazone*, m.p. 175—178°). Brown or black amorphous products are also formed in the above reactions. E. W. W.

Derivatives of morpholine. I. Addition to conjugated systems. V. E. Stewart and C. B. Pollard (J. Amer. Chem. Soc., 1937, **59**, 2702).—Morpholine and the appropriate ketone, CHAr:CH·COAr, in hot heptane give *Ph* β-N-*morpholino*-β-*phenyl*-, m.p. 80·5—81°, -β-p-*tolyl*-, m.p. 90—90·5°, and -β-p-*chlorophenyl*-*ethyl ketone*, m.p. 89·5—90°, p-*tolyl*, m.p. 90—90·5°, and p-*bromophenyl* β-N-*morpholino*-β-*phenylethyl ketone*, m.p. 99·6—100·2°. Some chalkones did not give such compounds owing to the ease of dissociation. The di-*p*-tolyl ketone forms the compound, but this dissociates when recrystallised. M.p. are corr. R. S. C.

Morpholine as a reagent for mobile halogen atoms and nitro-groups. R. H. Harradence and F. Lions (J. Proc. Roy. Soc. New South Wales, 1937, **70**, 406—412).—Compounds containing reactive halogen atoms or NO_2-groups when boiled with excess of morpholine for 2—3 hr. give well-cryst. derivatives of *N*-phenylmorpholine: 2-*nitro*-, m.p. 42°, 4-*nitro*-, m.p. 149—150°, and 2 : 4-dinitro-, from the corresponding Cl-compounds; 4-*chloro*-2-*nitro*-, m.p. 47°, and 2-*chloro*-4-*nitro*-, m.p. 127°, from 2 : 5- and 3 : 4-$C_6H_3Cl_2·NO_2$, respectively; 4 : 6-*dibromo*-2-*nitro*-, m.p. 105° (the corresponding *piperidine* derivative, m.p. 73°), from 3 : 5-*dibromo*-2-*iodonitrobenzene*, m.p. 82° (prepared from $NO_2·C_6H_3Br_2·NH_2$); 2-*nitro*-6-*methyl*-, m.p. 135—136°, from 1 : 2 : 6-$C_6H_3MeI·NO_2$ (5 hr. in boiling EtOH); 2 : 4-*dinitro*-6-*carboxy*-, m.p. 203—204° (decomp.) (*Me* ester, m.p. 106°), from chlorodinitrobenzoic acid; 2-*nitro*-4 : 5-*dimethoxy*-, m.p. 115—116°, from 4-bromo-5-nitro- or 4 : 5-dinitroveratrole; and 2-*nitro*-4 : 5-*di*-n-*butoxy*-, m.p. 75—76°, from 1 : 2 : 4 : 5-$C_6H_2(NO_2)_2(OBu^n)_2$. Morpholine is less reactive than piperidine towards *o*-chloro- and *o*-bromo-nitrobenzene. A. Li.

Nicotinylmorpholine. R. H. Harradence and F. Lions (J. Proc. Roy. Soc. New South Wales, 1937, **70**, 428—430).—Prolonged boiling of Et nicotinate with excess of morpholine gives *nicotinylmorpholine*, b.p. 192°/6 mm. (*picrate*, m.p. 174—175°; *methiodide*, m.p. 211—212°; *aurichloride*, m.p. 168°). A. Li.

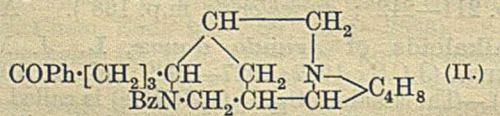
Alkaloids of *Arundo donax*, L. J. Madinaveitia (J.C.S., 1937, 1927—1929; cf. A., 1937, II, 125).—The alkaloid $C_{12}H_{13}O_2N$(NMe) is called *donaxarine*, m.p. 217°. Gramine (donaxine) with MeI–MeOH–KOH gives NMe_4I and 3-*methoxymethylindole*, m.p. 99—100°, and with MeI–MeOH forms NMe_3 and a substance similar to 3-*hydroxymethylindole*, m.p. 90°, obtained by reduction (PtO_2–H_2) of indole-3-aldehyde. Gramine and EtI–EtOH–KOH yield 3-*ethoxymethylindole*, m.p. 93—94°, and with EtI–$COMe_2$, *gramine ethiodide*, m.p. 176°, is obtained. There are indications of the presence of a third alkaloid with phenolic properties. F. R. S.

***Cactus* alkaloids. New alkaloid from mezcal buttons.** E. Späth and J. Bruck (Ber., 1937, **70**, [*B*], 2446—2450).—The non-phenolic bases of

fresh mezcal buttons are worked up roughly as sulphates and hydrochlorides and the mother-liquor from these salts is separated into seven base fractions by partial extraction with HCl in presence of NaCl. From the appropriate fraction mezcaline is mainly separated as the sulphate; the bases obtained from the mother-liquors are converted into their hydrochlorides, which by repeated treatment with MeOH–Et_2O yield *N-methylmezcaline hydrochloride*, m.p. 201—202° (corresponding *picrate*, m.p. 177·5—178·5°, *trinitro-m-tolyloxide*, m.p. 189·5—190·5°, and *p-nitrobenzoyl* derivative. *N-Methylmezcaline* [*methyl*-β-3 : 4 : 5-*trimethoxyphenylethylamine*] is obtained synthetically by converting mezcaline by PhCHO at 100° into *benzylidenemezcaline*, b.p. 190° (bath)/0·03 mm., and thence into the *methiodide*, which is readily hydrolysed to the required base. All the known alkaloids of this series are derivatives of β-3 : 4 : 5-trihydroxyphenylethylamine. H. W.

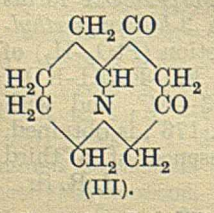
Tobacco alkaloids. XIII. New bases of tobacco. E. Späth and F. Kesztler (Ber., 1937, **70**, [*B*], 2450—2454).—Crude nicotine, freed from *l*- and *dl*-nornicotine, is transformed into its H *d*-tartrate, whereby the bulk of the nicotine is removed. The base, isolated from the mother-liquor of this salt, is allowed to crystallise again as H *d*-tartrate from a correspondingly smaller vol. of solution. Frequent repetition of this process leaves a small amount of a basic mixture, separated further by treatment with HCl in presence of NaCl and transformation of the fractions into the picrates. The presence of nicotyrine is thus established. l-*N-Methylanatabine*, $[\alpha]_D^{18}$ −171·4° in MeOH (*picrate*, m.p. 207—208°; *trinitro-m-tolyloxide*, m.p. 228—229° after softening at 226°), and *l-N*-methylanabasine, $[\alpha]_D^{15}$ −137·3° in MeOH, are also present; their prep. by the action of CH_2O and HCO_2H on anatabine and anabasine, respectively, is described. H. W.

Lupin alkaloids. XV. Oxidative degradation of phenyldehydrosparteine. Constitution of sparteine and lupanine. K. Winterfeld and M. Schirm (Arch. Pharm., 1937, **275**, 630—662; cf. A., 1937, II, 526).—Degradation products are obtained which confirm the structure previously assigned to sparteine. Phenyldehydrosparteine (I) and BzCl in KOH–H_2O–$COMe_2$ give *N-benzoyl-ω-phenylsparteone*



(II.)

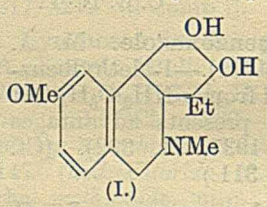
(II), an oil (*picrate*, m.p. 87—88°; *methiodide*, m.p. 73—75°, stable to $KMnO_4$), which gives deep-seated oxidation products with $KMnO_4$, but with CrO_3–H_2SO_4 under various conditions gives $(CH_2{\cdot}CO_2H)_2$, $NH_2{\cdot}[CH_2]_4{\cdot}CO_2H$, 3 : 5-*diketo-octahydropyridocoline* (III), an oil [*aurichloride*, m.p. 174° (decomp.); *reineckate*, decomp. 206—208°; *Me ether* of the enolic form, an oil (*reineckate*, decomp. 178—180°), absorbs 1 H_2 when hydrogenated; gives oily ketone derivatives; gives an oily pyrazoline], and the *lactone*



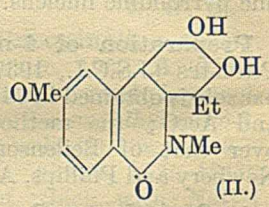
(III).

(IV), $CH_2<\begin{matrix}CH{:}C{\cdot}CH{\cdot}CH_2{\cdot}N\\CO{\cdot}O{\cdot}CH{\cdot}CO{\cdot}CH_2\end{matrix}>C_4H_8$, an oil [*reineckate*, sinters at 153°; unsaturated towards $KMnO_4$; gives an impure *Me* ester (*reineckate*, decomp. 85°)]. MnO_2–H_2SO_4 gives (III) and (IV), and HNO_3 gives (III). With HNO_3 (I) gives BzOH and (III). Clemmensen reduction of (III) gives a *base*, $C_{13}H_{23}N_2$ (*picrate*, m.p. 226°; *aurichloride*, decomp. 182—183°), *N*-methyl-2-piperidone, and a little sparteine (derived from lupanine present as an impurity). With HI–red P (III) gives (?) norlupinan, and electrolytic reduction gives piperidine. R. S. C.

***Lycoris* alkaloids. XI. Constitution of lycoramine.** H. Kondo and S. Ishiwata (Ber., 1937, **70**, [*B*], 2427—2437).—Lycoramine (I), m.p. 120°, $[\alpha]_D^{27}$ −98·2° [*platinichloride*, decomp. 245°; *perchlorate*, m.p. 138—139°; *methiodide*, decomp. 308°, or (+MeOH), m.p. 220° (decomp.)], contains 1 NMe, 1 OMe, and 2 OH (*lycoramine diacetate*, m.p. 95°). It does not contain a phenolic OH since it is insol. in alkali and does not give a OMe-derivative with Me_2SO_4. Lycoramine methohydroxide is very stable towards boiling 30% KOH but gives a little *methine base*, $C_{17}H_{25}O_3N{:}CH_2$ (*picrate*, m.p. 148°; *methiodide*, decomp. 213—214°). Lycoramine methochloride is transformed by the prolonged action of Na–Hg and

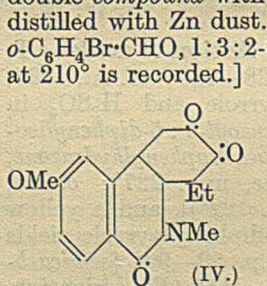


(I.)

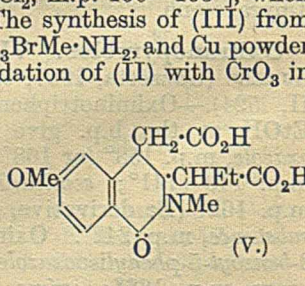


(II.)

boiling H_2O into *lycoraminemethylhydromethine-A*, $C_{18}H_{29}O_3N$, m.p. 96°, $[\alpha]_D^{18}$ −54·2° in EtOH (*hydrochloride*, m.p. 210—211°; *phenylurethane*, m.p. 150—151°; *methiodide*, decomp., 152—153°), and *lycoraminemethylhydromethine-B*, m.p. 145°, $[\alpha]_D^{18}$ +43·6° in EtOH (*hydrochloride*, m.p. about 210°; *methiodide*, decomp. 105—110°). Oxidation of lycoraminemethylhydromethine methohydroxide with cold, alkaline $KMnO_4$ gives $EtCO_2H$. Oxidation of (I) with cold $KMnO_4$ yields $H_2C_2O_4$, *m*-methoxyphthalic anhydride, and a neutral *substance* (II), m.p. 253°, $[\alpha]_D^{18\cdot5}$ +73·7° in $CHCl_3$, which contains 1 NMe, 1 OMe, and 2 OH (Ac_2 derivative). HIO_4 or $Pb(OAc)_4$ has little action on (II), which affords 1-*methylphenanthridine* (III), m.p. 80—82° after softening at about 78° [*picrate*, m.p. 217—218°; *styphnate*, m.p. 148° (decomp.); double *compound* with $HgCl_2$, m.p. 190—195°], when distilled with Zn dust. [The synthesis of (III) from *o*-$C_6H_4Br{\cdot}CHO$, 1 : 3 : 2-$C_6H_3BrMe{\cdot}NH_2$, and Cu powder at 210° is recorded.] Oxidation of (II) with CrO_3 in



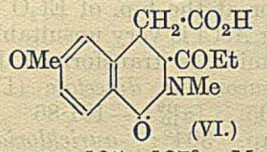
(IV.)



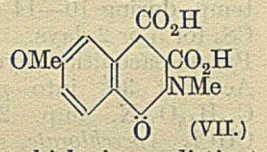
(V.)

AcOH yields an α-*diketo*-compound (IV), m.p. 220°, $[\alpha]_D^{17}$ +275·5° [*oximino*-derivative, m.p. 189—190°

(decomp.); *phenazine* derivative, $C_{23}H_{23}O_2N_3$, m.p. 175—180° (decomp.); p-*nitrophenylosazone*, decomp. 267—268°; *triazine* derivative, $C_{18}H_{20}O_3N_4$, decomp. 238°; *dioxime*, m.p. 257°, converted by 13N-NH_3 at 170° into the *furazan*, $C_{17}H_{19}O_3N_3$, m.p. 115—120° (decomp.)]. Oxidation of (IV) by $KMnO_4$ in $COMe_2$ containing Na_2CO_3 gives the *acid* (V), m.p. 222—223°, which does not react with *p*-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2$ and gives a resinous *Me*$_2$ ester when treated with CH_2N_2, the *acid* (VI), m.p. 119—120° (p-*nitrophenylhydrazone*,



(VI.)



(VII.)

decomp. 125—127°; *Me*$_2$ ester), which gives a distinct CHI_3 reaction when heated with I and KOH, *m*-methoxyphthalic anhydride, and an *acid* (VII), decomp. 261—262° and, after-resolidification, m.p. 240—241° (*Me*$_2$ ester, m.p. 152—153°), which gives the fluorescein and phenolphthalein reactions of *o*-dicarboxylic acids. The *Ag* salt of (VII) decomposes at about 270° into CO_2 and 6-*methoxy*-2-*methyldihydro*isocarbostyril, m.p. 50—51°, dehydrogenated by Pd–asbestos at 240—260° to 6-*methoxy*-2-*methyl*isocarbostyril, m.p. 96—98°, identical with the synthetic compounds. The following revised data are recorded: 2-*nitro*-4-*acet-toluidide*, m.p. 144°; 2 : 3-dinitro-4-acettoluidide, m.p. 170—171°, and -*p*-toluidine, m.p. 118—120°; 2 : 3-dinitrotoluene, m.p. 59—60°; 2-nitro-*m*-toluidine, m.p. 105—106°; 3-bromo-2-nitrotoluene, m.p. 28—29°; 3-*bromo*-o-*toluidine*, b.p. 105—107°/2—3 mm. (*Ac* derivative, m.p. 157—158°). H. W.

Crystallisation of ecgonine silicotungstate. (Cinematographic recording.) R. Hazard, J. Comandon, and P. de Fonbrune (Compt. rend., 1937, **205**, 922—924).—The freshly pptd. silicotungstate is amorphous; on keeping the mother-liquor deposits needle crystals, the amorphous form dissolving as formation of these proceeds. A small quantity of a third cryst. form is also produced, but is converted into the needle crystals by a similar process. A. J. E. W.

***Strychnos* alkaloids. XCVI. 9-Monohydroxybrucine, the analogue of ψ-strychnine.** H. Leuchs and K. Tessmar (Ber., 1937, **70**, [*B*], 2369—2373; cf. A., 1937, 435).—Brucine is very slowly converted by air in presence of $CuSO_4$–NH_3–H_2O into 9-*monohydroxybrucine* (*ψ-brucine*), $C_{23}H_{26}O_5N_2$ (I), m.p. 258—263° when crystallised from $COMe_2$ or AcOH, m.p. 268° when pptd. by NH_3 from hot solution, $[\alpha]_D^{20}$ −100°/*d* in $CHCl_3$, obtained more rapidly and in much better yield by oxidation in presence of Fehling's solution (under these conditions strychnine is rapidly attacked but the product is difficult to purify). (I) gives a *perchlorate*, decomp. 220—240°, and a (?) *Me ether*, m.p. about 100°. Brucine amine oxide (*perchlorate*, m.p. 210° (decomp.), $[\alpha]_D^{20}$ 0° in H_2O or H_2O–$COMe_2$, reduced by SO_2 to brucine, is obtained as by-product of the prep. of (I). PhCHO, (I), and NaOMe in boiling MeOH afford *benzylidene-ψ-brucine*, m.p. 165° (decomp.) after softening at 150°. Strongly lævorotatory N-*nitroso*-sec.-*ψ-brucine*, m.p. 248° (decomp.), is obtained from (I), $NaNO_2$, and dil. HCl at 0°. (I) is reduced by Zn and HCl to brucine, catalytically (PtO_2 in 50% AcOH) to *dihydro-ψ-brucine*, m.p. 258—260° (decomp.), $[\alpha]_D^{20}$ +29°/*d* in $CHCl_3$ free from EtOH (*perchlorate*; *Me ether*, m.p. 118° (decomp.), $[\alpha]_D^{20}$ +83°/*d* in $CHCl_3$, also +1MeOH). N-*Nitrosodihydro*-sec.-*ψ-brucine* has m.p. (indef.) 160—190° to a brown resin or m.p. 160—175° (decomp.) after being dried at 100°. H. W.

***Strychnos* alkaloids. XCVII. Methylations in the series of ψ- or 9-monohydroxy-strychnine and fission of the sixth and seventh rings in the strychnine molecule.** H. Leuchs (Ber., 1937, **70**, [*B*], 2455—2462).—The product of the action of MeI on ψ-strychnine Me ether (I) is the methiodide of the *N*-Me base $C_{22}H_{24}O_3N_2$ and therefore has the composition $C_{23}H_{27}O_3N_2I$ (cf. Leuchs, A., 1937, II, 435; Robinson and Blount, A., 1932, 1147). The base is hot, however, an intermediate since it does not add MeI at 37°. Probably the methiodide of the ether, :C(OMe)·N:MeI, is first produced and then passes partly with migration of Me into the *N*-Me_2 salt. The non-isomerised portion is ultimately hydrolysed and the OH imparts H to N so that the hydriodide of the NMe base results. This is converted by Me_2SO_4 into the quaternary salt, which is separated as the *perchlorate*, m.p. 285—293° (decomp.). The same salt is obtained from $C_{23}H_{27}O_3N_2I$ and $HClO_4$, thereby establishing its true nature. The migration of Me causes rupture of a ring linking in the strychnine mol. and union of two N rings one of which is five-membered and the other five-, six-, or seven-membered to a large ring. Certain valency relationships between NMe and CO appear to be retained which hinder the detection of the ketone. Reaction with semicarbazide or Clemmensen reduction could not be effected with any member of the series. In attempts to open the large ring the methoperchlorate of the base $C_{22}H_{24}O_5N_2$ is shown to pass by catalytic hydrogenation (PtO_2 in H_2O) mainly into the corresponding H_2-derivative, m.p. 150—200°, whilst the methiodide gives small amounts of a *base*, $C_{22}H_{28}O_5N_2$, m.p. 193° (vac.) after softening, and the *methiodide*, $C_{22}H_{26}O_3N_2MeI$, m.p. (anhyd.) 215—217°. Reduction of either salt by Na–Hg gives the *base*, $C_{23}H_{28}O_3N_2$, m.p. 170—172° (vac.) after softening at 165° (*perchlorate*, m.p. 243°), thus

$$CO<\begin{matrix}R{\cdot}CH_2{\cdot}CH_2\\ R'—C—CH_2\end{matrix}>N{:}Me_2I \longrightarrow$$

C:CMe·R'·CO·R·CH_2·$\dot{C}H_2$·NMe_2,HI. The Hofmann degradation occurs thus:

$$CO<\begin{matrix}R{\cdot}CH_2{\cdot}CH_2\\ CH—\dot{C}—CH_2\\ \quad\dot{C}\end{matrix}>NMe_2{\cdot}OH \xrightarrow{-H_2O}$$

$$OMe{\cdot}C<\begin{matrix}R{\cdot}CH_2{\cdot}CH_2\\ \dot{C}—\dot{C}—CH_2\\ \quad\dot{C}\end{matrix}>NMe$$

, the *product* having m.p. 188—190° (vac.).

(I) is transformed by PhCHO and 40% KOH in boiling MeOH into the benzylidene derivative, m.p. 153°, and by excess of MeI at room temp. into the *methiodide*, m.p. 267° (decomp.) after softening. Hydrogenation (PtO_2) of the latter gives the *base*, $C_{24}H_{32}O_3N_2$, m.p. 189—190° (vac.) [*hydriodide*, m.p.

260—268° (decomp.); *perchlorate*, m.p. 240—246°; *methiodide* (II), m.p. 295° (vac.; decomp.)]. Treatment of the methiodide, $C_{23}H_{26}O_3N_2$,MeI, with NaOMe in boiling MeOH gives an *isomeride*, m.p. 285—293° (decomp.), reduced by Na–Hg to the amorphous *base*, $C_{24}H_{30}O_3N_2$ (*perchlorate*, decomp. 135° after softening at 130°). H. W.

Strychnine and brucine. IX. R. Ciusa and V. Amoruso (Gazzetta, 1937, **67**, 723—727).—*iso*Strychnine [in the prep. of which new *forms* ($+H_2O$), m.p. 229°, and ($+2H_2O$), tabular, m.p. 219—222°, are obtained] with dil. HBr yields a *hydrobromide*, which with Br–H_2O gives, after treatment with aq. NH_3, *bromoisostrychnine* (I) ($+CHCl_3$), m.p. 140°, [α] 0° [*hydrobromide* (II) ($+H_2O$), m.p. 130°; *Bz* derivative, m.p. 162°, giving a *hydrochloride* ($+H_2O$), m.p. 180°]. With Br–AcOH, (II) forms *bromoisostrychnine perbromide*, decomposed by EtOH to a *substance*, $C_{23}H_{28}O_3N_2Br_4$. The lethal doses of (I) to the frog and the rabbit are 0·033 g. and 0·053 g. per kg., respectively. E. W. W.

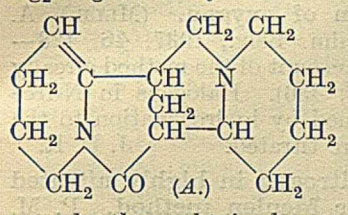
***Aconitum* alkaloids. XII. Oxidation of *Aconitum* alkaloids with nitric acid.** H. Suginome (Annalen, 1937, **533**, 172—182).—Oxidation of mesaconitine, aconitine, or oxonitine (I) by HNO_3 (*d* 1·43) according to Brady (J.C.S., 1913, **103**, 1821) gives in all cases *nitronitrosoaconitic acid* (II), $C_{18}H_{14}(OMe)_3(OH)(OAc)(OBz)(N{\cdot}NO)(NO_2)(CO_2H)$, decomp. 282°, $[\alpha]_D^{24}$ −33·2° in EtOAc. The physical properties of the acid vary somewhat according to the source [the highest yields and purest products are derived from (I)] but all specimens are converted by AcCl into *acetylnitroaconitic acid*, $C_{35}H_{38}O_{14}N_2$, m.p. 218—219°, $[\alpha]_D^{21}$ −15·0° in EtOAc, which requires 5 mols. of alkali for hydrolysis whereas the initial material requires 3 mols. Model experiments (to be described later) show that NO_2 in (II) is attached to N. Hydrolysis of (II) with $Ba(OH)_2$ in EtOH affords *nitronitrosoaconic acid*, $C_{22}H_{27}O_{11}N_3$, decomp. 298°, $[\alpha]_D^{20}$ −36·6° in $COMe_2$, which gives a well-cryst. yellow *Ba* salt. Lawson's acid, $C_{31}H_{35}O_{13}N_3$, m.p. 268°, appears to be identical with (II) (cf. A., 1936, 351). It seems certain that (II) does not contain a tetrahydro*iso*quinoline nucleus. AcCl converts (I) into *triacetyloxonitine*, m.p. 176—178°, whence (I) contains 3 OH; the last O gained during oxidation is very probably present as CO in juxtaposition to NH, thus accounting for the neutral reaction of (I). The formula of (I) is therefore $C_{18}H_{17}(OMe)_4(OH)_3(OAc)(OBz)(NH)(CO)$. H. W.

***Aconitum* alkaloids. XIII. New preparation of oxonine and pyroxonine.** K. Tamura (Annalen, 1937, **533**, 183—196).—*Oxonine penta-acetate* (I), decomp. 246°, $[\alpha]_D^{20}$ −77·09° in $CHCl_3$, is obtained by the oxidation of aconine penta-acetate or mesaconine penta-acetate with $KMnO_4$ in $COMe_2$ or by the action of AcCl on oxonine (II) at room temp. The 5 OH in aconine (III) and (II) must therefore be identical and, since the presence of :CO cannot be detected and that of an O bridge is improbable, it appears that the newly-introduced O exists in ·CO·NH_2. Oxonine is most conveniently made by transforming jesaconitine hydrobromide by AcCl at 35° into *jesaconitine triacetate*, decomp. 232° (*aurichloride*, decomp. 221°); this is oxidised by $KMnO_4$ in $COMe_2$, to *jesoxonitine triacetate* ($+2H_2O$), m.p. 177° and, after re-solidification, m.p. 235° (decomp.), $[\alpha]_D^{17\cdot8}$ −41·45° in $CHCl_3$, or, anhyd., decomp. 235°, which is hydrolysed to (II). Mesaconitine triacetate is similarly oxidised to *oxonitine triacetate* ($+7H_2O$), m.p. 178° and, after re-solidification, decomp. 235°, $[\alpha]_D^{17\cdot9}$ −50·80° in $CHCl_3$, or, anhyd., decomp. 233°. Acetylation of (III) is effected with AcCl at room temp. during 10—14 days, or at the b.p. of Et_2O or CS_2 for 5 or 2 days. Boiling AcCl is very unsuitable. Pyromesaconitine hydrobromide is transformed by AcCl at 36° into *pyromesaconitine diacetate* (IV) $C_{35}H_{45}O_{11}N$, m.p. 202—205°, $[\alpha]_D^{19}$ −101·86° in $CHCl_3$ (*perchlorate*, decomp. 304°; *aurichloride*, decomp. 225°), and an isomeric *base* (*perchlorate*, m.p. 193° after softening at 187°; *aurichloride*, decomp. 208°). $KMnO_4$ oxidises (IV) in $COMe_2$ to *pyroxonitine diacetate*, decomp. 170° after softening at 160°, $[\alpha]_D^{20}$ −115·49° in $CHCl_3$ (identical with that obtained from the base and AcCl at 36°), hydrolysed by 0·25N-$Ba(OH)_2$ in EtOH to pyroxinine, $C_{23}H_{33}O_9N$,0·5EtOH,H_2O, decomp. 264°. This with AcCl at 36° affords pyroxinine triacetate, $C_{29}H_{39}O_{12}N$, 1·5H_2O, m.p. 165° (*hydrochloride*, m.p. 158° and, after re-solidification, m.p. 219°; *aurichloride*). H. W.

Alkaloids of *Aconitum napellus*. W. Freudenberg and E. F. Rogers (J. Amer. Chem. Soc., 1937, **59**, 2572—2575).—The residual bases from the tubers of *A. napellus* contain *napelline*, $C_{22}H_{33}O_3N$, cryst. [*hydrobromide*, m.p. 229° (decomp. from 200°), $[\alpha]_D^{23}$ −42·7° in H_2O; *hydrochloride*, m.p. 220—222° (decomp.), $[\alpha]_D^{22}$ −93·9° in H_2O; *hydriodide*, m.p. 181—185° (decomp.)], *neoline*, $C_{24}H_{41}O_6N$, m.p. 153—154°, $[\alpha]_D^{23}$ +9·7° in EtOH [*hydrobromide*, m.p. 215° (decomp.), $[\alpha]_D^{23}$ +2·1° in H_2O; *hydrochloride*, decomp. 178—180°], with traces of *l*-ephedrine and *l*-sparteine. R. S. C.

Alkaloids of *Anabasis aphylla*. XIV. Structure of aphylline and aphyllidine. A. Orékhov (J. Gen. Chem. Russ., 1937, **7**, 2048—2062).—Aphyllidine (I) (A., 1932, 405), purified via the *perchlorate*, m.p. 210—212°, $[\alpha]_D$ +15° in MeOH, has m.p. 112—113°, and $[\alpha]_D$ +6·5° in MeOH; the higher [α] and lower m.p. previously reported were due to contamination with an unknown alkaloid, m.p. 162—164°, $[\alpha]_D$ +54·5° in MeOH. In light petroleum (I) and Br yield the *hydrobromide*, m.p. 210°, of *bromoaphyllidine* (II), m.p. 150—152° (*perchlorate*, m.p. 235°), attempted hydrogenation, reduction, and hydrolysis of which were unsuccessful. De-*N*-methylaphyllidine (III) is brominated in light petroleum to a Br_1-derivative, b.p. 190—193°/17 mm. (*perchlorate*, m.p. 180—183°), also prepared from the *methiodide*, m.p. 114—120°, of (II) and Ag_2O. In EtOH and HCl at 100° (I) gives *Et aphyllidate*, m.p. 210—212° (*picrate*, $+COMe_2$, m.p. 208—210°), showing that ring fission takes place. Hydrogenation of (I) (Pt catalyst) gives aphylline, which is thus 5 : 6-dihydroaphyllidine. Reduction of (I) in 50% H_2SO_4 with Pb electrodes gives *d*-sparteine. The methiodide, m.p. 121—122°, of de-*N*-dimethylaphyllidine, b.p. 240—242°/7 mm. (*perchlorate*, m.p.

180—182°), and Ag_2O in MeOH give hemiaphyllidylene, $C_{15}H_{19}ON$. In N-HCl (III) and H_2 (Pt catalyst) yield dihydrode-*N*-methylaphyllidine, m.p. 118—120° (methiodide, m.p. 234—235°), with which Ag_2O gives dihydrode-*N*-dimethylaphyllidine, b.p. 218—220°/5 mm. (*perchlorate*, m.p. 209—210°), the methiodide, m.p. 195°, of which gives dihydrohemiaphyllidylene, b.p. 206—207°/8 mm., with Ag_2O in MeOH; the compounds thus obtained are identical with, and of higher purity than, those obtained analogously from aphylline (*loc. cit.*). The structure of (I) is regarded as being *A*. R. T.



(*A*.)

Action of lead tetrachloride on primary and secondary halogenated arsines, and on tertiary arsines. G. J. Burrows and A. Lench (J. Proc. Roy. Soc. New South Wales, 1937, **70**, 294—299).—$PbCl_4$ at −5° in $CHCl_3$ converts $AsPhMe_2$ into $AsClPhMe_2$·OH, $AsPh_2Me$ into *diphenylmethyl-*, m.p. 132°, and $AsPhMeEt$ into *phenylmethylethyl-arsine dichloride*, m.p. 83°, (the last two are also obtained from the arsine and Cl_2). Similarly *o-* (but not *p-*)C_6H_4Me·$AsCl_2$ gives C_6H_4Me·$AsCl_4$, whilst *p*-C_6H_4Me·AsMeCl yields *p*-C_6H_4Me·$AsMeCl(OH)_2$, converted by H_2O into *p*-C_6H_4Me·AsMeO·OH, or by $PbCl_4$ in $CHCl_3$ above 10° into *p*-C_6H_4Me·$AsO(OH)_2$. No additive compounds of $PbCl_4$ with arsines could be isolated. A. Li.

Dihydroxydiphenylarsonium chloride. G. J. Burrows and A. Lench (J. Proc. Roy. Soc. New South Wales, 1937, **70**, 300—301).—Treatment of $(AsPh_2)_2O$ in $CHCl_3$ with dry Cl_2 yields $AsPh_2Cl(OH)_2$, m.p. 128°, and not the oxychloride $(AsPh_2Cl_2)_2O$ of La Coste and Michaelis (A., 1880, 396). A. Li.

Derivatives of diphenylmethylarsine. G. J. Burrows and A. Lench (J. Proc. Roy. Soc. New South Wales, 1937, **70**, 437—439).—$AsPh_2Me$ with Br in CCl_4 gives *diphenylmethylarsine dibromide*, m.p. 116° (decomp.), or *tetrabromide*, m.p. 63—64°; with I in $CHCl_3$ it gives the *di-iodide*, m.p. 104° (decomp.). $AsPh_2MeO$ and hot EtOH–HCl yield *hydroxydiphenylmethylarsonium chloride*, m.p. 147°. A. Li.

Mercuration and arsenation of benzothienone [2-benzoylthiophen]. A. W. Weitkamp and C. S. Hamilton (J. Amer. Chem. Soc., 1937, **59**, 2699—2702).—2-Benzoylthiophen with $Hg(OAc)_2$ and $HgCl_2$ in hot AcOH give *2-benzoyl-5-chloromercurithiophen* (I), m.p. 242°; $Hg(OAc)_2$ alone at 100° gives a 1 : 1 mol. *compound*, m.p. 202°, of *2-benzoyl-5-acetoxymercuri-* (not isolated) and *-4 : 5-diacetoxymercuri-thiophen* (II), the latter product being prepared from the mol. compound by $Hg(OAc)_2$ in OH·CH_2·CH_2·OMe. With KI_3 (I) gives *2-iodo-5-benzoylthiophen*, m.p. 129·5—130° (3-NO_2-derivative, m.p. 168°), also obtained from 2-iodothiophen, BzCl, and $SnCl_4$ in C_6H_6. Thiophen, C_6H_4I·COCl, and $SnCl_4$ yield 2-o-, m.p. 61°, -m-, m.p. 48°, and -p-*iodobenzoylthiophen*, m.p. 106·5°, which yield 5-*HgCl* derivatives, m.p. 225°, 252°, and 285° (decomp.), respectively; these derivatives with KI_3 yield *2-iodo-5-o-*, a glass (3-NO_2-derivative, m.p. 138—139°), -m-, m.p. 109°, and -p-*iodobenzoylthiophen*, m.p. 153°. With KI_3 (II) gives 2 : 3-*di-iodo-5-benzoylthiophen*, m.p. 80—90°. With KBr_3 (I) and (II) give *2-bromo-*, m.p. 76°, and 2 : 3-dibromo-*5-benzoylthiophen*, m.p. 80°, respectively. With $AsCl_3$ (I) gives *2-benzoylthienyl-5-dichloroarsine*, m.p. 113°, and thence *2-benzoylthienyl-5-arsinous oxide*. Either of these with NaOH–H_2O_2 gives *2-benzoylthienyl-5-arsinic acid*, m.p. 360° (decomp.; 1 H_2O lost at 140°). R. S. C.

Action of Grignard's reagent on silicon tetrafluoride. Fluorotriphenylmonosilane. G. V. Medox and N. Z. Kotelkov (J. Gen. Chem. Russ., 1937, **7**, 2007—2008).—SiF_4 and MgPhBr in Et_2O yield *fluorotriphenylsilicane*, m.p. 64°. R. T.

Complex compounds obtained from *p*-tolylstibine dichloride and *p*-tolyldiazonium chloride. II. A. B. Bruker and E. S. Machlis (J. Gen. Chem. Russ., 1937, **7**, 1880—1884).—*p*-C_6H_4Me·N_2Cl (I) and *p*-C_6H_4Me·$SbCl_2$ in AcOH yield a 1 : 1 *compound*, m.p. 90—92° (decomp.), converted by boiling 25% HCl into $(p\text{-}C_6H_4Me)_2SbCl_3$, m.p. 155° (lit. 143°). In presence of excess of (I) a 2 : 1 *compound*, m.p. 108—110°, is obtained, and this, when boiled with 25% HCl, gives $(p\text{-}C_6H_4Me\cdot)_2$, *p*-$C_6H_4Me$·$SbCl_4$, and the double *salt* *p*-C_6H_4Me·$SbCl_4$,NH_4Cl, not melting at 200°, and converted into *p*-C_6H_4Me·$Sb(OH)_2$ by shaking with H_2O. R. T.

Benzylstibines and their derivatives. I. Tzukervanik and D. Smirnov (J. Gen. Chem. Russ., 1937, **7**, 1527—1531).—CH_2PhCl, Mg, and $SbCl_3$ in Et_2O yield *tribenzylstibine oxide*, together with dibenzyl, PhCHO, and Sb_2O_3. The oxide is converted by HCl or HBr into *tribenzylstibine dichloride*, m.p. 100—101°, or *dibromide*, m.p. 107—109°. When the Grignard reaction is conducted with strict exclusion of air, the product is *tribenzylstibine*, m.p. 85—90°, which with excess of $SbCl_3$ gives *dibenzylchlorostibine dichloride*, m.p. 157—158°. This is converted by aq. Na_2CO_3 into *dibenzylstibine oxide*, $[(CH_2Ph)_2SbO]_2O$, which with HBr gives *dibenzylbromostibine dibromide*, m.p. 150—151° (decomp.). R. T.

Organic thallium derivatives. VII. Synthesis of organic thallium derivatives with the simpler substituents in the benzene ring. N. N. Melnikov and M. S. Rokitskaja (J. Gen. Chem. Russ., 1937, **7**, 1472—1477).—The *compounds* TlR_2X are prepared from RX, Mg, and TlX_3 in Et_2O: R = *m*-tolyl, X = Cl, m.p. 235°; R = *m*-tolyl, X = Br, m.p. 242°. $(OAc\cdot C_6H_4)_2Hg$ in boiling EtOH and $TlBr_3$ yield *di-p-acetoxyphenylthallium bromide*. $TlBr_3$ and *p*-CO_2H·C_6H_4·$B(OH)_2$ in boiling H_2O yield *di-p-carboxyphenylthallium bromide* (I), m.p. >260°. C_6H_4PhBr in Et_2O, Mg, and OBu^{β}·$B(OH)_2$ yield *diphenylylboric acid*, m.p. 185—190°, which with $TlCl_3$ or $TlBr_3$ in boiling H_2O gives *diphenylylthallium chloride*, decomp. at 240—245°, or *bromide*, not melting at 305°; the last with excess of $TlBr_3$ gives *diphenylylthallium dibromide* (II), m.p. 185° (decomp.). $(NO_2\cdot C_6H_4)_2TlCl$, m.p. 245° (decomp.), $(NO_2\cdot C_6H_4)_2TlBr$, m.p. 238° (decomp.), $NO_2\cdot C_6H_4\cdot TlCl_2$, m.p. 217° (decomp.), and

$NO_2{\cdot}C_6H_4{\cdot}TlBr_2$, m.p. 178° (decomp.), are prepared analogously to (I) and (II). R. T.

How to determine structural formulæ for proteins. W. D. Bancroft and H. F. Browning (J. Physical Chem., 1937, **41**, 1163—1170).—For studying the constitution of proteins a scheme is proposed, based on the determination of different forms of N (total, "stoicheiometric," and NH_3) in fractional hydrolysates, and in degradation products obtained in different ways. Dil. H_2SO_4 is preferred to HCl for hydrolysis. Some preliminary results for casein are recorded. F. L. U.

Relation between "fibrous" and "globular" proteins. W. T. Astbury (Nature, 1937, **140**, 968—969).—Accumulating *X*-ray evidence for the view that fibrous and globular proteins are constructed on a common plan is summarised. The chemical data of Bergmann and Niemann (A., 1937, III, 168) indicate a similar view. L. S. T.

Structure of the protein molecule. F. Halle (Kolloid-Z., 1937, **81**, 334—349).—A review.

Accidents in destruction of organic and biological substances with perchloric acid. E. Kahane (Z. anal. Chem., 1937, **111**, 14—17; cf. A., 1932, 71).—The action of $HClO_4$ on org. substances may become explosive in the absence of a diluent, such as H_2SO_4 or excess of $HClO_4$. J. S. A.

Determination of carbon and hydrogen content by combustion. M. W. Renoll, T. Midgley, jun., and A. L. Henne (Ind. Eng. Chem. [Anal.], 1937, **9**, 566—567).—Combustion of 0·1—0·2 g. in an electrically heated all-glass apparatus using an air current (cf. Smith *et al.*, A., 1933, 641) gives C and H correct to 0·01%. The at. wt. of C must be taken as 12·005. F. R. G.

Demands made on lead dioxide in micro-analysis [for carbon and hydrogen]. A. Friedrich (Mikrochem., 1937, **23**, 129—143).—The N liberated as NO_2 in the combustion of org. compounds varies from 5—30% in azo- or NH_2-compounds to 50% in NO_2- or NO-compounds, and is dependent on the rate of combustion and the catalyst used. The optimum amount of PbO_2 for use in micro-combustion tubes is discussed. J. S. A.

Micro-determination of sulphate solutions.—See A., I, 44.

Determination of deuterium in organic compounds. A. S. Keston, D. Rittenberg, and R. Schoenheimer (J. Biol. Chem., 1938, **122**, 227—237; cf. A., 1935, 1407).—The org. compound is burnt, H_2O formed is purified, and $[D_2O]$ in this H_2O determined by two independent methods, n and d being determined. Methods and apparatus are described. J. N. A.

Direct micro-determination of oxygen in organic substances by hydrogenation. Analysis of pure volatile compounds containing carbon, hydrogen, and relatively low percentages of oxygen. W. R. Kirner (Ind. Eng. Chem. [Anal.], 1937, **9**, 535—539).—A procedure similar to that of Hennig (A., 1936, 872; see also Unterzaucher and Bürger, A., 1937, II, 358) is described. H_2O formed is absorbed by anhyd. $CaSO_4$. The necessity of using an empirical blank val. is emphasised [cf. Lindner and Wirth, *ibid.* (1937)]. When the method is applied to sucrose the vals. are consistently low. F. R. G.

Micro-determination of oxygen. (Mlle.) A. Lacourt (Bull. Soc. chim. Belg., 1937, **46**, 428—433).—A more detailed account of the method already described (A., 1937, II, 436). Halogens in N-free compounds are determined by hydrogenation to the halogeno-acids, which are titrated. J. D. R.

Determination of nitrogen in highly nitrated substances by the ter Meulen method. P. M. Heertjes (Chem. Weekblad, 1937, **34**, 827).—Trustworthy results can be obtained with highly nitrated substances by using 1 g. of Ni containing 10% of ThO_2 per 10 mg. of sample, adding a few drops of an appropriate solvent (*e.g.*, $COMe_2$) to spread the substance throughout the catalyst mass, and heating at 100° for 1 hr. before heating to a higher temp. in order to disengage NH_3. Results for di- and trinitropyrocatechol ethylene ethers are discussed. S. C.

Halogenorganimetry. Determination of halogens in organic substances. J. A. Sanchez (J. Pharm. Chim., 1938, [viii], **27**, 5—18; cf. A., 1936, 1528).—The substance (0·02 g.) is heated with $KMnO_4$ and powdered pumice and an aq. solution of the powder is treated with H_2O_2. I is determined as IO_3'. For Cl, the neutralised filtrate is treated with $CaCO_3$ and the Cl determined titrimetrically. When the substance contains Br, the acidified solution of the fusion mixture is treated with MnO_2 and the Br liberated distilled into a solution of an alkali iodide; the I liberated is titrated. The method is widely applicable with an error of $<1\%$. J. L. D.

Determination of micro-quantities of iodine.—See A., I, 44.

Determination of acetyl, especially in *O*-acetyl compounds. E. P. Clark (Ind. Eng. Chem. [Anal.], 1937, **9**, 539).—If in the method described previously (A., 1937, II, 40) the reaction mixture is distilled at a rate such that it is conc. to approx. 15 c.c. during the collection of the 50 c.c. of distillate instead of steam-distillation at const. vol., all the AcOH is found in the distillate. L. S. T.

Diazometric analysis of dienes, and its applications. A. P. Terentiev (Prom. Org. Chim., 1937, **4**, 535—542).—The method is applicable to determination of *cyclo*pentadiene, $(CH_2{:}CMe{\cdot})_2$, $CHPh{:}CH{\cdot}CH{:}CH_2$, $CHMe{:}CH{\cdot}CMe{:}CH_2$, $CH_2{:}CCl{\cdot}CH{:}CH_2$, and pyrrole. R. T.

Micro-acetyl determination. Titration of weak bases. F. von Viditz (Mikrochim. Acta, 1937, **1**, 326—337).—A simplified form of apparatus is described. Phosphotungstic acid is used in place of p-$C_6H_4Me{\cdot}SO_3H$ as a hydrolysing agent, and dioxan as a solvent for Ac compounds of low solubility. The titration of weak acids by weak bases is discussed, and $NH_2{\cdot}[CH_2]_2{\cdot}OH$ is recommended for the titration of AcOH and other weak acids. The method gives satisfactory results with 0·7 mg. of phenacetin or 0·4 mg. of cellobiose octa-acetate. The possibility of a new

acidimetric method for the determination of fructose is pointed out. L. S. T.

Micro- and submicro-determination and identification of ethyl alcohol. II. Submicro-determination. III. Identification. M. Nicloux (Ann. Ferment., 1936, **1**, 513—529, 530—540; Chem. Zentr., 1936, i, 4189—4190).—II. A modification of the $K_2Cr_2O_7$ process is described, applicable to 0·1—0·5 mg. of EtOH (*e.g.*, in blood).

III. The oxidation of EtOH to AcOH requires the theoretical amount of $K_2Cr_2O_7$, whereas PrOH, $Bu^{\alpha}OH$, and $Bu^{\beta}OH$ require 1·21—1·26, 1·27, and 1·24—1·42 times the theoretical $K_2Cr_2O_7$, according to temp., and yield < the theoretical amount of the corresponding acids. J. S. A.

Rapid determination of primary and secondary alcohols by phthalisation in warm pyridine, and identification of the alcohols as their acid phthalates. S. Sabetay and Y. R. Naves (Ann. Chim. Analyt., 1937, [iii], **19**, 285—289; cf. A., 1937, II, 132).—Primary alcohols with an excess (2—4 times) of o-$C_6H_4(CO)_2O$ (I) in C_5H_5N (100°; 1 hr.) afford esters quantitatively; the extent of combination is determined titrimetrically after hydrolysis of excess of (I) with hot H_2O. Some *sec.* alcohols react similarly, but many do not as they are dehydrated or their groups exert steric influences on the phthalyl residue. Easily hydrolysed esters are determined after reaction at room temp. Many practical points dealing with the separation of these products are described. J. L. D.

Determination of glycerol and ethylene glycol in dilute aqueous solution. A. G. Hovey and T. S. Hodgins (Ind. Eng. Chem. [Anal.], 1937, **9**, 509—511).—The colour reactions of phenols in acid, neutral, and alkaline solution with glycerol (I) and $(CH_2{\cdot}OH)_2$ (II) show that (I) in presence of (II) is best detected by pyrocatechol and H_2SO_4, which gives a blood-orange colour at 140—145°. The colours given with the reagent by several polyhydric alcohols are recorded. The test fails in presence of aldehydes but may be used to detect acraldehyde (flocculent purple ppt.) in presence of (I). F. R. G.

Rapid hydrolysis of esters by potassium hydroxide in diethylene glycol. C. E. Redemann and H. J. Lucas (Ind. Eng. Chem. [Anal.], 1937, **9**, 521—522).—Sap. vals. of esters and oils are determined by hydrolysis with N-KOH in $(OH{\cdot}C_2H_4)_2O$ (I) at suitable temp. up to 130° followed by titration with 0·5N-HCl. Procedure for identification of esters using KOH in (I) allows ready separation of the alcohol. F. R. G.

Polarimetric titration of hydroxy-acids. F. Górski (Bull. Acad. Polonaise, 1937, **A**, 239—243).—Optically active OH-acids, *e.g.*, tartaric and malic acid, are determined by adding the enantiomorph to an aq. solution of the acid and NH_4 molybdate (I) until α is 0°. The method is accurate because the low $[\alpha]$ of the acid is changed by (I) to very high $[\alpha]$ of opposite sign). R. S. C.

Recognition and determination of traces of formaldehyde. J. M. Hambersin (Bull. Soc. chim. Belg., 1937, **46**, 519—524).—With β-$C_{10}H_7{\cdot}OH$ and H_2SO_4, CH_2O gives a pink colour which on boiling yields a pink ppt. The above pink colour serves for the recognition of, and in absence of other aldehydes (*e.g.*, MeCHO) for the colorimetric determination of, CH_2O by comparison with freshly prepared standards. Gravimetric determination is carried out by weighing the ppt. formed on boiling. J. D. R.

Use of drop analysis for investigation of medicaments. II. New test for amines, with especial consideration of *p*-phenylenediamine, and a new reaction for proteins. O. Frehden and L. Goldschmidt (Mikrochim. Acta, 1937, **1**, 338—353; cf. A., 1937, II, 476).—The formation of coloured Schiff's bases with furfuraldehyde (I) or p-$NMe_2{\cdot}C_6H_4{\cdot}CHO$ (II) in glacial AcOH provides a micro-test for primary and *sec.* amines. (I) gives mainly red to violet, and (II) orange-yellow to red, products. Colours and limiting sensitivities for numerous amines are tabulated. NH_2-acids, but not *tert.* amines, also react. The tests can be used with advantage in detecting adulteration of drugs and remedies; an example in which the adulterant was p-$C_6H_4(NH_2)_2$ is quoted. Primary aromatic amines can be detected by the formation of brown, red, or violet condensation products with a saturated AcOH solution of 5-nitroso-8-hydroxyquinoline or, with less sensitivity, with a 10% glacial AcOH solution of p-$NMe_2{\cdot}C_6H_4{\cdot}NO$. Condensed-ring systems such as $C_{10}H_7{\cdot}NH_2$ react best. Primary and *sec.* amines also yield coloured condensation products with a saturated solution of chloranil in dioxan; sensitivities and colours are tabulated. NH_2-acids and proteins do not react, but phenols interfere by giving red to violet colours. Free inorg. and org. bases must first be neutralised with AcOH. Aldehydes and carbohydrates are without effect. This test can be used on paper. (II) in glacial AcOH provides a test for proteins in presence of conc. HCl. L. S. T.

Effect of pyruvic acid on the determination of cystine and cysteine. M. X. Sullivan and W. C. Hess (J. Biol. Chem., 1938, **122**, 11—17).—$AcCO_2H$ has no effect on the colorimetric determination of cystine; in conc. solution it rapidly forms a complex with cysteine at p_H 6, which is decomposed by boiling for 10 min. with 2% HCl, yielding quant. vals. by the colorimetric method. P. G. M.

Chemistry of Jaffé's reaction for creatinine. A. Bolliger (J. Proc. Roy. Soc. New South Wales, 1937, **70**, 357—363).—Creatinine (1 mol.) in NaOH–EtOH and alcoholic picric acid (2 mol.) give an explosive red compound containing creatinine, picric acid, and NaOH (1 : 1 : 2 mol.), which is converted by HCl into the red isomeride of creatinine picrate, and is probably the red compound of Jaffé's reaction. A. Li.

Determination of phenanthrene. M. A. Ilinski and P. B. Roschal (Compt. rend. Acad. Sci. U.R.S.S., 1937, **17**, 120—124).—Determination of phenanthrene (I) (in mixtures with anthracene etc.) by prep., in xylene, of its picrate (which is weighed, and the amount in solution calc., after a second pptn. using the same mother-liquor) is not satisfactory.

Oxidation of phenanthraquinone (II) by CrO_3 varies with the amount of AcOH, H_2O, or H_2SO_4 present. Separation of (II) through its H sulphite compound is not complete, but (II) can be separated fairly well from anthraquinone by means of its oxime. The use of this to determine (I) will depend on a quant. method of oxidising (I) to (II). E. W. W.

Microchemical detection of some phenols. E. Eegriwe (Mikrochem., 1937, **23**, 173—175).—PhOH and *o*-cresol give rose-pink colorations when warmed with *m*-NO_2·C_6H_4·CHO and 63% H_2SO_4 at 65°. Other phenols give less sp. colorations or do not react. Orcinol gives a green fluorescence when treated with 1 : 2 : 4-CHO·$C_6H_3(OH)_2$ in HCl and then made alkaline. Other phenols do not react or give non-sp. fluorescence. J. S. A.

Determination of nitrogen in picric acid with hydrogen peroxide in strongly alkaline solution. A. Lecco and L. Lilić (Bull. Soc. Chim. Yougoslav., 1937, **8**, 77—82).—Utz's method gives results 2·5% too low with picric acid. Results for other NO_2-compounds are also tabulated. F. L. U.

Use of polarographs in determining ketones. G. T. Borcherdt, V. W. Meloche, and H. Adkins (J. Amer. Chem. Soc., 1937, **59**, 2171—2176).—The procedure described by Winkel and Proske (A., 1937, I, 152) is applied to mixtures of COPhMe and *p*-C_6H_4Cl·COMe. 0·001—1 mg. may be determined by comparison with the wave heights of standard solutions, the error being <2%. Methods of measuring polarographs are compared. F. R. G.

Spectrographic determination of 2-acetylpyrrole. S. A. Schou and M. Tønnesen (Dansk Tidsskr. Farm., 1937, **11**, 344—348).—2-Acetylpyrrole may be determined spectrographically by its maxima at 2810 A. in Et_2O, and 2880 A. in H_2O. In this way its partition coeffs. $H_2O/Et_2O = 0·13$ and H_2O/hexane = 5·5 have been measured. M. H. M. A.

Determination of diethylnicotinamide and bisdiethylphthalamide. K. A. Jackerott and F. Reimers (Dansk Tidsskr. Farm., 1937, **11**, 306—314).—*o*-$C_6H_4(CO·NEt_2)_2$, after 30 min. hydrolysis with boiling 2N-HCl, and *o*-C_5H_4N·CO·NEt_2 (I), untreated, are determined by Kjeldahl distillation and collection of the $NHEt_2$ in 0·1N-HCl. Care must be taken to avoid volatilisation of (I) and to ensure complete distillation of $NHEt_2$. M. H. M. A.

Determination of carbazole by its hydroxymethyl derivative. M. A. Iljinski and P. B. Roschal (Compt. rend. Acad. Sci. U.R.S.S., 1937, **17**, 117—120).—Carbazole (I) is determined by combining it with CH_2O to *N*-hydroxymethylcarbazole, hydrolysing this by heating with H_2O, oxidising the resulting CH_2O by Na_2O_2 to HCO_2Na, and titrating excess of NaOH. The method is satisfactory either with pure (I) or in presence of phenanthrene, anthracene, indole, or acridine. E. W. W.

Kapeller-Adler method for determining histidine.—See A., III, 151.

Action of potassium permanganate on sparteine. Effect on the determination of this alkaloid. A. Guillaume and (Mlle.) A. Proschell (Bull. Soc. Pharmacol., 1937, **44**, 475—478).—Sparteine is attacked by acidified $KMnO_4$, but only if an excess of $KMnO_4$ is present. Bourcet and Dugué's method (*ibid.*, 1930, **37**, 49) of determining sparteine is thus valid (cf. Jaretsky *et al.*, A., 1934, 708). R. S. C.

Indirect determination of cocaine in mixtures of cocaine and novocaine. S. N. Chakravarti and M. B. Roy (Current Sci., 1937, **6**, 219—220).—Novocaine (I) is determined as follows, and the cocaine (II) found by difference: an aq. solution of 2—10 mg. of mixture is treated with a slight excess of $NaNO_2$ in presence of a slight excess of dil. H_2SO_4, and 5 c.c. of 10% NaOH and 1 c.c. of 1% β-$C_{10}H_7$·OH are added; the colour produced is matched against suitable standards. M.p. data and curve are given for mixtures of hydrochlorides of (I) and (II). J. N. A.

Microchemical reaction for differentiating strychnine and brucine. A. Martini (Mikrochem., 1937, **23**, 164—167).—The alkaloids are distinguishable from the characteristic habit of the ppts. given with $RhCl_3$. J. S. A.

Comparative microscopic tests of anabasine and its related compounds, its purification, and some physical constants. A. G. Sokolov (Mikrochem., 1937, **23**, 147—148; cf. Zerbey *et al.*, A., 1937, II, 314).—Polemical. Pure anabasine is readily prepared and identified by means of its salt with H_2SiF_6. J. S. A.

Determination of thiol groups in proteins. R. Kuhn and P. Desnuelle (Z. physiol. Chem., 1938, **251**, 14—18; cf. A., 1935, 1252; Todrick and Walker, A., 1937, III, 130).—Thiol groups (*e.g.*, in native or denatured proteins) are determined colorimetrically by treatment with freshly prepared aq. solution of porphyrindine (porphyrexide acts in the same way but its colour interferes) which quantitatively dehydrogenates thiol to disulphide groups at room temp. The protein of the yellow enzyme and native ovalbumin contain no thiol groups but heat-denatured ovalbumin contains 0·58% of cysteine. W. McC.

Determination of amino-nitrogen in insoluble proteins. H. A. Rutherford, M. Harris, and A. L. Smith (J. Res. Nat. Bur. Stand., 1937, **19**, 467—477).—When treated with HNO_2, proteins and other NH_2-compounds liberate N_2 in two stages. The initial rapid stage or blank, which is due to spontaneous decomp. of HNO_2, depends on p_H, the size of the blank increasing with decreasing p_H. The blank is decreased by approx. 80% by means of a AcOH–NaOAc buffer of p_H 3·4—4·0. In the second stage, the rate at which N_2 is evolved decreases with increase in p_H. Extrapolation to zero time of the straight-line portions of time–N_2 evolved curves is considered to give vals. for the NH_2 content of proteins which are trustworthy and, for cryst. egg-albumin and collagen, compare favourably with vals. otherwise obtained. C. R. H.