BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

DECEMBER, 1940.

Preparation and properties of aliphatic hydrocarbons. L. SCHMERLING, B. S. FRIEDMAN, and V. N. IPATIEV (J. Amer. Chem. Soc., 1940, **62**, 2246—2249).—Hydrogenations below are effected in presence of Ni–kieselguhr at 100 kg. per sq. cm. $COMe{\cdot}CH{:}CMe_2$ and H_2 at 150° give $CHMeBu^{\beta}{\cdot}OH$ (70%), b.p. 128—131° (with 28% of $COMeBu^{\beta}$, b.p. 115—117°), dehydrated by Al_2O_3 (activated in this and other cases) at 427° to β-methylpentenes, b.p. 55—56°, which with H_2 at 50° give $CHMe_2Pr^{\alpha}$, b.p. 59·4—59·6°/750 mm., octane no. 71·5. Hydrogenation of $COMe{\cdot}CH_2{\cdot}CMe_2{\cdot}OH$ gives $OH{\cdot}CHMe{\cdot}CH_2{:}CMe_2{\cdot}OH$ (II), b.p. 194—195°, with much $Pr^{\beta}OH$. With Al_2O_3 at 427°, (I) gives, by way of the epoxy-compound, much MeCHO and $CMe_2{:}CH_2$ with some $COMe_2$ and $CHMe{:}CH_2$. With H_2–Cu–Ni at 200°, (I) gives only $Pr^{\beta}OH$. Hydrogenation of $COMeBu^{\gamma}$ at 200° gives $CHMeBu^{\gamma}{\cdot}OH$ (100%); $CHMeBu^{\gamma}{\cdot}OAc$ at 450° gives 90% of $CHBu^{\gamma}{:}CH_2$, b.p. 41—42°, hydrogenated in presence of Ni–Cu (not other catalysts) at 250° to a mixture of Pr^{β}_2 (85%), b.p. 57·4—57·5°/745 mm., octane no. 94, and $EtBu^{\gamma}$, b.p. 49·4—49·5°/753 mm., octane no. 93. $(CMe_2{\cdot}OH)_2$ and Al_2O_3 at 427° give 55—70% of $(CH_2{:}CMe)_2$, b.p. 68—70° (with 25—30% of $COMeBu^{\gamma}$), which with H_2 gives Pr^{β}_2, also obtained from $COMeBu^{\gamma}$ by way of $CHMeBu^{\gamma}{\cdot}OH$ and ($H_2C_2O_4$; 110—120°) $CMePr^{\beta}{:}CH_2 + (CMe_2{:})_2$. Hydrogenation (Ni–kieselguhr or Ni–Cu) of $CHMeBu^{\gamma}{\cdot}OH$ gives mixtures. $COMeBu^{\gamma}$ and MgMeBr give 85% of $CMe_2Bu^{\gamma}{\cdot}OH$, b.p. 128—129°, and thence (Al_2O_3–NiO; H_2; 250—260°/100 kg. per sq. cm.) $Pr^{\beta}Bu^{\gamma}$, b.p. 80·5—81°/748 mm., octane no. 100. Similarly, $(CMeEt{\cdot}OH)_2$ (prep. from COMeEt and Mg), b.p. 94—95°/10 mm., gives $(CHMeEt)_2$, b.p. 118—118·3°/750 mm., octane no. 84·5, and $CHMeEtBu^{\gamma}$, b.p. 110—110·5°/749 mm., octane no. 100. With Al_2O_3 at 325°, (II) gives $CMe_2{:}CMePr^{\beta}$, b.p. 114·5—114·9°/749·5 mm., and thence $CHMePr^{\beta}_2$, b.p. 112·3—112·4°/736 mm., octane no. 94·5. R. S. C.

High-temperature chlorination of paraffin hydrocarbons. W. E. VAUGHAN and F. F. RUST (J. Org. Chem., 1940, **5**, 449—471).—Mixtures of C_2H_6, C_2H_4, C_3H_8, EtCl, $Pr^{\alpha}Cl$, $Pr^{\beta}Cl$, or EtBr with Cl_2 diluted with CO_2 or N_2 are freed from O_2 by $CrSO_4$ or $CrCl_2$ and passed through heated tubes in the absence of light. The effluent mixtures are analysed by titration or by distillation. In the chlorination of C_2H_6 at moderate temp. reaction is expressed $d[HCl]/dt = k[Cl_2][C_2H_6]$ and the scheme $Cl_2 \rightarrow Cl + Cl$, $Cl + C_2H_6 \rightarrow C_2H_5 + HCl$, $C_2H_5 + Cl_2 \rightarrow EtCl + Cl$; $Cl + W \rightarrow$ chain ending. The chain nature of the reaction is further demonstrated by the inhibiting action of O_2. At or near the temp. at which uncontrollable reaction would occur in the absence of O_2 production of HCl occurs according to $d[HCl]/dt = k[Cl]^{1/2}[C_2H_6]^{3/2}/[O_2]$. Chlorination of C_2H_6 is highly dependent on the surface, which appears to produce Cl atoms and to terminate chains. Chlorination of C_3H_8 is very similar to that of C_2H_6. At ~250° approx. equal proportions of $Pr^{\alpha}Cl$ and $Pr^{\beta}Cl$ are formed. $Pr^{\alpha}Cl$ gives all three chlorides, the *sec.* H atoms being very reactive despite their smaller no. $Pr^{\beta}Cl$ is less reactive than $Pr^{\alpha}Cl$ probably because it has only one *sec.* H. EtCl is less reactive than C_2H_6. Large proportions of C_2H_4 are obtained at >280°; at 415° in absence of halogen but under otherwise comparable conditions EtCl scarcely yields C_2H_4 and HCl. The principal product is probably a consequence of a radical chain, $Cl + EtCl \rightarrow HCl + C_2H_4Cl$; $C_2H_4Cl + Cl_2 \rightarrow C_2H_4Cl_2 + Cl$. Small amounts of O_2 suppress the action almost completely whilst at higher temp. some change occurs. $CH_2{:}CHCl$, unsaturated dichloride, $CHMeCl_2$, $CMeCl_3$, and $(CH_2Cl)_2$ are also formed. EtBr at 278° affords EtCl, EtBr, C_2H_4, and a little C_2H_4ClBr. In mixtures of C_2H_6 and C_2H_4 the former is dominantly or almost exclusively the reactive component. The production of $CH_2{:}CH{\cdot}CH_2Cl$ from $CH_2{:}CHMe$ is thus explained. Chlorination of C_2H_6, C_3H_8, and *cyclo*pentane in the gas phase and of n-C_5H_{12} in the liquid phase is accelerated by $PbEt_4$. C_2Ph_6 is a useful catalyst in the liquid phase whilst CH_2N_2 is somewhat less effective than $PbEt_4$ in the gaseous state. H. W.

High-temperature chlorination of olefine hydrocarbons. F. F. RUST and W. E. VAUGHAN (J. Org. Chem., 1940, **5**, 472—503).—Dynamic studies of the interaction of C_2H_4 and Cl_2 can be made only in presence of a diluent (N_2). At 308° the total amount of addition is ⩾ that of substitution whereas at 346° the substitutive steps are dominant. The mol. % of tri- and tetra-chlorides are relatively const. and the principal variations are in the amounts of unsaturated and simple additive products. The formation of higher chlorides from $CH_2{:}CHCl$ is important in this connexion. At 485° there is extensive decomp. accompanied by formation of C_2H_2 undoubtedly by elimination of HCl from $CH_2{:}CHCl$. A simple relationship between rate of reaction and concn. of reactants could not be adduced. At low temp., where only addition occurs, increased surface causes an increase in the amount of reaction, probably as a result of catalysed bimol. association as well as initiation of chains. Glass wool is particularly effective. At higher temp. surface suppresses reaction, probably as a consequence of the termination of chains initiated in the gas phase. The chains

involve both addition and substitution at these temp. Controlled inhibition by O_2 does not persist to so high a temp. with olefines as with paraffins. The chain character of the gas-phase addition and substitution of olefines under certain conditions is further confirmed by the acceleration caused by $PbEt_4$; results with $CHMe{:}CH_2$ are even more striking. Other reactions unaffected by O_2 are association at the surface, gas-phase bimol. association, and gas-phase bimol. metathesis. Under analogous conditions $CHMe{:}CH_2$ yields mainly $CHMeCl{\cdot}CH_2Cl$ and $CH_2{:}CH{\cdot}CH_2Cl$. $CMe_2{:}CH_2$ at higher temp. reacts by addition and substitution. Below 240°, above which the reaction becomes violent, all activity is suppressed by 5% of O_2, showing that both changes involve radical chain mechanism. Low $[O_2]$ strongly catalyses the substitution of Cl into olefines whereas larger concns. cause the expected inhibition. Experimental conditions, especially temp., are very important in defining the magnitude of the effect, which appears to be much more pronounced although more critically dependent on the catalyst concn. with C_2H_4. $CHMe{:}CH_2$ and $(CHMe{:})_2$ are also subject to positive catalysis by O_2 but to a smaller extent. C_2H_6 is a powerful inhibitor of the O_2-catalysed Cl-substitution into olefines. The rate of production of HCl by substitution seems to vary linearly with $[C_2H_4]^2$, $[Cl_2]$, and $[O_2]$ for very small concns. The mechanism is one of chain initiation by radicals produced by interaction of olefine and O_2 rather than reaction of an association complex itself with Cl. Olefines act as inhibitors of the high-temp. chlorination of paraffins; $CHMe{:}CH_2$ appears the most effective. H. W.

Mechanism of polymerisation. V. Dimerisation of unconjugated pentadiene. A. Ahmad and E. H. Farmer (J.C.S., 1940, 1176—1178). —$\Delta^{\alpha\delta}$-Pentadiene (I) with 15% BF_3 in AcOH (24 hr.) gives iso*pentenyl acetate* (?), b.p. 138°, and $OAc{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}OAc$ (?). In light petroleum at −15° and 0°, BF_3 does not polymerise (I); with undiluted (I) it gives an undistillable polymeric oil. Below 225°, (I) alone does not polymerise. Under N_2 in an autoclave, (I) at 250° gives 15% polymerisation (7—8% of dimeride), and at 280—290°, 90% polymerisation (25% of di-, 10—15% of tri-, and 60—65% of higher poly-merides). Fractionation gives a dimeride (II), $C_{10}H_{16}$, b.p. 176° (mainly 1-methyl-2-allyl*cyclo*hexene), and a trimeride, b.p. 120—122°/1 mm. In $COMe_2$, (II) is oxidised by 4% aq. $KMnO_4$ to HCO_2H and an oily acid. Vapour of (II) with Pd–C at 178—181° gives an oil, b.p. 185°, of composition $\sim C_{10}H_{15}$ (C_6H_4MePr + methylpropyl*cyclo*hexane or dimethyldi*cyclo*octane), oxidised to *o*-$C_6H_4(CO_2H)_2$. Possible mechanisms are discussed. E. W. W.

Synthesis of polyenes. II. Reactions of β-methylallyl chloride with sodamide in liquid ammonia. M. S. Kharasch, W. Nudenberg, and E. Sternfeld (J. Amer. Chem. Soc., 1940, **62**, 2034—2036; cf. A., 1939, II, 498).—$CH_2{:}CMe{\cdot}CH_2Cl$ (I) (1·5) and $NaNH_2$ (1·7 mols.) in NH_3 give 27% of βε-*dimethyl*-n-*hexadiene* (II), m.p. −9°, b.p. 90·2°/200 mm. (cf. Bourguel *et al.*, A., 1930, 574), hydrogenated to Bu^{β}_2 and adding $(CH{\cdot}CO)_2O$ (III) in C_6H_6 at 80° to give 5-*methyl*-3-iso*propenyl*-1 : 2 : 3 : 6-*tetrahydrophthalic anhydride* (IV), m.p. 115—116°. $NaNH_2$ (0·88) and (I) (1 mol.) give α-*chloro*-βε-*dimethyl*-n-*hexadiene*, b.p. 33—34°/5 mm., 160°/752 mm. [with (III) gives (IV); with $NaNH_2$ gives (II)], and some (II). $CH_2{:}CH{\cdot}CH_2Cl$ (1) and $NaNH_2$ (0·5 mol.) give a *chlorohexadiene*, b.p. 46—47·5°/96 mm., and 30% of chloromethylvinyl*cyclo*hexene. The ultra-violet and infra-red absorption of (II) are determined. R. S. C.

Partial reduction of acetylenes to olefines by use of an iron catalyst. A. F. Thompson, jun., and S. B. Watt (J. Amer. Chem. Soc., 1940, **62**, 2555—2556).—Fe catalyst prepared from Fe–Al alloy and NaOH in EtOH at 100°/1000 lb. is excellent for reduction of acetylenes to olefines. Examples are $(C{\cdot}CMe_2{\cdot}OH)_2$ and $CH{:}C{\cdot}CMe{:}CH_2$ (gives $CH_2{:}CH{\cdot}CMe{:}CH_2$), but C_2Ph_2 gives $(CH_2Ph)_2$. R. S. C.

Fluorinated derivatives of ethane and ethylene. VI. Corrective data. A. L. Henne and E. G. Wiest (J. Amer. Chem. Soc., 1940, **62**, 2051—2052; cf. A., 1934, 1689).—The following data are recorded and shown to accord with expectation. $CCl_2{:}CF_2$, b.p. 18·9—19·0° (corr.). $CCl_3{\cdot}CClF_2$, m.p. 40·6°, b.p. 91·5°. $CCl_2Br{\cdot}CBrF_2$, f.p. 45·5°, b.p. 138·8—139·0° (corr.). $(CClBrF)_2$, f.p. 32·9—32·6°, b.p. 139·8—140·0° (corr.). $CCl_3{\cdot}CF_3$, f.p. 14·2°, b.p. 45·9° (corr.). R. S. C.

Peroxide effect in addition of reagents to unsaturated compounds. XXV. Effect of metals on the addition of hydrogen bromide to allyl bromide. M. S. Kharasch, W. R. Haefele, and F. R. Mayo (J. Amer. Chem. Soc., 1940, **62**, 2047—2051; cf. A., 1940, II, 61).—Promotion of abnormal additions by metals depends on ready reaction of the metal with HBr, and inability of the halide to promote the normal reaction or hinder the abnormal one. This is demonstrated for Fe, HBr, and $CH_2{:}CH{\cdot}CH_2Br$, and by the varying results with other metals. Fe induces also abnormal addition of HBr to $CH_2{:}CH{\cdot}CH_2Cl$. The reaction mechanism (discussed) is that for reaction without Fe. The mechanism proposed by Urushibara *et al.* (A., 1938, I, 628) for the normal addition is refuted. R. S. C.

Melibiotol and maltitol. M. L. Wolfrom and T. S. Gardner (J. Amer. Chem. Soc., 1940, **62**, 2553—2555).—Melibiose and H_2–Ni–kieselguhr in H_2O at 150°/190 atm. give melibiotol, m.p. 173° (lit., a syrup), $[\alpha]^{24}$ +116° in H_2O (*nonabenzoate*, m.p. 157°, $[\alpha]^{25}$ +123° in $CHCl_3$), hydrolysed to *d*-galactose and sorbitol. Maltitol nona-acetate is obtained cryst., having m.p. 86—87°, $[\alpha]^{20}$ +84° in $CHCl_3$ (cf. Karrer *et al.*, A., 1937, II, 83). Most of the $[\alpha]$ of these and similar α-glucosides is due to the lactol C. R. S. C.

Synthesis of esters of phosphoric acid related to phosphatides. H. N. Christensen (J. Biol. Chem., 1940, **135**, 399—401).—H_3PO_4 and $(CH_2)_2NH$ at 105° yield *aminoethyl* H_2 *phosphate*, m.p. 240° (decomp.). Cetyl alcohol in boiling CCl_4 yields, with $POCl_3$, cetyl, and with $Cl{\cdot}[CH_2]_2{\cdot}POCl_2$, β-*chloroethyl cetyl H phosphate*, m.p. 54·5°, converted by EtOH–NH_3 in a sealed tube at 110° into β-*aminoethyl cetyl H*

phosphate, m.p. 226° (decomp.) (corr.). All these acids are purified through the Ba salts. A. LI.

Factors influencing polysulphone formation. M. S. KHARASCH and E. STERNFELD (J. Amer. Chem. Soc., 1940, **62**, 2559—2560).—Ascaridole + aq. or alcoholic mineral acid catalyses formation of *polysulphones*, decomp. 210—235°, m.p. 125—160° (decomp.), and decomp. 245—265°, from CH_2:CH·CH_2Cl, CMe_2:CHMe, or CH_2:CHCl, respectively. CH_2:CH·CH_2Br and, more so, CHPh:CH·CH_2Br are inhibitors for this reaction. C_2HCl_3 and CMe_2:CHBu$^\gamma$ do not form polysulphones, but are not inhibitors. Other chain-breakers do not act as inhibitors. R. S. C.

Structure of compounds containing S–O and S–Cl bonds.—See A., 1940, I, 434.

Preparation of trioctoin. J. L. HARTWELL (Amer. J. Path., 1940, **16**, 313—316).—The prep. of pure *n*-C_7H_{15}·COCl and its condensation with glycerol in the presence of C_5H_5N to yield trioctoin are described. C. J. C. B.

Direct esterification of higher fatty acids with glycerol. III. Formation of mono- and di-stearin. S. KAWAI and H. NOBORI (J. Soc. Chem. Ind. Japan, 1940, **43**, 170B; cf. A., 1940, II, 336).—Stearic acid with 1·2 or 1·4 mols. of glycerol at 180° for several hr., then at 240—245° for 0·5—1 hr., yields mono- (20%) and di-stearin (up to 70%). A part of the product from commercial stearin sol. in 85% EtOH at 60° has emulsifying properties. A. LI.

Condensations. XIII. Alkylation of ethyl *iso*-butyrate and other esters by means of sodium triphenylmethyl and alkyl halides. B. E. HUDSON, jun., and C. R. HAUSER (J. Amer. Chem. Soc., 1940, **62**, 2457—2459).—CHR_2·CO_2Et, CPh_3Na, and R′I give good yields of CR_2R'·CO_2Et. Pr$^\beta CO_2Et$ thus gives 58% of CMe_2Et·CO_2Et, 42% of CH_2Ph·CMe_2·CO_2Et, and 55% of Bu$^\gamma CO_2Et$. CHMeEt·CO_2Et, b.p. 132° (corr.) (lit., 133·5°), gives 61% of *Et α-methyl-α-ethyl*-n-*valerate*, b.p. 81° (corr.)/20 mm. Bu$^\beta CO_2Et$ gives 22% of CHEtPr$^\beta$·CO_2Et. EtOAc, CH_2PhCl, and CPh_3Na do not react. R. S. C.

Compounds of lead halides with organic salts.—See A., 1940, I, 444.

Oxidation of [long-chain] unsaturated fatty acids.—See B., 1940, 725.

Linolenic acid and its isomerides. J. W. MCCUTCHEON (Canad. J. Res., 1940, **18**, B, 231—239; cf. A., 1938, II, 347).—Linolenic acid (prepared by a modification of Rollet's method, using Et_2O instead of AcOH), m.p. −16·25° to −17°, with Br in Et_2O yields the cryst. hexabromide (I), m.p. 181·9° (corr.), and two isomerides (sol. in Et_2O, separated by *iso*-C_5H_{11}·OH), one gummy, m.p. 145—150°, and the other liquid, both debrominated to an acid identical with that obtained from (I), and (?) with the natural acid. B.p./2·5—6·5 mm., *d*, *n*, and I val. of the Et ester are recorded. A. LI.

Action of lead tetra-acetate on hydroxylated fatty acids and related compounds. I. Hydroxylated oleic acid, ethyl oleate, and oleyl alcohol. II. Hydroxylated ricinoleic acid and castor oil. J. T. SCANLAN and D. SWERN (J. Amer Chem. Soc., 1940, **62**, 2305—2309, 2309—2311).—I. Hydroxylation of Et oleate, oleic acid, and oleyl alcohol is improved and the products are converted in AcOH by Pb_3O_4 into C_8H_{17}·CHO and CHO·$[CH_2]_7$·R (R = CO_2Et, CO_2H, or CH_2·OH). The effect of impurities on yields is described. Yields are poor with olive, peanut, and lard oils.

II. Hydroxyation and Pb_3O_4–AcOH oxidation of castor oil (not ricinoleic acid) gives CHO·$[CH_2]_7$·CHO, glycerol, and C_6H_{13}·CH:CH·CHO, b.p. 56—58°/0·1 mm. [semicarbazone, new m.p. 165—165·5°; 2 : 4-*dinitrophenylhydrazone*, m.p. 126°, previously reported (m.p. 124°) as derived from C_6H_{13}·CH(OH)·CH_2·CHO; oxidised by air to the acid, m.p. 0—1°, b.p. 135—138°/5 mm. (p-*phenylphenacyl* ester, m.p. 77·5—78°; amide, new m.p. 130—130·5°)]. R. S. C.

Action of hydrogen bromide and oxygen on various ethenoid compounds and the influence of pyrocatechol. O. SIMAMURA (Bull. Chem. Soc. Japan, 1940, **15**, 292—297).—A mixture of HBr and O_2 in the dark has no effect on solutions of C_2Ph_4, dimethylmaleic anhydride, or phenanthrene in C_6H_6. With Et αγ-dicarbethoxy-α-bromoglutaconate (I) in CCl_4, Br is liberated. With Et_2 αγ-dicarbethoxy-α-methylglutaconate in CCl_4 little Br is liberated and the product contains Br corresponding with the addition of a mol. of HBr. With CH_2:CPh_2 Br is liberated. Me_2 dimethylmaleate and Me_2 dimethylfumarate (II) behave as does (I). With the compound $C_{30}H_{42}O_{16}$, m.p. 86° (Guthzeit and Hartmann, A., 1910, i, 386), in CCl_4, Br is liberated. These reactions accord with the mechanism suggested by Urushibara *et al.* (A., 1938, II, 401). *o*-$C_6H_4(OH)_2$ markedly inhibits the reaction with (II) and with allyl bromide, presumably by suppressing the initial reaction of the chain. F. J. G.

Sulphonation reactions with sulphuryl chloride. II. Photochemical sulphonation of aliphatic acids with sulphuryl chloride. M. S. KHARASCH, T. H. CHAO, and H. C. BROWN (J. Amer. Chem. Soc., 1940, **62**, 2393—2397; cf. A., 1940, II, 3).—SO_2Cl_2 with lower aliphatic acids (except AcOH) in light gives β- or γ-sulphocarboxylic anhydrides and with higher acids gives sulphonyl chlorides by substitution in other positions. Varying amounts of Cl-acids are also obtained. A reaction mechanism is postulated involving Cl atoms and org. radicals. Properties of the anhydrides are reported. β-*Sulphopropionic* (I), m.p. 76—77°, and -iso*butyric anhydride*, b.p. 135—145° (decomp.)/3—5 mm., and (? β- or γ-) *sulpho*-n-*butyric anhydride*, an oil, are thus obtained. Bu$^\beta CO_2H$, *cyclo*hexanecarboxylic, and lauric acids give 25—60% of RSO_2Cl. *NH_2Ph sulphonanilido*-cyclo*hexanecarboxylate* is described. With H_2O the anhydrides give sulphocarboxylic acids, with NH_2Ph in C_6H_6 they give *NH_2Ph propion-*, m.p. 216°, and iso*butyr-anilide*-β-*sulphonate*, decomp. 238°, and -n-*butyranilide*-β- + -γ-*sulphonates*; with liquid NH_3, (I) gives *NH_4 propionamide*-β-*sulphonate*, m.p. 179°. R. S. C.

Derivatives of methylacraldehyde. R. L. SHRINER and A. G. SHARP (J. Amer. Chem. Soc.,

1940, **62**, 2245).—CH_2:CMe·CHO gives a *semicarbazone*, m.p. 197·5—198°, *p-nitro-*, m.p. 161—163°, and 2 : 4-*dinitro-phenylhydrazone*, m.p. 206—206·5°, and 1-*phenyl*-4-*methyl*-Δ^2-*pyrazoline*, m.p. 73—74°. R. S. C.

β-Diketones. Synthesis, structure, and bactericidal properties. C. D. Hurd and C. D. Kelso (J. Amer. Chem. Soc., 1940, **62**, 2184—2187).—Claisen condensation of COMeBu^a or COMe·C_6H_{13} with EtOAc gives COMe·CH_2·COBu^a (II), b.p. 83—85°/21 mm., and COMe·CH_2·CO·C_6H_{13}-*n*, b.p. 129—131°/33 mm., respectively. (II) is obtained (10%) also from CH_2Ac·COCl (III) and MgBu^{a}Br in Et_2O–N_2 at −25° and its structure is confirmed by condensation with N_2H_4 and oxidation of the product by $KMnO_4$ to pyrazole-3 : 5-dicarboxylic acid; with NH_2·CO·NH·NH_2 it gives 3-*methyl*-5-n-*butylpyrazole*-1-*carboxylamide*, m.p. 89—90°. *n*-C_7H_{15}·MgBr or *n*-C_8H_{17}·MgBr with (III) gives hendecane-, b.p. 93—95°/2—3 mm. (lit., 118°/5 mm.), and dodecane-βδ-dione, b.p. 104—105°/2—3 mm. (lit., 150°/15 mm.), respectively. *n*-C_6H_{13}·CHMe·MgBr and (III) give ε-*methylhendecane*-βδ-*dione*, b.p. 101—102°/2 mm. MgBu^{a}Br with (III) in Et_2O-air at −50° gives CH_2Ac·CO_2Bu^a, b.p. 95°/15 mm. (*semicarbazone*, m.p. 102°), also obtained from CHAc:CO and Bu^{a}OH. CHMe:CH·CO_2Et, (I), and NaOEt in xylene give 53% of Δ^β-*dodecene*-δζ-*dione*, m.p. 98—99°, with some CHMe[C(:CHMe)·CO_2Et]$_2$, b.p. 110—114°/5 mm. CH_2:CH·CO_2Et, (I), and NaOEt–EtOH give 54% of Δ^α-*hendecene*-γε-*dione*, m.p. 69—70°. In spite of formal resemblance of the dienolic forms of the diketones to alkylresorcinols, the saturated ketones are only weak bactericides against *B. typhosus* and ineffective against *S. aureus*. The unsaturated ketones are mildly effective against both organisms. R. S. C.

Reduction of aldoses at the dropping mercury cathode. Determination of the *aldehydo*-form in aqueous solutions. S. M. Cantor and Q. P. Peniston (J. Amer. Chem. Soc., 1940, **62**, 2113—2121).—Aldoses are reduced at the dropping Hg cathode, owing to presence of the *aldehydo*-form in highly mobile equilibrium with the cyclic forms. The amounts thus determined for four hexoses and four pentoses are correlated with rates of mutarotation. The amounts are very small except for allose and ribose. They are greater for pentoses than for hexoses, but in both cases are greatly influenced by configuration. R. S. C.

Mutarotation of *d*-glucose in absolute methanol and in ethanol–water mixtures.—See A., 1940, I, 442, 443.

Derivatives of the aldehydrol form of sugars. III. Carbon one asymmetry. M. L. Wolfrom, M. Konigsberg, and F. B. Moody (J. Amer. Chem. Soc., 1940, **62**, 2343—2349; cf. A., 1938, II, 126).—Demercaptalation (method: A., 1939, II, 202) of *d*-mannose Et_2 mercaptal penta-acetate (I) gives aldehydo-d-*mannose penta-acetate aldehydrol* (II), +$COMe_2$, m.p. 68—70°, $[\alpha]_D^{22}$ +24° → +9° in $CHCl_3$, $[\alpha]_D^{23}$ +26° (stable) in H_2O, which in air at < room temp. loses $COMe_2$ and gives a syrup (III). In MeOH, (III) gives aldehydo-d-*mannose penta-acetate Me semiacetal*, m.p. 102—104°, $[\alpha]_D^{23}$ +27·5° → +17° in $CHCl_3$, also obtained from (I) and converted by Ac_2O–H_2SO_4 into *aldehydo-d*-mannose hepta-acetate. *aldehydo-d*-Galactose penta-acetate aldehydrol has $[\alpha]_D^{20}$ +4° (stable) in H_2O. AcBr and (III) at room temp. give 1-*bromo*-aldehydo-d-*mannose hexa-acetate*, m.p. 115—116°, $[\alpha]_D^{22}$ +92° in $CHCl_3$. 1-*Bromo*-aldehydo-l-*rhamnose penta-acetate*, m.p. 112—113°, $[\alpha]_D^{25}$ −103° in $CHCl_3$, is similarly prepared. *aldehydo-d*-Mannose penta-acetate with Ac_2O–C_5H_5N at 0°, followed by 50% MeOH, gives α-l-*methoxy*-aldehydo-d-*mannose hexa-acetate*, m.p. 84—85°, $[\alpha]_D^{28}$ +23° in $CHCl_3$, and thence (Ac_2O–AcOH–$ZnCl_2$, followed by 50% MeOH) the β-*isomeride*, m.p. 95·5—96°, $[\alpha]_D^{31}$ +11° in $CHCl_3$, and ($AlCl_3$–$CHCl_3$) 1-*chloro*-l-*methoxy*-aldehydo-d-*mannose penta-acetate*, m.p. 116—118°, $[\alpha]_D^{28}$ +71° → +25° in 24 hr. in $CHCl_3$. α-, m.p. 103—104°, $[\alpha]_D^{24}$ +3·8°, and β-1-*Methoxy*-aldehydo-d-*glucose hexa-acetate*, m.p. 61—62°, $[\alpha]_D^{25}$ −3° in $CHCl_3$, α- (IV), m.p. 101°, $[\alpha]_D^{23}$ +3·5° in $CHCl_3$, and β-l-*methoxy*-aldehydo-d-*galactose hexa-acetate* (V), m.p. 123—124°, $[\alpha]_D^{22}$ +2·1° in $CHCl_3$, α-, m.p. 67—68°, $[\alpha]_D^{20}$ −34° in $CHCl_3$, and β-l-*methoxy*-aldehydo-l-*arabinose penta-acetate*, m.p. 76—77°, $[\alpha]_D^{23}$ −27° in $CHCl_3$, are prepared with the fully acetylated *aldehydo*-forms from the appropriate semiacetal. HCl–Et_2O at 0° converts (IV) or (V) into 1-chloro-1-methoxy-*aldehydo-d*-galactose penta-acetate, m.p. 155—156°, $[\alpha]_D^{25}$ −38° → +15° in 24 hr. in $CHCl_3$, $[\alpha]_D^{26}$ −53° → −42·5° in 10 hr. in C_6H_6; the corresponding OEt-compound suffers replacement of Cl by OH during all reactions in "anhyd." solvents. *l*-Arabinose Me_2 mercaptal tetra-acetate, $CdCO_3$, and $HgCl_2$ in boiling, abs. MeOH give the *Me_2 acetal tetra-acetate*, m.p. 81°, $[\alpha]_D^{20}$ −22° in $CHCl_3$, converted by 0·1N-NaOMe into l-*arabinose Me_2 acetal*, m.p. 121—122°, $[\alpha]_D^{22}$ +20° in H_2O; the *Et_2 acetal*, m.p. 109°, $[\alpha]_D^{22}$ +16° in H_2O, and its *acetate*, m.p. 59°, $[\alpha]_D^{23}$ −17·5° in $CHCl_3$, are similarly prepared. 1-Bromo-*aldehydo-d*-galactose hexa-acetate and Ag_2CO_3 in boiling abs. EtOH give *aldehydo-d*-galactose Et semiacetal. d-*Gluco*-d-*guloheptose Et_2 mercaptal hepta-acetate*, m.p. 99—100°, $[\alpha]_D^{25}$ −12° in $CHCl_3$, is obtained from the mercaptal by Ac_2O–C_5H_5N. R. S. C.

Use of the benzyl radical in synthesis of methylated sugars. II. 4 : 6-Dimethylgalactose. J. S. D. Bacon, D. J. Bell, and J. Lorber (J.C.S., 1940, 1147—1150).—That the dimethylgalactose obtained by Hirst *et al.* (cf. A., 1939, II, 495) from damson gum is not 4 : 6-*dimethyl*-α-*galactose* (I), m.p. 131—133°, $[\alpha]_D^{12}$ +133° → 76·9° in H_2O, is proved by synthesis of (I). 4 : 6-Benzylidene-β-methylgalactoside 2 : 3-diacetate gives (cf. Bell *et al.*, A., 1940, II, 205) the 4 : 6-*CH_2Ph* derivative, m.p. 132·5—133·5°, $[\alpha]_D^{20\cdot5}$ +50·2° (this and subsequent rotations in $CHCl_3$), of 2 : 3-*dibenzyl*-β-*methylgalactoside*, m.p. 70—71°, $[\alpha]_D^{18}$ +10·6°, which yields (Purdie) a 4 : 6-*Me_2* derivative, m.p. 68—69°, $[\alpha]_D^{17\cdot5}$ +3·05°. This with Na in EtOH yields 4 : 6-*dimethyl*-β-*methylgalactoside* (II), m.p. 140°, $[\alpha]_D^{20}$ −41·5°, hydrolysed (N-HCl) to (I). 4 : 6-Benzylidene-β-methylgalactoside gives a 2 : 3-*di*-p-*toluenesulphonate*, m.p. 168—170°, $[\alpha]_D^{20}$ +29·5°, hydrolysed to β-*methylgalactoside* 2 : 3-*di*-p-*toluenesulphonate*, m.p. 149—150°, $[\alpha]_D^{19}$ +18·4°. Purdie methylation of this gives the 2 : 3-*di*-p-*toluenesulphonate*,

a syrup, [α] +5—6°, of (II), from which it is also obtained. In cold MeOH–HCl (I) shows increasing [α], indicating that furanoside is not formed, and that there is Me at $C_{(4)}$; further (Purdie) methylation, hydrolysis, and treatment with EtOH–NH_2Ph gives 2 : 3 : 4 : 6-tetramethylgalactose anilide, m.p. 196—197°. With $NHPh{\cdot}NH_2$, (I) gives its osazone, identical with that prepared from 2 : 4 : 6-trimethylgalactose. E. W. W.

***iso*Propylidene derivatives of the mercaptals of monosaccharides. V. 5 : 6-*iso*Propylidene derivative of *d*-galactose dibenzyl mercaptal and the 6-methyl derivative of *d*-galactose.** E. Pacsu and S. M. Trister (J. Amer. Chem. Soc., 1940, **62**, 2301—2304).—The mercaptal, m.p. 112·5°, $[\alpha]_D^{20}$ +17·4° in $CHCl_3$ (A., 1939, II, 494), is proved to be 5 : 6-*iso*propylidenegalactose $(CH_2Ph)_2$ mercaptal and the structure of 6-methylgalactose (II) (Munro *et al.*, A., 1936, 826) is confirmed. HgO–$HgCl_2$–EtOH etc. converts (I) into 5 : 6-iso*propylidene*-β-*ethylgalactofuranoside*, a syrup, $[\alpha]_D^{22}$ −70·0° in H_2O, which consumes 1 HIO_4 (giving no CH_2O) and with MeI–Ag_2O gives 2 : 3-*dimethyl*-5 : 6-iso*propylidene*-β-*ethylgalactofuranoside*, a liquid, stable to HIO_4 and converted by 0·05N-HCl at 90° into 2 : 3-dimethylgalactose (III), $[\alpha]_D^{22}$ +64·7° → +80·9° in 90 min. in H_2O, $[\alpha]_D^{20}$ +17·2° in $CHCl_3$ [anilide, m.p. 128—129° (lit. 130—131°)]. The structure of (III) is confirmed by consumption of 2 HIO_4 and conversion by $NHPh{\cdot}NH_2$–AcOH into 3-methylgalactosazone, m.p. 176—179°, $[\alpha]_D^{17}$ +63·5° in C_5H_5N. Galactose $(CH_2Ph)_2$ mercaptal and H_2SO_4–$COMe_2$ at 0° give the CMe_2 derivative, methylated as Na salt by MeI (twice) to the ether, which with boiling HCl–EtOH–H_2O gives 6-methylgalactose $(CH_2Ph)_2$ mercaptal, m.p. 130°, $[\alpha]_D^{18}$ −27·1° in C_5H_5N. With HgO–$HgCl_2$ etc. this gives 6-*methyl*-β-*methylgalactofuranoside*, a syrup, $[\alpha]_D^{20}$ −78·7° in H_2O, hydrolysed by boiling 0·05N-HCl to (II), m.p. 113—114°, $[\alpha]_D^{18}$ +137·2° → +77·0° in 6 hr. in H_2O [consumes 4 HIO_4; phenylhydrazone, m.p. 117·5° (lit., 182—183°, 179°), $[\alpha]_D^{26}$ +22·4° → +13·6° in 24 hr. in C_5H_5N; osazone, m.p. 200°, $[\alpha]_D^{26}$ +141·0° → +91·8° in 24 hr. in C_5H_5N]. R. S. C.

Synthesis of 1-β-glucosidofructose. E. Pacsu (J. Amer. Chem. Soc., 1940, **62**, 2568).—A question of priority. R. S. C.

Sterol glucosides from expressed soya-bean oil. M. H. Thornton, H. R. Kraybill, and J. H. Mitchell, jun. (J. Amer. Chem. Soc., 1940, **62**, 2006—2008).—Treatment of crude expeller soya-bean oil with Al silicate and elution of the latter with $COMe_2$ gives sterol *glucosides*, darken at 250—255°, m.p. 267—270° (decomp.) (*tetra-acetate*, m.p. 165—166°, $[\alpha]_D^{20}$ −24·5° in $CHCl_3$), which with H_2SO_4–EtOH give Et glucoside (identified by conversion into *d*-glucobenziminazole) and sterols resembling those of the oil and containing ~24% of stigmasterol. R. S. C.

Composition of hemicellulose isolated from maple wood. R. L. Mitchell and G. J. Ritter (J. Amer. Chem. Soc., 1940, **62**, 1958—1959).—Hemicellulose fractions are prepared from maple holocellulose by boiling H_2O, cold 2% Na_2CO_3, cold 4% NaOH, and boiling 10% NaOH, successively. The products are isolated by pptn. by EtOH (from the aq. extract also by $COMe_2$). Uronic anhydride, xylan, OMe, Ac, and $[\alpha]_D$ are recorded for each fraction. Approx. min. mol. wts. (from I val.) increase from 1070 to 10,500. R. S. C.

Chemistry of wood. VII. Esters and ethers of the water-soluble polysaccharides of larch wood. F. C. Peterson, A. J. Barry, H. Unkauf, and L. E. Wise (J. Amer. Chem. Soc., 1940, **62**, 2361—2365; cf. A., 1935, 478).—Arabogalactans (I) from Eastern, Western, and European larch wood are similar. Fractional pptn. of the undegraded acetate, propionate, and benzoate gives fractions of similar acyl content but differing [α], reducing val., η, and araban content. (I) is thus not homogeneous. A fully methylated product (44·1% OMe) is prepared by Me_2SO_4–$COMe_2$–aq. NaOH. R. S. C.

Isolation of glucosamine and chondrosamine. Z. E. Jolles and W. T. J. Morgan (Biochem. J., 1940, **34**, 1183—1190).—The method for the isolation of 10—30 mg. of glucosamine (I) and chondrosamine takes advantage of the low solubility in H_2O of 2-*hydroxynaphthylidene-glucosamine*, m.p. 202—203°, $[\alpha]_{5461}$ +274° in MeOH (217° after 18 hr.) (*hydrochloride* sinters at 200°), and *-chondrosamine*, m.p. 175—178° (decomp.), $[\alpha]_{5461}$ +287° in MeOH (+258° after 18 hr.). Sugars and NH_2-acids do not interfere. The corresponding p-*nitrobenzylidene* compounds, decomp. 182—184° and 175—176°, the 4-*hydroxy*-3-*methoxybenzylidene* compounds, m.p. 184° (decomp.) and 153—155° (glucosamine compound, $[\alpha]_{5461}$ +64° in C_5H_5N), and the corresponding p-*nitrocinnamylidene* compounds, m.p. 187° (decomp.) and 172—173° respectively (glucosamine compound, $[\alpha]_{5461}$ +57·6° in C_5H_5N changing to +41·5° overnight), are described. Part of the NH_2-sugar of the sp. polysaccharide of *B. dysenteriæ* (Shiga) is (I). W. McC.

Aromatic sulphonic acids as reagents for amino-acids. D. G. Doherty, W. H. Stein, and M. Bergmann (J. Biol. Chem., 1940, **135**, 487—496).—The solubility in N-HCl at 0° of the salts of 26 aromatic sulphonic acids with 18 NH_2-acids has been investigated. The solubility products of the less sol. salts are recorded. Analyses of the following *sulphonates*, likely to be of use in the isolation or determination of NH_2-acids, are given: l-*leucine* (+H_2O), dl-*phenylalanine*, and l-*histidine* 2-*bromotoluene*-5-; l-*histidine* and l-*arginine* 3 : 4-*dichlorobenzene*-; dl-*phenylalanine* 2 : 5-*dibromo*- and 2 : 4 : 5-*trichlorobenzene*-; *glycine*, dl-*alanine*, l-*leucine*, dl-*phenylalanine* (+H_2O), l-*arginine*, and l-*histidine* O-*benzyl*-p-*phenol*- (+0·75H_2O); l-*leucine* (+H_2O), dl-*phenylalanine* (+H_2O), l-*tyrosine* (+H_2O), l-*arginine* (+0·5H_2O), and l-*lysine* O-(2 : 4-*dinitrophenyl*)-p-*phenol*- (+2H_2O); l-*leucine* and dl-*phenylalanine* O-p-*toluenesulphonyl*-p-*phenol*- (+H_2O); dl-*phenylalanine* (+2H_2O), l-*tyrosine*, and l-*arginine* 2 : 6-*diiodophenol*-4- (+2H_2O); *glycine*, l-*leucine*, l-*hydroxyproline*, dl-*phenylalanine*, l-*arginine* (+2H_2O), l-*histidine* (+H_2O), and l-*lysine* 5-*nitronaphthalene*-1- (+3H_2O); l-*leucine* (+2H_2O), l-*phenylalanine*, and l-*tyrosine* 2 : 4-*dinitro*-1-*naphthol*-7- (+H_2O); and l-*leucine* 2-*naphthol*-7-. Salts of arginine, histidine, and lysine contain 2 mols. of sulphonic to 1 of NH_2-acid.

The prep. of *NH*$_4$ O-(2 : 4-*dinitrophenyl*)- (+H_2O) and *Na* O-p-*toluenesulphonyl*-p-*phenolsulphonic acid* (+2H_2O), starting with *p*-OH·C_6H_4·SO_3Na, NaOH, and 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$ and *p*-C_6H_4Me·SO_2Cl respectively, is described. 1-$C_{10}H_7$·NO_2 with conc. H_2SO_4 yields *5-nitronaphthalene-1-sulphonic acid* (+2H_2O) (purified by the glycine salt), converted via the Na salt and acid chloride into the amide. A. Li.

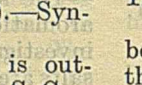
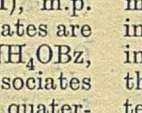
Preparation of alkylamino-acids and their electrometric titration. W. Cocker and J. O. Harris (J.C.S., 1940, 1290—1294; cf. A., 1937, II, 488).—SO_2Ph·NH·CH_2·CO_2H (I) and SO_2Ph·NH·CHMe·CO_2H (II) with RI at 100° yield N-*benzenesulphonyl*-N-n-*butyl*-, m.p. 101—102°, -n-*amyl*-, m.p. 84°, and -iso*butyl-glycine*, m.p. 90—91°, and -*ethyl*-, m.p. 145°, and -n-*propyl*-α-*alanine*, m.p. 117°, hydrolysed (60% H_2SO_4) to N-n-*butyl*-, m.p. 192° (inst.) (*phenylcarbamido*-compound, m.p. 127—128°), -n-*amyl*- (III), m.p. 201° (inst.) (*phenylhydantoin*, m.p. 111°), and -iso*butyl-glycine*, m.p. 188° (*phenylcarbamido*-compound, m.p. 86—87°), and N-*ethyl*-, m.p. 302—303° (inst.), and -n-*propyl*-α-*alanine*, m.p. 302—303°. The acid and basic dissociation consts. (K_A and K_B) of these acids, except (III), and those of glycine, NHMe·CH_2·CO_2H, NHEt·CH_2·CO_2H, NH_2·CHMe·CO_2H, and NHMe·CHMe·CO_2H, have been determined by electrometric titration (H_2 electrode). Substitution of NH_2 by alkyl slightly decreases K_A (K_A being const. for different alkyl groups), and considerably decreases K_B, in accordance with the "zwitterion" theory. (I) and (II) do not react with higher alkyl halides; the Et esters of (I) and (II) gave better alkylation, the nitriles better still. By hydrolysis (conc. HCl) of the alkylated nitrile, N-*benzenesulphonyl*-N-n-*hexylglycine*, m.p. 85—86°, is obtained. Partial hydrolysis (conc. H_2SO_4) of benzenesulphonyl-*n*-amylaminoacetonitrile yields the *amide*, m.p. 94°, hydrolysed (NaOH) in small yield to the acid. A. Li.

Synthesis of pantothenic acid. D. W. Woolley (J. Amer. Chem. Soc., 1940, **62**, 2251—2252).—Synthesis of Na pantothenate from OH·CH_2·CMe_2·CH(OH)·CO_2H and β-alanine is outlined. R. S. C.

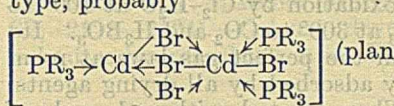
Reactions of nitriles and related compounds with sulphur in presence of amines. Synthesis of quaternary ammonium thiocyanates. C. R. McCrosky, F. W. Bergstrom, and G. Waitkins (J. Amer. Chem. Soc., 1940, **62**, 2031—2034).—At 200—210° NMe_4·CN gives NMe_3 and MeCN. NMe_3 does not recombine with MeCN or PhCN. MeCN, NMe_3, and S in MeOH at 200—210° give 25% of H_2O-sol. thiocyanates, including *NMe*$_4$ *thiocyanate* (I), m.p. 296—297°, and 10—25% of H_2O-sol. thiocyanates are formed by use of other nitriles, NH_2Ac, NH_4OBz, NH_2Bz, or NH_4OAc. (II) or (III) (below) dissociates at 200—210° to give by recombination mixed quaternary thiocyanates including (I). NH_3 also gives thiocyanates. MeSH, Me_2S, and probably other products are also formed in the above reactions. NMe_3 and EtSCN at 100—110° give *NMe*$_3$*Et thiocyanate* (II), m.p. 131—132°. *CH*$_2$*Ph*·*NMe*$_3$ *thiocyanate* (III), m.p. 117—118°, is obtained from CH_2Ph·SCN and NMe_3 in MeOH at room temp. (3 days). PhSCN and NMe_3 (excess) at 100—110° give a mixture; in MeOH at 200—210° they give (I). MeSeCN and NMe_3 at room temp. give *NMe*$_4$ *selenocyanate*, m.p. 267—268° (decomp.). R. S. C.

Hydrogen cyanide. XII. Asymmetry of the tetrapolymeride of hydrogen cyanide. L. E. Hinkel and T. I. Watkins (J.C.S., 1940, 1206—1208). —The aminoiminosuccinonitrile (I) structure proposed (cf. Hinkel *et al.*, A., 1937, II, 433) for $(HCN)_4$ (II) is confirmed. In EtOAc, (II) gives the dl-δ-*camphorsulphonate*, m.p. 176—182° (variable) (decomp.), of (I), which in boiling EtOAc gives the l-*diastereoisomeride*, m.p. 237° (decomp.), strongly lævorotatory in C_5H_5N, which is hydrolysed in H_2O to an optically inactive base. E. W. W.

Manufacture of trichloroacetonitrile.—See B., 1940, 726.

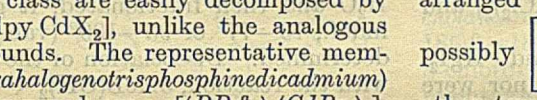
Constitution of complex metallic salts. XI. Structure of the tertiary phosphine and arsine derivatives of cadmium and mercuric halides. R. C. Evans, F. G. Mann, H. S. Peiser, and D. Purdie. **XII. Bridged compounds containing two different metallic atoms. XIII. Stability of the 4-covalent auric complex.** F. G. Mann and D. Purdie (J.C.S., 1940, 1209—1230, 1230—1235, 1235—1239; cf. A., 1939, I, 61; II, 536).—XI. *tert.* Phosphines and arsines yield three types of compounds with Cd halides: class 1, $[\{R_3P(As)\}_2CdX_2]$; class 2, $[\{R_3P(As)\}_2(CdX_2)_2]$; class 3, $[\{R_3P(As)\}_3(CdX_2)_2]$, whilst five types are obtained with Hg^{II} halides: class A, $[\{R_3P(As)\}_2HgX_2]$; class B, $[\{R_3P(As)\}_2(HgX_2)_2]$; class C, $[\{R_3P(As)\}_2(HgX_2)_3]$; class D, $[\{R_3P(As)\}_2(HgX_2)_4]$; class E, $[\{R_3P(As)\}_3(HgX_2)_2]$. Members of class 1 are prepared by shaking aq. CdX_2 or CdX_2 in EtOH with the theoretical amount of PR_3 or AsR_3; they vary in stability, some discarding half their PR_3 or AsR_3 and changing to the corresponding compound of class 2. The structure is probably  (valency bonds in normal type lie in the plane of the paper, those in heavy type project tetrahedrally above, those in dotted type tetrahedrally below, this plane). Preps. of the following members of this class (*dihalogenobis-phosphine-* or *-arsine-cadmium*) are given: $[(PEt_3)_2CdI_2]$, m.p. 132—134°; $[(PEt_3)_2CdBr_2]$, m.p. 103—104°; $[(PPr^a_3)_2CdCl_2]$, an unstable oil; $[(PPr^a_3)_2CdBr_2]$, m.p. 75—77°; $[(PPr^a_3)_2CdI_2]$, m.p. 72—73°; $[(PBu^a_3)_2CdBr_2]$ and $[(PBu^a_3)_2CdI_2]$, oils; $[(PPh_3)_2CdBr_2]$, m.p. 225—226°; $[(PPh_3)_2CdI_2]$, m.p. 243°; $[(AsEt_3)_2CdI_2]$, m.p. 79—81°; $[(AsPr^a_3)_2CdI_2]$, m.p. 27—29°. Class 2 compounds are formed by interaction of class 1 compounds with 1 mol. of CdX_2 in hot EtOH; they are usually more stable than those of class 1. The most likely structure is the tetrahedral *trans*-symmetric structure,  . With 2 : 2′-dipyridyl in COMe$_2$ $[(PEt_3)_2(CdI_2)_2]$ yields white *di-iododipyridylcadmium*, $[dpy\ CdI_2]$, which, on account of its lower solubility in H_2O and org. solvents than $[dpy\ HgI_2]$,

is recommended for use in gravimetric determination of Cd or dipyridyl. Preps. of the following members of this class (*dihalogenobisphosphine-* or *-arsine-μ-dihalogenodicadmium*) are given: $[(PMe_3)_2(CdBr_2)_2]$, m.p. 195—198°; $[(PMe_3)_2(CdI_2)_2]$, m.p. 174—176° (decomp.); $[(PEt_3)_2(CdBr_2)_2]$, m.p. 163—164°; $[(PEt_3)_2(CdI_2)_2]$, m.p. 141°, which in EtOH is an equilibrium mixture $[(PEt_3)_2(CdI_2)_2] \rightleftharpoons [(PEt_3)_2CdI_2] + CdI_2$; $[(PPr^a_3)_2(CdBr_2)_2]$, m.p. 105—106°; $[(PPr^a_3)_2(CdI_2)_2]$, m.p. 123—125°; $[(AsEt_3)_2(CdBr_2)_2]$, m.p. 175—178° (decomp.); $[(AsEt_3)_2(CdI_2)_2]$, m.p. 80—81° (decomp.); $[(AsPr^a_3)_2(CdI_2)_2]$, m.p. 114—116·5°. Crystallographic data are given for $[(PEt_3)_2(CdBr_2)_2]$, $[(PPr^a_3)_2(CdI_2)_2]$, and $[(AsPr^a_3)_2(CdI_2)_2]$; all are monoclinic and isomorphous. *X*-Ray examination of $[(PEt_3)_2(CdBr_2)_2]$ indicates that the crystals belong to the holohedral class $2/m$ of the monoclinic system; space-group $P2_1/a$, 2 mols. per unit cell. Compounds of class 3 are prepared by interaction of CdX_2 with appropriate members of class 1, or by interaction of appropriate members of classes 1 and 2 (2 : 1 mol.). These compounds are stable when solid but dissociate in org. solvents, from which, however, they can be recrystallised unchanged; they appear to be of new structural type, probably

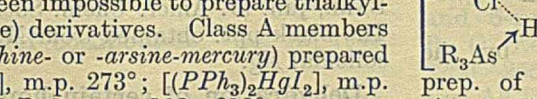


(planes of valency bonds unindicated)

Compounds of this class are easily decomposed by dipyridyl, giving $[dpy\ CdX_2]$, unlike the analogous class E Hg^{II} compounds. The representative members of this class (*tetrahalogenotrisphosphinedicadmium*) which have been prepared are: $[(PPr^a_3)_3(CdBr_2)_2]$, m.p. 126—128°; $[(PBu^a_3)_3(CdBr_2)_2]$, m.p. 93—94·5°; $[(PBu^a_3)_3(CdI_2)_2]$, m.p. 100—101°. The two tetrabromides of this class have orthorhombic crystals showing perfect cleavage parallel to {001} and 4 mols. per unit cell. The space-group of the PBu^a_3 derivative is $P2_12_12_1$, which indicates that the mol. need not possess any intrinsic symmetry. It is, however, not an intimate lattice compound of $[(PBu^a_3)_2CdBr_2]$ and $[(PBu^a_3)_2(CdBr_2)_2]$ as might be deduced from its mode of prep. Class A of the Hg^{II} derivatives are prepared by analogous methods to class 1 of the Cd compounds; they have the same structure and differ only in that it has been impossible to prepare trialkylphosphine (or -arsine) derivatives. Class A members (*dihalogenobis-phosphine-* or *-arsine-mercury*) prepared are: $[(PPh_3)_2HgCl_2]$, m.p. 273°; $[(PPh_3)_2HgI_2]$, m.p. ~250°; $[(AsPh_3)_2HgBr_2]$, m.p. 182—212°; $[(AsPh_3)_2HgI_2]$, m.p. 197°. Class B of the Hg^{II} compounds resemble class 2 of the Cd derivatives in prep. and in possessing the tetrahedral "bridged" *trans*-symmetric structure. The following members (*dihalogenobis-phosphine-* or *-arsine-μ-dihalogenodimercury*) have been prepared and studied: $[(PEt_3)_2(HgBr_2)_2]$, m.p. 106°; $[(PEt_3)_2(HgI_2)_2]$, m.p. 121—123°; $[(PPr^a_3)_2(HgBr_2)_2]$, m.p. 133°; $[(PPr^a_3)_2(HgI_2)_2]$, α-form, white blunt-ended needles, m.p. 114—115°, β-form, yellow but turning white at 104—107° and having m.p. 113—115° either alone or mixed with α-form; the α-form is converted at room temp. in the solid state or in org. solvent into opaque yellow β-form; $[(PBu^a_3)_2(HgBr_2)_2]$, m.p. 116°; $[(PBu^a_3)_2(HgI_2)_2]$, pale yellow, m.p. 84—85° yields, with dipyridyl in $COMe_2$, $[dpy\ HgI_2]$; $[\{P(n\text{-}C_5H_{11})_3\}_2(HgI_2)_2]$, m.p. 54—55°; $[(PPh_3)_2(HgCl_2)_2]$, m.p. 306—309°; $[(PPh_3)_2(HgBr_2)_2]$, m.p. 240—250° (decomp.); $[(AsEt_3)_2(HgCl_2)_2]$, m.p. 162—163°; $[(AsEt_3)_2(HgI_2)_2]$, m.p. 87—88°; $[(AsPr^a_3)_2(HgBr_2)_2]$, m.p. 91—92°; $[(AsPr^a_3)_2(HgI_2)_2]$, m.p. 107—108°; $[(AsBu^a_3)_2(HgBr_2)_2]$, m.p. 86—87°; $[(AsBu^a_3)(HgI_2)_2]$, m.p. 55—56°; $[(AsPh_3)_2(HgCl_2)_2]$, m.p. 251—253°; $[(AsPh_3)_2(HgBr_2)_2]$, m.p. 219°. From crystallographic data on $[(AsEt_3)_2(HgI_2)_2]$, $[(PPr^a_3)_2(HgBr_2)_2]$, and $[(AsPr^a_3)_2(HgI_2)_2]$ it is concluded that, unlike the class 2 Cd derivatives, the Hg^{II} compounds are morphologically different. $[(AsPr^a_3)_2(HgI_2)_2]$ and $[(AsPr^a_3)(CdI_2)_2]$ are isomorphous and have approx. identical cell dimensions. The space-group is $P2_1/a$. Hg^{II} derivatives of class C (*bisphosphine(arsine)trismercuric halide*), prepared by the interaction of the appropriate class B derivative and HgX_2 in hot EtOH or $COMe_2$ solution, are: $[(PEt_3)_2(HgBr_2)_3]$, m.p. 130°; $[(PEt_3)_2(HgI_2)_3]$, m.p. 109—110°; $[(PPr^a_3)(HgCl_2)_3]$, m.p. 113—114°; $[(PBu^a_3)_2(HgCl_2)_3]$, m.p. 72—74°; $[(AsEt_3)_2(HgI_2)_3]$, m.p. 114—115°; $[(AsPr^a_3)_2(HgCl_2)_3]$, m.p. 105°; $[(AsBu^a_3)_2(HgBr_2)_3]$, m.p. 62—64°; $[(AsBu^a_3)_2(HgI_2)_3]$, m.p. 63—65°. Crystallographic analysis indicates that these are two distinct structures in compounds of this class. $[(AsEt_3)_2(HgI_2)_3]$ forms orthorhombic crystals and there are 4 mols. per unit cell structurally arranged to give a non-centro-symmetrical mol., possibly

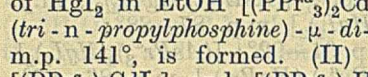
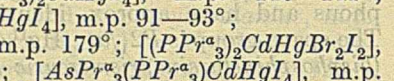


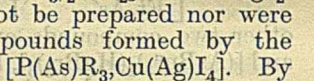
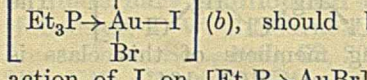
The other two compounds examined, $[(AsPr^a_3)_2(HgCl_2)_3]$ and $[(AsBu^a_3)_2(HgBr_2)_3]$, have colourless, isomorphous monoclinic crystals and possess a centre of symmetry, space-group $P2_1/a$, 2 mols. per unit cell, the whole forming a bridged mol., *e.g.*, $[(Bu^a_3As)BrHgBr_2HgBr(Bu^a_3As)]$, for which a complete analysis has been carried out and interat. distances and valency angles are given. Mols. of class D (*bisphosphine(arsine)tetrakismercuric halide*) have 2 mols. per unit cell and space-group $P2_1/c$ or $P2_1/m$. Crystallographic data are incomplete but it is almost certain that these mols. have a tetrahedral symmetrical structure, *e.g.*,



The prep. of the following members of this class is given: $[(PEt_3)_2(HgCl_4)_4]$, m.p. 163—164°; $[(PEt_3)_2(HgBr_2)_4]$, m.p. 149—151°; $[(AsEt_3)_2(HgCl_2)_4]$, $COMe_2$, m.p. 112—114°; $[(AsEt_3)_2(HgCl_2)_4]$, prisms, m.p. 138°. I-derivatives could not be prepared. On the other hand, only I-derivatives of class E (*tetrahalogenotris-phosphine-* or *-arsine-dimercury*) could be prepared, usually by the interaction of HgI_2 in aq. KI with excess of phosphine (or arsine). These compounds closely resemble class 3 Cd compounds but are extremely stable to 2 : 2′-dipyridyl. The following have been prepared: $[(PPr^a_3)_3(HgI_2)_2]$, m.p. 124—125°; $[(PBu^a_3)_3(HgI_2)_2]$, m.p. 102°; $[(AsEt_3)_3(HgI_2)_2]$, m.p. 58—70°; $[(AsPr^a_3)_3(HgI_2)_2]$, m.p. 84—85·5°; $[(AsBu^a_3)_3(HgI_2)_2]$, m.p. 74—75°.

The stability and inter-relations of the various classes are discussed. Under analogous conditions of prep. ZnX_2 forms no compounds with $P(As)R_3$ in H_2O but some reaction occurs in EtOH.

XII. When $[(PPr^{\alpha}_3)_2CdI_2]$ (I) is boiled with 1 mol. of HgI_2 in EtOH $[(PPr^{\alpha}_3)_2CdHgI_4]$ (II), *di-iodobis(tri-n-propylphosphine)-μ-di-iodocadmium-mercury*, m.p. 141°, is formed. (II) is also formed from $[(PPr^{\alpha}_3)_2CdI_4]$ and $[(PPr^{\alpha}_3)_2HgI_4]$, indicating that both parent substances must be dissociated in hot EtOH to $PPr^{\alpha}_3 \rightarrow CdI_2$ and $PPr^{\alpha}_3 \rightarrow HgI_2$ radicals. (II) probably has the structure  . Other compounds prepared are: $[(PBu^{\alpha}_3)_2CdHgI_4]$, m.p. 140—141°; $[(n\text{-}C_5H_{11}\cdot Cd(PPr^{\alpha}_3)HgI_4]$, m.p. 91—93°; $[(PPr^{\alpha}_3)_2CdHgBr_4]$, m.p. 179°; $[(PPr^{\alpha}_3)_2CdHgBr_2I_2]$, needles, m.p. 138°; $[AsPr^{\alpha}_3(PPr^{\alpha}_3)CdHgI_4]$, m.p. 121—123°. *Dibromobis(tri-n-propylarsine)-μ-dibromo-palladium-mercury* was obtained as orange crystals, m.p. 89—90°, by boiling equiv. quantities of $[(AsPr^{\alpha}_3)_2PdBr_2]$ and $HgBr_2$ in EtOH. This was the only compound of this type which could be prepared; its probable structure is  . No reaction occurred between $[(PBu^{\alpha}_3)_2PdI_2]$ and HgI_2. $[(PPr^{\alpha}_3)_2PdCl_2]$ and $HgCl_2$ gave $[(PPr^{\alpha}_3)_2(PdCl_2)_2]$ and $[(PPr^{\alpha}_3)_2(HgCl_2)_2]$. $[(PEt_3)_2PdCl_2]$ and $HgCl_2$ gave $[(PEt_3)_2(PdCl_2)_2]$ and $[(PEt_3)_2(HgCl_2)_4]$. $[(PBu^{\alpha}_3)_2(PdI_2)_2]$ and $[(PBu^{\alpha}_3)_2(HgI_2)_2]$ gave $[(PBu^{\alpha}_3)_2PdI_2]$ and HgI_2. Pd–Cd compounds could not be prepared nor were bridged $Cu^{I}(Ag)$–Hg^{II} compounds formed by the interaction of HgI_2 and $[P(As)R_3,Cu(Ag)I_4]$. By adding PPr^{α}_3 (3 mols.) to AgI (1 mol.) and HgI_2 (1 mol.) in aq. KI, followed by vigorous shaking, white needles of *di-iodobis(tri-n-propylphosphine)mercury*, $[(PPr^{\alpha}_3)_2HgI_2]$, m.p. 117—119°, were obtained.

XIII. 2-Covalent Au^{I} compounds readily combine with 1 mol. of a halogen to give 4-covalent Au^{III} compounds. The Au^{I} compounds are linear and hence, if two halogen atoms enter the *trans*-position, two isomeric mols., *e.g.*,  (*a*) and  (*b*), should be obtained by the action of I on $[Et_3P\rightarrow AuBr]$ or by the action of IBr on $[Et_3P\rightarrow AuI]$. From the fact that in all such mixed halogen Au^{III} complexes only one form is encountered it is concluded that the groups around the 4-covalent Au atom possess considerable mobility and only the more stable isomeride occurs. The relative stabilities of the trihalogeno-derivatives is discussed. Attempts to introduce acid radicals other than halides into the Au^{III} complex have failed. The Au^{III} are readily reduced to Au^{I} by passing SO_2 into their EtOH solutions at room temp. and the more electronegative halogen atoms are preferentially removed; *e.g.*, with SO_2 $[PEt_3AuCl_2I]$ gave $[PEt_3AuI]$ and with $COMe_2$ $[PEt_3AuClBrI]$ gave $[PEt_3AuI]$.

Preps. of the following compounds are given: Au compounds, *monobromo(trimethylphosphine)gold*, $[PMe_3AuBr]$, m.p. 225° (decomp.); *monobromo(triethylphosphine)gold*, $[PEt_3AuBr]$, m.p. 87°. (A corr. val. for the m.p. of $[PEt_3AuCl]$ is given as 84—85°.) Au^{III} compounds, *trihalogeno(triphosphine)gold*, $[PMe_3AuBr_3]$, m.p. 162°; $[PEt_3AuCl_3]$, m.p. 121°; $[PEt_3AuCl_2Br]$, m.p. 119—120°; $[PEt_3AuClBr_2]$, m.p. 128—129°; $[PEt_3AuBr_3]$, m.p. 129°; $[PEt_3AuCl_2I]$, m.p. 105—106°; $[PEt_3AuClBrI]$, m.p. 107—108°; $[PEt_3AuBr_2I]$, m.p. 109°; $[PEt_3AuClI_2]$, m.p. 94—95°; $[PEt_3AuBrI_2]$, m.p. 90—91°; $[PEt_3AuI_3]$, m.p. 77°; $[PPr^{\alpha}_3AuClBr_2]$, m.p. 145°. *Toluene-3:4-bis(thiotriethylphosphine gold)*, m.p. 124—125°, has also been prepared.

W. R. A.

Methylboric acid and its anhydride. Methylboron fluorides. A. B. Burg (J. Amer. Chem. Soc., 1940, **62**, 2228—2234).—Me_3BO_3 and MgMeI give impure *methylboric acid* (I) (cf. Khotinsky *et al.*, A., 1909, i, 864; Snyder *et al.*, A., 1938, II, 87), which by repeated passage over < the calc. amount of partly dehydrated gypsum gives trimeric *methylboric anhydride* [*trimethyltriborine trioxan*] (II), $(MeBO)_3$, m.p. −38° (vac.), b.p. 79° (extrapolated from the v.p.). (II) is analysed by oxidation by Cl_2–H_2O at 100° to H_3BO_3 and by HNO_3 at 300° to CO_2 and H_3BO_3. Its vapour deviates from the perfect gas laws at room temp. It is strongly adsorbed by all drying agents, least by $CaSO_4$. When treated with <1 mol. of H_2O and then fractionated, it gives pure (I), m.p. indef., 73—77° or 95—100° (vac.), for which v.p. are determined. Dissociation of the vapour of (I) agrees with the reaction, $3MeB(OH)_2 \rightleftharpoons (MeBO)_3 + 3H_2O$, for which $\Delta H = 9300$ g.-cal. and $\Delta F^{\circ} = 9300 - 22{\cdot}31T$. The stable *compounds*, $(MeBO)_3,NH_3$ (III) and $(MeBO)_3,NMe_3$, and the unstable *compound*, $(MeBO)_3,2NH_3$ (IV), are prepared, but $(MeBO)_3,3NH_3$ does not exist. V.p. of these compounds and the dissociation of (III) are recorded. BF_3 and (II) give high yields of *B Me difluoride*, $BMeF_2$, m.p. −130·5°, b.p. −62·3°. $(Me_2B)_2O$ and BF_3 give similarly *B Me$_2$ fluoride*, BMe_2F, m.p. −147·4°, b.p. −42·2°. Cyclic structures are assigned to (II), (III), and (IV), the 2 NH_3 of (IV) being united as $B\leftarrow NH_3\leftarrow NH_3$.

R. S. C.

Grignard reagent. M. Kilpatrick and E. A. Barr, jun. (J. Amer. Chem. Soc., 1940, **62**, 2242).—The black ppt. obtained from Mg and org. halides is colloidal Mg. R. S. C.

Dehydration of certain homologues of *cyclo*pentanol. III. J. I. Denisenko and A. D. Naber (J. Gen. Chem. Russ., 1940, **10**, 193—201).—1-δ-Phenylbutyl*cyclo*pentanol and anhyd. $H_2C_2O_4$ (2 hr. at 130—135°) give 1-δ-phenylbutyl-Δ^1-*cyclo*pentane (I) in 85% yield. With P_2O_5 or conc. H_2SO_4 the product is 1-cyclo*pentyl*-1:2:3:4-*tetrahydronaphthalene*, b.p. 140—141°/3 mm., also obtained from (I) and H_2SO_4. R. T.

Isolation of carotene from green plant tissue.—See A., 1940, III, 944.

Molecular compounds of aromatic hydrocarbons with nitro-compounds and with antimony trihalides.—See A., 1940, I, 412.

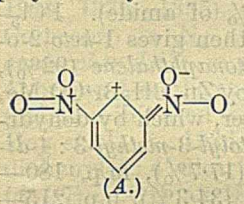
Synthesis and properties of mono-*n*-alkylbenzenes. I. Alkylation of benzene. G. SHEN, T. Y. JU, and C. E. WOOD (J. Inst. Petroleum, 1940, **26**, 475—487).—The efficacy of seven methods for synthesising higher *n*-alkylbenzenes is considered. The best is the reduction (Pd or Clemmensen) of ketones obtained by the Friedel–Crafts reaction. A. LI.

4-Phenyl*cyclo*hexene. C. C. PRICE and J. V. KARABINOS (J. Amer. Chem. Soc., 1940, **26**, 2243).—4-Phenyl*cyclo*hexene, prepared from CH_2:CHPh and $(CH_2{:}CH)_2$ (cf. Alder *et al.*, A., 1938, II, 131), has b.p. 88—90°/16 mm., n_D^{20} 1·5420, d_4^{20} 0·9715. This confirms the structure of the 3-isomeride (A., 1940, II, 276). R. S. C.

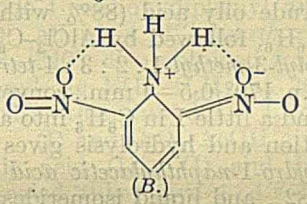
Rate of nitration of benzene.—See B., 1940, 724.

***s*-Tri-*p*-tolylbenzene.** T. R. SAMPEY (J. Amer. Chem. Soc., 1940, **62**, 1953).—*s*-$C_6H_3(C_6H_4Me\text{-}p)_3$, m.p. 170—171°, is best (67—70%) prepared by heating *p*-$C_6H_4Me{\cdot}COMe$ (10 g.) with $KHSO_4$ (2 g.) or conc. H_2SO_4 (0·2—0·3 c.c.) and $K_2S_2O_7$ (2 g.) at 190° for 6 hr. R. S. C.

Acidity of aromatic nitro-compounds towards amines. Effect of double chelation. G. N. LEWIS and G. T. SEABORG (J. Amer. Chem. Soc., 1940, **62**, 2122—2124).—Colours developed by aromatic polynitro-hydrocarbons and NH_3 or amines (not



(*A*.)



(*B*.)

alkali hydroxides) are interpreted as due to addition to the resonance form (type *A*) to give doubly chelated compounds of type (*B*). This is supported by the effects of substitution in either component. R. S. C.

Presence of indole in "practical" α-methylnaphthalene. M. S. KHARASCH, S. S. KANE, and H. C. BROWN (J. Amer. Chem. Soc., 1940, **62**, 2242—2243).—"Practical" α-$C_{10}H_7Me$ is shown to contain 1—2% of indole by condensation with $(COCl)_2$ to give 3-indolylglyoxalyl chloride. Pure 1-$C_{10}H_7Me$ does not discolour in air. R. S. C.

Organic molecular compounds.—See A., 1940, I, 436.

Preparation of 1 : 5-dimethylnaphthalene. (MISS) E. W. J. BUTZ (J. Amer. Chem. Soc., 1940, **62**, 2557).—1-Keto-5-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene is obtained from *o*-C_6H_4MeBr in six stages, no separation of isomerides being required at any stage. With MgMeI it gives a carbinol, dehydrated by I–CO_2 at 200° to a mixture which with Pd–C at 250° gives 1 : 5-$C_{10}H_6Me_2$, m.p. 80° (picrate, m.p. 137°). R. S. C.

Methyl and dimethyl derivatives of cholanthrene. L. F. FIESER and D. M. BOWEN (J. Amer. Chem. Soc., 1940, **62**, 2103—2108).—Prep. of 1 : 4-$C_{10}H_6Me{\cdot}SO_3K$ and thence of 1 : 4-$C_{10}H_6MeBr$ is modified. The derived Grignard reagent with 4-cyanohydrindene (I) in boiling Et_2O–C_6H_6–N_2 gives a ketimine hydrochloride, hydrolysed by conc. HCl–AcOH–PhMe to 4-4′-*methyl*-1-*naphthoylhydrindene* (85%), m.p. 84·6—85·1°, which at 400—410° gives a difficultly separable mixture of 6-*methylcholanthrene* (24%), m.p. 204·2—205·2° (*picrate*, m.p. 208·4—209°), and (?) cholanthrene. 4-Cyano-7-methylhydrindene gives similarly 4-4′-*methyl*-1′-*naphthoyl*-7-*methylhydrindene* (81%), m.p. 130·2—131·2°, b.p. 230°/1 mm., and 6 : 20-*dimethylcholanthrene* (30%), m.p. 175·8—176·5° (*picrate*, m.p. 199·8—200·2°). The preps., *p*-$C_6H_4Me{\cdot}NHAc \rightarrow$ 1 : 3 : 4-$C_6H_4MeCl{\cdot}NHAc \rightarrow$ 1 : 3 : 4-$C_6H_3MeCl{\cdot}NH_2 \rightarrow$ 1 : 3 : 4-$C_6H_3MeClBr$, are modified. 1 : 3 : 4-$C_6H_3MeCl{\cdot}MgBr$ and $CH(OEt)_3$ in Et_2O give an aldehyde, which with $CH_2(CO_2H)_2$ and C_5H_5N at 100° yield 2-*chloro*-4-*methylcinnamic acid* (21%), m.p. 223·7—224°. 2% Na–Hg then gives β-3-*chloro*-*p*-*tolylpropionic acid*, m.p. 96·6—97·4°, which with PCl_5–C_6H_6 and then $AlCl_3$–CS_2 at 0° (later 30°) yields 4-*chloro*-6-*methylhydrind*-1-*one* (95%), m.p. 104—104·5°. This is reduced (Clemmensen) to 4 *chloro*-6-*methylhydrindene*, b.p. 128—132°/27 mm., converted by CuCN–C_5H_5N–MeCN at 240—250° into 4-*cyano*-6-*methylhydrindene* (61%), b.p. 138—139°/10 mm., which with conc. HCl at 180—200° gives 6-*methylhydrindene*-4-*carboxylic acid*, m.p. 158·6—159·3°, or with 1-$C_{10}H_7{\cdot}MgBr$ gives 4-1′-*naphthoyl*-6-*methylhydrindene* (94%), b.p. 205—210°/1·5 mm., and thence 22-*methylcholanthrene* (27%), m.p. 154·5—155° (*picrate*, m.p. 173·6—174°). 4-4′-*Methyl*-1′-*naphthoylhydrindene* (89%), b.p. 230°/1·5 mm., and 6 : 22-*dimethylcholanthrene* (23%), m.p. 161·7—162·4° (*picrate*, m.p. 185·6—186°), are similarly obtained. Preps. of 8-chloro-1-bromo- and thence of 8-chloro-1-methylnaphthalene (II) are improved. With CuCN–C_5H_5N–MeCN at 240°, (II) gives 1-*cyano*-8-*methylnaphthalene* (III) (79%), m.p. 95—95·5°, hydrolysed by boiling KOH–aq. EtOH to 8-*methyl*-1-*naphthoamide*, m.p. 208·7—209·4° (could not be converted into the acid). The Li derivative from (II) with (I) gives a ketimine hydrochloride (37%), which resists hydrolysis. The Mg derivative from 7-bromo-4-methylhydrindene (modified prep.) with (III) in C_6H_6–Et_2O gives 8-*methyl*-1-*naphthyl* 7-*methyl*-4-*hydrindenyl ketimine hydrochloride* (29%), cryst., which resists hydrolysis. M.p. are corr. R. S. C.

Synthesis of 1′-methyl-1 : 2-benzanthracene and 5-methylchrysene. W. E. BACHMANN and R. O. EGERTON (J. Amer. Chem. Soc., 1940, **62**, 2250—2553).—4-Methylphenanthrene, $(CH_2{\cdot}CO)_2O$, and $AlCl_3$ in $PhNO_2$ at −15° give γ-*keto*-γ-5-*methyl*-3-*phenanthryl*-n-*butyric acid* (I), m.p. 195—196·5°, also obtained from 3-acetyl-5-methylphenanthrene by bromination (the 3-$CH_2Br{\cdot}CO$ compound melts at 105—107°), condensation with $CH_2(CO_2Et)_2$, etc. Zn–Hg–HCl–AcOH–PhMe then gives γ-5-*methyl*-3-*phenanthryl*-n-*butyric acid*, m.p. 92—94°, which with $SOCl_2$–C_5H_5N–Et_2O, followed by $SnCl_4$–C_6H_6, gives 5-*keto*-1′-*methyl*-5 : 6 : 7 : 8-*tetrahydro*-1 : 2-*benzanthracene*, m.p. 153·5—154·5°. Reduction (as above) thereof gives 1′-*methyl*-5 : 6 : 7 : 8-*tetrahydro*-1 : 2-*benzanthracene*, m.p. 83·5—84·5° (*picrate*, m.p. 140·5—142°), dehydrogenated by Pd–C at 300—320° to 1′-methyl-1 : 2-benzanthracene. 1-*Bromoacetyl*-4-

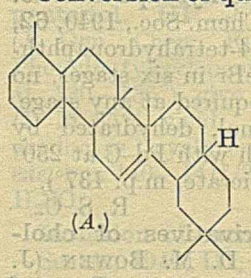
methylphenanthrene (prep. from the 1-Ac derivative), m.p. 80—82°, gives *γ-keto-γ-4-methyl-1-phenanthryl-n-butyric acid*, m.p. 133—136°, reduced to *γ-4-methyl-1-phenanthryl-n-butyric acid* (II), m.p. 152—152·5°, also obtained by reduction of the mother-liquors from (I). 1-Keto-4-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene, $CH_2Br{\cdot}CO_2Me$, Zn, and a trace of I in C_6H_6–Et_2O give an ester, which by hydrolysis (cold, dil. HCl) and dehydrogenation (Pd–C; 240—260°) yields *4-methyl-1-phenanthrylacetic acid*, m.p. 188—189°. By the Arndt–Eistert procedure this affords successively *β-4-methyl-1-phenanthrylpropionic acid*, m.p. 155—156°, and (II). Cyclisation of (II) as above yields *1-keto-11-methyl-1 : 2 : 3 : 4-tetrahydrochrysene*, m.p. 139·5—140·5°, reduced to *11-methyl-1 : 2 : 3 : 4-tetrahydrochrysene*, m.p. 71—72° (*picrate*, m.p. 141—142°), which with Pd–C at 300—320° gives 5-methylchrysene, new m.p. 118—118·8° (corr.) [picrate, m.p. 141—142° (corr.); *s*-$C_6H_3(NO_2)_3$ derivative, m.p. 171—173°]. 1- and 3-Methylchrysene have m.p. 256·5—257° (corr.) and 172·5—173° (corr.), respectively. R. S. C.

Polycyclic aromatic hydrocarbons. XXV. 1- and 2-Alkyl derivatives of 3 : 4-benzphenanthrene. J. L. Everett and C. L. Hewett (J.C.S., 1940, 1159—1162).—3 : 4-Benz-1-phenanthroyl chloride (cf. Hewett, A., 1940, II, 212) gives 3 : 4-*benz-1-phenanthramide*, m.p. 238—239°, which with MgMeI, followed by hydrolysis (conc. HCl–AcOH), yields *1-acetyl-3 : 4-benzphenanthrene*, m.p. 95—96°, b.p. 227°/0·5 mm., the *semicarbazone*, m.p. 180° (decomp.), of which with NaOEt at 180° (18 hr.) gives *1-ethyl-3 : 4-benzphenanthrene*, m.p. 66—67°, b.p. 200°(bath)/0·5 mm. (*picrate*, m.p. 116—117°). The following are prepared similarly: *1-propionyl-*, m.p. 94·5—95° (*semicarbazone*, m.p. 229—230°), and *1-n-propyl-3 : 4-benzphenanthrene*, m.p. 67—68° (*picrate*, m.p. 93—94°). *Me* 3 : 4-*benz-1-phenanthroate*, m.p. 96·5—97·5° (the *Et* ester, m.p. 81—82°, gives poor results), with MgMeI followed by NH_4Cl–ice and picric acid yields the *picrate*, m.p. 94—95°, of *1-isopropenyl-*, hydrogenated (Pd) to *1-isopropyl-3 : 4-benzphenanthrene*, m.p. 76—77° [*picrate*, $2C_{21}H_{18},3C_6H_3O_7N_3$, m.p. 105—106°; *compound*, m.p. 112·5—113°, with $C_6H_3(NO_2)_3$]. 3 : 4-Benz-2-phenanthroic acid (*loc. cit.*) gives the corresponding *chloride*, m.p. 110—111°, and the *amide* (I), m.p. 228—229°, which with *o*-$C_6H_4(CO)_2O$ or with MgMeI yields the *nitrile*, m.p. 128—129°, sublimes 150°/0·7 mm. With MgMeI followed by hydrolysis, (I) gives *2-acetyl-*, m.p. 111·5—112·5° (*semicarbazone*, m.p. 235—236°), converted as before into 2-ethyl-3 : 4-benzphenanthrene, new m.p. 67—68° (picrate, new m.p. 83—84°). Similarly the *semicarbazone*, m.p. 211—212°, of *2-propionyl-*, m.p. 115·5—116·5°, b.p. 230—234°/0·4 mm., gives *2-n-propyl-3 : 4-benzphenanthrene*, m.p. 71·5—72·5° (*picrate*, m.p. 103·5—104°). 3 : 4-*Benz-2-phenanthranilide*, m.p. 214—215°, in $C_2H_2Cl_4$ with PCl_5 followed by $SnCl_2$–Et_2O–HCl gives 3 : 4-*benz-2-phenanthraldehyde*, m.p. 130·5—131·5°, b.p. 260°(bath)/0·4 mm. (*semicarbazone*, m.p. 240—241°), reduced to 2-methyl-3 : 4-benzphenanthrene. E. W. W.

Synthesis of 4 : 5-dimethylchrysene. M. S. Newman (J. Amer. Chem. Soc., 1940, **62**, 2295—2300).—Synthesis of 4 : 5-*dimethylchrysene* (I) is difficult but is achieved by the following reactions, which introduce both Me at an early stage and effect the fourth ring-closure at a distance from their interference. Only the final dehydrogenation gives trouble. Many of the oily products are mixtures of stereoisomerides. $CH_2Ph{\cdot}MgCl$ and dry $(CH_2O)_3$ in Et_2O give 62·4% of impure or 42% of pure (f.p. 35·0°, b.p. 109°/12 mm.) *o*-$C_6H_4Me{\cdot}CH_2{\cdot}OH$ [phenylurethane, m.p. 79·0—79·6°; obtained also in 55% yield from *o*-C_6H_4MeBr and $(CH_2O)_3$ in Et_2O] (and $Ph{\cdot}[CH_2]_2{\cdot}OH$), which with $SOCl_2$ and a drop of C_5H_5N in C_6H_6 gives 89% of *o*-$C_6H_4Me{\cdot}CH_2Cl$ (II), b.p. 84°/14 mm., and 11% of a polymeride. NaCN in boiling, aq. EtOH converts (II) into *o*-$C_6H_4Me{\cdot}CH_2{\cdot}CN$ (III) (86%), b.p. 225·5°/14 mm. $CH_2Ph{\cdot}CHMe{\cdot}OH$ (prep. from MgPhBr and propylene oxide in boiling Et_2O), b.p. 105·5—107°/14—15 mm. (phenylurethane, m.p. 88·2—88·8°), with PBr_3–C_6H_6, first at room temp. and later boiling, or with 48% HBr gives $CH_2Ph{\cdot}CHMeBr$ (IV), b.p. 112·5—114°/20—21 mm., the structure of which is proved by conversion of the derived Grignard reagent by CO_2 into $CH_2Ph{\cdot}CHMe{\cdot}CO_2H$, b.p. 172—173°/23 mm. (amide, m.p. 106—107°). (III), (IV), and $NaNH_2$ give *γ-phenyl-α-o-tolylisovaleronitrile* (63%), b.p. 159—160°/1 mm., hydrolysed by alkali at 150° only to the *amide*, m.p. 115—122°, but by boiling 6 : 8 : 47 (vol.) H_2O–H_2SO_4–AcOH (62 hr.) to the crude oily acid (88% with 6·6% of amide). PCl_5–C_6H_6, followed by $AlCl_3$–C_6H_6, then gives *1-keto-2-o-tolyl-3-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene* (92%), b.p. 170°/0·5—1 mm., converted by Zn, $CH_2Br{\cdot}CO_2Me$, and a little I in C_6H_6 into an ester, which by dehydration and hydrolysis gives *2-o-tolyl-3-methyl-3 : 4-dihydro-1-naphthylacetic acid* (V) (17·7%), m.p. 180—182°, and liquid isomerides (VI) (34·3%), b.p. 215—223°/7—8 mm. Hydrogenation of (V) gives an oily *H_4-acid*, which with, successively, PCl_5–C_6H_6, $AlCl_3$–C_6H_6, $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$, and S at 230° gives (I), m.p. 164·0—164·8° [*s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 131—132°; picrate unobtainable]. No (I) is obtained from (VI). The chrysene structure of (I) is proved by absorption max. at 2740 (log ε 5·11) and 3440 A. (log ε 4·34) and a point of inflexion at 3800 A. (log ε 2·87). M.p. are corr. R. S. C.

Isolation and identification of fluoranthrene from carbon black. J. Rehner, jun. (J. Amer. Chem. Soc., 1940, **62**, 2243—2244).—Isolation of fluoranthrene from commercial "thermatomic C" is described. R. S. C.

Conversion of quillaic acid into a hydrocarbon. G. A. R. Kon and H. R. Soper (J.C.S., 1940, 1335).—The CO ester obtained by oxidation and reduction of Me quillaate is reduced by hot NaOEt and N_2H_4, with simultaneous removal of CO_2Me, to *norhederobetulene* (*A*), $C_{28}H_{46}$, having m.p. 154°, $[\alpha]_D$ +33° in hexane.



(*A*.)

A. Lr.

Aromatic amines and 2-fluoro-5 : ω-dinitrostyrene. D. E. Worrall and H. T. Wolosinski (J. Amer. Chem. Soc., 1940, **62**, 2449).—F enhances

the addition of bases to $CHAr{:}CH{\cdot}NO_2$ less than does Cl, Br, or I. o-*Fluoro-ω-nitrostyrene* (I) (prep. in ~60% yield from o-$C_6H_4F{\cdot}CHO$, $MeNO_2$, and a little NMe_3), m.p. 56·5—57·5° (ω-*Br*-derivative, m.p. 89—90°), and fuming HNO_3 give the 5-NO_2-derivative, m.p. 142—143°. With NH_2Ar this gives α-*nitro*-β-*anilino*-, m.p. 134—135°, -β-m-, m.p. 105—106°, and -β-p-*toluidino*-, m.p. 116—117°, and -β-*phenylhydrazino*-, m.p. 103—104°, -β-2-*fluoro*-5-*nitrophenylethane*, and with benzidine gives NN′-*di*-(β-*nitro*-α-2-*fluoro*-5-*nitrophenylethyl*)*benzidine*, m.p. 139·5—140·5°. o-$C_6H_4Me{\cdot}NH_2$, $OMe{\cdot}C_6H_4{\cdot}NH_2$, NH_2OH, p-$C_6H_4Me{\cdot}NH{\cdot}NH_2$, and NH_3 do not react. A *compound*, $C_{28}H_{24}O_4N_4F_2$, m.p. 134—135°, is obtained from benzidine and ? (I). R. S. C.

Condensation of sulphanilamide with an enol. N^4-α-Bromotetronylsulphanilamide. W. D. Kumler (J. Amer. Chem. Soc., 1940, **62**, 2560—2561).—p-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ (I) and α-bromotetronic acid at 110—120° or in boiling AcOH, dioxan, or (best, 31%) PhMe give N^4-α-*bromo*-β-*tetronylsulphanilamide*, a very weak acid, which does not couple, is not toxic (orally) to mice, and equals (I) in efficiency against β-hæmolytic streptococci. p-$NHAc{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ does not condense. R. S. C.

Quaterphenyl. I. Some dihydroxy-derivatives. J. Harley-Mason and F. G. Mann (J.C.S., 1940, 1379—1385).—4′-Iodo-4-methoxydiphenyl and Cu-bronze in N_2 at 280° afford 4 : 4‴-*dimethoxyquaterphenyl* (I), m.p. 338—340°, also obtained from 4′-bromo-4-methoxydiphenyl–Mg–EtBr–C_6H_6 at 30° (reaction initiated with EtBr), then anhyd. $CuCl_2$ (cf. Hey *et al.*, A., 1936, 991). (I) and CrO_3–AcOH give diphenyl-4 : 4′-dicarboxylic acid (II). (I) and HI (*d* 1·7)–AcOH at 180° (sealed tube) give 4 : 4‴-*dihydroxyquaterphenyl*, m.p. 419—422° [purified through the *diacetate* (III), m.p. 325° (decomp.); *di*(*chloroacetate*), decomp. 360° without melting], which has no œstrogenic properties and could not be oxidised to the corresponding quinone [AcOH–CrO_3 gives (II)]. p-$C_6H_4I{\cdot}C_6H_4{\cdot}NO_2$-$p$, new m.p. 212—214° (improved prep.), and Cu-bronze at 235—245° yield 4 : 4‴-*dinitroquaterphenyl*, m.p. 317—320°, sublimes at 320°/0·01 mm. (could not be prepared from quaterphenyl), oxidised by CrO_3–AcOH to 4-*nitrodiphenyl*-4′-*carboxylic acid*, m.p. 338—340°, and reduced by $SnCl_2$–AcOH–HCl (decomp. of the stannichloride by 20% aq. NaOH) to 4 : 4‴-*diaminoquaterphenyl*, m.p. 312—315° (partial decomp.), sublimes at 310—320°/0·01 mm. (Ac_2 derivative, m.p. 385°), converted by the diazo-reaction, followed by acetylation, into (III). Diacetylbenzidine (IV)–Ac_2O–AcOH at 5° with nitrous fumes give NN′-*bisnitrosoacetylbenzidine*, explodes at 84—87°, which with excess of PhOMe affords a little (IV) only. p-$C_6H_4Br{\cdot}N_2Cl$–PhOMe–aq. NaOH give 4′-*bromo*-2-*methoxydiphenyl* (V), m.p. 63—64°, b.p. 200—201°/18 mm., and -4-methoxydiphenyl (VI), m.p. 144—145°. p-$C_6H_4I{\cdot}N_2Cl$ similarly affords 4′-*iodo*-2-*methoxydiphenyl* (VII), m.p. 61—63°, b.p. 140—143°/0·05 mm., the 4-OMe-isomeride, m.p. 182—183°, and p-$C_6H_4I_2$. Tetrazotised benzidine and an excess of PhOMe give no identifiable product. 4′-Nitro-2-hydroxydiphenyl yields (Ac_2O) 4′-*nitro*-2-*acetoxy*-, m.p. 142—145°, and (Me_2SO_4–aq. NaOH at 60°) -2-*methoxy-diphenyl*, m.p. 62—63°; the latter and reduced Fe–AcOH–70% EtOH give the 4′-NH_2-compound (*hydrochloride*; *Ac* derivative, m.p. 147—148°) and thence (diazo-reaction) (V) and (VII). (VII) and (V) are converted [as for (I)] into 2 : 2‴-*dimethoxyquaterphenyl* (VIII), m.p. 188—191° [oxidised to (II)], whence the 2 : 2‴-$(OH)_2$-compound, m.p. 238—240° [oxidised to (II); *diacetate*, m.p. 221—224°; *di*(*chloroacetate*), m.p. 166—169°; *di*-o-*nitrobenzoate*, m.p. 190—192°]. (V) and (VI), added alternately to Mg–Et_2O–EtBr followed by anhyd. $CuCl_2$, give (I), (VIII), and 2 : 4‴-*dimethoxy*-, m.p. 223—224°, and thence -*dihydroxy-quaterphenyl*, m.p. 268—270° [oxidised to (II); *diacetate*, m.p. 189—192°; *di*(*chloroacetate*), m.p. 158—160°; *di*-o-*nitrobenzoate*, m.p. 206—208°]. A. T. P.

Aldehyde–resorcinol condensations. J. B. Niederl and H. J. Vogel (J. Amer. Chem. Soc., 1940, **62**, 2512—2514).—m-$C_6H_4(OH)_2$ and RCHO in 10% H_2SO_4 at 100° give *compounds*, $CHR<^{X{\cdot}CHR{\cdot}X}_{X{\cdot}CHR{\cdot}X}>CHR$ [X = 4 : 6 : 1 : 3-$(OH)_2C_6H_2<$], $+H_2O$, in which R = Me and Et, and $+2H_2O$, in which R = Bu^β, all having m.p. >300° (decomp.). These give *octa-acetates*, m.p. 282° (decomp.), 242° (decomp.), and >300° (decomp.), and -*propionates*, m.p. 222° (decomp.), 114° (decomp.), and —, and *Me*$_8$ *ethers* (prep. by Me_2SO_4 and 30% NaOH), $+H_2O$, m.p. 256° (decomp.), 227° (decomp.), and —, respectively. R. S. C.

Aralkyl ethers of phenols.—See B., 1940, 781, 782.

Hexœstrol [4 : 4′-dihydroxy-γδ-diphenylhexane]. W. F. Short (Chem. and Ind., 1940, 703).—The prep. of hexœstrol Me_2 ether from Mg and anethole hydrobromide (Docken *et al.*, A., 1940, II, 342) has been previously patented (B.P. 523,320, B., 1940, 701). H. W.

Crystalline vitamin-*A* palmitate and vitamin-*A* alcohol. J. G. Baxter and C. D. Robeson (Science, 1940, **92**, 203—204).—The prep. of vitamin-*A* alcohol (I), new m.p. 63—64° (cf. A., 1939, III, 601), from rich fish-liver oils is described. The average extinction coeff. at 328 mμ. of 18 preps. is 1725, whilst that calc. from the blue val. is 1700. The extinction coeff. of the (I)–$SbCl_3$ blue colour is 4700 at 622 mμ. Palmityl chloride, (I), and quinoline in $CHCl_3$ at −15° give the palmitate (II), m.p. 26—28°, which has an average extinction coeff. of 940, whilst that calc. from the blue val. is 933 at 328 mμ. The extinction coeff. of the (II)–$SbCl_3$ blue colour is 2490 at 620 mμ. The distilled esters from a fish-liver oil, vitamin-*A* β-naphthoate, (II), and β-carotene are equally stable in refined cottonseed oil when exposed at comparable concns. to air in the dark. The potency of (I) is $>2{\cdot}7 \times 10^6$ U.S.P. units per g. L. S. T.

Synthesis of γ-4-hydroxy*cyclo*hexyl-*n*-propyl alcohol, a product of the hydrogenation of lignin. E. Bowden and H. Adkins (J. Amer. Chem. Soc., 1940, **62**, 2422—2423).—p-$OMe{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO_2Et$ [prep. in 82% yield from p-$OMe{\cdot}C_6H_4{\cdot}CHO$ (I), EtOAc, and Na at <0°], m.p. 48—50°, b.p. 132°/1 mm., with H_2–Raney Ni in EtOH

at 80—90°/100 atm. gives *p*-OMe·C_6H_4·$[CH_2]_2$·CO_2Et, b.p. 103°/0·1 mm., converted by HI (*d* 1·7) into *p*-OH·C_6H_4·$[CH_2]_2$·CO_2H (II), m.p. 128—129°, also obtained less well from (I), $CH_2(CO_2Et)_2$, and piperidine etc. The Et ester, b.p. 140°/0·2 mm., of (II), prepared by H_2SO_4–EtOH, is hydrogenated (Raney Ni; EtOH; 175—200°/150 atm.) to *Et* β-4-*hydroxycyclohexylpropionate*, b.p. 102—103°/0·2 mm., which with H_2–Cu chromite in EtOH at 250°/200 atm. gives γ-4-hydroxy*cyclo*hexyl-*n*-propyl alcohol (93%), b.p. 125—127°/1 mm. (cf. A., 1938, II, 332), identified by oxidation to the 4-CO-acid, m.p. 60—65° (2 : 4-dinitrophenylhydrazone, m.p. 125—127°, which in hot EtOH gives the derivative, m.p. 90—94°, of the Et ester). *Et* p-*methoxybenzylmalonate* has b.p. 138°/0·1 mm. R. S. C.

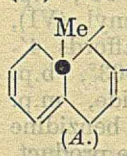
Action of magnesium phenyl bromide on anthraquinones. C. F. H. Allen and A. Bell (J. Amer. Chem. Soc., 1940, **62**, 2408—2412; cf. A., 1938, II, 147).—Good yields of 9 : 10-dihydroxy-9 : 10-diphenyl-9 : 10-dihydroanthracenes are obtained from the appropriate anthraquinones and MgPhBr in Bu_2O. 9 : 10-*Dihydroxy*-2 : 9 : 10-*triphenyl*-, m.p. 203°, -9 : 10-*diphenyl*-2 : 3-*dimethyl*-, m.p. 227°, -2 : 3 : 9 : 10-*tetraphenyl*-, m.p. 294°, and -9 : 10-*diphenyl*-1 : 2-*tetramethylene*- (I), m.p. 226°, -9 : 10-*dihydroanthracene* are thus prepared. In the naphthacene series diols and diketones (formed by a 1 : 4-addition of MgPhBr) are formed if Mg is absent, but presence of Mg and thus of Mg + $MgBr_2$ leads to their gradual decomp. by heat to hydrocarbons; in this series PhMe is preferable to Bu_2O as solvent. Heating (I) at 150° gives 45% of 9 : 10-*diphenyl*-1 : 2-*tetramethyleneanthracene*, m.p. 295°. R. S. C.

Free radicals and radical stability. XI. Methyltriphenylmethyls. S. T. Bowden and T. L. Thomas. **XII. Fluorotriphenylmethyl and the reactivity of halogen substituents in free radicals.** S. T. Bowden and T. F. Watkins (J.C.S., 1940, 1242—1249, 1249—1257; cf. A., 1940, II, 302).—XI. Substitution of Me in CPh_3·OH increases the basicity of the carbinols (2 : 5-Me_2 > *p*- > *o*- > *m*-Me), and the halochromism of the sulphates, but in lesser degree than OMe. Both sulphates and neutral radicals (in C_6H_6) change colour on exposure to sunlight. The Me-substituted formates decompose more slowly than the OMe-derivatives, and the conductivity of the chlorides in liquid SO_2 is > that of CPh_3Cl (*p* > *o* > *m*). The rate of isomerisation of the neutral radicals to colourless products in C_6H_6 in the dark (measured photo-electrically or tintometrically) is in the order *p*- > *m*- ≫ *o*-Me or 2 : 5-Me_2. Diphenyl-*m*-tolyl- (best prepared from Me *m*-toluate and MgPhBr), m.p. 65°, and 2 : 5-*dimethyltriphenylcarbinol* (from 2 : 5 : 1-$C_6H_3Me_2$·COPh and MgPhBr), m.p. 108·5° (reduced by Zn + AcOH to the *-methane*, m.p. 91°), with HCl in Et_2O + $CaCl_2$ yield the *-methyl chlorides*, m.p. 71° and 128·5°, respectively. The corresponding free radicals absorb O_2 in Et_2O (at about the same rate as CPh_3) giving the *peroxides*, m.p. 155° and 157°, respectively, together with isomeric compounds (oils), and with I gives iodides which dissociate to a greater extent than CPh_3I. Mol. wt. determinations on C_6H_6 solutions of the free radicals show that they have a greater radical stability than CPh_3; evaporation of such solutions yields oils.

XII. *p*-F increases the basicity of CPh_3·OH, enhances the halochromism of its salts, and raises the decomp. temp. of the formate by 30° (the decomp. then proceeds normally). p-*Fluorotriphenylcarbinol*, m.p. 121—122° (from *p*-C_6H_4F·CO_2Et and MgPhBr), yields, via the chloride (I), m.p. 91—92°, a radical (II), m.p. 115—124°, which with O_2 yields the *peroxide*, m.p. 169°. On keeping in the dark, solutions of (II) change colour, and absorb less O_2 (amount decreases with time; an isomeride is formed which does not absorb O_2). Mol. Ag, when shaken with freshly prepared (II), removed part of the F giving a secondary radical, showing that this F is more reactive than that of CPh_3F. This behaviour is discussed from the viewpoint of the quinonoid hypothesis. F is also replaced by SO_4 on shaking (I) with Ag_2SO_4 in $PhNO_2$. Mol. wt. determinations in C_6H_6 solutions show that the unimol. stability of (II) is ~20%. A. Li.

Sterols. XCIX. Sterols from various sources. R. E. Marker and A. C. Shabica (J. Amer. Chem. Soc., 1940, **62**, 2523—2525).—Hydrolysis (EtOH–KOH) of the EtOH extract of "Cantharides Russian" (Spanish flies) gives the urine hydrocarbon (I), m.p. 64°, β-sitosterol, and sterol *carbinols*, m.p. 69° (mol. wt. 256) and 201° (mol. wt. 381). Ant eggs and mare's non-pregnancy urine yield cholesterol as sole pure product pptd. by digitonin. Mexican flies yield (I) and a *sterol* (II), m.p. 149—151° (*acetate*, m.p. 130°). Chicken fæces yield sitosterol and (II). Sheep fæces yield sitostanol, (I), and a trace of carbinol, m.p. 75—79°. R. S. C.

Sterol group. XLI. New epimerisation process. (Miss) J. Barnett, I. M. Heilbron, E. R. H. Jones, and K. J. Verrill (J.C.S., 1940, 1390—1393).—$Al(OPr^{\beta})_3$ in boiling xylene converts sterols into their epimeric forms; the yields are variable. Thus, cholesterol, lumisterol (I), neoergosterol, or cholestanol gives *epi*cholesterol (II), m.p. 140·5°, $[\alpha]_D^{20}$ −34° in $CHCl_3$ (10% yield after resolution with digitonin) (*benzoate*, m.p. 99·5°, $[\alpha]_D^{20}$ −29° in $CHCl_3$), *epi*lumisterol (III), m.p. 113° (40%) [after resolution of the racemate, m.p. 156—158°, $[\alpha]_D^{20}$ +199° in $CHCl_3$, of (I) + (III), with digitonin], *epi*neoergosterol (15%), or *epi*cholestanol (4%), respectively. The use of C_6H_6 or PhMe gives poorer yields. An equilibrium is established, as (III) and $Al(OPr^{\beta})_3$ in xylene (? C_6H_6) afford some (I) (as the above racemate). Ergosterol similarly in xylene gives an impure ergostatetraene, m.p. 83—93°; in C_6H_6, however, in N_2 in the dark for 160 hr., a little solid, m.p. 175—182° (? *epi*-ergosterol), separable by adsorption (Al_2O_3) into fractions, m.p. 185—190° and 173—176°, is obtained. (II) and $COMe_2$–$Al(OBu^{\gamma})_3$–C_6H_6 afford 3-keto-Δ^4-cholestene. Sublimation in high vac. (10^{-3} mm.) of ergostatrienol (*epiallo*-ergosterol) (IV) or its acetate in presence of $FeCl_3$ (I or $HgCl_2$ are ineffective) gives the same hydrocarbon, m.p. 86—87°, probably (*A*), as obtained by Windaus *et al.* (A., 1939, II, 212). Irradiation in $COMe_2$ solution, or shaking with PtO_2–MeOH, has no effect on



(*A.*)

(IV); adsorption of the acetate on alumina gives a little of a substance, m.p. 131—132° (? *epi-iso*ergosteryl acetate). A. T. P.

Constitution of α-spinasterol. E. Fernholz and W. L. Ruigh (J. Amer. Chem. Soc., 1940, **62**, 2341—2343).—α-Spinasterol (I) with O_3 in AcOH gives *d*-CHEtPr$^{\beta}$·CHO. Its benzoate with H_2–Pd-black in Et_2O gives α-spinastenyl benzoate (II), m.p. 89°, $[\alpha]_D^{23}$ +11° in $CHCl_3$, and thence (5% KOH–EtOH) α-spinastenol, m.p. 115°, $[\alpha]_D^{23}$ +24° in $CHCl_3$ (acetate, m.p. 118°, $[\alpha]_D^{23}$ +16° in $CHCl_3$), identical with α-stigmastenol and its derivatives. (I) is unaffected by Pd. It is therefore $\Delta^{8:14,\ 22:23}$-stigmastadien-3-ol. α-Stigmastenyl benzoate [= (II)] is obtained by reduction (as above) of 7-dehydrostigmasteryl benzoate. R. S. C.

Sterols. CI. Structure of ψ-sarsasapogenin. R. E. Marker, E. M. Jones, and J. Krueger (J. Amer. Chem. Soc., 1940, **62**, 2532—2536).—The formula previously assigned (cf. A., 1940, II, 171) to ψ-sarsasapogenin (I) is supported by reactions described. The composition of Δ^{16}-pregnene-3 : 20-dione (II) and non-identity of dihydro-ψ-sarsasapogenin (III) with dihydrosarsasapogenin (IV) are confirmed. *Deoxy-ψ-sarsasapogenin* (prep. from deoxysarsasapogenin by Ac_2O at 200° followed by hydrolysis with EtOH–KOH), m.p. 130°, and H_2–PtO_2 in AcOH at 3 atm. give *dihydrodeoxy-ψ-sarsasapogenin*, m.p. 128—129°. H_2O_2–AcOH at 70° oxidises (I) or (III) to (after hydrolysis with MeOH–KOH) a *substance*, $C_{27}H_{44}O_5$, m.p. 253—254°, and a small amount of a *lactone*, m.p. 282—285°. Sarsasapogenin acetate with H_2O_2–AcOH at 70°, followed by KOH–MeOH, gives pregnane-3 : 16 : 20-triol, but bromosarsasapogenin acetate and (IV) are unaffected. $KMnO_4$ and (I) in ~65% AcOH at 15° give (II). O_3 converts (I) in $CHCl_3$ or its diacetate in AcOH into pregnen-3(β)-ol-20-one, but (III) is barely affected. Tetrahydrosarsasapogenin and Ac_2O (? at 200°) give a product, whence 5% KOH–EtOH yields *tetrahydrosarsasapogenin 16-acetate*, m.p. 155°. R. S. C.

Simple synthesis of α-substituted crotonic acids. H. Spiegelberg (Festschr. E. C. Barell [Basel], 1936, 212—216; Chem. Zentr., 1937, i, 4926). —OH·CHMe·CHR·CO_2Et (R = alkyl or aralkyl), obtained by reduction of CHRAc·CO_2Et or CHR:CAc·CO_2Et, is converted by PCl_5 into a mixture of CHMeCl·CHR·CO_2Et and CHMe:CR·CO_2Et; hydrolysis (aq. EtOH–KOH) of the mixture then gives CHMe:CR·CO_2H. *Et* β-*hydroxy*-α-*benzylbutyrate*, b.p. 158—160°/12 mm., from CHPh:CAc·CO_2Et by H_2–Ni–MeOH–$NHEt_2$ (first at 40—60° and then at 80—90°) or from CH_2Ph·CHAc·CO_2Et by Al–Hg in moist Et_2O, thus affords α-*benzylcrotonic acid*, m.p. 99°. Solubility data (H_2O; Et_2O) are given for α-benzylcrotonamide, -anilide, and -benzylamide; α-*n*- and -*iso*-butylcrotonamide; α-benzyl- and α-*n*-butyl-crotonylcarbamide. The amides have some hypnotic activity. H. B.

Preparation of salicylates of primary alcohols. E. Le Sech (Rev. Marques Parfum., 1937, **15**, 45—46; Chem. Zentr., 1937, i, 3628).—When *o*-ONa·C_6H_4·CO_2Me is heated with CH_2Cl·CH_2·OH and a primary alcohol (ROH), group exchange occurs and *o*-OH·C_6H_4·CO_2R is formed. Salicylates of sesquiterpene alcohols can thus be prepared. *Santalyl salicylate* has b.p. 200—235°/6 mm. H. B.

Bromo-derivatives of aromatic esters. L. Rosenthaler (Pharm. Acta Helv., 1937, **12**, 8—9; Chem. Zentr., 1937, i, 4497).—*p*-OH·C_6H_4·CO_2Me, *o*-NH_2·C_6H_4·CO_2Me, and Me anisate with Br in AcOH give *Me* 3 : 5-*dibromo*-4-*hydroxybenzoate*, m.p. 123—124°, 3 : 5-*dibromoanthranilate*, m.p. 90°, and 3-*bromoanisate*, m.p. 99—100°, respectively.
o-OAc·C_6H_4·CO_2H and Br in H_2O + $CaCO_3$ afford 3 : 5-*dibromoacetylsalicylic acid*, m.p. 163°. H. B.

Constitution of anacardic acid, principal constituent of cashew-nut shell oil. G. D. Gokhale, M. S. Patel, and R. C. Shah (Current Sci., 1940, **9**, 362—363).—*n*-$C_{14}H_{29}$·CO_2Ph by Fries transformation yields *o*- and *p*-OH·C_6H_4·CO·$C_{14}H_{29}$, reduced (Clemmensen) to o-, m.p. 54—55°, and p-*pentadecylphenol*, m.p. 72·5°, both different from tetrahydroanacardol (I) (Smit, A., 1931, 840). Since (I) gives a Br_3-derivative and anacardol Me ether is oxidised to *m*-OMe·C_6H_4·CO_2H, (I) is *m*-OH·C_6H_4·$C_{15}H_{31}$, and anacardic acid is 2 : 6 : 1- or
2 : 4 : 1-OH·C_6H_3($C_{15}H_{27}$)·CO_2H. A. Li.

Synthesis of iodohippuric acids. II. 2 : 3 : 5- and 3 : 4 : 5-Tri-iodohippuric acid. C. J. Klemme and J. H. Hunter (J. Org. Chem., 1940, **5**, 508—511; cf. A., 1940, II, 277).—2 : 3 : 5 : 1-$C_6H_2I_3$·CO_2H and $SOCl_2$ give the *chloride*, m.p. 85—86° after softening at 80—84°, which with aq. NH_2·CH_2·CO_2Na followed by HCl affords 2 : 3 : 5-*tri-iodohippuric acid*, m.p. 255·5—257° after darkening at 250—255°. 4 : 3 : 5 : 1-NH_2·$C_6H_2I_2$·CO_2H, m.p. >350°, from *p*-NH_2·C_6H_4·CO_2H and ICl in 12·5% HCl, is converted into 3 : 4 : 5 : 1-$C_6H_2I_3$·CO_2H, m.p. 289—290°. This with $SOCl_2$ yields 3 : 4 : 5-*tri-iodobenzoyl chloride*, m.p. 138—139°, which is transformed into 3 : 4 : 5-*tri-iodohippuric acid*, m.p. 242—243°. H. W.

Optically active monosubstituted succinic acids and [their] derivatives. (Miss) M. Naps and I. B. Johns (J. Amer. Chem. Soc., 1940, **62**, 2450—2457).—Resolution of the *dl*-acid by brucine gives *d*-, m.p. 198·5—199·0°, $[\alpha]_D^{32}$ +135·5° in EtOH, and *l*-anisylsuccinic acid, m.p. 196—199°, $[\alpha]_D^{29}$ −122·0° in EtOH [*brucine* salts, 1 *d*-acid, 1 base, m.p. 197—200°, and 1 *l*-acid, 2 base, +2H_2O, m.p. 136·5—137°; *anhydrides*, m.p. 92·5—93·0°, $[\alpha]_D^{31}$ +95·2°, $[\alpha]_D^{29\cdot5}$ −94·9° in EtOH, respectively; d-*amic acid*, m.p. 166—169°, $[\alpha]_D^{29}$ (partly hydrolysed sample) +104·3° in EtOH (N-*Me* derivative, m.p. 174—175°, $[\alpha]_D^{29}$ +143·0° in EtOH); d-*anilic acid*, m.p. 148—150°, $[\alpha]_D^{30}$ +154·0° in EtOH; d-*anil*, m.p. 165—166°, readily racemised, $[\alpha]_D^{29}$ +29·3° in C_6H_6]. *o*-C_6H_4Cl·CHO, CN·CH_2·CO_2Na, and aq. NaOH at 40° give α-*cyano*-β-*o*-*chlorophenylacrylic acid*, m.p. 208—209°, the *Et* ester (prep. by HCl–EtOH), m.p. 51—52°, of which with NaCN in 50% aq. EtOH at 100° gives the oily dicyano-ester, converted by boiling, conc. HCl into dl-o-*chlorophenylsuccinic acid*, m.p. 173—174° (sublimes at 167°) (*anhydride*, m.p. 122·0°; *amic acid*, softens at 156°, m.p. 164°; N-*methylimide*, m.p. 129—131°; *anil*, m.p. 143—144°). Strychnine then yields the d- (I), m.p. 166—168°, $[\alpha]_D^{28}$ +115·0° in EtOH, and

l-*acid*, m.p. 166—168°, $[\alpha]_D^{32}$ −101·3° in EtOH [*strychnine* salts, *d*-acid, *l*-base, +2H_2O, m.p. 126—128°, and *l*-acid, *l*-base, m.p. 138°; d-, $[\alpha]_D^{31}$ +45·2° in EtOH, ±0° in $CHCl_3$, and l-, $[\alpha]_D^{31}$ −45·7° in EtOH, -*anhydride*, m.p. 145—146°; d-*amic acid*, m.p. 164—165°, $[\alpha]_D^{32}$ +19·0° in EtOH, racemises in hot H_2O (N-*Me* derivative, m.p. 156—158°, $[\alpha]_D^{34}$ +104·3° in EtOH); d-*anilic acid*, m.p. 169—170°, $[\alpha]_D^{32}$ +130·7° in EtOH; d-*anil*, m.p. 180—181°, $[\alpha]_D^{29}$ −27·6° in EtOH]. *d*-CO_2H·CHPh·CH_2·CO_2H (II), m.p. 173—174°, $[\alpha]_D^{26}$ +148·1° in EtOH (corresponding *l*-acid, m.p. 173°, $[\alpha]_D^{30}$ −147·8° in EtOH), gives an anhydride, m.p. 82°, $[\alpha]_D^{29}$ +99·4° in EtOH, *amic acid*, m.p. 141—145°, $[\alpha]_D^{31\cdot5}$ +52·8° in EtOH, racemised and partly hydrolysed in boiling H_2O (N-*Me* derivative, m.p. 159—160°, partly racemised, $[\alpha]_D^{28}$ +34·8° in EtOH), *anilic acid*, m.p. 125—127°, $[\alpha]_D^{31}$ +151·8° in EtOH, and *anil*, forms, m.p. 165—166° and 140—141°. Hydrogenation (PtO_2, EtOH) of (I) or (II) gives d-cyclo*hexylsuccinic acid*, m.p. 95·5—96·0°, $[\alpha]_D^{30}$ +26·3° in EtOH (*anhydride*, m.p. 43·0°, $[\alpha]_D^{31}$ +9·5° in EtOH; *anilic acid*, m.p. 172—172·5°, $[\alpha]_D^{31}$ +32·2° in EtOH; *anil*, m.p. 143·5—144·5°, $[\alpha]_D^{31}$ −41·1° in EtOH); *dl-cyclo*hexylsuccinic acid, new m.p. 146°, is similarly prepared. *d*-Methylsuccinic acid, m.p. 110—111°, $[\alpha]_D^{28}$ +11·7° in H_2O [d-, m.p. 64—65°, $[\alpha]_D^{29}$ +32·1° in EtOH, and *l*-anhydride, $[\alpha]_D^{30}$ −32·6° in $CHCl_3$; d-, $[\alpha]_D^{31}$ +11·4° in EtOH, and *l*-, $[\alpha]_D^{32}$ −10·9° in EtOH, -*anilic acid*, m.p. 143—145°; d-, $[\alpha]_D^{31}$ +4·5° in EtOH or $CHCl_3$, and l-, $[\alpha]_D^{32\cdot5}$ −5·5° in $CHCl_3$, -*anil*, m.p. 125—126°], are also described. [α] are given also for other λ. Ring-closure results in a marked decrease in α except for the Me derivatives. Solvent effects are noted for several of the compounds.

R. S. C.

Chemiluminescence of hydrazides of carboxylic acids. II. E. S. Vasserman and G. P. Mikluchin (J. Gen. Chem. Russ., 1940, **10**, 202—206).—The cyclic *hydrazides* of 4-*nitronaphthalic*, m.p. 336° (decomp.), of *diphenic*, m.p. 246° (decomp.), of 4-*aminodiphenic*, m.p. 140°, and of cis-1 : 2-*dihydro*-, sublimes at 270°, and cis-4 : 5-*dihydro-phthalic acid*, m.p. 253° (decomp.), have been prepared by heating the appropriate anhydrides with N_2H_4 in EtOH. Chemiluminescence is observed when H_2O_2 is added to alcoholic solutions of the hydrazides, the most intense effect being given by the two last named.

R. T.

Reactions of aldehydes with amines. I. With *o*-aminophenol. F. G. Singleton and C. B. Pollard (J. Amer. Chem. Soc., 1940, **62**, 2288—2289).—*o*-NH_2·C_6H_4·OH and RCHO under any of 5 sets of conditions give *o*-, m.p. 104·5°, *m*-, m.p. 132°, and *p*-NO_2·C_6H_4·CH:, m.p. 161° (cf. lit.), m-, m.p. 105° (corr.), and p-C_6H_4Me·CH:, m.p. 108·5° (corr.), o-C_6H_4Cl·CH:, m.p. 94° (corr.), and 5 : 2 : 1-NO_2·C_6H_3Cl·CH:, m.p. 164° (corr.), derivatives.

R. S. C.

Addition reactions of unsaturated α-keto-acids. VI. (Miss) M. Reimer and (Miss) E. Tobin (J. Amer. Chem. Soc., 1940, **62**, 2515—2520; cf. A., 1938, II, 494).—p-*Bromobenzylidenepyruvic acid* (I) (prep. from *p*-C_6H_4Br·CHO and $AcCO_2H$ in 25% KOH–MeOH), m.p. 143° (hydrates in air) and +H_2O, m.p. 120°, and its *Me*, m.p. 122°, and *Et* ester, m.p. 77°, are sensitive to light, a dimeric *Et* ester, m.p. 167—168°, being very readily formed. H_2O_2 converts the Na salt of (I) into *p*-C_6H_4Br·CH:CH·CO_2H. Br and anhyd. (I) in dry $CHCl_3$ give a stable *dibromide* (II), m.p. 133° (decomp.), and +H_2O, softens at 100°, m.p. 120° (gas) (*Me* ester, m.p. 113°), which in boiling H_2O gives colourless β-*bromo*-p-*bromobenzylidene-pyruvic acid* (III), m.p. 144—145° (decomp.), and +H_2O, cryst. (*Me* ester, m.p. 101°, prep. by CH_2N_2 only; *Na* salt), but in 1% Na_2CO_3 at room temp. gives a yellow isomeric *acid* (IV), m.p. 141—143° [*Me* ester, m.p. 75°, prep. by MeOH–HCl; with H_2O_2–Na_2CO_3 gives a *bromo*-p-*bromocinnamic acid*, m.p. 221° (*Me* ester, m.p. 72°)]. When heated at the m.p. or slowly in H_2O, (IV) gives (III). Dissolution in Na_2CO_3 converts (III) into (IV). (II) is accompanied by an isomeride (not obtained pure), which in 2% Na_2CO_3 gives 4 : ω-*dibromostyrene*, m.p. 81°, oxidised by $KMnO_4$ to *p*-C_6H_4Br·CO_2H. (III) is probably *p*-C_6H_4Br·C$\lessgtr^{H\leftarrow O}_{CBr\cdot CO}$>C·OH and (IV) the unchelated form.

R. S. C.

Condensations. XI. Condensations of active hydrogen compounds effected by boron trifluoride and aluminium chloride. D. S. Breslow and C. R. Hauser. **XII. General theory for carbon–carbon condensations effected by acidic and basic reagents.** C. R. Hauser and D. S. Breslow (J. Amer. Chem. Soc., 1940, **62**, 2385—2388, 2389—2392; cf. A., 1940, II, 308).—XI. PhCHO with COPhMe and BF_3 gives CHPh:CH·COPh (I) (61%) and CHPh(CH_2·COPh)$_2$, with $CH_2(CO_2Et)_2$ (II) and BF_3 gives CHPh[$CH(CO_2Et)_2$]$_2$ (III) [identified as CHPh(CH_2·CO_2H)$_2$ (43·6%)], with (II) and $AlCl_3$ gives CHPh:$C(CO_2Et)_2$ (IV) and some (III), and with Ac_2O and BF_3 gives 4·5% of CHPh:CH·CO_2H, but it does not react with EtOAc and BF_3. (II), (IV), and BF_3 give (III), but CHPh:CH·CO_2Et and (II) do not react. (II), (I), and BF_3 probably give COPh·CH_2·CHPh·$CH(CO_2Et)_2$; Et_2 2-benzoyl-1 : 3 : 5-triphenyl-Δ^1-*cyclo*hexene-4 : 4-dicarboxylate and, after hydrolysis, COPh·CH_2·CHPh·CH_2·CO_2H are isolated. 23·1% of CH_2Ph·CHAc·CO_2Et is obtained from CH_2Ac·CO_2Et, CH_2PhCl, and BF_3 at room temp.

XII. The author's theories of condensation reactions are expanded to include reactions induced by acidic catalysts. Such catalysts exert their effect on the electron-accepting component by forming an "active" co-ordination complex. CHPh:NPh, (II), and BF_3,Et_2O give 26·5% of NHPh·CHPh·$CH(CO_2Et)_2$. NHPh·CHPh·CHAc·CO_2Et and BF_3 in Et_2O give PhCHO and CH_2Ac·CO_2Et, and in $COMe_2$ give CH_2Ac·CO_2Et, NH_2Ph, and CHPh:CAc·CO_2Et. CH_2Ac·CO_2Et, Pr^β_2O, and BF_3 give 70·9% of CHPr$^\beta$Ac·CO_2Et, 40·4% being similarly obtained by Pr$^\beta$OH.

R. S. C.

β-Naphthyl derivatives of ethanolamine and *N*-substituted ethanolamines. T. Immediata and A. R. Day (J. Org. Chem., 1940, **5**, 512—527).—Gradual addition of $AlCl_3$ to $C_{10}H_8$ and AcCl in cold $PhNO_2$ and fractionation of the product from EtOH gives a 35—40% yield of 2-acetonaphthone, m.p. 53° (picrate, m.p. 82°), converted by Br in AcOH into ω-bromo-2-acetonaphthone (I), m.p. 80° (picrate,

m.p. 93°), which with $(CH_2)_6N_4$ in $CHCl_3$ followed by conc. HCl gives ω-amino-2-acetonaphthone, isolated in 40—44% yield as the hydrobromide; the oxime could not be obtained. Gradual addition of NH_2Me in dry EtOH to (I) in dry Et_2O gives the unstable ω-methylamino-2-acetonaphthone (*oxime*, m.p. 143°), isolated as the *hydrochloride* in 12—15% yield. The following-2-*acetonaphthones* are described: ω-*ethylamino-*, m.p. 68° (*oxime*, m.p. 121°; *hydrochloride*, m.p. 220—222°); ω-n-*butylamino-*, m.p. 82° (*oxime*, m.p. 113°; *hydrochloride*, m.p. 208°); ω-*benzylamino-*, m.p. 84° (*oxime*, m.p. 116·5°; *hydrochloride*, m.p. 207—208°); ω-cyclo*hexylamino-*, m.p. 125° (*hydrochloride*, m.p. 209—210°; *oxime hydrochloride*, m.p. 201—202°); ω-*dimethylamino-*, free base very unstable (*oxime*, m.p. 148°; *hydrochloride*, m.p. 216—217°); ω-*diethylamino-*, free base very unstable (*oxime*, m.p. 121·5°; *hydrochloride*, m.p. 199°); ω-*dibenzylamino-*, m.p. 109° (*oxime*, m.p. 114°; *hydrochloride*, sublimes without melting at 198°); ω-*piperidino-*, m.p. 84° (*oxime*, m.p. 122°; *hydrochloride*, m.p. 213°); ω-*morpholino-*, m.p. 120·5° (*oxime*, m.p. 154—155°; *hydrochloride*, m.p. 223—224°). The ketone salts are hydrogenated (10% Pd–C in EtOH) at atm. pressure thus giving the following -α-2-*naphthylethanols*; β-*amino-*, m.p. 113·5° [*hydrochloride* (II), m.p. 186°]; β-*methylamino-* (III), m.p. 109° (*hydrochloride*, m.p. 152°); β-*ethylamino-* (IV), m.p. 110·5° (*hydrochloride*, m.p. 189·5°); β-n-*butylamino-* (V), m.p. 95·6° (*hydrochloride*, m.p. 190°); β-*benzylamino-* (VI), m.p. 136·5° (*hydrochloride*, m.p. 194·5°); β-cyclo*hexylamino-* (VII), m.p. 98° (*hydrochloride*, m.p. 224°); β-*dimethylamino-*, (VIII), m.p. 53° (*hydrochloride*, m.p. 143·5°); β-*diethylamino-* (IX), m.p. 42° (*hydrochloride*, m.p. 142·5°); β-*dibenzylamino-* (X), m.p. 132° (*hydrochloride*, m.p. 210°); β-*piperidino-* (XI), m.p. 98·5° (*hydrochloride*, m.p. 213°); β-*morpholino-* (XII), m.p. 120·5° (*hydrochloride*, m.p. 223—224°). (II) is transformed by BzCl at 100° into β-*amino*-α-2-*naphthylethyl benzoate hydrochloride*, m.p. 206—206·5°; attempts to prepare the corresponding free base lead to β-*benzamido*-α-2-*naphthylethanol*, m.p. 207·8°. Similarly obtained are the *benzoate hydrochloride of* (III), m.p. 193—194°, and β-*benzmethylamido*-α-2-*naphthylethanol*, m.p. 134·5°; *benzoate hydrochloride* of (IV), m.p. 178—179°, and β-*benzethylamido*-α-2-*naphthylethanol*, m.p. 125°; *benzoate hydrochloride* of (V), m.p. 151°, and β-*benz*-n-*butylamido*-α-2-*naphthylethanol*, m.p. 126—127°; *benzoate hydrochloride* of (VI), m.p. 208°, and β-*benzbenzylamido*-α-2-*naphthylethanol*, m.p. 82°; *benzoate hydrochloride* of (VII), m.p. 192—193°, and β-*benz*cyclo*hexylamido*-α-2-*naphthylethanol*, m.p. 68°; *benzoate hydrochloride* of (VIII), m.p. 225°, and the *base*, m.p. 69°; *benzoate hydrochloride* of (IX), m.p. 178°, and free *base*, m.p. 84°; *benzoate hydrochlorides* of (X), (XI), and (XII), m.p. 205—206°, 209°, and 204—205°, respectively, and the corresponding *bases*, m.p. 111·2°, 69°, and 105°, respectively. All m.p. are corr.

H. W.

Friedel–Crafts reaction. V. Action of acetic anhydride and benzoyl chloride on methyl β-resorcylate. R. D. Desai and (Miss) K. S. Radha (Proc. Indian Acad. Sci., 1940, **12**, **A**, 46—49; cf. A., 1939, II, 23).—2 : 4 : 5 : 1-$(OH)_2C_6H_2Ac{\cdot}CO_2Me$, m.p. 124° (improved method of prep.), is converted by 1 mol. of Ac_2O into *Me* 2 : 4-*dihydroxy*-3 : 5-*diacetylbenzoate*, m.p. 113°, also obtained from Me β-resorcylate (I) and Ac_2O (2 mols.). The *acid*, m.p. 175° (p-*nitrophenylhydrazone*, m.p. >280°; *semicarbazone*, m.p. >280°), is transformed by HCl–AcOH at 160—170° into 2 : 4 : 1 : 3-$C_6H_2Ac_2(OH)_2$, m.p. 95—96° (lit., m.p. 85—87°). (I), BzCl, and $AlCl_3$ afford *Me* 2 : 4-*dihydroxy*-5-*benzoylbenzoate*, m.p. 129—130° (2 : 4-*dinitrophenylhydrazone*, m.p. >270°; *semicarbazone*, m.p. >270°); the corresponding *acid*, m.p. 232—233°, is decarboxylated to 4 : 1 : 3-$C_6H_3Bz(OH)_2$. *Me* 2 : 4-*dihydroxy*-5-*benzoyl*-3-*acetylbenzoate*, m.p. 126—127°, gives a 2 : 4-*dinitrophenylhydrazone*, m.p. >290°. *Me* 2 : 4-*dihydroxy*-3 : 5-*dibenzoylbenzoate*, m.p. 119—120°, is hydrolysed to the *acid* (+H_2O), m.p. 235—236° (2 : 4-*dinitrophenylhydrazone*, m.p. >280°; *semicarbazone*, m.p. >290°), which is decarboxylated to 2 : 4 : 1 : 3-$C_6H_2Bz_2(OH)_2$, m.p. 102°.

H. W.

Preparation of *iso*phorones.—See B., 1940, 782.

Cyclone series. V. S. Abramov and C. L. Mitropolitanskaja (J. Gen. Chem. Russ., 1940, **10**, 207—209).—Cyclone (I) and $CH_2{:}CH{\cdot}CH_2{\cdot}OH$ or $CH_2{:}CH{\cdot}CH_2Cl$ in C_6H_6 (8 hr. at 180—200°) afford 2 : 5-endo*keto*-2 : 3 : 4 : 5-*tetraphenyl*-1 : 2 : 5 : 6-*tetrahydrobenzyl alcohol*, m.p. 85—86°, or *chloride*, m.p. 115—118°, respectively. $CH_2{:}CH{\cdot}CH_2Ph$ and (I) give 3 : 4 : 5 : 6-*tetraphenyl*-1 : 2-*dihydrodiphenylmethane*, m.p. 158—160°, whilst styrene affords 1 : 2 : 3 : 4 : 5-*pentaphenyl*-5 : 6-*dihydrobenzene*, m.p. 157—158°.

R. T.

Synthetic experiments utilising perinaphthan-7-one. L. F. Fieser and M. D. Gates, jun. (J. Amer. Chem. Soc., 1940, **62**, 2335—2341).—1-$C_{10}H_7{\cdot}CH_2Cl$ [prep. from $C_{10}H_8$, $(CH_2O)_3$, and HCl in AcOH improved to give a 51·5% yield] and $CHNa(CO_2Et)_2$ give the Et_2 ester, b.p. 167—171°/1·5—2 mm., and thence 1-$C_{10}H_7{\cdot}[CH_2]_2{\cdot}CO_2H$, m.p. 156—156·6° [Me ester, m.p. 35—36·5°; amide, m.p. 103—104° (lit., 140°, 85°, 133°)]. With $AlCl_3$ or $SnCl_4$ this gives mixtures, but in HF gives readily 81% of perinaphthan-7-one (I), m.p. 82·6—83·2° [oxime, new m.p. 127—128°; *semicarbazone*, m.p. 232—233° (decomp.)], with a little 4 : 5-benzhydrindone, m.p. 120·6—121·4° [oxime, m.p. 229—231° (decomp.)] (cf. Cook *et al.*, A., 1934, 519). The structure of (I) is proved by Clemmensen–Martin reduction to perinaphthane (A., 1938, II, 356). With *o*-$C_6H_4Cl{\cdot}MgBr$, (I) gives a crude carbinol, dehydrated in boiling AcOH to mixed, rearranged anhydro-derivatives, which after hydrogenation (PtO_2; AcOH) gives a product, b.p. 178—180°/1 mm.; interaction thereof with CuCN–MeCN–C_5H_5N at 230—240° gives 1- (II) (18·6%), m.p. 144·7—145·4°, and 3-o-*cyanophenylperinaphthane* (III) (13·4%), m.p. 122·5—123·8°, and a eutectic mixture (18·3%), m.p. 104·3—106·3°, thereof. Acid hydrolysis of (II) and (III) is unsuccessful but hot KOH–aq. EtOH gives 76% of 1-o-*carbamyl-*, m.p. 173—174·5°, 17% of 1-o-*carboxy-* (IV), m.p. 173·7—174·7°, 77·5% of 3-o-*carbamyl-*, m.p. 194·2—196·5° [hydrolysed to (V) by conc. HCl–AcOH], and 16·5% of 3-o-*carboxy-* (V), m.p. 187·9—188·5°, *-phenylperinaphthane*. In HF, (V) gives 3 : 4-trimethylenebenzanthr-7-one, m.p. 217·2—218·4°, and (IV) gives 4 : 4′-*trimethylene*-2 : 3-*benzfluorenone*,

m.p. 187—189° (rapid), 201—203° (slow heating), or 190° (preheated bath) resolidifying with m.p. 201—203° (absorption spectrum resembles that of 2 : 3-benzfluorenone but not that of 1 : 2-benzanthr-10-one). M.p. are corr. R. S. C.

Constitution of the chlorobenzanthrone obtained by direct chlorination of benzanthrone. G. Charrier and E. Ghigi (IX Congr. int. quim. pura apl., 1934, **4**, 309—316; Chem. Zentr., 1937, i, 4361—4362).—The chlorobenzanthrone, m.p. 183°, is probably the 3-derivative. Oxidation (CrO_3) gives anthraquinone-1-carboxylic acid whilst fusion with KOH affords *iso*violanthrone. Oxidative fission ($KMnO_4$, aq. NaOH, 85—90°) gives a *chlorodiphenyl*-2(or 3) : 2′-*dicarboxylic*-3(or 2)-*glyoxylic acid*, m.p. 245—250° (softens at 225°), which is converted by MnO_2–H_2SO_4 into a substance, m.p. 237—238°, and by distillation with CaO into (probably) *p*-C_6H_4PhCl and a substance, m.p. 140—160°. H. B.

Sterols. CV. Preparation of testosterone and related compounds from sarsasapogenin and diosgenin. R. E. Marker (J. Amer. Chem. Soc., 1940, **62**, 2543—2547).—*allo*Pregnan-20-one and $K_2S_2O_8$–H_2SO_4–K_2SO_4 in AcOH at 25° give 30—35% each of 21-*acetoxy*all*opregnan*-20-*one* (I), m.p. 197—200° [*semicarbazone*, m.p. 242—244° (decomp.)], and 17(α)-androstanyl acetate (isolated by hydrolysis to androstan-17(α)-ol and purification of the H succinate). Hydrolysis of (I) by boiling $KHCO_3$–MeOH gives *allo*-*pregnan*-21-*ol*-20-*one*, m.p. 115—117°, oxidised by CrO_3 to ætio*all*ocholanic acid. 3(α)-Acetoxypregnan-20-one and $K_2S_2O_8$ give similarly products hydrolysed to ætiocholane-3(α) : 17(α)-diol and a little *epi*pregnanolone and ætiolithocholic acid. 3-Acetoxy-Δ⁵-pregnen-20-one (as dibromide) gives similarly Δ⁵-androstene-3(β) : 17(α)-diol, m.p. 176—178°, identified by oxidation to androstene-3 : 17-dione. 4-Bromopregnane-3 : 20-dione gives products, which, after removal of HBr by C_5H_5N, contain deoxycorticosterone, which was hydrolysed (without isolation) by $KHCO_3$–MeOH and then oxidised to 3-*keto*-Δ⁵-*ætiocholenic acid*, m.p. 249—253° (reduced by Na–EtOH to 3(β)-hydroxy-ætio*all*ocholanic acid); the residual 17-acetoxy-compounds afford, after hydrolysis (1% MeOH–KOH), testosterone and progesterone. 2-Bromocholestanone, 4-bromocoprostanone, cholestanol and its acetate resist oxidation by $K_2S_2O_8$. R. S. C.

Steroids. III. Partial oxidation of 3 : 5 : 6-triols and oxidation with permanganate of 5 : 6-unsaturated steroids. M. Ehrenstein and M. T. Decker (J. Org. Chem., 1940, **5**, 544—560).—Partial oxidation ($CrO_3 \equiv 1O$) of androstane-3(β)-5 : 6-(*trans*)-triol-17-one yields *androstane*-3(β) : 5-*diol*-6 : 17-*dione*, m.p. 282—284° (3-*monoacetate*, m.p. 197·5—199°, $[\alpha]_D^{26}$ +17·0° in $COMe_2$). Dehydro*iso*androsterone acetate is oxidised by $KMnO_4$ in $COMe_2$ to a mixture of substances including 5 : 6(α)-*oxido*-, m.p. 188—190°, $[\alpha]_D^{26}$ +58·4° in $COMe_2$, and 5 : 6(β)-*oxido*- (I), m.p. 221—222·5°, $[\alpha]_D^{26}$ +10° in $COMe_2$, *-androstan*-3(β)-*ol*-17-*one acetate* both of which with aq. $COMe_2$–H_2SO_4 undergo ring opening to *androstane*-3(β)-5 : 6-(trans)-*triol*-17-*one* 3-*monoacetate*, m.p. 234—235°, transformed by oxidation into *androstane*-3(β) : 5-*diol*-6 : 17-*dione* 3-*monacetate*, m.p. 234—235°, and by acetylation into the 3 : 6-*diacetate*, m.p. 216·5—217°, $[\alpha]_D^{26}$ ±0° in $COMe_2$. The dehydro*iso*androsterone oxide of Uschakov *et al.* (A., 1938, II, 65) and Miescher *et al.* (A., 1938, II, 174) is acetylated to (I). Oxidation ($KMnO_4$ in AcOH) of cholesteryl acetate gives a mixture of substances separated chromatographically into appreciable amounts of *cholestane*-3(β) : 5-*diol*-6-*one* 3-*monoacetate*, m.p. 226·5—228·5°, and β-*cholesterol oxide acetate*, m.p. 114—117°. Analogous oxidation of pregnenolone acetate affords a mixture of substances from which 5 : 6-*oxidopregnane*-3(β)-*ol*-20-*one acetate*, m.p. 163—165° (oxime, m.p. 219—221°), *pregnane*-3(β) : 5-*diol*-6 : 20-*dione* 3-*monoacetate*, m.p. 222·5—224° [oxime, m.p. 262—264° (decomp.)], and a small amount of *pregnane*-3(β) : 5 : 6-*triol*-20-*one* 3-*monoacetate*, m.p. 226—228° (oxime, m.p. 221—223°), are isolated. The mechanism of the oxidation ($KMnO_4$) of 5 : 6-unsaturated steroids is discussed. *Androstane*-3(β) : 5 : 6(cis)-*triol*-17-*one* 3 : 6-*diacetate* has m.p. 253—254°, $[\alpha]_D^{26}$ +63·6° in $COMe_2$. H. W.

Sterols. CIII. Oxidation of pregnanetriols. R. E. Marker and D. L. Turner (J. Amer. Chem. Soc., 1940, **62**, 2540—2541).—*allo*Pregnane-3 : 16 : 20-triol, $Al(OPr^B)_3$, and *cyclo*hexanone (excess) in PhMe give Δ¹⁶-*allo*pregnene-3 : 20-dione, reduced by H_2–Pd–$BaSO_4$ in Et_2O at 1·7 atm. to *allo*pregnane-3 : 20-dione. Sarsasapogenin acetate and $K_2S_2O_8$–H_2SO_4–K_2SO_4 in AcOH at room temp. give (after hydrolysis) pregnane-3(β) : 16 : 20-triol, m.p. 227—228° (lit. 223—226°), oxidised (as above) to (probably) Δ¹⁷:²⁰-*pregnene*-3 : 16-*dione*, m.p. 179—182°. R. S. C.

6-Methyl-Δ⁴-androstene-3 : 17-dione. O. S. Madaeva, M. I. Uschakov, and N. F. Koscheleva (J. Gen. Chem. Russ., 1940, **10**, 213—216).—Δ⁵-Androstene-3 : 17-diol and BzO_2H in $CHCl_3$ yield *androstene*-3 : 17-*diol* 5 : 6-*oxide*, m.p. 198—199° [*diacetate*, m.p. 165—165·5° (corr.)], which with MgMeI in Et_2O affords 6-*methylandrostane*-3 : 5 : 17-*triol*, m.p. 117—120° (3 : 17-*diacetate*, m.p. 176·3—177·9°). This is oxidised (CrO_3 in AcOH) to 6-*methylandrostan*-5-*ol*-3 : 17-*dione*, m.p. 187—188°, converted by HCl in $CHCl_3$ into 6-*methyl*-Δ⁴-*androstene*-3 : 17-*dione*, m.p. 163·5—167°. R. T.

Preparation and properties of derivatives of inositol. F. A. Hoglan and E. Bartow (J. Amer. Chem. Soc., 1940, **62**, 2397—2400).—Prep. of inositol from [best (9·5%), light] starch steep water is modified. Oxidation to 1 : 2 : 3 : 5 : 6 : 4-O·$C_6(OH)_4$·O (I) is best (35—40%) effected by HNO_3 (*d* 1·42) at room temp. The Na salt and the so-called "K rhodizonate" are salts of (I) and lead to the same products. The coloured *compounds*, (I),$2NH_2Ar$ (9 bases used; 6 others do not react), 22 inorg. salts of (I), and the (? tetra-)benzoate, m.p. 266—270° (decomp.), propionate, m.p. 231° (decomp.), butyrate, m.p. 237° (decomp.), *iso*butyrate, m.p. 121°, valerate, m.p. 241° (decomp.), *iso*valerate, m.p. 218° (decomp.), *iso*hexoate, m.p. 222—225° (decomp.), octoate, m.p. 224° (decomp.), and decoate, m.p. 208—211° (decomp.), are described. R. S. C.

1-Alkylthiolanthraquinones.—See B., 1940, 782.

Dependence of physiological action on chemical constitution. I. Difference in odour of *d*-, *l*-,

and *dl*-derivatives of amino- and diamino-methylenecamphor. B. K. Singh and A. B. Lal (Proc. Indian Acad. Sci., 1940, **12**, A, 230—234).—The order of intensity of odour of 5- and 3-nitro-*o*-toluidino- and of 2 : 5- and 2 : 3-toluylenesdiamino-methylenecamphor is $l > dl > d$ in each case. Hypotheses relating odour to chemical constitution are discussed. H. W.

Dependence of optical rotatory power on chemical constitution. XVIII. Rotatory dispersion of stereoisomeric 3-nitro-*o*-toluidino-, 5-nitro-*o*-toluidino-, 2 : 3-toluylenediamino-, and 2 : 5-toluylenediamino-methylenecamphor. B. K. Singh and A. B. Lal (Proc. Indian Acad. Sci., 1940, **12**, A, 157—178).—Hydroxymethylene-*d*-camphor in 90% EtOH and 5-nitro-*o*-toluidine in 70% AcOH at 0° afford 5-*nitro*-o-*toluidinomethylene*-d-*camphor*, m.p. 161—162°; the l- and dl-*camphor* compounds have m.p. 162° and 170°, respectively. 3-*Nitro*-o-*toluidinomethylene*-d-, -l-, and -dl-*camphor* have m.p. 98°, 98°, and 122°, respectively. 2 : 5-*Toluylenediaminomethylene*-d-, m.p. 215°, -l-, m.p. 217°, and -dl-, m.p. 136° -*camphor* are described. M.p. 115°, 116°, and 116° are recorded for 2 : 3-*toluylenediaminomethylene*-d-, -l-, and -dl-*camphor*. Rotatory powers in MeOH, $COMe_2$, C_6H_6, EtOH, C_5H_5N, and $CHCl_3$ are recorded at 35° for $\lambda = 5036$, 5218, 5460, 5780, 5812, 6102, 6362, 6438, and 6707 A. NO_2 at $C_{(5)}$ has a greater effect on the rotatory power than at $C_{(3)}$. The introduction of additional optically active centres does not result in a corresponding increase in the vals. of [α]. The influence of Me on [α] is irregular. The order of [α] in different solvents does not run parallel with the sequence of their dielectric consts., MeOH > EtOH > $COMe_2$ > C_5H_5N > $CHCl_3$ > C_6H_6. H. W.

Kinetics of mutarotation of hydroxymethylene-*d*-camphor.—See A., 1940, I, 443.

Volatile plant substances. XII. Structure of aromadendrene. Y. R. Naves and E. Perrottet (Helv. Chim. Acta, 1940, **23**, 912—925).—Repeated fractional distillation of the sesquiterpenes from oil of *Eucalyptus globulus*, Labill, gives aromadendrene (I), b.p. 114°/6 mm., α_{5461} +5·96° ($l = 1$?) hydrogenated (PtO_2) to dihydroaromadendrene (II), b.p. 104—104·5°/4 mm., α_{5461} −13·36° ($l = 1$?), and ozonised to aromadendrone, m.p. 83·5—84°, α_{5461} +5·02° ($l = 1$?) in EtOH. Evidence of more than one ethylenic linking has not been obtained. (I) absorbs only 1 H_2 and (II) appears saturated particularly towards $C(NO_2)_4$. The observation of Radcliffe *et al.* (A., 1938, II, 416) that aromadendrol is saturated towards $C(NO_2)_4$ and does not absorb H_2 is confirmed and it is found that oxygenated hydroazulenes are readily and completely hydrogenated. Fixation of halogens does not give any useful information probably on account of decyclisation. According to Rossmann's method (I) and (II) unite with 2·1 and 1 mol. of Br, respectively. Data are given for parachor, dispersion, dipole moment, and ultra-violet absorption and Raman spectra. H. W.

Sesquiterpenes. XLIV. Carbon skeleton of guaiol and of guaiazulene. P. A. Plattner and L. Lemay (Helv. Chim. Acta, 1940, **23**, 897—907).—Hydrogenation of guaiol (*dinitrobenzoate*, m.p. 137—137·5°) in presence of PtO_2 in *cyclo*hexane, EtOH, EtOAc with or without AcOH, or in AcOH leads to only 33% absorption of H_2 whereas hydrogenation with Raney Ni–H_2 at 100°/100 atm. affords dihydroguaiol (I), m.p. 78—79°, $[\alpha]_D$ −54° in $COMe_2$ (*dinitrobenzoate*, m.p. 150°, $[\alpha]_D$ −14·2°), and a dextrorotatory isomeride (II), $[\alpha]_D$ ~+40° (dinitrobenzoates, m.p. 135° and 144°). The dihydroguaiene (III) obtained from (I) and Ac_2O at 150°, $AlCl_3$ at 255°, BzCl in C_5H_5N followed by distillation, and $KHSO_4$ at 150—160° has b.p. 123—124°/11 mm., $[\alpha]_D$ −43·8° in EtOH, b.p. 124°/11 mm., $[\alpha]_D$ −59° in EtOH, $[\alpha]_D$ −57°, and b.p. 128—131°/13 mm., $[\alpha]_D$ −42·3° in EtOH, respectively. Ozonisation of (III) gives notable amounts of CH_2O and $COMe_2$ and the product is transformed by Zn dust into a *ketone*, $C_{12}H_{20}O$, b.p. 100—120°/3 mm. [*semicarbazone* (IV), m.p. 205—206°, $[\alpha]_D$ −81·4°], a neutral *material*, $C_{15}H_{20}O_2$, b.p. 130—136°/3 mm., probably a mixture of the expected CO-aldehyde and a neutral peroxidic *substance*, $C_{15}H_{26}O_3$, b.p. 169°/3 mm. Prolonged keeping of the neutral products gives a cryst. *substance*, $C_{15}H_{26}O_2$, m.p. 168·5—169·5°. Similar treatment of (II) leads to a *semicarbazone*, m.p. 196—197°, $[\alpha]_D$ +17·5°, whilst crude dihydroguaiol affords a *semicarbazone*, m.p. 199—200°, $[\alpha]_D$ +46°; neither compound depresses the m.p. of (IV). Aq. $H_2C_2O_4$ transforms (IV) into 2 : 6-*dimethyldi*cyclo-[0 : 3 : 5]-*decanone*, b.p. 130—131°/11 mm., $[\alpha]_D$ −107·4° in EtOH, reduced (Raney Ni in EtOH at room temp.) to 2 : 6-*dimethyldi*cyclo-[0 : 3 : 5]-*decanol*, b.p. 130—134°/10 mm. This is converted by $KHSO_4$ at 200° followed by S at 230° into 1 : 4-dimethylazulene [additive compound, m.p. 177—178°, with $C_6H_3(NO_2)_3$; picrate, m.p. 142—143°]. All m.p. are corr. H. W.

Triterpene resinols and related acids. XI. Oxidation of acetyloleanolic acid and of methyl acetyloleanolate with perbenzoic acid. C. W. Picard and F. S. Spring (J.C.S., 1940, 1387—1390).—Oxidation with BzO_2H of Me acetyloleanolate gives the oxide, m.p. 215—217° (corr.) [cf. m.p. 201—204° (corr.), Ruzicka *et al.*, A., 1937, II, 510], which with dil. HCl is isomerised to Me ketoacetyldihydrooleanolate. Similarly treatment of acetyloleanolic acid yields hydroxyacetyloleanolic acid lactone, m.p. 333°, characterised by formation of a Ac_2 derivative, and oxidation (CrO_3–AcOH) to ketoacetyloleanolic acid lactone. F. R. S.

Oxidation of lupenyl esters. E. R. H. Jones and R. J. Meakins (J.C.S., 1940, 1335—1339).—An examination of the absorption spectra of ketolupeol, ketolupenyl benzoate and acetate (I) (cf. Ruzicka *et al.*, A., 1939, II, 330), and *ketolupenyl acetate semicarbazone*, m.p. 251° (decomp.) [2 : 4-dinitrophenylhydrazone, m.p. 252° (decomp.)], has revealed that these ketones are αβ-unsaturated. Ozonolysis of (I) gives CH_2O (33% yield) and the acetate-acid, m.p. 260—261°, previously obtained by Duerden *et al.* (A., 1939, II, 170), which is hydrolysed to the OH-acid, $C_{28}H_{48}O_3$ (*Me* ester, m.p. 220—221°, $[\alpha]_D^{20}$ −22° in $CHCl_3$), also obtained by ozonolysis of lupenyl acetate in $CHCl_3$, but in AcOH an *acetate-acid*, $C_{31}H_{50}O_4$, m.p. 285—286° (decomp.), $[\alpha]_D^{20}$ −9·7° in

$CHCl_3$ [Me ester, m.p. 242—245° (decomp.)], is also isolated. F. R. S.

(A) **Abietic acid.** G. Dupont, J. Dubourg, and G. Rouris. (B) **Pyroabietic acid.** G. Dupont and J. Dubourg (Monit. Produits chim., 1936, **18**, No. 211, 8—11, 11—15; Chem. Zentr., 1937, i, 4109).—(A) Anomalies observed in the analysis, mol. wt. determination, and amount of H_2O eliminated during heating, of abietic acid (I) are due to the presence of a small amount of H_2O of crystallisation. Crystallisation from H_2O-containing solvents gives (I), m.p. 173°, $C_{20}H_{30}O_2 + \frac{1}{3}$ or $\frac{1}{4}H_2O$, which when heated or recrystallised from anhyd. C_6H_6, xylene, CCl_4, or CS_2 affords anhyd. (I), m.p. 151—153°, and not abietic anhydride. This contains 1 OH (Zerevitinov) and with abs. EtOH–NH_3, –NaOEt, and –KOH gives the normal NH_4, m.p. 121—122°, Na, and K salt, respectively, which are converted into gels under the action of moisture.

(B) The final product of isomerisation (heat; acid) of resin acids is not (I), which is converted at 190—200° into dextrorotatory products. *Pyroabietic acid*, m.p. 155—159°, $[\alpha]_{5461}$ +54·2°, isomeric and isomorphous with (I), has been isolated from a 20 year-old resin oil and from Aleppo turpentine after heating at 250°/80 hr. H. B.

Lignin and related compounds. L. Fractionation of acetylated cell wall constituents of red oak wood. Q. P. Peniston, J. L. McCarthy, and H. Hibbert (J. Amer. Chem. Soc., 1940, **62**, 2284—2288; cf. A., 1940, II, 348).—Extraction of red oak wood meal with Et_2O–C_6H_6 and aq. alkali, and treatment of the product with Ac_2O–H_2SO_4 at 25°, 29°, and 35° gives products, the solubility of which in $CHCl_3$ is 47·7, 73·3, and 78·4% (averages), respectively. Solubility thus parallels, and owes its increase to, fission of the macromols. Fractionation of the product by dioxan and $CHCl_3$ and pptn. from dioxan by MeOH gives products of widely differing composition. One fraction contained 87% of lignin. Sol. "carbohydrate" fractions could not be freed from OMe and probably contained combined lignin. In the natural wood the lignin, pentosans, and cellulose are probably partly but not entirely combined. R. S. C.

Sterols. C. Diosgenin. R. E. Marker, T. Tsukamoto, and D. L. Turner (J. Amer. Chem. Soc., 1940, **62**, 2525—2532).—Reactions of diosgenin (I) are interpreted in accordance with Marker's sapogenin formulæ. (I), isolated from *Dioscorea tokoro*, Makino, is stable to HCl–EtOH. With $Al(OPr^{\beta})_3$–PhMe-*cyclo*hexanone or with Br–AcOH, CrO_3, and then Zn dust, it gives Δ^4-*tigogenone* (II), m.p. 186—188°, hydrogenated (Pd–$BaSO_4$; Et_2O; 10 lb.) to *iso*sarsasapogenone (= smilagenone), which with $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ gives *iso*sarsasapogenin (= smilagenin). Na–EtOH reduces (II) to tigogenin (oxidised by CrO_3 to tigogenone) and Ac_2O at 200° isomerises it to ψ-Δ^4-*tigogenone* (III), an oil, reconverted into (II) by HCl–MeOH and reduced (H_2–Pd–$BaSO_4$; Et_2O; 5 lb.) to ψ-sarsasapogenone. CrO_3–AcOH oxidises (III) to $\Delta^{4:16}$-*pregnadiene*-3 : 20-*dione*, m.p. 182—185°, which with Na–EtOH gives *allo*pregnane-3(β) : 20(α)-diol (IV) and with H_2–Pd–$BaSO_4$ gives progesterone (V) and pregnane-3 : 20-dione. With Ac_2O at 195—200°, (I) gives ψ-*diosgenin* (VI), *forms*, m.p. 190—192° and 172—174°, the oily acetate of which by Br, CrO_3, Zn dust, and finally alkaline hydrolysis of the ketonic products gives $\Delta^{5:16}$-*pregnadien*-3-*ol*-20-*one*, m.p. 212—214°. This is reduced (Na–EtOH) to Δ^5-*pregnenediol*, m.p. 170—174° (and an isomeride), which is oxidised (Br, CrO_3, Zn) to (V) and hydrogenated (PtO_2; Et_2O; 3 atm.) to (IV). (VI) is reconverted by HCl–EtOH into (I) and hydrogenated (PtO_2; AcOH; 3 atm.) to *tetrahydro*-ψ-*diosgenin* (= *dihydro*-ψ-*tigogenin*), m.p. 202—205°, obtained also similarly from ψ-tigogenin and oxidised (CrO_3) to Δ^{16}-*allo*pregnenedione. R. S. C.

Sterols. CII. Chlorogenin. R. E. Marker, E. M. Jones, and D. L. Turner (J. Amer. Chem. Soc., 1940, **62**, 2537—2540).—The structure of chlorogenin (I) (A., 1940, II, 99) is confirmed and the OH are shown to be at 3(β) and 6(α). Na–EtOH reduces chlorogenone (II) to (I), but H_2–PtO_2 in EtOH at 3 atm. gives β-*chlorogenin*, m.p. 246—248° (*diacetate*, m.p. 120°; *dibenzoate*, m.p. 198—200°), further hydrogenated in AcOH to *dihydro*-β-*chlorogenin*, m.p. 209—210°. Cholestane-3 : 6-dione and Na–EtOH give the diol, m.p. 215—216°, also obtained from the 3-ol-6-one (Windaus, A., 1917, i, 265). Diosgenin and CrO_3–AcOH give $\Delta^{4:5}$-*diosgen*-3 : 6-*dione*, m.p. 194—195°, converted by Zn dust in AcOH into 6-*keto-tigogenone* [= (II); identity confirmed by reduction with Na–EtOH and H_2–PtO_2]. The mother-liquors from the oxidation of crude digitogenin afford (II) and the corresponding $C_{(5)}$-epimeride (cf. Windaus, A., 1926, 409). R. S. C.

Sterols. CVI. Sapogenins. XXXV. The supposed trillarigenin. R. E. Marker and J. Krueger (J. Amer. Chem. Soc., 1940, **62**, 2548—2549).—"Trillarigenin" (A., 1938, III, 837) is a ~7 : 3 mixture of diosgenin (I) and *trillin* (II), $C_{33}H_{52}O_8$, +0·5H_2O, m.p. 275—280° (decomp.). Vigorous hydrolysis of trillarin gives (I) and glucose; mild hydrolysis gives (II), which by vigorous hydrolysis affords (I) and glucose (identified as osazone). (II) gives a *tetra*-(? *penta*-)*acetate*, m.p. 202—203°, hydrolysed by 5% KOH–MeOH to (II) and hydrogenated (PtO_2; AcOH; 70°/3 atm.) to the H_4-*acetate*, which with boiling HCl–EtOH affords dihydrotigogenin. Hydrogenation (PtO_2) of (II) in MeOH containing a trace of AcOH at 1 atm. gives *dihydrotrillin*, +0·5H_2O, m.p. 270°, hydrolysed to tigogenin. (II) is thus *diosgenin* 3-*glucoside*. R. S. C.

Sclerotiorin, $C_{20}H_{20}O_5Cl$, m.p. 206—207°, metabolic product of *Penicillium sclerotiorum*, Van Beyma.—See A., 1940, III, 868.

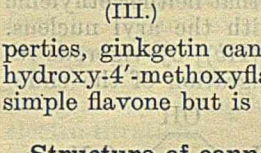
Structure of monocrotaline. IV. Monocrotalic acid. R. Adams and R. S. Long (J. Amer. Chem. Soc., 1940, **62**, 2289—2294).—The formula previously (A., 1940, II, 29) proposed for monocrotalic acid (I) and another considered are improbable in view of the properties of synthetic products.

COMe·CHMeBr and $CHNa(CO_2Et)_2$ in boiling Et_2O, PhMe, or PhMe–EtOH give *Et* α-*carbethoxy*-β-*methyllævulate* (II), b.p. 130—135°/3 mm. [2 : 4-*dinitrophenylhydrazone*, m.p. 118—119° (corr.)], hydrolysed

by boiling KOH–EtOH to *α-carboxy-β-methyl-lævulic acid*, m.p. 127—128° (corr.; decomp.), which at 130—140° gives CHMeAc·CH_2·CO_2H, b.p. 115—118°/3 mm. [*p*-nitrophenylhydrazone, m.p. 160—162° (corr.) (lit., 168—169°)]. The Na salt of (II) with MeI in boiling, abs. EtOH or PhMe–EtOH (less well, C_6H_6) gives *Et α-carbethoxy-αβ-dimethyl-lævulate* (III) (76%), b.p. 116—117°/2·5 mm., converted by boiling KOH–EtOH into the liquid dicarboxylic acid, which at 120° gives CHMeAc·CHMe·CO_2H (= monocrotic acid) (IV), b.p. 117—118°/3·5 mm. {Me ester, b.p. 97—98°/20 mm. [2 : 4-*dinitrophenylhydrazone, forms*, m.p. 107—109° (corr.) and 121—122°, obtained also from Me monocrotate (cf. *loc. cit.*)]}, and a little αβγ-trimethylangelicalactone (V). Boiling, conc. HCl converts (III) directly into (IV), but has no effect on (I). CO_2Et·CHAc·CHMe·CO_2Et, b.p. 107°/2 mm. [2 : 4 *dinitrophenylhydrazone*, m.p. 99—100° (corr.)], with Na and MeI in C_6H_6 or EtOH (less well, Et_2O) gives *Et β-carbethoxy-αβ-dimethyl-lævulate*, b.p. 110—115°/2 mm. {also obtained (25% yield) from CHMeAc·CO_2Et [2 : 4-*dinitrophenylhydrazone*, m.p. 56—57° (corr.)] and CHMeBr·CO_2Et}, which in conc. HCl at room temp. gives *β-carbethoxy-αβ-dimethyl-lævulic acid* (VI), b.p. 154—158°/2·5 mm., and (IV). Alkaline hydrolysis of (VI) gives (IV) and *meso*-(·CHMe·$CO_2H)_2$; that of Me monocrotalate gives (IV) and CO_2 with a little (V). Acid hydrolysis of Me dihydroanhydromonocrotalate gives the acid, m.p. 131—132°, $[\alpha]_D^{30}$ +3·80°, but alkali gives a mixture. R. S. C.

Derivatives of coumarin-3-carboxylic acid; a new class of synthetic medicinal. F. von Werder (Merck's Jahresber., 1936, **50**, 88—101).—*o*-OH·C_6H_4·CHO, $CH_2(CO_2Me)_2$, and a little piperidine at room temp. give *Me coumarin-3-carboxylate*, m.p. 116·5°. The following esters are prepared from the free acid (I) or the acid chloride (II): *Pr*$^{\alpha}$, m.p. 73°, *Pr*$^{\beta}$, m.p. 89°, *Bu*$^{\alpha}$, m.p. 67°, *CCl*$_3$·*CMe*$_2$, m.p. 176°, *CH*$_2$*Ph*, m.p. 92°, and diethylaminoethyl (*hydrochloride*, m.p. 215°). The appropriate amine and (II) afford *coumarin-3-carboxy-allylamide*, m.p. 130°, *-carbethoxyamide*, m.p. 183—184° (from NH_2·CO_2Et), *-ethylamide*, m.p. 132—133°, *-hexadecylamide*, m.p. 108—110°, *-phenylethylamide*, m.p. 178—179°, *-benzylamide*, m.p. 154°, -p-*anisidide*, m.p. 215—216°, -p-*phenetidide*, m.p. 206—207°, *-diethylaminoethylamide hydrochloride*, m.p. 187°, *-diethylamide* (III), m.p. 77—78°, *-dimethylamide*, m.p. 144—145°, *-dipropylamide*, m.p. 80—81°, *-diallylamide*, m.p. 132°, *-di*-iso-, m.p. 137°, and -sec.-*butylamide*, m.p. 148°, *-diphenylamide*, m.p. 236°, *-di-β-phenylethylamide*, m.p. 119—120°, *-dibenzylamide*, m.p. 143°, *-methylpropylamide*, m.p. 109—110°, -iso*butyl-*, m.p. 102—103°, and -iso*amyl-allylamide*, m.p. 79°, *-piperidide*, m.p. 179—180°, *-methyl-*, m.p. 111—112°, and *-benzyl-*p-*phenetidide*, m.p. 160°, *-diacetonamide*, m.p. 127—129°, and -s-*diethylcarbamide*, m.p. 148—149°. *Et* β-*coumarin-3-carboxylamido-α-phenyl-α-methylpropionate* has m.p. 111—112°. The following salts of (I) are prepared in $COMe_2$: dl-, m.p. 196°, and l-*ephedrine*, m.p. 145°, *papaverine*, m.p. 129°, *eupaverine*, m.p. 134°, *quinine*, m.p. 137—139°, *sparteine*, m.p. 157°, β-*methylamino-α*-p-*aminophenylpropyl alcohol*, m.p. 182°, and (?) 6 : 7-*methylenedioxy*-1-3′ : 4′-*methylenedioxyphenyl*-3-*methyl*-iso*quinoline*, m.p. 174°. 3 : 2 : 1-CH_2:CH·CH_2·C_6H_3(OH)·CHO, $CH_2(CO_2Et)_2$, and piperidine give *Et* 8-*allylcoumarin-3-carboxylate*, m.p. 88° (free *acid*, m.p. 147°); *phenanthrocoumarin-3-carboxylic acid*, m.p. 196°, is similarly obtained (as impure Et ester, m.p. 165°) from 3-phenanthrol-4-aldehyde. Pharmacological data are reported; (III) is a powerful sedative whilst (I) is a sedative in small and a hypnotic in large doses. Ch. Abs. (*b*)

Derivatives of 5 : 6 : 4′- and 5 : 8 : 4′-trihydroxyflavones, and a note on the structure of ginkgetin. W. Baker and W. H. C. Simmonds (J.C.S., 1940, 1370—1374).—2-*Anisoyloxy*-3 : 6-*dimethoxyacetophenone*, m.p. 131°, with $NaNH_2$ in PhMe gives 2-*hydroxy*-3 : 6 : 4′-*trimethoxydibenzoylmethane*, m.p. 138—139°, which with NaOAc–AcOH is finally rearranged to 5 : 8 : 4′-*trimethoxyflavone* (I), m.p. 161°. Partial demethylation of (I) with $AlCl_3$ affords the 5-*OH*-compound, m.p. 146° (*Ac* derivative, m.p. 200°). 2-Hydroxy-6-benzyloxyacetophenone is methylated (Me_2SO_4) to the 6-*benzyloxy*-2-*methoxy*-compound, m.p. 74°, which is hydrolysed (AcOH–HCl) to the 2-hydroxy-6-methoxy-derivative. 2-*Anisoyloxy*-5 : 6-*dimethoxyacetophenone*, m.p. 99°, is rearranged ($NaNH_2$–PhMe) to 2-*hydroxy*-5 : 6 : 4′-*trimethoxydibenzoylmethane*, m.p. 69°, which is further converted (AcOH–NaOAc) into 5 : 6 : 4′-*trimethoxyflavone* (II), m.p. 164°. Partial demethylation of (II) gives 5-*hydroxy*-6 : 4′-*dimethoxyflavone*, m.p. 173° (*Ac* derivative, m.p. 182·5°). Complete demethylation of (II) with AcOH–HBr yields 5 : 6 : 4′-*trihydroxyflavone*, m.p. 298° (*Ac*$_3$ derivative, m.p. 209°), also obtained by complete demethylation (HBr–AcOH) of (I), re-orientation of the OH groups having occurred through opening and subsequent closing of the flavone ring in the alternative direction. By comparison of properties, ginkgetin cannot be either 5 : 8- or 5 : 6-dihydroxy-4′-methoxyflavone; it is probably not a simple flavone but is best represented by (III).



(III.)

F. R. S.

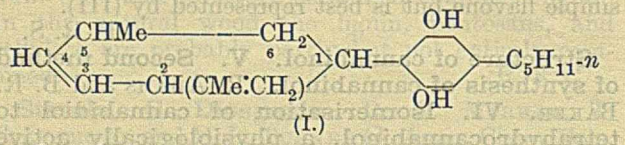
Structure of cannabinol. V. Second method of synthesis of cannabinol. R. Adams and B. R. Baker. **VI. Isomerisation of cannabidiol to tetrahydrocannabinol, a physiologically active product. Conversion of cannabidiol into cannabinol.** R. Adams, D. C. Pease, C. K. Cain, and J. H. Clark. **VII. Synthesis of a tetrahydrocannabinol which possesses marihuana activity.** R. Adams and B. R. Baker. **VIII. Position of the ethylenic linkings in cannabidiol. Marihuana activity of tetrahydrocannabinols.** R. Adams, S. Loewe, D. C. Pease, C. K. Cain, R. B. Wearn, R. B. Baker, and H. Wolff (J. Amer. Chem. Soc., 1940, **62**, 2401, 2402—2405, 2405—2408, 2566—2567; cf. A., 1940, II, 354).—V. Olivetol, Et 5-methyl*cyclo*hexanone-2-carboxylate, and $POCl_3$ in C_6H_6 give 57% of 1-*hydroxy*-9-*methyl*-3-n-*amyl*-7 : 8 : 9 : 10-*tetrahydro*-6-*dibenzpyrone* [6″-*hydroxy*-5′-*methyl*-4″-n-*amyl*-3′ : 4′ : 5′ : 6′-*tetrahydrodibenzopyrone*], m.p. 180—181° (corr.) (*acetate*, m.p. 82·5—84°), which with S at 255—260° gives 1-hydroxy-9-methyl-

3-*n*-amyl-6-dibenzopyrone (61%), m.p. 184—185° (corr.), and thence (MgMeI) cannabinol.

VI. Isomerisation of cannabidiol (I) to tetrahydrocannabinol, (II*a*) $[\alpha]_D^{32}$ ~—165° and (II*b*) $[\alpha]_D^{32}$ ~—240°, is detailed (cf. *ibid.*, 355). Dehydrogenation of (II) to cannabinol and hydrogenation (PtO_2) to hexahydrocannabinol (III) are detailed. (II) and (III) have marihuana activity.

VII. Et *cyclo*hexanone-2-carboxylate, orcinol (IV), and $POCl_3$ in C_6H_6 give 6″-*hydroxy*-4″-*methyl*-3′ : 4′ : 5′ : 6′-*tetrahydrodibenzopyrone* (V), m.p. 243—245° [*acetate* (VI), m.p. 126—127°] (cf. Ahmad *et al.*, A., 1938, II, 198), which with MgMeI gives a product, converted by HI into 6″-*hydroxy*-2 : 2 : 4″-*trimethyl*-3′ : 4′ : 5′ : 6′-*tetrahydrodibenzopyrone*, m.p.136—138°. 5-Methyl*cyclo*hexane-1 : 3-dione, *o*-$C_6H_4Br{\cdot}CO_2H$, and $Cu(OAc)_2$ give 71% of 6″-*keto*-4″-*methyl*-3″ : 4″ : 5″ : 6″-*tetrahydrodibenzopyrone*, m.p. 148—150° (corr.), dehydrogenated by S at 255—260° to 6″-*hydroxy*-4″-*methyldibenzopyrone* (VII) (45%), m.p. 249—251° (*acetate*, m.p. 144—146°), obtained also (83%) similarly from (V). Dehydrogenation of (VI) causes partial hydrolysis, completion of which by HCl–EtOH yields (VII). Et 5-methyl*cyclo*hexanone-2-carboxylate, (IV), and $POCl_3$ in C_6H_6 give 6″-hydroxy-4″ : 5′-dimethyl-3′ : 4′ : 5′ : 6′-tetrahydrodibenzopyrone (62%), m.p. 262—263° (Ahmad *et al.*, *loc. cit.*, 260°), which with MgMeI gives 6-*hydroxy*-2 : 2 : 4″ : 5′-*tetramethyl*-3′ : 4′ : 5′ : 6′-*tetrahydrodibenzopyran* (77%), m.p. 115·5—116°. 6-*Hydroxy*-2 : 2 : 5′-*trimethyl*-4″-*n*-*amyl*-3′ : 4′ : 5′ : 6′-*tetrahydrodibenzopyran* [a *tetrahydrocannabinol*] (VIII), b.p. 191—192°/1 mm., is similarly prepared and has marihuana activity. M.p. are corr.

VIII. The absorption spectrum of (I) [log ϵ 3·18; cf. log ϵ 3·05 for (II)] and failure of (I) to react with $(CH{\cdot}CO)_2O$ show that the ethylenic linkings in (I) are not conjugated. Differences between physical consts. of (VIII) and (II) show that neither ethylenic linking in (I) is conjugated with the aryl nucleus. Change of [α] of (II) [(II*a*) → (II*b*)] by vigorous reagents is held to be due to migration of the endo-



(I.)

cyclic ethylenic linking, probably from the 3 : 4 to the 4 : 5 position. (I) thus has the structure shown. Relative physiological potencies are: marihuana red oil 1, (I) 0, (II*a*) 2·5±0·66, (II*b*) 1·75±0·25, (III) 0·70±0·10, (VIII) 0·20±0·07, synthetic hexahydrocannabinol 0·15±0·05. (II*a*) and (II*b*) give acetates, $[\alpha]_D^{34}$ —167° and —229°, and Me ethers, $[\alpha]_D^{32}$ —240° and —226°, respectively. R. S. C.

[Projected] synthesis of cannabinol. G. Powell and T. H. Bembry (J. Amer. Chem. Soc., 1940, **62**, 2568—2569).—Et *cyclo*hexanone- and 5-methyl*cyclo*hexanone-2-carboxylate with orcinol or olivetol in H_2SO_4 give pyrones, converted by MgMeI into diols or tetrahydropyrans, which may be later dehydrogenated (cf. Adams *et al.*, A., 1940, II, 355). Thus are obtained 2 : 2 : 5″-*trimethyl*-3′ : 4′ : 5′ : 6′-*tetrahydro*-, m.p. 69°, 2 : 2 : 5″-*trimethyl*-, m.p. 58°, and 6″-*methoxy*-2 : 2 : 4″-*trimethyl*-*dibenzopyran*, 6″-*hydroxy*-5′-*methyl*-4″-*n*-*amyl*-3′ : 4′ : 5′ : 6′-*tetrahydrodibenzopyrone*, m.p. 172—173°, and 2′-*hydroxy*-6′-*methoxy*-4′ : 3-*dimethyl*-6-α-*hydroxy*isopropyl-1 : 2 : 3 : 4-*tetrahydrodiphenyl*, m.p. 105—106°. R. S. C.

***Cannabis indica*. V. Synthesis of cannabinol.** R. Ghosh, A. R. Todd, and S. Wilkinson (J.C.S., 1940, 1393—1396).—The *Et* ester, m.p. 48°, of 2′ : 4′-*dimethoxyphenyl*-Δ¹-cyclo*hexene*-2-*carboxylic acid*, m.p. 153—154°, prepared from 7-hydroxy-3 : 4-*cyclo*hexenocoumarin (I) and NaOH, is dehydrogenated with S, followed by demethylation (HBr) and hydrolysis to 7-*hydroxy*-3 : 4-*benzocoumarin*, m.p. 233°, also obtained by dehydrogenation with Pd–C of 7-acetoxy-3 : 4-*cyclo*hexenocoumarin or of (I) with Se. Dehydrogenation (Pd–C) of 6″-acetoxy-2 : 2 : 4″-trimethyl-3′ : 4′ : 5′ : 6′-tetrahydrodibenzopyran yields 6″-*hydroxy*-2 : 2 : 4″-*trimethyldibenzopyran*, m.p. 164°. Similar treatment of 5-acetoxy-5′-methyl-7-*n*-amyl-3 : 4-*cyclo*hexenocoumarin affords 5-*hydroxy*-5′-*methyl*-7-*n*-*amyl*-3 : 4-*benzocoumarin*, m.p. 187° (*acetate*, m.p. 98°). The *acetate*, b.p. 140—145°/10^{-3} mm., of 6″-hydroxy-2 : 2 : 5′-trimethyl-4″-n-amyl-3′ : 4′ : 5 : 6′-tetrahydrodibenzopyran is similarly converted (Pd–C) into 6″-*hydroxy*-2 : 2 : 5′-*trimethyl*-4″-n-*amyldibenzopyran*, b.p. 160—165°/10^{-2} mm., identical with natural cannabinol (Adams *et al.*, A., 1940, II, 354, give m.p. 75—76°). The acetate of 6-hydroxy-5′-methyl-3 : 4-*cyclo*hexenocoumarin with MgMeI gives 5″-*hydroxy*-2 : 2 : 5′-*trimethyl*-3′ : 4′ : 5′ : 6′-*tetrahydrodibenzopyran*, b.p. 130—135°/10^{-2} mm., of which the acetate is dehydrogenated to 5″-hydroxy-2 : 2 : 5′-trimethyldibenzopyran. F. R. S.

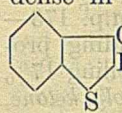
Non-crystalline constituents of *Tephrosia virginiana* roots. L. D. Goodhue and H. L. Haller (J. Amer. Chem. Soc., 1940, **62**, 2520—2522).—Roots of *T. virginiana*, L., contain 7·4% of total extractives ($CHCl_3$), including 2·4% of rotenone. The alkali-sol. portion of the resin yields unidentified phenols and a little tephrosin (I), dehydrorotenone, and, after "mol." distillation, a substance, m.p. 76°, insol. in alkali. Extraction of a 90% AcOH solution of the neutral portion with light petroleum removes an oil, mainly sesquiterpenes with a small amount of a drying oil. The residual neutral resin contains *l*-deguelin [racemisation by MeOH–KOH gives 20% of *dl*-deguelin (II) and hydrogenation gives *l*-dihydrodeguelin] and, after adsorption on C, further amounts of (I) and (II), with a resin, which by "mol." distillation yields a yellow *substance*, $C_{20}H_{18}O_2(OMe)_2$, m.p. 125°, α 0 in C_6H_6, and Clark's substance, $C_{20}H_{19}O_3{\cdot}OMe$, m.p. 131°, $[\alpha]_D^{20}$ —95·5° in C_6H_6. R. S. C.

Thiophen derivatives. II. N. K. Chakrabarty and S. K. Mitra (J.C.S., 1940, 1385—1387).—Thionation of Et β-carbethoxy-α-ethyl-lævulate gives in small yield 5-*ethoxy*-2-*methyl*-4-*ethylthiophen*-3-*carboxylic acid*, m.p. 105°; the corresponding 2 : 4-Me_2 compound, m.p. 125°, de-ethylated to the 5-*hydroxy*-2 : 4-*dimethyl* derivative, m.p. 140°, is similarly obtained. In the prep. of the following the thioketonic ester is added to emulsified Na in C_6H_6 and the α-halogenated fatty ester added: *Et* β-(α′-*carbethoxyethylthio*)*crotonate*, b.p. 124°/5 mm., *Et* α-(α′-

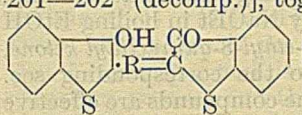
carbethoxyethylthio)ethylidenemalonate, b.p. 125°/5 mm., and *Et* β-*carbethoxymethylthiocrotonate*, b.p. 116°/9 mm. The action of Na on the appropriate thioether gives *Et* 3-*hydroxythiophen*-5-*acetate* (I), b.p. 96°/5 mm., and -5-α-*propionate*, b.p. 116°/5 mm., m.p. 53°, and *Et* 3-*hydroxy*-2-*methylthiophen*-5-*acetate*, b.p. 104°/5 mm. $SOCl_2$ and EtI with (I) afford respectively *Et* 3-*chloro*-, b.p. 128°/8 mm., and 3-*ethoxy-thiophen*-5-*acetate*, b.p. 102°/5 mm. F. R. S.

Benzene-*o*-bisthioindoxyl.—See B., 1940, 726.

Polymethine dyes of the 3-hydroxythionaphthen series. I. Condensation of 3-hydroxythionaphthen with *NN'*-diphenylformamidine and with the dianils of malonic and glutaconic aldehydes. N. N. Sveschnikov and I. I. Levkoev (J. Gen. Chem. Russ., 1940, **10**, 274—280).—3-Hydroxythionaphthen and NPh:CH·NHPh or the dianils of malonic or glutaconic aldehydes condense in EtOH solution, giving anils of the type



[R = CH·; R = ·CH:CH·CH·, m.p. 217—218° (decomp.); R = ·CH:CH·CH:CH·CH·, m.p. 201—202° (decomp.)], together with dyes of the type



[R = ·CH·; R = ·CH:CH·CH·, m.p. 255—257° (decomp.); R = ·CH:CH·CH:CH·CH·, m.p. 240—242° (decomp.)]. The anils are readily converted into the dyes by heating with HCl–EtOH. Increase in the length of the polymethine chain shifts the absorption max. of alkaline or acid solutions of the dyes towards the red. R. T.

5-Keto-4 : 4-dialkyldihydropyrroles. R. Zumbrunn (Festschr. E. C. Barell [Basel], 1936, 206—211; Chem. Zentr., 1937, i, 4787—4788).—5-Keto-4 : 5-dihydropyrroles unsubstituted at $C_{(4)}$ condense with AlkCHO and ketones in presence of bases, *e.g.*, $NHEt_2$; the resulting alkylidene derivatives are reduced catalytically to the 4-alkyl derivatives, which can be obtained directly by the action of $NaNH_2$ and alkyl halide in boiling C_6H_6. Mono- or di-allylation at $C_{(4)}$ can be effected with CH_2:CH·CH_2Br in aq. EtOH + Cu; catalytic reduction then gives the Pr derivatives. Various Et 5-keto-4 : 4-dialkyl-4 : 5-dihydropyrrole-3-carboxylates have been prepared; the free acids could not be obtained by hydrolysis owing to ring fission (by acids) or non-reaction. *Et* 5-*keto*-1 : 2-*dimethyl*-4-*ethylidene*- and 5-*keto*-2-*methyl*-4-*ethyl*-4-*diethylaminoethyl*-4 : 5-*dihydropyrrole*-3-*carboxylates* appear new. 5-Keto-2-methyl-4 : 5-dihydropyrrole could not be obtained from (?) CHO·$[CH_2]_2$·CO_2Et or $(OEt)_2$CMe·$[CH_2]_2$·CO_2Et (I) and NH_3. NH_2Ph and (I) give *Et* γ-*anilovalerate*, which could not be converted (heat; NaOEt) into a pyrrole. *Et* γ-*anilinovalerate* does not eliminate EtOH at 250°; the free acid passes into 1-*phenyl*-5-*methyl* 2-*pyrrolidone* at <100°. H. B.

Synthesis of soporifics of the pyridine series. O. Schnider (Festschr. E. C. Barell [Basel], 1936, 195—205; Chem. Zentr., 1937, i, 4642).—$CEt_2Ac·CO_2Et$ and HCO_2Et are condensed to OH·CH:CH·CO·CEt_2·CO_2Et, which is converted by NH_3 into NH_2·CH:CH·CO·CEt_2·CO_2Et and thence (alkali) into 2 : 4-diketo-3 : 3-diethyl-1 : 2 : 3 : 4-tetrahydropyridine (I). This procedure is not of general applicability although the corresponding 3 : 3-diallyl derivative (II) can be similarly prepared; (II) is also obtained by allylation of 2 : 4-diketo-1 : 2 : 3 : 4-tetrahydropyridine in aq. EtOH in presence of a trace of Cu. Similar allylation of 2 : 4-diketo-6-methyl-1 : 2 : 3 : 4-tetrahydropyridine (III) [from NH_2·CMe:CH·CO_2Et (IV), $CH_2(CO_2Et)_2$, and NaOEt with subsequent hydrolysis] gives its 3 : 3-diallyl derivative (V). The *N*-Et derivative of (III) is formed on ethylation (EtBr); this differs from 2 : 4-diketo-6-methyl-3-ethyl-1 : 2 : 3 : 4-tetrahydropyridine [prep. from (IV) and $CHEt(CO_2Et)_2$], alkylation [other than allylation, which occurs at $C_{(3)}$] of which affords *N*-derivatives. The allyl compounds are reduced to the corresponding Pr derivatives. (V), which is a soporific [as is (I)], and its analogues are more strongly lipotropic than the 5 : 5-dialkylbarbituric acids; *N*-alkylation leads to neutral, strongly lipotropic compounds with enhanced soporific properties. H. B.

α-Pyridinium compounds of higher fatty acids.—See B., 1940, 778.

Preparation of certain quinaldine methiodides. V. A. Alexeeva (J. Gen. Chem. Russ., 1940, **10**, 263—270).—4-Chloroquinaldine (I) and Me_2SO_4 (30 min. at —5°, 30 min. at room temp., then 20 min. at 100°) give the corresponding dimethosulphate, which with aq. KI yields 4-*chloroquinaldine methiodide* (II), decomp. at 222—223°. The Cl atom of (II) is highly reactive; (II) with NH_2Ph (2 hr. at 120°) gives 4-*anilino*-, m.p. 264° (80%), with NHPh·NH_2 gives 4-*phenylhydrazino*-, m.p. 235° (97%), and with NH_2Me gives 4-*methylamino-quinaldine methiodide*, m.p. 290° (90%). (I) and excess of MeI (26 hr. at 100°) give 4-*iodoquinaldine methiodide*, m.p. 230° (decomp.) (22%). The products are conveniently analysed for halogens by Pringsheim combustion, followed by electro-titration. R. T.

Carbazolecarboxyl chlorides.—See B., 1940, 762.

Nitro- and amino-benz[f]quinolines and derivatives. W. J. Clem and C. S. Hamilton (J. Amer. Chem. Soc., 1940, **62**, 2349—2352).—Naphth-2′ : 1′ : 2 : 3-pyridine (I) [prep. in 18·5% yield from β-$C_{10}H_7$·NH_2, glycerol (II), H_2SO_4, and H_3AsO_4 at 140°], m.p. 93°, with HNO_3 (*d* 1·5) and H_2SO_4 at —15° gives the 5′-NO_2-compound (40%), m.p. 174°, converted by nitration at 0° into the 5′ : 7′-$(NO_2)_2$-compound, m.p. 250°, which is similarly obtained from (I). 6 : 2-NO_2·$C_{10}H_6$·NH_2, (II), H_3BO_2, and H_2SO_4 at 140° give 6′-*nitronaphth*-2′ : 1′ : 2 : 3-*pyridine* (34%), m.p. 240°. Hydrogenation (Raney Ni; $COMe_2$; 2·67 atm.) of the appropriate NO_2-compound gives 5′-, m.p. 175° (lit., 158°) (*Ac*, m.p. 235°, *CHPh*:, m.p. 101°, *CH_2Ph*, m.p. 152—154°, m-*NO_2·C_6H_4·CH*:, m.p. 182—183°, and m-*NH_2·C_6H_4·CH_2*, m.p. 141—144°, derivative; *mono*- and *di-hydrochloride*, m.p. >300°), 6′- (III), m.p. 222—224° (*dihydrochloride*, m.p. >300°; *Ac*, m.p. 212—213°, and *CHPh*: derivative, m.p. 148—

151°), and 8′-*aminonaphth*-2′ : 1′ : 2 : 3-*pyridine* (IV), m.p. 156—157° (*mono-* and *di-hydrochloride*, m.p. >300°; *Ac* derivative, m.p. 152—154°), and the 5′ : 7′-$(NH_2)_2$-compound, m.p. 245—246°. The structure of (III) and (IV) is proved by oxidation to quinoline-5 : 6-dicarboxylic acid. 6-Chloro-4-methylnaphth-2′ : 1′ : 2 : 3-pyridine and NH_2·$[CH_2]_2$·OH at 180° give 6-β-*hydroxyethylamino*-4-*methylnaphth*-2′ : 1′ : 2 : 3-*pyridine*, m.p. 148—149°, which with $POCl_3$ at 110° gives 6-*vinylamino*-4-*methylnaphth*-2′ : 1′ : 2 : 3-*pyridine*, m.p. 163—164°. R. S. C.

5 : 5-Dianisylhydantoin.—See B., 1940, 823.

Pyrimidines. CLXV. Reaction of thiocarbamide with 5 : 5-dibromo-hydroxyhydrouracil and -barbituric acid. T. B. Johnson (J. Amer. Chem. Soc., 1940, **62**, 2269—2271).—5 : 5-Dibromohydroxyhydrouracil in EtOH or H_2O gives quantitatively 5-bromouracil (I) and HOBr and may thus be used as an oxidising agent. With NH_2·C(:NH)·SH in EtOH or H_2O it give (I), S, HBr, and CN·NH_2; no uracil-5-ψ-thiocarbamide is obtained (cf. 5 : 5-dibromobarbituric acid). R. S. C.

Synthesis of *iso*cytosine. W. T. Caldwell and H. B. Kime (J. Amer. Chem. Soc., 1940, **62**, 2365).—Prep. of *iso*cytosine from guanidine hydrochloride, malic acid, and 15% oleum at <5° is described. R. S. C.

Synthesis of compounds related to cinchonine and quinine. B. K. Nandi (Proc. Indian Acad. Sci., 1940, **12**, A, 1—19).—Et quinoline-3-carboxylate (I) and EtOAc in boiling C_6H_6 are transformed by NaOEt free from EtOH into *Et* 3-*quinoloylacetate* (*Cu* salt, m.p. 202—203°) which could not be distilled unchanged but is converted by 25% H_2SO_4 at 100° into 3-*quinolyl Me ketone* (II), m.p. 98° (*semicarbazone*, m.p. 235°; *phenylhydrazone*, m.p. 202°). Passage of Br through (II) dissolved in 45% HBr at 70—75° leads to 3-*quinolyl* CH_2Br *ketone* (III), unstable, m.p. 120° [*hydrobromide*, m.p. 215° (decomp.)], which with piperidine in C_6H_6 at ~5° affords 3-*quinolyl piperidinomethyl ketone* (IV), b.p. 165—168°/15 mm. (*monohydrobromide*, m.p. 245—246° after becoming brown at 230°; *dipicrate*, m.p. 139—141°). Reduction (H_2–Pd in conc. HBr) of (IV) yields 3-β-*piperidino*-α-*hydroxyethylquinoline*, m.p. 93—94° (*dipicrate*, m.p. 161—163°). $NHEt_2$ and (III) in Et_2O at room temp. give non-cryst. 3-*quinolyl* CH_2·NEt_2 *ketone* (*monohydrobromide*, m.p. 142—145°; *dipicrate*, m.p. 150—151°), which could not be distilled unchanged; it is reduced to 3-β-*diethylamino*-α-*hydroxyethylquinoline*, m.p. 89—90° (*dipicrate*, m.p. 139—141°). Non-cryst. 3-*quinolyl* CH_2·NMe_2 *ketone* [*dihydrochloride*, m.p. 157—158°; *dipicrate*, m.p. 147—149° (decomp.)] is reduced to 3-β-*dimethylamino*-α-*hydroxyethylquinoline*, an oil (*dihydrochloride*, m.p. 171—173°; *Ac* derivative, m.p. 139°). (I) and *N*-benzoylhomocincholoiponic ester (V) are condensed by NaOEt to *Et* α-3-*quinoloyl*-β-1′-*benzoyl*-3′-*ethyl*-4′-*piperidylpropionate*, an oil (*Cu* derivative, m.p. 251° after darkening at ~237°), which could not be distilled unchanged and is hydrolysed by boiling 17% HCl to β-3′-*ethyl*-4′-*piperidylethyl* 3-*quinolyl ketone*, b.p. 225°/9 mm. (*phenylhydrazone dipicrate*, m.p. 195—197°). This in N-HCl and Et_2O at room temp. is transformed by dropwise addition of NaOBr into the 1′-*Br*-compound, m.p. 137—139°, which does not give a methiodide and is transformed by boiling NaOEt–EtOH into 3′-*quinolyl* 8-3-*ethylquinuclidyl ketone*, m.p. 122—124° (*monopicrate*, m.p. 167—168°); it is hydrogenated (Pd in 5% HCl) to 3′-*quinolyl*-8 : 3-*ethylquinuclidylmethanol*, m.p. 225—226° [*dihydrochloride*, m.p. 261—263°; *platinichloride*, m.p. 286—289° (decomp.)]. Et 2-methoxyquinoline-3-carboxylate (VI), EtOAc, and NaOEt in boiling C_6H_6 afford 2-*methoxy*-3-*quinolyl Me ketone*, m.p. 110—112° (*phenylhydrazone*, m.p. 177°). The corresponding CH_2Br *ketone*, m.p. 126—127°, yields the *piperidinomethyl ketone*, m.p. 69—71° [*monohydrobromide*, m.p. 251—256° (decomp.)], reduced to 2-*methoxy*-3-β-*piperidino*-α-*hydroxyethylquinoline*, m.p. 102—104°, the CH_2·NEt_2 *ketone*, m.p. 134—136°, reduced to 2-*methoxy*-3-β-*diethylamino*-α-*hydroxyethylquinoline*, m.p. 78—79°, and the CH_2·NMe_2 *ketone* (*dihydrochloride*, m.p. 177°), reduced to 2-*methoxy*-3-β-*dimethylamino*-α-*hydroxyethylquinoline*, an oil (*dihydrochloride*, m.p. 167—169°; *dipicrate*, m.p. 173—175°). (V) and (VI) yield the corresponding propionate, hydrolysed by a large excess of boiling 17% HCl to 3-*ethyl*-4-*piperidyl* 2′-*methoxy*-3′-*quinolyl ketone*, b.p. 197—200°/5 mm. (*phenylhydrazone dipicrate*, m.p. 188—189°). The corresponding 1-*Br*-*ketone*, m.p. 158—162°, is transformed by NaOEt in boiling EtOH into 2′-*methoxy*-3′-*quinolyl* 3-*ethyl*-8-*quinuclidyl ketone*, m.p. 155—156°, reduced to the corresponding sec. *alcohol*, m.p. 259—261°. The compounds are effective against paramecia but those related to cinchonine are ineffective against avian malaria; those related to quinine have not been tested. H. W.

New test for hydroxylamine by formation of "indo-oxine" [5-(8′-hydroxy-5′-quinolinyl)-imino-8-keto-5 : 8-dihydroquinoline]. R. Berg and (Frl.) E. Becker (Ber., 1940, **73**, [*B*], 172—173; cf. Monti *et al.*, A., 1935, 500).—With 1% 8-hydroxyquinoline (I) in EtOH, a solution containing NH_2OH,HCl (II) (1 in 12×10^6) with 2N-Na_2CO_3 gives a green coloration; at higher concns. of (II), after keeping in air, a brown *Na* salt of "*indo-oxine*" [5-(8′-*hydroxy*-5′-*quinolyl*)*imino*-8-*keto*-5 : 8-*dihydroquinoline*], m.p. 253—254°, separates. This has no indophenol properties. E. W. W.

Melamine preparation. P. P. McClellan (Ind. Eng. Chem., 1940, **32**, 1181—1186).—The literature of melamine (I) and related products is reviewed. (I) is now a comparatively cheap commercial product and commercial methods of prep. are compared. Solubility of (I) in H_2O is 0·5, 2·5, or 5·5% at 25°, 75°, or 90°, respectively. Pyrolysis of anhyd. CN·NH_2, guanidine (II) salts alone, or dicyanodiamidine (III) alone or in presence of solvents at atm. pressure does not give high yields of (I). Heating together (III) and (II), either dry or in presence of NH_3, improves the method. High yields of (I) are obtained by heating (II) under pressure in presence of free NH_3; some CN·NH_2, (II), and diguanide are also formed. The latter method is not improved materially by use of equimols. of CN·NH_2 and (III). The complete mechanism of the formation of (I) is not clear. A. T. P.

Phthalocyanines.—See B., 1940, 784.

Metalloporphyrins. I. Co-ordination with nitrogenous bases. Theoretical relations. W. M. CLARK, J. F. TAYLOR, T. H. DAVIES, and C. S. VESTLING. **II. Cobalt and manganese meso-porphyrins in co-ordination with nitrogenous bases.** J. F. TAYLOR and W. M. CLARK. **III. Co-ordination of nitrogenous bases with iron meso-, proto-, and hæmato-porphyrins.** T. H. DAVIES. **IV. Co-ordination of iron copro- and ætio-porphyrins with nitrogenous bases.** C. S. VESTLING. **V. Spectrophotometric study of pyridine [iron] coproporphyrin I.** W. M. CLARK and M. E. PERKINS (J. Biol. Chem., 1940, **135**, 543—568, 569—595, 597—622, 623—641, 643—657; cf. Barron, A., 1937, III, 450).—I. A nomenclature for metalloporphyrins and their co-ordination compounds is proposed. Equations are developed for relating potentiometric and spectrophotometric data with the state of equilibrium between oxidised and reduced metalloporphyrin and the co-ordinating base.

II. The prepn. of mangani- (I), $C_{34}H_{36}O_4N_4MnOH$, and *cobalto-mesoporphyrin* (II), $C_{34}H_{36}O_4N_4Co$ [from $Co(OAc)_2$ and mesoporphyrin IX hydrochloride in glacial AcOH in absence of air], and their Me_2 esters, is described. Potentiometric titration (reduction with $Na_2S_2O_4$ in the dark or with phthiocol) of systems containing (I) or (II) and C_5H_5N, nicotine, or α-picoline shows that there is no evidence of polymerisation, that 1 equiv. per mol. is concerned in the oxidation–reduction process, and that $\Delta E_h/\Delta p_H = 0$ (E_h = electrode potential referred to H_2 standard). It appears that 2 mols. of C_5H_5N associate with 1 of manganomesoporphyrin, and with 1 or more of (I), and (from consideration of the Debye–Hückel simplified equation) that the net charge of nicotine Mn^{+++}-mesoporphyrin is 1, that of the Mn^{++}-compound, 2. In absence of co-ordinating base, these systems showed no stable potential. Spectroscopic measurements could not be satisfactorily interpreted. Molar extinction coeffs. for various λλ of (I) and Co^{+++}-mesoporphyrin, and log transmittance curves for Co^{+++}- and Co^{++}-mesoporphyrins in presence of nicotine, C_5H_5N, and CN′ are given. No Cr mesoporphyrin could be obtained. Cu and Ni mesoporphyrins show no reversible oxidation–reduction properties.

III. Potentiometric and spectrophotometric results indicate the following. 1 equiv. per Fe is concerned in the reduction of ferri-meso-, -proto-, and -hæmato-porphyrin IX in presence of nicotine, C_5H_5N, α-picoline, or CN′. Oxidant and reductant of the nicotine Fe protoporphyrin system are dimeric in H_2O, monomeric in 47% H_2O–EtOH, within the p_H range used. Other things being const., $-\Delta E_h/\Delta p_H = 0{\cdot}06$ for all cases except CN′, when it is 0. Changes of E with increasing concn. of co-ordinating base show that ferro- co-ordinate better with bases than ferri-porphyrins, 2 mols. of base per Fe co-ordinating with the former, 1 or 2 with the latter. In absence of base, fluctuating potentials are observed. It is suggested that ferriporphyrins in alkaline solution are associated with 1 OH^- per Fe, and that CN^- ions compete successfully with this OH^-, neutral bases only with difficulty, if at all.

IV. The synthesis of coproporphyrin I (III) by a modification of Fischer's method is described. Spectroscopic measurements show that the reaction Fe^{++} + porphyrin → ferroporphyrin + $2H^+$ is favoured by bases, and the reverse reaction by acids; hence excess of NaOAc is used in preparing Fe porphyrins. Potentiometric titration of C_5H_5N, nicotine, and CN′ complexes of Fe-(III) in buffered aq. alkali, and of C_5H_5N Fe ætioporphyrin I (IV) in alkaline, buffered 75% H_2O–EtOH show that all species are monomeric and that 1 equiv. per mol. is involved in the oxidation–reduction. At high concns. of co-ordinating base, other things being const., $-\Delta E_h/\Delta p_H = 0{\cdot}06$ for C_5H_5N (IV) or for C_5H_5N or nicotine Fe (III). 1 Mol. of ferro-(III) co-ordinates with 2 mols. of base, the dissociation consts. of these complexes increasing in the order CN′, nicotine, C_5H_5N. 1 Mol. of ferri-(III) co-ordinates with 2 mols. of cyanide, (?) mols. of other bases. The significance of the distinctive apparent dissociation consts. of C_5H_5N or nicotine ferri-(III) is discussed.

V. A photo-electric spectrophotometer is described. Photometric results confirm that 2 mols. of C_5H_5N co-ordinate concurrently with 1 mol. of ferro- or ferri-coproporphyrin. The former shows no sign of acid ionisation between p_H 8·5 and 12·4. Dissociation consts. of these complexes are given. A. LI.

Coumaronesulphonamidobenztriazoles. — See B., 1940, 824.

Synthesis and excretion of trigonelline. H. P. SARETT, W. A. PERLZWEIG, and E. D. LEVY (J. Biol. Chem., 1940, **135**, 483—485).—Trigonelline (I) hydrochloride and *H sulphate*, m.p. 199—200°, are synthesised by modifications of the methods of Winterstein *et al.* (A., 1918, i, 35). Distillation of (I) with conc. alkali gives a 96—98% yield of NH_2Me. The product of heating (I) at 75° with 6N-KOH and NH_4 salts or $CO(NH_2)_2$ gives a colour identical with that of nicotinic acid with the Bandier–Hald modification of the König reaction (A., 1939, II, 196). Normal human subjects excrete daily 1—3 mg. of nicotinic acid (II) and derivatives, 30—50 mg. of (I) (determination based on the above reaction). (II) ingested in small doses is excreted largely as (I). A. LI.

Alkaloids of Chinese drug Pai Pu. H. M. LEE and K. K. CHEN (J. Amer. Pharm. Assoc., 1940, **29**, 391—394).—The drug (*Stemona* species; total alkaloids 1·77%) contains the alkaloids *paipunine*, $C_{24}H_{37}O_4N$, m.p. 105·5—106·5°, $[\alpha]_D^{25}$ −53·7° in $COMe_2$, and *sinostemonine*, $C_{21}H_{36}O_5N$, m.p. 138—138·5°, $[\alpha]_D^{25}$ −37° in H_2O, the main pharmacological properties of which are described. F. O. H.

New formula for chaksine, the alkaloid of *Cassia absus*, and some experiments on its constitution. H. R. KAPUR, K. N. GAIND, K. S. NARANG, and J. N. RAY (J. Indian Chem. Soc., 1940, **17**, 281—284).—Contrary to Siddiqui *et al.* (A., 1936, 350), chaksine is $C_{11}H_{21}O_3N_3$, not $C_{12}H_{21}ON_3$. The hydriodide, m.p. 180°, sulphate (I), m.p. 317° (decomp.), *hydrochloride* (II), m.p. 178°, *hydrobromide*, m.p. 186°, and *nitrate* (III), m.p. 220° (decomp.), are described. Addition of (III) to ice-cold H_2SO_4 leads to *nitrochaksine sulphate*, m.p. 176° (decomp.). HNO_2 transforms (II) into a nitrogenous *compound*, m.p. 221° (decomp.). Oxidation of (I) with H_2O_2 and $FeSO_4$ affords CH_2O. With $KMnO_4$ in alkaline

solution (I) is oxidised ($KMnO_4$) to $H_2C_2O_4$ and (after esterification) two *Et* esters, b.p. 80°/3 mm. and 100—105°/3 mm., respectively. H. W.

Tetra-aryl-phosphonium,-arsonium, and -stibonium salts. I. New method of preparation. J. Chatt and F. G. Mann (J.C.S., 1940, 1192—1196).—$AsPh_2Cl$ (I) with $AsCl_3$ and $AlCl_3$ (II) at 280° gives free As, C_6H_6 and, after treatment with aq. KI, $AsPh_4I$ (IV). When (II) is heated at ≯280° with $AsCl_3 + 3C_6H_6$, with $AsPhCl_2$, with (I), with $AsPh_3$ or, best, with $AsPh_3$ + PhBr, followed in each case by KI, (IV) is again obtained, in varying yield. With PPh_3 at 280°, and KI, (II) gives no PPh_4I, which is, however, formed if 1 PhBr is present. $SbPh_3$, 1 PhBr, and (II), followed by KBr or KI, give *tetraphenylstibonium bromide* (V), m.p. 210—218° (according to rate of heating), or *iodide*, m.p. ~200°, best obtained from (V). E. W. W.

Stereochemistry of 3-covalent arsenic. Isomeric forms of 5 : 10-di-*p*-tolyl-5 : 10-dihydroarsanthren. J. Chatt and F. G. Mann (J.C.S., 1940, 1184—1192).—Physical evidence indicates that the 3-covalent As has a pyramidal configuration with an intervalency angle of ~97°.

o-$C_6H_4<^{As(C_6H_4Me)}_{As(C_6H_4Me)}>C_6H_4$-*o* should therefore be folded along the As–As axis, and should exist in two isomeric forms, a third form being impossible owing to the position of the ·C_6H_4Me groups. Arsanthren dichloride and *p*-C_6H_4Me·MgBr give α-, m.p. 178—179°, and β-5 : 10-*di*-p-*tolyl*-5 : 10-*dihydroarsanthren*, m.p. 179—181° [no third form but a small quantity of *tri*-p-*tolylenediarsine* (?), m.p. 216—217°]. Both α- and β-isomerides with Br followed by aq. NH_3 give the same 5 : 10-*di*-p-*tolyl*-5 : 10-*dihydroarsanthren tetrahydroxide*, m.p. ~318—325° (decomp.), which is dehydrated to the *dioxide*; in the tetrahydroxide the C–As–C angles have become 120° and the three rings and ·C_6H_4Me groups are co-planer. The isomerides with MeI form α- (+EtOH), m.p. 140—177°, anhyd. m.p. 176—179° (slight efferv.), and β-5 : 10-*di*-p-*tolyl*-*dihydroarsanthren monomethiodide* (+H_2O), m.p. 174—179°, anhyd. m.p. 176—179°. The As atoms in the ditolyl compounds show a marked reluctance to assume simultaneously the 4-covalent condition. The dimethiodide, disulphide, and monosulphide-monomethiodide could not be prepared, but a very stable *dibromide*, m.p. 298—300° (decomp.), which probably has the quinonoid structure, and a *monosulphide*, m.p. 198—201°, have been isolated. F. R. S.

Methoxy-mercurials from *cis*- and *trans*-styryl cyanide. W. H. Brown and G. F. Wright (J. Amer. Chem. Soc., 1940, **62**, 1991—1994).—*cis*-CHPh:CH·CN reacts faster than the *trans*-isomeride with $Hg(OAc)_2$ and a little HNO_3 in MeOH and gives a better yield. Equilibrium mixtures contain 99% of the product, but the second-order velocity coeffs. fall with time owing to destruction of the catalyst. The structure of the products, cis-, m.p. 121°, and trans-β-*methoxy*-β-*phenyl*-α-*acetoxymercuripropionitrile*, m.p. 96°, is proved by conversion by Br–$CHCl_3$ into (?) OMe·CHPh·CHBr·CO·NH_2, m.p. 219—223°, and a little OMe·CHPh·CHBr·CO_2H. R. S. C.

Catalysis in the formation of α-methoxymercurials from ethylenes. A. M. Birks and G. F. Wright (J. Amer. Chem. Soc., 1940, **62**, 2412—2421).—When *trans*-(CHPh:)$_2$ (I) is kept with $Hg(OAc)_2$ in MeOH at room temp., HgOAc is gradually pptd. (cf. A., 1935, 1515). Heating with a second equiv. of $Hg(OAc)_2$ then gives 20% of (CHPh·OMe)$_2$. This is also formed when OMe·CHPh·CHPh·HgCl from *cis*-(CHPh:)$_2$ is heated with $Hg(OAc)_2$. Thus failure to isolate the mercurichloride from (I) is due to the consumption thereof to give (CHPh·OMe)$_2$ as fast as it is formed. The accelerating action of HNO_3 in these and kindred additions is due to its peroxide content. 0·1 equiv. of Bz_2O_2 or ascaridole leads to 24% of *Hg* αβ-*diphenyl*-β-*methoxyethyl chloride*, m.p. 125—126°, from (I) (BF_3 is not catalytic); reaction is slow, but after longer periods complex mixtures are formed. Peroxides initiate interaction of CHPh:CH·CN (II) with $Hg(OAc)_2$ in MeOH, but the reaction soon stops as the peroxide is destroyed; HNO_3 owes its utility in these reactions to its continuously generating small amounts of peroxide. Interaction of CHPh:CH·COPh (III) with $Hg(OAc)_2$ in MeOH at 35° is accelerated by impurities in the salt and slightly by Me_2O_2 but is slightly retarded by AcO_2H, much retarded by MeCN or (II), and most retarded by C_5H_5N or its acetate. Et_2S_2 also retards the reaction of (III), but itself reacts to give SEt·Hg·OAc in equilibrium with Et_2S_2 and $Hg(OAc)_2$. BF_3 accelerates the reaction of *cis*- or *trans*-(II), but simple addition is not the sole reaction. BF_3 greatly accelerates reaction of (III), but an equilibrium is set up: (III) + $Hg(OAc)_2$ + MeOH ⇌ AcOH + OMe·CHPh·CH(COPh)·Hg·OAc ⇌ Hg[CH(COPh)·CHPh·OMe]$_2$ ⇌ ($HgCl_2$) OMe·CHPh·CH(COPh)·HgCl. A reaction mechanism for the catalysis is postulated. β-*Methoxy*-β-*phenyl*-α-*chloromercuripropiophenone*, m.p. 150—151°, *Hg*^{II} *ethylmercaptide acetate*, SEt·Hg·OAc, m.p. 131—132°, a *salt*, $C_4H_7O_5B$, b.p. 60°/8 mm., and β-*methoxy*-β-*phenyl*-α-*chloromercuripropionitrile*, m.p. 174° from *cis*- (II) and 124·5° from *trans*-(II), are described. R. S. C.

Mercurated carvacrol. J. B. Abcede and A. C. Santos (J. Amer. Pharm. Assoc., 1940, **29**, 362—364).—Carvacrol with $Hg(OAc)_2$ in AcOH–EtOH yields *di*(*acetoxymercuri*)*carvacrol* (I), m.p. 192—195° (decomp.); the reaction products treated with saturated aq. NaCl afford di(chloromercuri)carvacrol, decomp. 216—218° (cf. Burt, A., 1936, 619). (I) with 10% aq. NaOH gives the Na salt (?), decomp. 180°, and, when subsequently treated with CO_2, the *oxide*, decomp. 223—250°, of di(hydroxymercuri)carvacrol. F. O. H.

Interconversion reactions of organolithium compounds. H. Gilman, W. Langham, and F. W. Moore (J. Amer. Chem. Soc., 1940, **62**, 2327—2335).—General principles of metallation and halogen–Li interconversion are discussed. Prep. and manipulation of organo-Li compounds are improved. The amounts of $ArCO_2H$ obtained from PhBr, PhI, *m*-C_6H_4ClI, *p*-C_6H_4ClBr, *p*-$C_6H_4Br_2$, *o*-, *m*-, and *p*-C_6H_4MeBr, *p*-C_6H_4MeI, *p*-C_6H_4PhBr, *o*- and *p*-C_6H_4Br·OMe, and *p*-C_6H_4I·OMe, usually in petroleum ether or Et_2O, under varying conditions are reported.

1 : 3 : 5-$C_6H_3Br_3$ gives $LiC_6H_3Br_2$. Replacement of one and partly of two Br occurs with 1 : 2 : 5-$C_6H_3MeBr_2$, *p*-$C_6H_4Br_2$, (*p*-$C_6H_4Br)_2$, 2 : 4 : 6 : 1-$C_6H_2Br_3$·OMe, and (*p*-$C_6H_4Br)_2O$. In light petroleum at room temp. CHPh:CHBr and $LiBu^a$ give CHPh:CHBu^a and $(CHPh:CH)_2$, but, if boiled, give 23% of CHPh:CHLi (with CO_2 gives *trans*-CHPh:CH·CO_2H); in Et_2O 42·5% of CPh:CLi [gives (CPh:C·CO_2H)] is obtained. R. S. C.

Relative reactivities of organometallic compounds. XXXII. Indium triphenyl. H. Gilman and R. G. Jones (J. Amer. Chem. Soc., 1940, **62**, 2353—2357; cf. A., 1940, II, 316).—The order of increasing reactivity is $InPh_3 > GaPh_3 > TlPh_3$. In general, increasing activity parallels decreasing ionisation potentials of the metals. $InPh_3$ (prepared in 65—81% yield from $HgPh_2$ and In in N_2 at 130°), m.p. 208° (lit., 291°), oxidises and hydrolyses rapidly in air, does not react with Hg in boiling C_6H_6, and gives the Michler ketone colour reaction anomalously only if used in excess. With O_2 in C_6H_6 it gives ~17% of PhOH and 20% of Ph_2. It reacts slowly with CO_2, giving after 4 hr. in boiling xylene 18% of BzOH. With 1 mol. of PhCHO in boiling C_6H_6 it gives 82% of CHPh$_2$·OH with $InPh_2I$ and $InPhI_2$, but with 0·3 mol. gives 20% of PhCHO; equilibrium occurs thus: $InPhI_2 \rightleftharpoons InPh_2I + InI_3$ and $InPh_2I \rightleftharpoons InPh_3 + InI_3$, both $InPhI_2$ and $InPh_2I$ yielding CHPh$_2$·OH by interaction with PhCHO. With CHPh:CH·COPh it gives only (92%) CHPh$_2$·CH_2·COPh. All the Ph radicals react with BzCl: in C_6H_6 40% and in petroleum ether 31% of $COPh_2$ is obtained; $InPh_2I$ in $CHCl_3$ gives 70% of $COPh_2$. With $COPh_2$ in boiling xylene it gives 58% of CPh$_3$·OH. It does not react with EtOBz or PhCN. R. S. C.

Carboxylic acids of phthaloyl-thionaphthen and -selenophen.—See B., 1940, 727.

Diphenyl series. IV. Diphenylyl derivatives of phosphorus, arsenic, and antimony. D. E. Worrall (J. Amer. Chem. Soc., 1940, **62**, 2514—2515; cf. A., 1930, 1195).—*o*-C_6H_4PhCl (I), PCl_3, Na, and a trace of $SbCl_3$ in boiling C_6H_6 give *tri*-o-*diphenylylphosphine*, m.p. 151—152° after softening [*oxide* (prep. by Br or Cl_2, followed by KOH–EtOH), m.p. 184—185°; *methiodide*, m.p. >250° (decomp.), with Ag_2O gives Ph_2]. $AsCl_3$, (I), and Na in boiling C_6H_6 give *tri*-o-*diphenylylarsine*, m.p. 190° [*dihydroxide*, m.p. 237—238°; *methiodide*, m.p. ~154° (decomp.), with Cl_2 gives the iodochloride, m.p. 172—174° (decomp.)]. Use of $SbCl_3$ gives similarly *tri*-o-*diphenylylstibine*, m.p. 208—209° [*dibromide*, m.p. 152—154°; dichloride, m.p. 174—175°; *dihydroxide*, m.p. 243—244°], which with $SbCl_3$ in xylene at 220—250° gives *mono*-o-*diphenylylstibine hydroxychloride*, m.p. 201—202°, converted by NH_3–EtOH into the *oxide*, m.p. 195—196°, and by Cl_2–H_2O into *diphenylylstibinic acid*, m.p. ⩾300°. R. S. C.

Relative reactivities of organometallic compounds. XXXIV. Thallium phenyl. H. Gilman and R. G. Jones (J. Amer. Chem. Soc., 1940, **62**, 2357—2361).—Reactions of *Tl triphenyl* in boiling xylene are interpreted as due to pyrolysis to Ph_2 and reactive TlPh, much Tl being also formed. $TlPh_3$, prepared from $TlPh_2Br$ and LiPh in warm xylene, has m.p. 169—170° (N_2; softens at 167°; decomp. 180—185°). In boiling xylene, $TlPh_3$ and CO_2 give 70% of BzOH and 73% of Ph_2; possibility of this reaction proceding by way of *$TlPh_3$ benzoate* (prep. from $TlPh_3$ and BzOH in boiling C_6H_6), m.p. 259—260°, is excluded by the stability thereof in boiling xylene. $TlPh_3$ with $COPh_2$ in boiling xylene gives a little CPh$_3$·OH and with PhCN a little $COPh_2$, with Ph_2 in both cases, but it does not react with EtOBz. TlCl reacts with LiPh at −70°, probably to form TlPh; Tl and Ph_2 are the products isolated. $TlPh_2Br$ does not react with BzCl in boiling C_6H_6 or PhMe. With Na in liquid NH_3, $TlPh_2Br$ gives $TlPh_3$, NaBr, and Tl, the $TlPh_3$ being isolated by conversion into TlPh$_2$·OBz. $LiBu^a$ and $TlPh_3$ give a solution whence CO_2 yields 66% of BzOH. AgBr and MgEtBr in Et_2O at 0° give AgEt, which decomposes spontaneously to give 48% of C_4H_{10} and 3·5% of C_2H_4. R. S. C.

Hydrolysis of ovalbumin in presence of acids and salts at various temperatures. I. Time of hydrolysis in autoclave and acid hydrolysis of autoclave hydrolysates. II. Effect of acids, salts, and temperature on hydrolysis in autoclave. A. B. Silaev (Kolloid. Shurn., 1938, **4**, 593—602, 603—609).—I. In the initial stages of hydrolysis in an autoclave there is rapid formation of NH_3. As heating proceeds, the hydrolytic fission of the protein almost ceases, but deamination of the products, possibly both intermediate and final products, continues rapidly. Examination of the acid hydrolysis of the autoclave hydrolysate suggests that the mechanism of deamination is different in these two types of hydrolysis.

II. Prolonged hydrolysis with 2% H_2SO_4 in an autoclave at 180° does not effect complete resolution of the protein into NH_2-acids, but concurrent with the hydrolysis there is deamination of the NH_2-acids, which is not retarded by increase of [H_2SO_4], or much affected by the presence of salts or H_3BO_3. Rise in temp. from 150° to 180° for 3 hr. hydrolysis doubles the rate of hydrolysis and the rate of deamination. Deamination is largely to be ascribed to pyrolysis, at the autoclave temp., of relatively unstable NH_2-acids formed at the beginning of hydrolysis. R. C.

Volatile aldehydes liberated by periodic acid from protein hydrolysates. A. J. P. Martin and R. L. M. Synge (Nature, 1940, **146**, 491—492).—HIO_4 in aq. $NaHCO_3$ rapidly liberates MeCHO from threonine. Serine, alanine, cystine, tyrosine, arginine, etc. gave no volatile aldehyde. After hydrolysis (HCl), wool, casein, and gelatin yield MeCHO, and wheat gluten MeCHO and EtCHO with HIO_4–$NaHCO_3$; β-hydroxynorvaline may thus be present in the gluten hydrolysate. L. S. T.

Analysis of proteins. XII. Dephosphocaseose or depocaseose. T. J. R. Macara and R. H. A. Plimmer (Biochem. J., 1940, **34**, 1431—1448; cf. A., 1939, II, 294).—The prep. of depocasein (I) and depocaseose (II) by the action of 1% NaOH at 37° for 24 hr. on caseinogen (III) is described, and the amounts of the individual NH_2-acids in (I)

and (II) are determined. (I) and (II) have low P content and both contain less N than does (III), whilst (II) contains slightly more N and S than does (I). (II) contains less arginine, tyrosine, and glutamic acid, and more lysine and methionine, than does (III), whilst (I) contains more arginine, tyrosine, and glutamic acid, and less lysine, histidine, and methionine, than does (III). Both (I) and (II) contain less threonine and β-hydroxyamino-acids than (III), but more are present in (II) than in (I). Assuming that 1 mol. of cystine is present for each mol. of (I) and (II), the mol. wt. of the latter are 80,000 and 100,000, respectively. It is concluded that 1% NaOH scarcely affects the peptide linkings in (III), but hydrolyses the ester linkings by which H_3PO_4 is bound and approx. half of the dicarboxylic acid amide groups, and separates the complex system of (III) into the two main components (I) and (II), which may or may not be homogeneous. J. N. A.

Preparation of Nessler's reagent.—See A., 1940, I, 444.

Apparatus for determination of sulphur by the evolution method.—See A., 1940, I, 446.

Microchemical technique. IV. Micro-determination of mercury and halogen in organo-mercuric halides. G. O. Stonestreet and G. F. Wright (Canad. J. Res., 1940, **18**, B, 246—251).—Br and Cl are determined by heating with $Ag_2Cr_2O_7$–$K_2Cr_2O_7$–conc. H_2SO_4 in O_2 (Zacherl *et al.*, A., 1932, 709), and Hg in the residue by titration with dithizone (Winkler, B., 1936, 168). In some cases further heating with fuming HNO_3–H_2SO_4 is necessary to complete the decomp. A. Li.

Quantitative analysis of mixtures of polyethylene glycols by fractional distillation. S. Perry and H. Hibbert (J. Amer. Chem. Soc., 1940, **62**, 2561—2562).—Such analysis is accurate (96—99·8%). R. S. C.

Ketoses. XVIII. Van Slyke procedure for determination of β-hydroxybutyric acid. H. Blunden, L. F. Hallman, M. G. Morehouse, and H. J. Deuel, jun. (J. Biol. Chem., 1940, **135**, 757—759).—Experiments on the Van Slyke method with pure Ca Zn *l*- and *dl*-β-hydroxybutyrate, and with the Et *dl*-β-ester containing traces of $CH_2Ac{\cdot}CO_2Et$, give vals. for the wt. of Hg ppt. equiv. to 1 g. of β-hydroxybutyrate of 9·51, 9·68, and 9·62, respectively. A. Li.

Determination of benzoic acid. R. W. Sutton and O. Hitchen (Analyst, 1940, **65**, 502).—Unless the air oven described by Monier-Williams (B., 1927, 502) is copied in full detail, either a higher temp. (180°) or a longer time of sublimation than specified by him may be required for the quant. sublimation of BzOH. J. W. S.

Micro-methods for determination of sphingomyelin and choline.—See A., 1940, III, 946.

Chemical determination of thiamin by a modification of Melnick-Field method.—See A., 1940, III, 818.

Determination of morpholine. I. S. Shupe (J. Assoc. Off. Agric. Chem., 1940, **23**, 824—831).—Pptn. and colour tests for morpholine (I) are described and titration data given. With CS_2 (I) yields *morpholine morpholyldithiocarbamate*, sublimes at >100°, reduced by $K_3Fe(CN)_6$ to a thiuram disulphide (?), m.p. 150—151°. The prep. of *benzene*-, m.p. 119°, and *p-bromobenzene-sulphonyl-morpholine*, m.p. 153°, is described. Methods of determining (I) in creams and ointments, based on steam-distillation and titration with acid and on quant. conversion into the above derivatives, are described. F. O. H.

Identification of traces of barbituric acid by a modification of the Parri reaction. E. Sellés (Anal. Fís. Quím., 1940, **36**, 115—118).—2×10^{-6} g. of a 0·01% solution of barbituric acid in Et_2O or EtOH may be detected by micro-technique on addition of a drop of the solution to paper saturated with 1% $Co(NO_3)_3$ in EtOH followed by a drop of 5—10% aq. NH_3 added at the edge of the paper. F. R. G.

Micro-crystallographical detection of uric acid. G. Denigès (Bull. Trav. Soc. Pharm. Bordeaux, 1937, **75**, 73—78; Chem. Zentr., 1937, i, 4833).—Uric acid deposited on acidification of an alkaline solution, or on addition of H_2O to a conc. H_2SO_4 solution followed by washing with H_2O, gives characteristic crystals after ~5 min. A. J. E. W.

Microchemistry of xanthine. G. Denigès (Bull. Trav. Soc. Pharm. Bordeaux, 1937, **75**, 79—80; Chem. Zentr., 1937, i, 4833).—Xanthine separates as characteristic crystals on dilution of its conc. H_2SO_4 solution. A. J. E. W.

Quantitative characteristics of nicotine colour reaction with cyanogen bromide and β-naphthylamine. L. N. Markwood (J. Assoc. Off. Agric. Chem., 1940, **23**, 792—800; cf. B., 1939, 1171).—The optimum p_H for the reaction is ~10; neutralisation to phenolphthalein is recommended. When alkaline solutions of nicotine (I) are neutralised with AcOH, HCl, or H_2SO_4, sensitivity is greatest with AcOH and least with HCl. NaCl and, to a greater extent, Na_2SO_4 have a desensitising effect. Conditions for max. development of colour [which, for concns. of (I) >8 mg.-%, follows Beer's law] are described. F. O. H.

Turbidimetric determination of nicotine as phosphotungstate. L. N. Markwood (J. Assoc. Off. Agric. Chem., 1940, **23**, 800—804).—Nicotine (1—6 μg. per ml.) is determined by photometric measurement of the turbidity produced by phosphotungstic acid in presence of dil. H_2SO_4. F. O. H.

Micro-chemical tests for alkaloids. C. K. Glycart (J. Assoc. Off. Agric. Chem., 1940, **23**, 746—747).—Eserine is detected by PbI_2 reagent and stovaine by the characteristic crystal picture given by $AuCl_3$ reagent in presence of conc. HCl. F. O. H.

Nature of the Feulgen reaction with nucleic acid. H. N. Barber and J. R. Price (Nature, 1940, **146**, 335).—The effect of C_5H_5N and piperidine (A., 1940, II, 319) is not equiv. chemically to the Feulgen reaction, but is due to their basicity. Three of the purines used by Semmens (*loc. cit.*) gave no colour reaction. The Feulgen reaction is regarded as sp. for the potential ·CHO of chromatin. L. S. T.