BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

NOVEMBER, 1939.

Electric moments in some homologous series.—See A., 1939, I, 511.

Free radicals and their importance in chemical reactions. E. OLIVERI-MANDALÀ (Chim. e l'Ind., 1939, **21**, 342—345).—A lecture. O. J. W.

Reaction between methyl radicals.—See A., 1939, I, 568.

Activation of hydrogen in catalytic reactions of hydrocarbons.—See A., 1939, I, 529.

Production of ethane, quinhydrone, and potassium cupric cyanide by a.c. electrolysis.—See A., 1939, I, 530.

Kinetics of thermal decomposition of tetramethylmethane.—See A., 1939, I, 526.

Aromatisation of *n*-octane and *n*-decane in the presence of nickel–alumina catalyst. V. I. KOMAREWSKY and C. H. RIESZ (J. Amer. Chem. Soc., 1939, **61**, 2524—2525).—When passed over Ni–Al_2O_3 in N_2 at 300°, *n*-C_8H_{18} gives CH_4, H_2, and PhMe (10%, formed by way of PhEt). *n*-$C_{10}H_{22}$ at 350° gives CH_4, H_2, PhMe (2%), and *iso*paraffins (1·6%). *iso*-C_8H_{18} and di*iso*amyl at 300—350° give olefines, but no aromatic compounds. R. S. C.

Reactions of olefines with solid cuprous halides.—See A., 1939, I, 531.

Preparation of acetylene in the interrupted discharge.—See A., 1939, I, 573.

Radiochemical polymerisation of acetylene.—See A., 1939, I, 574.

Reactions in concentrated sulphuric acid. XV. Relationships in the case of acetylene. J. MILBAUER and Z. MILBAUER (Chem. Obzor, 1939, **14**, 69—73).—Mathematical relationships are given correlating various factors which affect the reaction of C_2H_2 with H_2SO_4 under various conditions. F. R.

Reactions in concentrated sulphuric acid. XVI. Selenium and tellurium as catalysts.—See A., 1939, I, 528.

Chemical methods of concentrating radioactive halogens.—See A., 1939, I, 532.

Fluorinated derivatives of propane. III. A. L. HENNE and M. W. RENOLL (J. Amer. Chem. Soc., 1939, **61**, 2489—2491; cf. A., 1938, II, 467).—Previous conclusions on the course of fluorination of C_3Cl_8 and C_3HCl_7 are borne out and expanded. Structures of F_3-derivatives are proved. Probable structures are assigned to F_4-derivatives, partly on the basis of m.p. Fluorination of C_2Cl_5·$CClF_2$ or $CCl_2(CCl_2F)_2$ yields only *ααββγ-pentachloro-αγγ-trifluoropropane*, m.p. −4·9°, b.p. 152·3°, which in turn yields *αββγ-tetrachloro-ααγγ-tetrafluoropropane*, m.p. −42·9°, b.p. 112·0°. $CHCl(CCl_2F)_2$ yields, with much decomp., *ααβγ-tetrachloro-αγγ-trifluoropropane*, b.p. 128·7°, converted by alcoholic alkali into $CHCl(CO_2Et)_2$, decomposed by Cl_2 in light, and on further fluorination yielding impure $CHCl(CClF_2)_2$. $CHCl_2$·CCl_2·$CClF_2$ yields *ααβγ-tetrachloro-βγγ-trifluoropropane* (I), b.p. 129·8°, which at high temp. affords, with decomp., *ααβ-trichloro-βγγγ-tetrafluoropropane* (II), b.p. 89·8°. Chlorination of (I) gives *αααβγ-pentachloro-βγγ-trifluoropropane*, m.p. −14·8°, b.p. 153·3°; that of (II) yields *αααβ-tetrachloro-βγγγ-tetrafluoropropane*, m.p. −15·8°, b.p. 112·3°, which with Zn–EtOH yields *αα-dichloro-βγγγ-tetrafluoro-Δ$^{\alpha}$-propene*, b.p. 43·5° (*dibromide*, m.p. 35·5—37°, b.p. 154°). R. S. C.

Pure ethyl alcohol for absorption spectrophotometry.—See A., 1939, I, 582.

Aromatisation of fatty alcohols. V. I. KOMAREWSKY, C. H. RIESZ, and G. THODOS (J. Amer. Chem. Soc., 1939, **61**, 2525—2527).—When passed over Cr_2O_3–Al_2O_3 at 450—500°, aliphatic alcohols undergo successive dehydration (very rapid) and cyclisation–dehydrogenation. Thus, *n*-C_7H_{15}·OH or $CHPr^{\alpha}_2$·OH yields PhMe; *n*-C_6H_{13}·OH gives C_6H_6; *n*-C_8H_{17}·OH gives PhEt (4·5%), PhMe (3%; by fission of PhEt), *o*-, *m*- (trace), and *p*-xylene (7%; by isomerisation of PhEt), and higher aromatic compounds (32·7%). H_2, CO_2, and CO are also determined; production of CO and CO_2 indicates aldehyde formation. Approx. heats of activation for aromatisation and formation of CO, respectively, are *n*-C_7H_{15}·OH 59,700, —; $CHPr^{\alpha}_2$·OH 57,600, 31,100; *n*-C_6H_{13}·OH 62,000, 14,200 kg.-cal. R. S. C.

Interconversion of crotyl alcohol and methylvinylcarbinol in aqueous sulphuric acid. W. G. YOUNG, K. NOZAKI, and (MISS) R. WARNER (J. Amer. Chem. Soc., 1939, **61**, 2564—2565).—$CHMe{:}CH{\cdot}CH_2{\cdot}OH$ and $CH_2{:}CH{\cdot}CHMe{\cdot}OH$ are interconvertible by 3·7—7·4N-H_2SO_4 at room temp., some ether also being formed. The relative rates of the reactions depend on the concn. of the acid. R. S. C.

[Tri]chloro[*iso*]butanol. A. G. FISHBURN and H. B. WATSON (J. Amer. Pharm. Assoc., 1939, **28**, 491—493).—$OH{\cdot}CMe_2{\cdot}CCl_3$ (+0·5H_2O), m.p. 77° (anhyd., m.p. 96·2°), is prepared by interaction of $COMe_2$ (100 g.), $CHCl_3$ (40 g.), and KOH (7 g. in saturated EtOH solution) for 15 min.; KCl is removed by filtration and $COMe_2$ + $CHCl_3$ by distillation, H_2O being added to the residue. The yield (calc. on $CHCl_3$) is 25% of theory. F. O. H.

Preparation of unsaturated higher alcohols. III. S. KOMORI (J. Soc. Chem. Ind. Japan, 1939,

42, 246—247B).—The reduction of the Et ester of the acids from rice oil and of Et erucate has been studied at temp. varying between 310° and 343° in the presence of Mg–Cr, Cd–Cr (I), Hg–Cr, Sr–Cr, Co–Cr (II), and Mn–Cr (all as oxides) obtained by decomp. of the requisite metallic chromate. (I) and (II) are excellent for the hydrogenation of an unsaturated fatty ester to a corresponding unsaturated alcohol. H. W.

Partly *O*-methylated hexitols. III. Synthesis of αγδε-tetramethyl-*l*-rhamnitol. R. S. TIPSON and P. A. LEVENE (J. Biol. Chem., 1939, **130**, 235—242; cf. A., 1939, II, 466).—3 : 4-Dimethyl-1 : 2-methylorthoacetyl-*l*-rhamnose (modified prep.), m.p. 67—68°, $[\alpha]_D^{25}$ +40·6° in H_2O, and boiling 0·5N-HCl give 2 : 3-dimethyl-*l*-rhamnose, new m.p. 102—103°, b.p. 99°/0·1 mm., reduced by H_2–Raney Ni at 125°/1650 lb. in H_2O to γδ-*dimethyl*-l-*rhamnitol*, m.p. 105°, $[\alpha]_D^{24}$ −25·5° in abs. EtOH. H_2SO_4 and anhyd. $CuSO_4$ in $COMe_2$ then give βγ-*dimethyl*-αβ-iso*propylidene*-l-*rhamnitol*, b.p. 73°/0·1 mm., $[\alpha]_D^{25}$ −8·2° in $COMe_2$, converted by MeI–Ag_2O into the γδε-Me_3 derivative, b.p. 64°/0·25 mm., $[\alpha]_D^{29}$ −6·6° in $COMe_2$, which is hydrolysed by boiling 0·2N-H_2SO_4 to γδε-*trimethyl*-l-*rhamnitol*, b.p. 99—100°/0·1 mm., $[\alpha]_D^{20}$ −14·8° in abs. MeOH. CPh_3Cl and then BzCl in C_5H_5N convert this into the α-*CPh_3 ether* β-*benzoate*, a syrup, which in boiling AcOH–H_2O (4 : 1) yields γδε-*trimethyl*-l-*rhamnitol* β-*benzoate*, b.p. 140°/0·1 mm., $[\alpha]_D^{29}$ −16·4° in $COMe_2$ (and some αβ-*dibenzoate*, b.p. 145—170°/0·1 mm., $[\alpha]_D^{29}$ −20·5° in $COMe_2$), converted by Ag_2O–MeI into αγδε-*tetramethyl*-l-*rhamnitol* β-*benzoate*, b.p. 130°/0·1 mm., $[\alpha]_D^{28}$ −9·1° in $COMe_2$, and thence by boiling 0·4N-$Ba(OH)_2$ into αγδε-*tetramethyl*-l-*rhamnitol*, b.p. 87°/0·25 mm., $[\alpha]_D^{20}$ −8·1° in abs. EtOH. R. S. C.

Structure of the di*iso*propylidenedulcitols. R. M. HANN, W. D. MACLAY, and C. S. HUDSON (J. Amer. Chem. Soc., 1939, **61**, 2432—2442).—To avoid ambiguity, dulcitol is numbered as *D,L*-galactitol. α- (I) and β-Di*iso*propylidenedulcitol (II) are shown to be structural isomerides, containing 1 and 2 primary OH, respectively. OH·C·C·OH is absent from (I) and (II), as neither is affected by aq. $NaIO_4$ or $Pb(OAc)_4$ in AcOH unless hydrolysis, *e.g.*, by keeping or heat, occurs. 0·4M-HIO_4 removes CMe_2: and thus oxidises (I) and (II). With Ac_2O–C_5H_5N, (II) yields the αζ-*diacetate* (III), m.p. 134°, which, owing to its insolubility, is useful for separating (I) and (II) and readily regenerates (II) by NaOMe or $Ba(OMe)_2$. The αζ-*$(CPh_3)_2$ ether*, m.p. 233—234°, of (II) is prepared. The αζ-*di*-p-*toluenesulphonate*, m.p. 165—166° of (II) and NaI in hot $COMe_2$ give the αζ-*di*-*iodide*, m.p. 108—109°, confirming the free OH at α and ζ positions. Dulcitol "β"-dibenzoate (IV), previously called the "α"-dibenzoate, yields *dulcitol* αζ-*dibenzoate* βγδε-*tetra*-*acetate*, m.p. 225—226°. Hot 9% AcOH hydrolyses (III) to *dulcitol* αζ-*diacetate*, m.p. 167—168°, which consumes 3 $Pb(OAc)_4$ in AcOH and with $NaIO_4$ yields 2 HCO_2H. $Pb(OAc)_4$ similarly oxidises (IV) as expected to OBz·CH_2·CHO (isolated as semicarbazone or acid). (I) yields similarly βγεζ-di*iso*propylidene-D,L-*galactitol* αδ-*diacetate*, m.p. 89°, αδ-*di*-p-*toluenesulphonate*, m.p. 101°, and α-*iodide* δ-p-*toluenesulphonate*, m.p. 120—121°; it leads to D,L-*galactitol* αδ-*dibenzoate*, m.p. 170—171°, resolidifies, remelts 202—203° [transformation into (IV)] [consumes 2 $Pb(OAc)_4$ or 2 $NaIO_4$ (gives only a trace of HCO_2H)], and αδ-*dibenzoate* βγεζ-*tetra*-*acetate*, m.p. 113°. With CPh_3Cl in C_5H_5N, followed by Ac_2O, (I) gives βγεζ-*di*isopropylidene-D,L-*galactitol* δ-*acetate* α-*CPh_3 ether*, m.p. 107—108°. The dibenzoate (prep. by BzCl–quinoline) (V), m.p. 183—184°, of (II) with hot 80% AcOH gives (IV), new m.p. 209°. With BzCl in quinoline, (I) gives 66% of (IV) and 11% of βγεζ-di*iso*propylidene-*D,L*-galactitol αδ-dibenzoate, m.p. 82—83°, previously called the "β"-dibenzoate; the migration of CMe_2: is catalysed by quinoline (or, less well, C_5H_5N) hydrochloride. The structures of (IV) and its isomerides are confirmed by debenzoylation by NaOMe. M.p. are corr. R. S. C.

Oxidation of ethyl disulphide by hypobromite ion.—See A., 1939, I, 527.

Di(carbethoxymethanesulphonyl)dialkylmethanes. R. L. SHRINER, J. M. CROSS, and E. H. DOBRATZ (J. Amer. Chem. Soc., 1939, **61**, 2001—2003).—The CO_2Et of $CAlk_2(SO_2·CH_2·CO_2Et)_2$ destroys the toxic and hypnotic actions of the compounds. $SH·CH_2·CO_2H$, $COAlk_2$, and HCl at <0° give 82—96% of ββ-*di*(*carboxymethylthiol*)-n-*propane*, m.p. 134—135°, γγ-*di*(*carboxymethylthiol*)-n-*pentane*, m.p. 125—126°, δδ-*di*(*carboxymethylthiol*)-n-*heptane*, m.p. 133—134°, and εε-*di*(*carboxymethylthiol*)-n-*nonane*, m.p. 86—87°, converted by HCl, abs. EtOH, and anhyd. $MgSO_4$ into the *Et* esters, b.p. (I) 152—153°/1·8 mm., 162—163°/2 mm., 178—179°/3 mm., and 183—184°/3 mm., respectively. These esters are very readily hydrolysed by acid, and, when distilled give, except (I), $SH·CH_2·CO_2Et$ (HgCl derivative, new m.p. 105°) and γ-*carbethoxymethylthiol*-Δ^β-n-*pentene*, b.p. 78·5°/2 mm., δ-*carbethoxymethylthiol*-Δ^γ-n-*heptene*, b.p. 90°/1·8 mm., and ε-*carbethoxymethylthiol*-Δ^δ-n-*nonene*, b.p. 108°/1·8 mm., respectively. Addition of solid $KMnO_4$ to 10% H_2SO_4 and the esters in CCl_4 (not other methods) gives 32—42% of ββ-*di*(*carbethoxymethanesulphonyl*)-n-*propane*, m.p. 84—85°, γγ-*di*(*carbethoxymethanesulphonyl*)-n-*pentane*, m.p. 73—74°, δδ-*di*(*carbethoxymethanesulphonyl*)-n-*heptane*, m.p. 90—91°, and εε-*di*(*carbethoxymethanesulphonyl*)-n-*nonane*, m.p. 74—75°, some hydrolysis also occurring. M.p. are corr. R. S. C.

Application of high temperatures in preparative organic work. A. J. VAN PELT, jun. (Chem. Weekblad, 1939, **36**, 613—614).—A review of the recent work of Wibaut *et al.* on the high-temp. halogenation of C_5H_5N and quinoline and the pyrolysis of various acetates. S. C.

Effect of the silent electric discharge on the synthesis of monochloroacetic acid. Y. ISOMURA (Bull. Chem. Soc. Japan, 1939, **14**, 258—270).—In the prep. of $CH_2Cl·CO_2H$ (I) from AcOH and Cl_2 using red P as a catalyst, activation of the Cl_2 by the silent electric discharge gives an increase of 15—100% in the yield as compared with activation by direct sunlight. With Brückner's (B., 1928, 254) catalyst (I + red P + PCl_5; 2 : 2 : 1) and solar activation of the Cl_2 a yield of 66% is obtained but it is difficult to remove all the I from the product on distillation.

However, by reducing the amount of I in the catalyst to 0·1—0·2 part and activating the Cl_2 by the silent electric discharge the yield is increased to 80% and the I can be eliminated by distillation at 180—190°. With red P alone as catalyst large amounts of AcCl are formed and the P does not act simply as a carrier of Cl_2. The equation $2P + AcOH + 9Cl_2 = 2AcCl + 6HCl + 4(I) + 2POCl_3$ is therefore proposed instead of $AcOH + Cl_2 = (I) + HCl$, which appears to apply with the more complex catalyst. T. H. G.

Rate of hydration of crotonic acid. Rate of dehydration of β-hydroxybutyric acid. Equilibrium between these acids in dilute aqueous solution.—See A., 1939, I, 570.

Chromatographic separation of palmitic and stearic acids from their mixture with oleic acid. C. MANUNTA (Helv. Chim. Acta, 1939, **22**, 1156—1160).—The mixture, dissolved in light petroleum, is adsorbed on $MgSO_4,0·5H_2O$ or franconite and the column is developed by washing with light petroleum. Division of the column, extraction of the parts by Et_2O, and repeated chromatographic separation of the fractions thus obtained yields fairly pure palmitic (I) and stearic (II) acids. (I) is more strongly adsorbed than is (II). F. O. H.

Intermolecular oxidation of linoleic acid. M. BRAMBILLA (Annali Chim. Appl., 1939, **29**, 303—314; cf. A., 1939, II, 47).—Linoleic acid, heated to 325° in N_2, yields H_2O, CO_2, $EtCO_2H$, $PrCO_2H$, hexoic, glutaric, and sebacic acid, and an unsaponifiable, carbonaceous residue which, on fractionation, affords $C_{10}H_{20}$, $C_{14}H_{28}$, $C_{16}H_{32}$, $C_{20}H_{40}$, $C_{28}H_{54}$, and $C_{32}H_{62}$. The mechanism of the degradation is discussed. F. O. H.

Acid, $C_{15}H_{22}O_3$, m.p. 118·5°, and lactone, $C_{15}H_{18}O_2$, m.p. 60·5°, from oil of kostus root.—See A., 1939, III, 950.

Improved [organic] procedures. K. M. SEYMOUR (J. Chem. Educ., 1939, **16**, 285—287).—Directions for the prep. of $H_2C_2O_4$ from $(CH_2·OH)_2$ and HNO_3 are given. Advantages of using $(CH_2Cl)_2$ instead of ethers as a solvent are pointed out. In the prep. of NH_2Ph by Degering's method (A., 1936, 1359) the yield is much increased by substituting $(CH_2Cl)_2$ for the ether. An improved method for the prep. of NH_2Ac is described. L. S. T.

Polynuclear complex chromioxalates.—See A., 1939, I, 575.

Itaconic acid, metabolic product of *Aspergillus terreus*.—See A., 1939, III, 1010.

Influence of temperature on aqueous solutions of *l*-malic acid.—See A., 1939, I, 564.

Dibenzyl sebacate. R. E. BURNETT and J. J. RUSSELL (J. Amer. Chem. Soc., 1939, **61**, 2246).—$(CH_2Ph)_2$ *sebacate*, m.p. 28·3°, b.p. 257° (uncorr.)/4 mm., is prepared from the acid and alcohol. R. S. C.

Synthesis of aldehydes by Stephen's method. J. W. WILLIAMS (J. Amer. Chem. Soc., 1939, **61**, 2248—2249).—Stephen's method gives the following yields of RCHO: R = Ph 97, β- 91 and α-$C_{10}H_7$ 7, *p*- 77 and *o*-tolyl 9, CH_2Ph 33, *iso*-C_7H_{15} 31%, and $OH·[CH_2]_2$ 0. R. S. C.

Formation of acetaldehyde from succinic acid by quinone catalysis.—See A., 1939, III, 939.

Reversed aldol condensation. H. FRAENKEL-CONRAT (Science, 1939, **90**, 114).—On digestion with H_2O at 37° α-keto-γ-acetoxyvaleric acid dissolves within a few days forming $AcCO_2H$, AcOH, and MeCHO. The next higher homologue behaves similarly, but aldol, acetaldol, $OAc·CHMe·CH_2·CO_2H$, and $OAc·CHMe·CH_2·COMe$ are stable under these conditions. An acid p_H of the solution or an acid group in the mol. appears to be necessary for the decomp., as well as a CO β to an esterified OH. These reactions indicate that the readily fermentable hexose diphosphate is a ketose, with one PO_4 in position 4. L. S. T.

Keten generator. C. H. LI (Science, 1939, **90**, 143).—In the apparatus described and illustrated, $COMe_2$ vapour is decomposed by a W filament at bright-red heat, and unchanged $COMe_2$ and keten polymerides are removed by a condenser and a special trap immersed in ice + salt. Keten is passed into the solution through a sintered-glass plate. L. S. T.

Oxidation of simple sugars. A. QUARTAROLI and A. RATTU (Annali Chim. Appl., 1939, **29**, 296—302).—The oxidation by O_2 of monosaccharides in presence of $FeSO_4$ involves the formation of FeO_2; this reacts with the acceptor with production of Fe_2O_3. The oxidation product, if in sufficient concn., prevents pptn. of basic Fe salts. Examples of such systems in buffered solution are described. F. O. H.

Preparation of fully methylated carbohydrates and their derivatives. E. PACSU and S. M. TRISTER (J. Amer. Chem. Soc., 1939, **61**, 2442—2444).—Methylation of carbohydrates is difficult owing to incomplete reaction of $CH_2·OH$. Sugars, partly methylated by Me_2SO_4 or MeI–Ag_2O, are fully methylated thereafter by one treatment with Na in Et_2O, PhMe, etc., followed by MeI. Prep. of octamethylsucrose is described. R. S. C.

Tetrose sugars. IV. Structure of a methyl-*d*-erythroside. Mutarotation of *d*-arabinoseoxime. R. C. HOCKETT and C. W. MAYNARD, jun. (J. Amer. Chem. Soc., 1939, **61**, 2111—2115; cf. A., 1938, II, 126).—*d*-Arabinoseoxime, m.p. 136—137°, $[\alpha]_D^{20}$ −84° → (unimol.) −13·5° in H_2O, with Ac_2O–NaOAc–dioxan or Ac_2O–C_5H_5N gives *d*-arabononitrile tetra-acetate, m.p. 120—121° (corr.), $[\alpha]_D^{20}$ −33·3° in $CHCl_3$, and thence *d*-erythrosediacetamide. With 0·6N-H_2SO_4 at 100° (for 0·1N-H_2SO_4 k = 0·0175), this gives syrupy *d*-erythrose, which with 1% HCl–MeOH gives *methyl*-d-*erythroside* (I), b.p. 78—98°/1—2 mm., $[\alpha]_D^{20}$ variable, −5·34° to 0° in $CHCl_3$. Me_2SO_4–60% NaOH converts (I) into dimethylmethyl-*d*-erythroside, b.p. 135—145°/1—2 mm., oxidised by HNO_3 (*d* 1·2) at 85—90° to *meso*-$[·CH(OMe)·CO_2H]_2$. 1 mol. of $Pb(OAc)_4$ is consumed by (I) in $CHCl_3$, the reaction having the fast rate characteristic of *cis*-diols and yielding with Br–$SrCO_3$ Sr *D'*-methoxydiglycollate (58% of α- and 42% of β-), $[\alpha]_D^{20}$ −8·94° in H_2O. R. S. C.

Quantitative formation of furfuraldehyde and methylfurfuraldehyde from pentoses and methylpentoses. E. E. Hughes and S. F. Acree (J. Res. Nat. Bur. Stand., 1939, **23**, 293—298; cf. A., 1939, II, 7).—During rapid steam-distillation in 12% HCl saturated with NaCl the conversion of arabinose and rhamnose is slower than that of xylose, but theoretical yields of furfuraldehyde (I) and methylfurfuraldehyde, respectively, are obtained. Addition of salts to raise the distillation temp. to >112° increases the initial rate of formation of (I) from xylose and arabinose, but decreases the yields. To ensure complete conversion it is desirable to take samples ≯0·1 g. when determining pentoses by this method. J. W. S.

Action of silver salts of organic acids on bromoacetyl sugars. New form of *l*-rhamnose tetra-acetate. R. S. Tipson (J. Biol. Chem., 1939, **130**, 55—59).—AgOAc or AgOBz with bromoacetyl derivatives of sugars gives compounds having *trans*-OAcyl on $C_{(1)}$ and $C_{(2)}$. Thus are obtained l-*rhamnose tetra-acetate*, b.p. 129—130°/0·1 mm., $[\alpha]_D^{25}$ −61·7° in $CHCl_3$, and d-*xylose* l-*benzoate triacetate*, m.p. 147—147·5°, $[\alpha]_D^{27}$ −70·3° in $CHCl_3$. R. S. C.

Mutarotation of tetramethyl-α-*d*-glucopyranose and -mannopyranose. B. C. Hendricks and R. E. Rundle (J. Amer. Chem. Soc., 1939, **61**, 2103—2105).—The mutarotations of tetramethyl-α-*d*-glucose and -mannose at 0° and 25° are first-order reactions. Heats of activation are similar to those of the non-methylated sugars. R. S. C.

Substitution of glucose in position 4. II. β-Benzylglucoside 2 : 3-diacetate and its derivatives. A. L. Raymond, R. S. Tipson, and P. A. Levene (J. Biol. Chem., 1939, **130**, 47—54; cf. A., 1933, 54).—β-Benzylglucoside [prep. from glucosidyl bromide tetra-acetate by $CH_2Ph{\cdot}OH$, followed by $Ba(OMe)_2$–MeOH] with PhCHO and $ZnCl_2$ and then Ac_2O–C_5H_5N gives 4 : 6-*benzylidene*-β-*benzylglucoside* 2 : 3-*diacetate*, m.p. 208—209°, $[\alpha]_D^{20}$ −108·4° in $CHCl_3$, hydrolysed by 0·25N-HCl to β-*benzylglucoside* 2 : 3-*diacetate* (I), m.p. 116—117°, $[\alpha]_D^{23}$ −67·4° in $COMe_2$, $[\alpha]_D^{25}$ −85·9° in EtOH. With *p*-$C_6H_4Me{\cdot}SO_2Cl$–C_5H_5N, (I) gives β-*benzylglucoside* 2 : 3-*diacetate* 4 : 6-*di*-p-*toluenesulphonate*, m.p. 143—144°, $[\alpha]_D^{26}$ −34·0° in $COMe_2$, which with NaI–$COMe_2$ at 100° gives β-*benzylglucoside* 6-*iodide* 2 : 3-*diacetate* 4-p-*toluenesulphonate*, m.p. 125—126°, $[\alpha]_D^{27}$ −67·4° in $COMe_2$. Ac_2O–$CHCl_3$ at room temp. converts (I) into the 2 : 3 : 6-*triacetate*, cryst., b.p. 190—195°/0·1 mm., $[\alpha]_D^{25}$ −55·4° to −57·8° in $COMe_2$. Addition of *p*-$C_6H_4Me{\cdot}SO_2Cl$ in $CHCl_3$ to (I) in C_5H_5N gives β-*benzylglucoside* 2 : 3-*diacetate* 6-p-*toluenesulphonate*, cryst. R. S. C.

***iso*Propylidene derivatives of the mercaptals of monosaccharides. IV. 4 : 5-*iso*Propylidene derivative of the dibenzyl mercaptan and of the dimethyl acetal of *d*-galactose.** E. Pacsu, S. M. Trister, and J. W. Green (J. Amer. Chem. Soc., 1939, **61**, 2444—2448).—Prep. of 4 : 5- (I), m.p. 102·5—103°, $[\alpha]_D^{20}$ +31·0° in $CHCl_3$, and (?) 5 : 6-*isopropylidenegalactose* $(CH_2Ph)_2$ *mercaptal*, m.p. 112·5°, $[\alpha]_D^{20}$ +17·4° in $CHCl_3$, is detailed (cf. A., 1930, 197; 1936, 1491). The structure of (I) follows from formation of a *CPh*$_3$ *ether*, amorphous, and from the following reactions. With $HgCl_2$–HgO–MeOH, (I) gives 4 : 5-iso*propylidenegalactose* Me_2 *acetal* (II), m.p. 125—126°, $[\alpha]_D^{20}$ +37·4° in H_2O (2 : 3 : 6-*triacetate*, m.p. 55°, $[\alpha]_D^{20}$ +17·8° in $CHCl_3$), which is incompletely methylated by MeI–Ag_2O (5 treatments), but after final treatment with Na–MeI yields the syrupy 2 : 3 : 6-*Me*$_3$ *ether*. Hydrolysis by 0·05N-HBr at 60—70° and subsequent oxidation by Br at 35—40° then gives 2 : 3 : 6-*trimethyl*-γ-*galactonolactone*, m.p. 97—98°, [α] −32·9° → −21·3° in H_2O in 3 days, which consumes 1 HIO_4. 1 HIO_4 is consumed also by (II) to yield glyoxal (isolated as bisphenylhydrazone) and 2 : 3-*iso*propylidene-*d*-threose, characterised by hydrolysis to *d*-threose (osazone) and oxidation thereof to *d*-threonic acid (brucine salt) and thence to *l*-[·$CH(OH){\cdot}CO_2H]_2$. R. S. C.

Cardiac glycosides. XV. Periplocin, the genuine cardiac glycoside of *Periploca graeca*. A. Stoll and J. Renz (Helv. Chim. Acta, 1939, **22**, 1193—1208).—The stems and bark of *P. graeca* are extracted with EtOH and the extract is evaporated to dryness in vac. The residue is treated with $Pb(OH)_2$ and then with H_2O–EtOH–$CHCl_3$ in varied proportions. The crude glycoside is transformed by Ac_2O and C_5H_5N at room temp. into *periplocin tetra-acetate*, m.p. 195°, $[\alpha]_D^{20}$ +20·0° in abs. EtOH, which is hydrolysed by the requisite amount of $Ba(OMe)_2$–MeOH to periplocin, (I), $C_{36}H_{56}O_{13}$, m.p. 209° when slowly heated or m.p. 224° (decomp.) in bath pre-heated to 200°, $[\alpha]_D^{20}$ +22·9° in MeOH, +23° in EtOH. Hydrolysis of (I) with 0·1N-H_2SO_4 at 25° and then at 40—50° yields periplogenin, $C_{23}H_{34}O_5$, m.p. 232° after softening at 165—170°, $[\alpha]_D^{20}$ +29·8° in MeOH, and *periphlobiose*, $C_{13}H_{24}O_9$, decomp. 160—170° after softening at ~120° greatly dependent on the mode of heating and moisture content, $[\alpha]_D^{20}$ +30·8° in H_2O (c = 0·276). Strophanthobiase hydrolyses (I) rather more readily than it does *k*-strophanthin-β, giving glucose and periplocymarin, $C_{30}H_{46}O_8$, m.p. 143—145° after softening at 135°, $[\alpha]_D^{20}$ +30·2° in 95% EtOH, +27·6° in MeOH. *Periplobiose penta-acetate*, m.p. 184°, $[\alpha]_D^{20}$ +19·5° in $CHCl_3$ (c = 0·353), differs from *strophanthobiose penta-acetate*, m.p. 162°, $[\alpha]_D^{20}$ +13·2° in $CHCl_3$, although each sugar is formed from glucose and cymarose. H. W.

***p*-Nitrophenol-β-galactoside, m.p. 170°, $[\alpha]_D^{20}$ −74·7° in H_2O (tetra-acetate, m.p. 138°).**—See A., 1939, III, 940.

Quercetin-3-galactoside, +1·5H_2O, m.p. 235—237°, $[\alpha]_D^{24}$ −51·6°.—See A., 1939, III, 951.

Molecular size of starch by the mercaptalation method. M. L. Wolfrom, D. R. Myers, and E. N. Lassettre (J. Amer. Chem. Soc., 1939, **61**, 2172—2174).—By hydrolysis of potato starch with conc. HCl at 0° in presence of EtSH (excess), isolation of the product as acetate, and S determination, it is shown that the product contains 17 glucose units after 0·5 and 2 units after 26 hr. [α] of mixtures of the starch and HCl at 0° are recorded at various times. Graphic analysis indicates 20±4 glucose units per mol. of the original starch. R. S. C.

Enzyme–protein complex which phosphorylates glycogen: reversible enzymic synthesis of glycogen.—See A., 1939, III, 940.

Polysaccharides. XXXII. Molecular constitution of rice starch. E. L. HIRST and G. T. YOUNG. **Examination in the ultracentrifuge.** J. ST. L. PHILPOT (J.C.S., 1939, 1471—1481, 1481—1482).—Methylstarch (I) prepared by direct methylation (Me_2SO_4–NaOH) in air or N_2, or prepared via the acetate, shows mol. wts., determined by η in *m*-cresol, varying from 175,000 to 600,000. Independently of the mode of prep. of (I) and irrespective of the mol. wt., the method of end-group assay shows a const. % of tetramethylglucose (II) and indicates a repeating unit of 24—30 glucose units. The observed proportion of (II) cannot be explained by random hydrolysis of long chains of similarly united residues and it is concluded that viscous methylstarches are composed of a large no. of repeating units joined together laterally, forming side-chains. Thus, a viscous methylstarch (mol. wt. ~500,000), disaggregated by heating with $H_2C_2O_4$ in $COMe_2$–H_2O and methylated (Me_2SO_4–NaOH), yields a substance (III) of mol. wt. ~20,000 (by osmotic pressure and ultracentrifuge measurements) corresponding with 3 repeating units (90 glucose residues). On hydrolysis (AcOH–HCl) this material gives the same yield of (II) as do the viscous methylstarches, but the yield of dimethylglucose is very small. From consideration of the conditions of the disaggregation process it is concluded that in the starch mol. the repeating units, each consisting of a chain of 30 glucose residues, are linked to a non-terminal glucose residue of another unit by primary valencies of the glycosidic type. The relationship between η and mol. wt. in the methylstarch series is discussed and an empirical method is suggested for the utilisation of η measurements in the determination of approx. mol. sizes.

Ultracentrifuge examination of (III) indicates that the material is essentially homogeneous, of min. mol. wt. 18,700, and that the mols. are spherical in shape.

J. D. R.

Constitution of the mucilage from the bark of *Ulmus fulva* (slippery elm mucilage). I. Aldobionic acid obtained by hydrolysis of the mucilage. R. E. GILL, E. L. HIRST, and J. K. N. JONES (J.C.S., 1939, 1469—1471).—Partial hydrolysis (N-H_2SO_4) of the mucilage extracted by H_2O from the inner bark yields (as *Ba* salt) an aldobionic acid (I), which when methylated (TlOH–MeI followed by MeI–Ag_2O) and hydrolysed yields αβγ-trimethyl-*d*-galacturonic acid and 3 : 4-dimethyl-*l*-rhamnose; (I) is therefore 2-*d*-galacturonido-*l*-rhamnose, identical with the aldobionic acid from flax-seed mucilage (cf. Tipson *et al.*, A., 1939, II, 298). J. D. R.

Constitution of damson gum. II. Hydrolysis products from methylated degraded (arabinose-free) damson gum. E. L. HIRST and J. K. N. JONES (J.C.S., 1939, 1482—1490).—The polysaccharide *A* from damson gum (cf. A., 1938, II, 394) on repeated methylation (TlOH–MeI and finally MeI–Ag_2O) yields a methylated polysaccharide (I) containing uronic anhydride, purified by fractional pptn. by light petroleum from $CHCl_3$. Hydrolysis of (I) with N-HCl followed by treatment with HCl–MeOH and fractional distillation yields 2 : 3 : 4-trimethylmethyl-*d*-xylose (⅛ part), tetramethylmethyl-*d*-galactose (1 part), 2 : 3 : 4- (1 part) and 2 : 4 : 6-trimethylmethyl-*d*-galactose (1 part) (*anilide*, m.p. 179°, $[\alpha]_D^{19}$ −92° in $COMe_2$ → +38° in 22 hr.), and 4 : 6-dimethylmethyl-*d*-galactose (1 part) (*anilide*, m.p. 207°, $[\alpha]_D^{20}$ −174° in C_5H_5N), which on oxidation (Br) yields γε-*dimethyl*-d-*galactonolactone*, a syrup, $[\alpha]_D^{20}$ +78° in MeOH, +91° in H_2O → +45° in 60 hr., converted by liquid NH_3 into γε-*dimethyl*-d-*galactonamide monohydrate*, m.p. 164°, $[\alpha]_D^{26}$ +54° in H_2O. From the acidic part of the hydrolysis products of (I) are isolated αβγ-trimethyl-*d*-glycuronic acid (1 part) and αβ-dimethyl-*d*-glycuronic acid (1 part), which when oxidised (Br) and esterified yields *dimethylsaccharolactone Me ester*, m.p. 101°.

J. D. R.

Constitution of cellulose with special regard to hydrolytic experiments.—See A., 1939, I, 511.

Kinetics of thermal decomposition of methylamines.—See A., 1939, I, 528.

General synthesis of α-amino-acids by means of ethyl benzamidomalonate. C. A. REDEMANN and M. S. DUNN (J. Biol. Chem., 1939, **130**, 341—348).—OH·N:C(CO_2Et)$_2$ (prep. by Bu^nO·NO) is reduced by H_2–Raney Ni to NH_2·CH(CO_2Et)$_2$, which with BzCl in H_2O containing C_5H_5N gives NHBz·CH(CO_2Et)$_2$, m.p. 73—74° (lit., 61°). With NaOEt–EtOH, followed by an alkyl or aralkyl iodide, this gives the *C*-alkyl-ester, hydrolysed and decarboxylated, best by boiling HBr, to the α-NH_2-acid. Phenylalanine, leucine, aspartic acid, and valine are thus prepared. For serine and threonine the condensation with RI should be effected in C_6H_6 or PhMe etc. (no details given). R. S. C.

Synthesis of α-aminopelargonic acid. T. B. JOHNSON (J. Amer. Chem. Soc., 1939, **61**, 2485—2487).—*n*-C_6H_{13}·CHO, hydantoin, and NaOAc in AcOH give n-*heptylidene*-, m.p. 157—159°, reduced by $SnCl_2$ to n-*heptyl-hydantoin*, m.p. 142—143°, which, by prolonged boiling with aq. $Ba(OH)_2$, gives α-*amino*-n-*nonoic acid*, decomp. 236—256° (*hydrochloride*).

R. S. C.

(A) Stereoisomerides of γ-amino-β-hydroxybutyric acid. M. TOMITA and Y. SEIKI. **(B) Stereoisomerides of *iso*serine.** Y. SEIKI (J. Biochem. Japan, 1939, **30**, 101—105, 107—112).—(A) *X*-Ray diagrams of *l*- and *d*-γ-amino-β-hydroxybutyric acid-I or of the *l*- and *d*-forms of acid-II are identical; that of acid-I, however, differs from that of acid-II (cf. A., 1927, 1058). Acid-II has a ring, and -I an open-chain, structure (cf. Bergmann and Lissitzin, A., 1930, 459).

(B) The conclusions of Tomita *et al.* (A., 1932, 1118) are confirmed by *X*-ray studies and the structure of the isomerides is further discussed.

F. O. H.

Racemisation of benzyl-*l*-cysteine. Preparation of *d*-cystine. J. L. WOOD and V. DU VIGNEAUD (J. Biol. Chem., 1939, **130**, 109—114).—*d*-Cystine (I) is best prepared by treating *S*-benzyl-*l*-cysteine (prep. from *l*-cystine by Na, followed by CH_2PhCl, in liquid NH_3) with Ac_2O–NaOH at 45—50°

and hydrolysing the resulting *dl-N*-Ac compound by HCl. S-*Benzyl*-dl-*cysteine*, m.p. 213—215°, thus produced is converted by Ac_2O in 90% HCO_2H at 55—60° into the N-*CHO* derivative, m.p. 136·5°, which is resolved by brucine to yield the d-*salt*, $[\alpha]_D^{21}$ −25° in H_2O, and thence S-*benzyl*-d-*cysteine*, $[\alpha]_D^{25}$ −22·5° in N-NaOH. Na in liquid NH_3 then yields (I), $[\alpha]_D^{20}$ +224° in N-HCl. R. S. C.

Decomposition of cysteine in aqueous solution. J. I. Routh (J. Biol. Chem., 1939, **130**, 297—304).—When boiled in air or N_2 with dil. aq. NaCl (0·48 g. per l.) cysteine (I) decomposes more slowly than cystine (II) (A., 1939, II, 11) but yields (II), H_2S, and NH_3, with products similar to sulphenic and sulphinic acids which cause a progressive decrease in the p_H of the solutions during heating. The progressive decrease in the NH_2-content and the non-formation of free S indicate that the mechanism of the decomp. of (I) differs from that of (II). J. W. S.

Conversion of methionine into cystine. Radioactive sulphur. H. Tarver and C. L. A. Schmidt (J. Biol. Chem., 1939, **130**, 67—80).—S containing ^{35}S is converted successively into FeS, H_2S, $CH_2Ph{\cdot}SH$, $CH_2Ph{\cdot}S{\cdot}[CH_2]_2{\cdot}Cl$, $o\text{-}C_6H_4(CO)_2N{\cdot}C(CO_2Et)_2{\cdot}[CH_2]_2{\cdot}S{\cdot}CH_2Ph$, *phthalimidobenzylthiolmalonic acid*, m.p. 110—111° (decomp.; corr.), *S*-benzylhomocysteine, and methionine. When this methionine (but not Na_2SO_4 containing $Na_2{}^{35}SO_4$), is fed to or injected intravenously into rats, it is converted into radioactive cystine. The change probably proceeds thus: $SH{\cdot}[CH_2]_2{\cdot}CH(NH_2){\cdot}CO_2H \rightarrow SH{\cdot}CHMe{\cdot}CH(NH_2){\cdot}CO_2H \rightarrow SH{\cdot}CH(NH_2){\cdot}CO_2H$. R. S. C.

Stability of the keto-acid from methionine. H. Waelsch and E. Borek (J. Amer. Chem. Soc., 1939, **61**, 2252).—Deamination of methionine (I) by kidney slices gives a ketone (II), $C_5H_8O_3S$, isolated as *dinitrophenylhydrazone* (~20%), m.p. 149°. If the incubated solution is deproteinised and boiled in 2N-NaOH–N_2, MeSH is formed (isolated as Hg salt) and must be derived from the (II) as (I) is stable to alkali. R. S. C.

Di-(βγ-dihydroxypropyl)oxamide and its nitration products. T. Domański and J. Skudrzyk (Rocz. Chem., 1939, **19**, 427—432).—$[OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}]_2$ (I) was obtained by the reactions: glycerol + HCl → chlorohydrin (II) (+NaOH) → glycide (+NH_3) → $NH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$ (III) (+$Et_2C_2O_4$) → (I); (II)+NH_3 → (III) (+$H_2C_2O_4$) → oxalate → (I). (I) nitrated (HNO_3 *d* 1·38, H_2SO_4 *d* 1·84) at <10° yields *NN'-di-(βγ-dihydroxypropyl)oxamide tetranitrate*, m.p. 142·5°. This is a strong explosive, of high stability. Its properties resemble those of $(NO_2{\cdot}NMe{\cdot}CO{\cdot})_2$. R. T.

Use of mercuric acetate in organic preparations. I. Mercury compounds of amides and imides. N. V. S. Rao and T. R. Seshadri (Proc. Indian Acad. Sci., 1939, **10**, A, 1—5).—Good yields of pure $o\text{-}C_6H_4(CO)_2NHg$ (I) and $(\cdot CH_2{\cdot}CO)_2NHg$ are quickly obtained from the respective imide and $Hg(OAc)_2$ in EtOH. With 1 mol. of $Hg(OAc)_2$ in EtOH, $CO(NH_2)_2$ gives *mercuricarbamide*, $CO(NH)_2Hg$, m.p. >340° (yellow at 230°) [which may replace (I) pharmaceutically], but with 2 mols. of $Hg(OAc)_2$ gives *di(acetoxymercuri)carbamide*, $CO(NH{\cdot}HgOAc)_2$, decomp. ~270°. NH_2Ac and $Hg(OAc)_2$ at 180° give Hg, AcOH, and a mixture. NH_2Ac (2 mols.) and $Hg(OAc)_2$ (1 mol.) in EtOH give N-*acetoxymercuriacetamide*, m.p. 195° (decomp.); larger proportions of $Hg(OAc)_2$ give a *product* (Hg 72, N 3·9%), m.p. 225° (decomp.). R. S. C.

Attempts to prepare optically active ethyleneimine derivatives containing an asymmetric nitrogen atom. R. Adams and T. L. Cairns (J. Amer. Chem. Soc., 1939, **61**, 2464—2467).—*p*-$C_6H_4Br{\cdot}SO_2Cl$ and $OH{\cdot}[CH_2]_2{\cdot}NH_2$ in 10% NaOH at 50—70° give p-*bromobenzenesulphon*-β-*hydroxyethylamide* (I), m.p. 93·5—95°, converted by $SOCl_2$ into the β-*Cl*-compound, m.p. 150—152·5°, which with hot, 1% KOH regenerates (I). p-*Bromobenzenesulphon*-β-*hydroxy*isobutylamide (II) (similarly prepared), m.p. 96·5—98°, is converted by 48% HBr into *p*-$C_6H_4Br{\cdot}SO_2{\cdot}NH_2$ (III), by P_2O_5 into 4-p-*bromobenzenesulphon*-1 : 1 : 6 : 6- or -1 : 1 : 5 : 5-*tetramethylmorpholide*, m.p. 145—147°, with some (III), and by boiling, conc. HCl into p-*bromobenzenesulphon*-β-*chloro*isobutylamide (IV), m.p. 123—128°. 10% NaOH at 100° converts (IV) into (II) (~50%) and 1-p-*bromobenzenesulphon*-2 : 2-*dimethylethyleneimide* (46%), m.p. 79·5—81·5°; KOH–EtOH gives (II) and an oil. Distillation of $OH{\cdot}CMe_2{\cdot}CH_2{\cdot}NH_2$ with aq. H_2SO_4 gives β-*methylallylamine* (V), b.p. 76·7—77·7°/746 mm. (*hydrochloride*, m.p. 190—191°; *picrate*, m.p. 202—206°; p-$C_6H_4Br{\cdot}SO_2$, m.p. 74—76°, and *thiocarbamide* derivatives, m.p. 78—79°). $CH_2{:}CMe{\cdot}CH_2Cl$ and *o*-$C_6H_4(CO)_2NK$ at 150° give N-β-*methylallylphthalimide*, m.p. 88·5—90°, converted by N_2H_4 into (V). p-*Bromobenzenesulphon*-β-*hydroxy*-ββ-*diphenylethylamide* (VI), m.p. 151—153°, does not yield the β-Cl-compound; with $SOCl_2$ or, best, P_2O_5 in C_6H_6 it gives p-*bromobenzenesulphon*-ββ-*diphenylvinylamide*, m.p. 197—198°, oxidised by CrO_3 to $COPh_2$. The camphor- and α-bromocamphor-sulphonamide analogues of (II) and the α-bromocamphorsulphonamide analogue of (VI) are oils. M.p. are corr. R. S. C.

Explosion of ethyl azide in presence of diethyl ether.—See A., 1939, I, 568.

Detection of chloride in chlorovinylarsine (lewisite). C. Froger (Compt. rend., 1939, **209**, 351).—Passage of $CHCl{:}CH_2{\cdot}AsCl_2$ (I) vapour through Draeger's detector tube (SiO_2 gel) followed by a little Br–H_2O and aq. fluorescein shows an eosin-coloured region where Br has not reacted with (I). The reaction occurs only with high concns. of (I). (I) adsorbed on SiO_2 reacts with 1% OsO_4 to give a black ppt.; 25 mg. of (I) per cu.m. of air can be detected. EtOH, Et_2O, and $COMe_2$ do not react with OsO_4; acraldehyde reacts. J. L. D.

[Coupling organic radicals by means of the Grignard reagent.] J. H. Gardner and L. Joseph (J. Amer. Chem. Soc., 1939, **61**, 2551—2552; cf. A., 1930, 76).—$MgBu^{\beta}Br$ and AgBr give 37·5% of $Bu^{\beta}{}_2$, and $CHMeEt{\cdot}MgBr$ gives 13% of $(CHMeEt)_2$. No rearrangement occurs. R. S. C.

Introduction of racemic organic molecules into some optically active complex ions of cobalt and chromium.—See A., 1939, I, 576.

Relative dissymetric synthesis and rotation-dispersion in cobaltic complexes of the α-amino-acids.—See A., 1939, I, 533.

Investigation of the isomeric dichlorobis-ethylenediaminocobaltic chlorides by means of a radioactive isotope of chlorine.—See A., 1939, I, 576.

New class of ammines. Complex thio-molybdates and thiotungstates.—See A., 1939, I, 532.

Complex compounds of platinum [chloride] and butadiene.—See A., 1939, I, 533.

Oxygen effect in the reaction of *cyclo*propane with bromine and with hydrogen bromide. M. S. KHARASCH, M. Z. FINEMAN, and F. R. MAYO (J. Amer. Chem. Soc., 1939, **61**, 2139—2142).—In absence of O_2, reaction of *cyclo*propane (I) and Br is very slow in light or dark. O_2, Bz_2O_2, or ascaridole accelerates the reaction, particularly in the light. O_2, Bz_2O_2, *o*-$C_6H_4(OH)_2$, O_2+$NHPh_2$, or H_2O accelerates the slow reaction of 0·1 mol. of HBr with (I), but *o*-$C_6H_4(OH)_2$+O_2 has less effect than O_2 alone; light has little effect. A chain mechanism involving Br atoms is suggested for both reactions. O_2 or light has no effect on the reaction with 1 mol. of HBr, but *o*-$C_6H_4(OH)_2$, H_2O, AcOH, or C_6H_4Me·SH accelerates the reaction in absence of O_2; a competing non-at. mechanism is suggested. R. S. C.

Synthesis of antirachitic vitamins. I. Synthesis of γ-2-methylene*cyclo*hexylidene-Δ^{α}-propene. N. A. MILAS and W. L. ALDERSON, jun. (J. Amer. Chem. Soc., 1939, **61**, 2534—2537).—2-Dimethylaminomethyl*cyclo*hexanone (prep. described) and CH_2:CH·CH_2·MgBr in Et_2O give 2-dimethylaminomethyl-1-allyl*cyclo*hexanol (I), b.p. ~112—117°/5 mm. (*acetate*, b.p. 129—130°/9 mm.), the unstable bromide (prep. by PBr_3 in C_6H_6) of which is converted by KOH at 175°/vac. into γ-2-*dimethylaminomethyl*cyclo*hexylidene*-Δ^{α}-*propene*, b.p. 126·5—128°/10 mm. (absorption max. at 236 mμ., mol. extinction coeff. 10,500), obtained also less well directly from (I) by various methods of dehydration ($KHSO_4$ gives a good yield of a rearranged product, b.p. 100—103°/9 mm.). The amine gives a methiodide, which, when treated with Ag_2O etc. and distilled at 60°/5 mm., gives γ-2-*methylene*cyclo*hexylidene*-Δ^{α}-*propene*, b.p. 62—63°/7 mm. (absorbs 3 H_2). This has the unsaturated system of an antirachitic vitamin and has an absorption max. at 255 mμ. with a mol. extinction coeff. 19,000. R. S. C.

Reduction of diazonium salts to hydrocarbons with alkaline formaldehyde. R. Q. BREWSTER and J. A. POJE (J. Amer. Chem. Soc., 1939, **61**, 2418—2419).—Addition of ArN_2Cl to aq. NaOH–CH_2O gives the ArH from the following NH_2Ar: NH_2Ph 60; *o*- and *p*-C_6H_4Me·NH_2 80; *o*- 75 and *p*-OMe·C_6H_4·NH_2 72; *o*- 75 and *p*-OEt·C_6H_4·NH_2 65; *m*-4-$C_6H_3Me_2$·NH_2 80; *p*- 50 and *o*-C_6H_4Cl·NH_2 55; *p*- and *o*-NH_2·C_6H_4·OPh 60; *o*- and *p*-NH_2·C_6H_4·O·C_6H_4Me-*p* 50; 2 : 5 : 1-$C_6H_3Cl_2$·NH_2 10; *o*-NH_2·C_6H_4·CO_2H 25; *o*- 20, *m*- 10, and *p*-NO_2·C_6H_4·NH_2 10%. The method succeeds best when EtOH fails and vice versa. R. S. C.

Possible dimorphism of trinitrobenzene. T. URBAŃSKI and J. SIMON (Rocz. Chem., 1939, **19**, 487—491).—Nitration of *m*-$C_6H_4(NO_2)_2$ with HNO_3 and 60% oleum gives *s*-$C_6H_3(NO_2)_3$ (I), m.p. 121°, or a substance, m.p. 61—62°, presumably identical with that described by Radcliff and Pollitt (A., 1921, i, 233) as being a polymorph of (I). This product is shown to be a mixture of *m*-$C_6H_4(NO_2)_2$ 35—50 and (I) 50—65%. R. T.

Rearrangement of toluene derivatives by aluminium chloride. J. F. NORRIS and H. S. TURNER (J. Amer. Chem. Soc., 1939, **61**, 2128—2131).—$AlCl_3$–HCl at 50—100° causes rearrangement and disporportionation of *o*-, *m*-, and *p*-C_6H_4MeCl or *p*-cresol, but not of *o*-, *m*-, or *p*-C_6H_4Me·NO_2 (at 100°; tars formed at 150°) or *p*-C_6H_4Me·NMe_2. The ratio of the products depends on the temp., time of heating, and amount of $AlCl_3$. With 0·1 mol. of $AlCl_3$ at 96° for 4·25 hr., the ease of rearrangement is *o*- < *m*- < *p*-C_6H_4MeCl. Thermal analysis of mixed isomerides, C_6H_4MeCl, is described. R. S. C.

Use of *n*-butyl chlorosulphonate and chlorosulphite in the Friedel–Crafts reaction. C. BARKENBUS, R. L. HOPKINS, and J. F. ALLEN (J. Amer. Chem. Soc., 1939, **61**, 2452—2453).—With $ClSO_3Bu^{\alpha}$ (1 mol.) and $AlCl_3$ (2 mols.), at 0—5°, C_6H_6 (9 mols.) gives CHPhMeEt (19), *m*-$C_6H_4(CHMeEt)_2$ (26·6), and PhCl (11·2%); PhMe gives *m*- (32·4) and *p*-C_6H_4Me·$CHMeEt$ (19·6) with *o*- (21·8) and *p*-C_6H_4MeCl (6·2%) and products halogenated in the side-chain. Higher-boiling products are also formed. $ClSO_2Bu^{\alpha}$, C_6H_6, and $AlCl_3$ give CHPhMeEt and S compounds. R. S. C.

Ferric chloride as a condensing agent. W. M. POTTS and R. J. DODSON (J. Amer. Chem. Soc., 1939, **61**, 2553).—$FeCl_3$ gives a better yield (82%) of $PhBu^{\gamma}$ from C_6H_6 and $Bu^{\gamma}OH$ at room temp. than does $AlCl_3$, but causes only an indefinite reaction with CHMeEt·OH and none with $Bu^{\alpha}OH$. R. S. C.

Rearrangement of the xylenes by aluminium chloride. J. F. NORRIS and G. T. VAALA (J. Amer. Chem. Soc., 1939, **61**, 2131—2134).—The ratio of the three isomerides obtained from each xylene by $AlCl_3$ depends on the temp. Rearrangement is accelerated by increase in the amount of $AlCl_3$, but not by HCl (increases decomp.) or $FeCl_3$. R. S. C.

Chlorinations with sulphuryl chloride. I. Peroxide-catalysed chlorination of hydrocarbons. M. S. KHARASCH and H. C. BROWN (J. Amer. Chem. Soc., 1939, **61**, 2142—2150).—Traces of org. peroxides enormously accelerate chlorination of many org. compounds by SO_2Cl_2, making this a practical reagent. Yields are usually excellent and reaction times short. Boiling *cyclo*hexane does not react with SO_2Cl_2 in the dark and only to the extent of 25% in 6 hr. in light; 0·001 mol. of Bz_2O_2 or (n-$C_{11}H_{23}$·CO_2)$_2$ (I) causes complete reaction in 15—30 min. in the dark; animal C in rather large amount or CuCl (0·2 mol.) is less effective, but S, I, PCl_5, HCl, SO_2, and O_2 are useless.

The products are chloro- and dichloro-*cyclo*hexanes. n-C_7H_{16} gives α- and *sec.*-chloroheptane. Pr^aCl gives $CHMeCl{\cdot}CH_2Cl$ and $CH_2(CH_2Cl)_2$. Bu^aCl gives αβ-, αγ-, and αδ-dichlorobutane. $CHMeCl{\cdot}CH_2Cl$ gives $CHMeCl{\cdot}CHCl_2$, $CMeCl_2{\cdot}CH_2Cl$, and $CHCl(CH_2Cl)_2$. $(CH_2Cl)_2$ gives $CHCl_2{\cdot}CH_2Cl$. Pr^aBr gives $CHMeCl{\cdot}CH_2Br$, $CH_2Cl{\cdot}CH_2{\cdot}CH_2Br$, and products of higher b.p. $(CHCl_2)_2$ and $CHCl_3$ are unaffected. In general, CH_2 is more readily substituted than Me, and Cl depresses further substitution at the same C. PhMe similarly gives ~100% of CH_2PhCl or, with an excess of SO_2Cl_2, $CHPhCl_2$, but further substitution does not occur. p-C_6H_4MeCl (gives p-$C_6H_4Cl{\cdot}CH_2Cl$), PhEt (gives mainly CHPhMeCl), $PhPr^\beta$ (gives mainly $CPhMe_2Cl$), $PhBu^\gamma$ (gives mainly $CPhMe_2{\cdot}CH_2Cl$), m-xylene [gives only m-$C_6H_4(CH_2Cl)_2$], and $CHPh_3$ (gives CPh_3Cl), but not o- or p-$C_6H_4Me{\cdot}NO_2$, or CH_2Ph_2, react similarly. Fluorene and 2-$C_{10}H_7Me$ undergo nuclear chlorination. Sometimes use of a solvent (CH_2Cl_2, $CHCl_3$, CCl_4, C_6H_6, PhCl, or o-$C_6H_4Cl_2$) is advantageous, and the less stable (I) is preferable to Bz_2O_2 when reaction is slow. CH_2Ph_2, a slow stream of O_2, I, S, p-$C_6H_4Me{\cdot}NO_2$, $SOCl_2$, PCl_3, or *iso*-$C_5H_{11}{\cdot}O{\cdot}NO$ inhibits chlorination, *e.g.*, of PhMe or *cyclo*hexane, but AcCl, AcOH, and $COPh_2$ have no effect. Bz_2O_2 and SO_2Cl_2 at 70—80° slowly give PhCl, SO_2, and CO_2. A chain mechanism for chlorination involving Cl atoms is suggested.

R. S. C.

Action of chlorine on thiocyanates. T. B. Johnson and I. B. Douglass (J. Amer. Chem. Soc., 1939, 61, 2548—2550).—RSCN and aq. Cl_2 at 0°—room temp. give ~75% yields of RSO_2Cl (prep. when R = Me or Et, described) and CNCl. $CH_2Ph{\cdot}SCN$ at 0—2° gives CNCl and $CH_2Ph{\cdot}SO_2H$, converted in air into $(CH_2Ph{\cdot}SO{\cdot})_2$ or by CH_2PhCl into $(CH_2Ph)_2SO_2$; at 20—30° it gives $CH_2Ph{\cdot}SO_2Cl$, obtained also from $CH_2Ph{\cdot}SO_2H$ by aq. Cl_2 at 20—30°.

$CH_2Ph{\cdot}S{\cdot}C(NH){\cdot}NH_2,HCl$ gives only $CH_2Ph{\cdot}SO_2Cl$ (76%). Prep. of $PhSO_2Cl$ from PhSCN is more difficult.

R. S. C.

Kinetics of sulphonation of nitrobenzene by sulphur trioxide.—See A., 1939, I, 570.

Derivatives of *o*- and *p*-nitrobenzenesulphinic acids.—See B., 1939, 1077.

Validity of the structure assigned to *cyclo*octatetraene: pyrolysis of diquaternary ammonium hydroxides related to Δ^α- and Δ^β-butene. C. D. Hurd and L. R. Drake (J. Amer. Chem. Soc., 1939, 61, 1943—1945).—*Trimethyl*-n-*butylammonium bromide*, m.p. 197—198° (sealed tube), is converted by Ag_2O in H_2O into the hydroxide, which, when heated, finally at 250°, in N_2 gives only Δ^α-butene. αβ-*Butylenedi*(*trimethylammonium bromide*) (prep. from $CHEtBr{\cdot}CH_2Br$ and NMe_3 at room temp.) gives similarly 44% of CEt:CH (absorbed by alkaline $KHgI_3$) and 56% of $CHMe{:}C{:}CH_2$ (absorbed by 82% H_2SO_4). βγ-*Butylenedi*(*trimethylammonium bromide*) [similarly prepared from $(CHMeBr)_2$] gives 42—47% of $(CH_2{:}CH)_2$ (absorbed by molten maleic anhydride) and 58—53% of a mixture (absorbed by 82% H_2SO_4) of $(:CMe)_2$ and $CHMe{:}C{:}CH_2$. The structure of the *cyclo*octatetraene of Willstätter *et al.* (A., 1912, i, 17; 1913, i, 348) is thus uncertain, as it was deduced from successive Hofmann degradations assumed to give only conjugated ethylenic linkings.

R. S. C.

Synthesis of polyenes. I. Hexatriene and its polymerides. M. S. Kharasch and E. Sternfeld (J. Amer. Chem. Soc., 1939, 61, 2318—2322).—$NaNH_2$ in liquid NH_3 causes smooth coupling of halides of weakly negative radicals, if the C carrying the halogen also carries H. Thus, addition of $NaNH_2$ (1 mol.) to $CH_2{:}CH{\cdot}CH_2Cl$ (I) (1 mol.) gives 24—30% of $(CH_2{:}CH{\cdot}CH{:})_2$ (II), b.p. 76—78°, and 41—33% of 3-*vinyl*-4-*butadienyl*-Δ^1-cyclo*hexene* (III), b.p. 50—55°/3 mm. Addition of (I) (1·33 mols.) to $NaNH_2$ (2 mols.) gives 50% of (III) with some 4-β-2′-*vinyl*-$\Delta^{3'}$-cyclo*hexenylvinyl*-3-*vinyl*-Δ^1-cyclo*hexene*, b.p. 70—80°/10^{-4} mm. [absorbs 5 H_2 in MeOH; does not react with $(:CH{\cdot}CO)_2O$ (IV)], and (?) 3-2′-*vinyl*-$\Delta^{3'}$-cyclo*hexenyl*-5-β-2″-*vinyl*-$\Delta^{3''}$-cyclo*hexenylvinyl*-Δ^1-cyclo*hexene*, b.p. 120—133°/10^{-4} mm. [absorbs 6 H_2 in MeOH; does not react with (IV)]. Addition of $NaNH_2$ (2) to (I) (3 mols.) gives 50% of 4-*chloromethyl*-3-*vinyl*cyclo*hexene*, b.p. 44—48°/8 mm. [reduced (H_2–PtO_2; 2·7 atm.) to 1-methyl-2-ethyl*cyclo*hexane], and less (II). The structure of (III) follows from its reaction with (IV) in C_6H_6 at 90—100° to give an adduct, hydrolysed to the *dicarboxylic acid*, $C_{16}H_{20}O_4$, m.p. 178°, and from its hydrogenation (4 H_2) in MeOH to give 1-*ethyl*-2-n-*butyl*cyclo*hexane*, b.p. 208°, obtained also by interaction of 2-ethyl*cyclo*hexanone with $MgBu^aBr$, dehydration of the resulting carbinol by I, and finally hydrogenation (PtO_2) in AcOH at 2·5 atm.

R. S. C.

Addition of alkali metals to stilbenes. G. F. Wright (J. Amer. Chem. Soc., 1939, 61, 2106—2110).—Contrary to Schlenk *et al.* (A., 1928, 1031), addition of Na, K, or Li to stilbene (I) or *iso*stilbene gives a mixture of stereoisomerides. The reaction mechanism is discussed. Impure (I) is recovered (with one exception) from the reaction. Reaction is fastest in $(CH_2{\cdot}OMe)_2$ (II) and good in Et_2O, but in C_6H_6 must be initiated by PhCl, and barely occurs in light petroleum (III) (b.p. 60—70°). The ratio of products depends on the solvent and on the characterising agent. With Li in Et_2O, CO_2 gives 55% of *meso*- and 26% of *dl*-$(CHPh{\cdot}CO_2H)_2$ (IV); in (II) (Na or Li), only a trace of and, in C_6H_6 (Na or Li) or (III), no (IV) was isolated (purification is difficult) although the crude acid was a mixture. In (II) (Na), Me_2SO_4 gives 45% of $(CHPhMe)_2$, b.p. 132—134°/6 mm., and 20% of the isomeride, m.p. 124°, the 4 : 4′-$(NO_2)_2$-derivatives, m.p. 133° and 256°, respectively, of which with CrO_3–AcOH give 90% of p-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$.

R. S. C.

Effect of substitution on the dissociation of hexa-arylethanes. VII. *m*- and *p*-Phenyl groups. C. S. Marvel, M. B. Mueller, and E. Ginsberg (J. Amer. Chem. Soc., 1939, 61, 2008—2010; cf. A., 1939, II, 103).—χ for 3·6% solutions in C_6H_6 at 25° indicates 11—12% of dissociation for $(m$-$C_6H_4Ph{\cdot}CPh_2)_2$ (I) and 13—14% for $(p$-$C_6H_4Ph{\cdot}CPh_2)_2$ (10% in 7% solution). These figures and the known 60% dissociation of $C_2(C_6H_4Ph$-$m)_6$ show that the *m*- are about as strongly dissociated as the p-C_6H_4Ph derivatives, which does not accord with a relation of the stability of the free radicals with the

no. of possible resonance forms. Colour is no guide to the degree of dissociation. *m*-$C_6H_4Ph{\cdot}MgBr$ (prep. with aid of a little EtBr) and $COPh_2$ give m-*phenyltriphenylcarbinol* (II), m.p. 104—105°, converted by HCl–$CaCl_2$–Et_2O followed by EtOH into the *Et ether* (III), m.p. 78—79°. Hot, pure AcCl converts (II) or (III) into the *carbinyl chloride*, m.p. 86—87°, which with Ag gives (I) and thence by air m-*phenyltriphenylmethyl peroxide*, m.p. 164—165°. R. S. C.

Cyclisation of dieninenes. VII. Dehydrogenation of *trans*-dodecahydrophenanthrene. *trans*-1-Keto-3 : 4-dialkyloctahydronaphthalenes. C. S. Marvel, R. Mozingo, and E. C. Kirkpatrick (J. Amer. Chem. Soc., 1939, **61**, 2003—2008).—The structure of the *trans*-Δ^{11}-dodecahydrophenanthrene of Marvel *et al.* (A., 1936, 1101; 1938, II, 48) is confirmed. Its relative resistance to Se excludes a spiran structure; with Pd–C at 300—320° it gives only phenanthrene; H_2–Raney Ni reduces the 9-CO of the parent ketone only at 185°/100—200 atm. (proof of steric hindrance), yielding mixed, waxy tetradecahydrophenanthr-9-ols, b.p. 136—138°/2 mm. Formation of phenanthrene derivatives by Se-dehydrogenation of 1 : 2-dialkylnaphthalene derivatives (cf. A., 1938, II, 48) is confirmed. Addition of 1-acetylenyl*cyclo*hexanol (prep. in 69% yield from *cyclo*hexanone, C_2H_2, and $CMe_2Et{\cdot}OK$ in $CMe_2Et{\cdot}OH$–Et_2O at −15°), b.p. 77—78°/17 mm., followed by $COMeBu^{\alpha}$, to MgEtBr in Et_2O gives 1-*γ-hydroxy-γ-methyl-*Δ^{α}*-heptinenyl*cyclo*hexanol*, b.p. 124—126°/1 mm., dehydrated by $KHSO_4$ at 190—200° to 1-*γ-methyl*-n-*hept*-Δ^{γ}-*en*-Δ^{α}-*inenyl*-Δ^{1}-cyclo*hexene*, b.p. 143—148°/21 mm., which with boiling 87% HCO_2H gives 38% of trans-1-*keto*-3-*methyl*-4-n-*propyl*-1 : 2 : 5 : 6 : 7 : 8 : 9 : 10-*octahydronaphthalene* (I), b.p. 107—108°/1 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 124—125°). Zn–Hg–18% HCl–AcOH reduction of (I) yields a mixture (II), $C_{14}H_{24}$, b.p. 115—120°/14 mm., containing some 6-methyl-5-*n*-propyl-1 : 2 : 3 : 4 : 7 : 8 : 9 : 10-octahydronaphthalene and 19% of a hydroazulene (absorption spectrum; Br–AcOH test of the mixture). With Se at 390—400°, (II) gives blue and mixed colourless compounds; the absorption spectrum of the mixture indicates presence of 35—40% of *trans-as*-octahydrophenanthrene. R. S. C.

Synthesis of phenanthrene derivatives. III. 9-Methylphenanthrene. C. K. Bradsher and R. W. H. Tess (J. Amer. Chem. Soc., 1939, **61**, 2184—2185; cf. A., 1939, II, 362).—Cyclisation of *o*-$C_6H_4Ph{\cdot}CMe(OH){\cdot}CH_2X$ (*A*) by 2 : 1 AcOH–40% HBr gives the following yields of 9-methylphenanthrene: X = OMe 50, OPh 32, $O{\cdot}C_{10}H_7$-β 23, NEt_2 10, and Cl <1%, calc. on the ketone used. If X = OPh, $AlCl_3$ in CS_2 gives a 10% yield. Prep. of $COMe{\cdot}CH_2{\cdot}OPh$, b.p. 117—124°/19 mm., $COMe{\cdot}CH_2{\cdot}O{\cdot}C_{10}H_7$-β, m.p. 69—72°, and of (*A*) (from *o*-$C_6H_4Ph{\cdot}MgI$ and $COMe{\cdot}CH_2X$ except for X = OMe which is obtained from MgMeI and *o*-$C_6H_4Ph{\cdot}CO{\cdot}CH_2{\cdot}OMe$) is described. R. S. C.

Synthesis of 9 : 10-dialkyl-1 : 2-benzanthracenes. W. E. Bachmann and J. M. Chemerda (J. Amer. Chem. Soc., 1939, **61**, 2358—2361).—Conversion of 9 : 10-dimethoxy-9 : 10-dimethyl-9 : 10-dihydro-1 : 2-benzanthracene (I) into 9 : 10-dimethyl-1 : 2-benzanthracene (II) by Na (A., 1938, II, 270) involves formation of 9-sodio-10-methoxy-9 : 10-dimethyl-9 : 10-dihydro-1 : 2-benzanthracene, followed by transannular loss of NaOMe, because (*a*) 1 mol. of the ether reacts with 2 Na, (*b*) the final product is present as hydrocarbon, (*c*) the reaction mixture remains almost colourless, (*d*) when (I) and (II) compete for Na, only (I) reacts, and (*e*) (II) is not obtained by interaction of its Na_2 derivative with (I). Some 9 : 10-dialkyl derivatives are prepared. 9 : 10-*Diethoxy*-9 : 10-*dimethyl*-9 : 10-*dihydro*-1 : 2-*benzanthracene*, m.p. 172—173·5°, is obtained from the 9 : 10-$(OH)_2$-compound by H_2SO_4–EtOH and with Na in C_6H_6–Et_2O gives 61% of (II); the Pr^{α}_2, Pr^{β}_2, and Bu^{α}_2 ethers could not be thus obtained. 9 : 10-*Dimethoxy*-9 : 10-*di*-n-*propyl*-9 : 10-*dihydro*-1 : 2-*benzanthracene* (similarly prepared), m.p. 176·5—177·5°, gives 95% of 9 : 10-*di*-n-*propyl*-1 : 2-*benzanthracene*, m.p. 100·5—101° (*picrate*, m.p. 107·5—108°). MgEtBr and 5-keto-5 : 6 : 7 : 8-tetrahydro-1 : 2-benzanthracene (III) give a carbinol, converted by Pd–C in N_2 at 310—320° into 5-ethyl-1 : 2-benzanthracene (IV) (65%), m.p. 118—119° (lit. 120°), and by $KHSO_4$ at 150—160° into 5-*ethyl*-7 : 8-*dihydro*-1 : 2-*benzanthracene*, m.p. 110—112°, which with Pd–C at 330—340° gives 70% of (IV). $Na_2Cr_2O_7$ in AcOH at 70° oxidises (IV) to the quinone, which with MgMeI etc. affords 9 : 10-dihydroxy-, m.p. 201·5—204·5°, and 9 : 10-*dimethoxy*-9 : 10-*dimethyl*-5-*ethyl*-9 : 10-*dihydro*-1 : 2-*benzanthracene*, m.p. 197—200°, and 9 : 10-*dimethyl*-5-*ethyl*-1 : 2-*benzanthracene* (80%), m.p. 107—108°. Addition of $CH_2{:}CH{\cdot}CH_2Br$ to (III) and Mg in C_6H_6–Et_2O gives 84% of 5-*hydroxy*-5-*allyl*-5 : 6 : 7 : 8-*tetrahydro*-1 : 2-*benzanthracene*, m.p. 82—82·5°, converted by Pd–C–N_2 at 300° into 5-*n*-propyl-1 : 2-benzanthracene (V). $MgPr^{\alpha}Br$ and (III) in C_6H_6–Et_2O give impure 5-hydroxy-5-*n*-propyl-5 : 6 : 7 : 8-tetrahydro-1 : 2-benzanthracene, m.p. 107—108·5°, which yields (V) by heating with HCO_2H and then with Pd–C. 5-*n*-Propyl-1 : 2-benzanthraquinone yields successively 9 : 10-dihydroxy-, m.p. 161·5—163°, and 9 : 10-*dimethoxy*-9 : 10-*dimethyl*-5-n-*propyl*-9 : 10-*dihydro*-1 : 2-*benzanthracene*, m.p. 157—159°, and 9 : 10-*dimethyl*-5-n-*propyl*-1 : 2-*benzanthracene*, m.p. 84—85°. 9 : 10-*Dimethoxy*-9 : 10-*dimethyl*-9 : 10-*dihydro*-1 : 2 : 5 : 6-*dibenzanthracene* (obtained from the diol by H_2SO_4–MeOH–C_6H_6), m.p. 310—320° (decomp.), and Na in Et_2O–C_6H_6 give 85% of 9 : 10-dimethyl-1 : 2 : 5 : 6-dibenzanthracene [*dipicrate*, m.p. 175°; *peroxide*, m.p. 206—207° (decomp.) or 218—219° (decomp.; preheated at 200°)]. R. S. C.

Synthetic experiments in the chrysene series. L. F. Fieser, L. M. Joshel, and A. M. Seligman (J. Amer. Chem. Soc., 1939, **61**, 2134—2139).—Addition of $OMe{\cdot}CH_2{\cdot}CN$ (prep. from $CH_2Cl{\cdot}OMe$ and CuCN in 81·6% yield), b.p. 120—120·6°, to 1-$C_{10}H_7{\cdot}MgBr$ in Et_2O–C_6H_6 gives α-*C*$_{10}H_7$ *CH*$_2{\cdot}$*OMe ketone*, b.p. 144—146°/1 mm. (*semicarbazone*, m.p. 166·4—167·8°), which with MgMeCl affords α-*methoxy*-β-1-*naphthylpropan*-β-*ol*, m.p. 56·4—60·4°, b.p. 138—142°/1·5 mm., in 80% over-all yield (reversing the order of the Grignard reactions gives only a 12%

yield). $KHSO_4$ at 165—180° then gives α-1-*naphthylpropaldehyde* (I) (61%), b.p. 130—132°/2 mm. (*semicarbazone*, m.p. 203—204°), and its *enol Me ether* (16%), b.p. 120—122°/15 mm., hydrolysed by hot 20% HCl to (I). Fe powder and 1 : 1 AcOH–H_2O reduce (I) to 1-$C_{10}H_7$·CHMe·CH_2·OH, b.p. 144—147°/3 mm. (3 : 5-*dinitrobenzoate*, m.p. 125·5—126·5°), which with most reagents gives impure halides, but with PCl_5 in C_6H_6 affords the *chloride*, b.p. 114—116°/1 mm. This probably has the normal structure, since the Grignard reagent (II) (obtained with difficulty) and solid CO_2 give 1-$C_{10}H_7$·CHMe·CH_2·CO_2H. Dehydration of the oily carbinol from (II) and 2-methyl*cyclo*hexanone gives ~25% of α-2-*methyl*-Δ^1-cyclo*hexenyl*-β-1-*naphthylpropane*, b.p. ~200—225°/2 mm. $AlCl_3$ in CS_2 at 0° then gives 1 : 6a-*dimethyl*-1 : 2 : 2a : 3 : 4 : 5 : 6 : 6a-*octahydrochrysene*, b.p. ~220—240°/2 mm., which with Se at 320° yields 2-methylchrysene [*s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 189·8—190·6°] (9%) by loss and migration of Me. Mg *cyclo*hexyl chloride and (I) in Et_2O, first at <0° and then at room temp., give α-cyclo*hexyl*-β-1-*naphthyl*-n-*propyl alcohol*, m.p. 59—61°, which with P_2O_5 at 150° or $KHSO_4$ at 160—180°, followed by $AlCl_3$ in CS_2, gives an oil, converted by Se at 320° in very poor yields into a (?) methylchrysene, m.p. 90—100° [$C_6H_3(NO_2)_3$ *compound*, m.p. 232—235° after sintering], and a (?) spiran [$C_6H_3(NO_2)_3$ *compound*, m.p. 107—109°]. Mg 2-methyl*cyclo*hexyl chloride and (I) lead by similar reactions to an oil, which on dehydration gives small amounts of chrysene and another impure compound. *o*-C_6H_4Cl·MgBr and (I) give a carbinol, dehydrated by $KHSO_4$ to mixed isomeric α-*o*-*chlorophenyl*-β-1-*naphthyl*-Δ^{α}-*propenes*, b.p. 150—180°/1 mm., which with KOH (fusion or in quinoline) gives tars. *o*-C_6H_4Br·MgI and (I) give an impure carbinol. M.p. are corr.

R. S. C.

Hydrobromides of 3 : 5-dibromo-*o*- and -*p*-toluidine and 5 : 6-dibromo-*m*-4-xylidine. A. Wróbel (Rocz. Chem., 1939, **19**, 393—395).—The *hydrobromides*, m.p. 225° (decomp.), 221°, and 228° (decomp.), respectively, are decomposed by H_2O. R. T.

Use of nitrobenzenesulphenyl chloride in identification of amines. J. H. Billman and E. O'Mahony (J. Amer. Chem. Soc., 1939, **61**, 2340—2341).—*o*-NO_2·C_6H_4·SCl and NH_3 or the appropriate amine in Et_2O or Et_2O–H_2O give *o*-nitrobenzenesulphenamide, m.p. 124—125° (decomp.) [350° (decomp.)] (figures in parentheses or brackets are m.p. of the *hydrochlorides*), *o-nitrobenzenesulphen*-p-*anisidide*, m.p. 138—138·5° [220° (decomp.)], -anilide, new m.p. 88·5—89° (198°), -p-*bromoanilide*, m.p. 146—146·5° [? (decomp.)], -p-*chloroanilide*, m.p. 143·5—144° [194° (decomp.)], -n-*butyl*-, m.p. 27—28° (142—142·5°), -cyclo*hexyl*-, m.p. 51·5—52° (206—207°), -*diethyl*-, an oil (215—223°), -*dimethyl*-, m.p. 62·5—63° (171°), -*ethyl*-, m.p. 32·5—33° (108°), -*methyl*-, m.p. 35·5—36° (225—226°), and -n-*propyl*-, an oil (157—158°), β-, new m.p. 202—202·5° (254°), and -α-*naphthyl-amide*, m.p. 130·5—131° after softening at 125° [260° (decomp.)], -N-*methylanilide*, m.p. 86—86·5° (121—122°), -o-, m.p. 115·5—116° (215°), -m-, m.p. 106·5—107° (228°), and -p-*toluidide*, m.p. 136—136·5° (243°), from which the amines are regenerated in nearly 100% yield by HCl–Et_2O. M.p. are corr.

R. S. C.

Effect of temperature on the nitration of *p*-cymene. Synthesis of 6-nitrocarvacrylamine and certain derivatives. G. C. Kyker and R. W. Bost (J. Amer. Chem. Soc., 1939, **61**, 2469—2470).—Nitration of *p*-cymene (best at −10° to −12°) to the 2 : 6-$(NO_2)_2$-derivative and reduction thereof by $(NH_4)_2S$ to 6-nitrocarvacrylamine, m.p. 52° (lit. 52°, 80—82°) (Ac derivative, m.p. 114—115°), is improved.

R. S. C.

New reaction of sulphonamides. *p*-Cresol–tyrosinase reagent. F. Wyss-Chodat and R. Paillard (Arch. Sci. Phys. nat., 1939, [v], **21**, Suppl., 50—53).—Sulphanilamide, *p*-NH_2·C_6H_4·SO_2·NH·C_6H_4·SO_2·NMe_2-*p*, 2-*p*-aminobenzenesulphonamidopyridine, di-*p*-acetamidophenyl sulphone, and *p*-NH_2·C_6H_4·SO_2·CH_2·CO·NH_2 give colours (varying shades of red) with *p*-cresol–tyrosinase, whereas *p*-CH_2Ph·NH·C_6H_4·SO_2·NH_2 and Na_2 *p*-αγ-disulpho-γ-phenylpropylaminobenzenesulphonamide do not. J. L. D.

Schiff base hydrochlorides. Test for arylamines. J. V. Scudi, H. D. Ratish, and J. G. M. Bullowa (J. Amer. Chem. Soc., 1939, **61**, 2554—2555).—A yellow colour, stable for several days but not to alkali, is produced by condensing arylamines of sulphanilamide type with, best, CHPh:CH·CHO in, best, H_2SO_4–abs. EtOH. Halochromic salts of Schiff's bases are produced. *Cinnamylidene-sulphanilamide*, m.p. 213—215° (decomp.) [*hydrochloride*, m.p. 203—205° (decomp.)], and -*sulphapyridine*, m.p. 208—210° (decomp.) [*hydrochloride*, m.p. 178—180° (decomp.)], are described. R. S. C.

Sulphanilamide derivatives. I. R. Adams, P. H. Long, and A. J. Johanson. **II.** R. Adams, P. H. Long, and A. Jeanes (J. Amer. Chem. Soc., 1939, **61**, 2342—2346, 2346—2349).—I. The following are prepared. Figures in parentheses are anti-streptococcal and -meningococcal activity, respectively, relative to *p*-NH_2·C_6H_4·SO_2·NH_2 = 4, but the new compounds are generally less toxic. *p*-Propion-, new m.p. 226·5—227·5° (2, 3), *p*-*n*-butyr-, new m.p. 236—237° (1, 4), *p*-*iso*butyr-, new m.p. 248—249° (0—1, 4), and *p*-*n*-valer-amidobenzenesulphonamide, new m.p. 209—210° (3, —). p-*Acetamidobenzenesulphon*-β-*hydroxyethylamide*, m.p. 150—151° (0, 4), -*di*-(β-*hydroxyethyl*)*amide*, m.p. 158—159° (0, 1), -γ-, m.p. 133·5—135° (0, 1), and -β-*hydroxy*-n-*propylamide*, m.p. 166—167° (1, 0), -β-*hydroxy*isobutylamide, m.p. 185—187° (0—1, 2), -βγ-*dihydroxy*-n-*propylamide*, m.p. 132—133° (0, 0), -N-*methyl*-N-βγδεζ-*pentahydroxy*-n-*hexylamide*, m.p. 87—91° (0, 0—1), -2′-*hydroxy*cyclo*hexylamide*, m.p. 218° (0, 0). p-*Propionamidobenzenesulphon*-β-*hydroxy*-n-*propyl*-, m.p. 148° (0, 3), and -iso*butylamide*, m.p. 172—172·5° (1, 3). p-n-*Butyramidobenzenesulphon*-β-*hydroxyethyl*-, m.p. 139° (0, 1), -*di*-(β-*hydroxyethyl*)-, m.p. 114—115° (0, 1), -β-*hydroxy*-n-*propyl*-, m.p. 127—128° (0, 2), and -β-*hydroxy*isobutyl-*amide*, m.p. 166° (0—1, 4). p-iso*Butyramidobenzenesulphon*-β-*hydroxy-ethyl*-, m.p. 116·5° (2, 1), -n-*propyl*-, m.p. 144° (0—1, 3), and -iso*butyl-amide*, m.p. 173°

(0—1, 4). p-n-*Valeramidobenzenesulphon*-β-*hydroxy*-n-*propyl*-, m.p. 121·5° (0—1, 4), and -iso*butyl*-*amide*, m.p. 136—136·5° (0—1, 3). p-iso*Valeramidobenzenesulphon*-β-*hydroxy*iso*butylamide*, m.p. 146—147° (0, 0). p-*Aminobenzenesulphon*-β-*hydroxyethyl*-, m.p. 95—97° (2, 3), -di-(β-hydroxyethyl), m.p. 109—110° (2, 0—1), -γ-, m.p. 123—124° (0—1, 4), and -β-*hydroxy*-n-*propyl*-, m.p. 115—116° (1, 4), -β-*hydroxy*iso*butyl*-, m.p. 102—103° (0, 4), -βγ-*dihydroxy*-n-*propyl*-, m.p. 102—104° (0, 4), and -2′-*hydroxy*cyclo*hexyl*-*amide*, m.p. 141—142° (0, 0). p-*Methylaminobenzenesulphon*-β-*hydroxy*-n-*propylamide*, m.p. 90—91°. p-*Acetethylamido*-, m.p. 134°, and p-*ethylamino*-*benzenesulphon*-β-*hydroxy*iso*butylamide*, m.p. 131·5° (0, —). p-*Benzylaminobenzenesulphon*-β-*hydroxyethylamide*, m.p. 115—116° (0—1, —). p-*Carbethoxyamidobenzenesulphon*-*amide*, m.p. 241—242° (1, 1), -β-*hydroxy*-*ethylamide*, m.p. 176° (1, 4), and -n-*propylamide*, m.p. 132° (0—1, 2), and -*morpholide*, m.p. 157—158° (0, 2). p-*Acetamido*-, m.p. 165—166° (1, 2), p-*propionamido*-, m.p. 189—190° (1, 1), p-n-, m.p. 191—193° (1, 2), and p-iso*butyramido*-, m.p. 147° (0—1, 0—1), and p-*amino*-*benzenesulphonmorpholide*, m.p. 217° (0—1, 0—1). p-p′-*Acetamido*-, m.p. 127—128° (0, 0), p-p′-*amino*-, m.p. 123—125° (0, 4), and p-p′-*carbethoxyamido*-*benzenesulphonamidobenzenesulphon*-β-*hydroxy*-n-*propylamide*, m.p. 175—177° (0, 4). p-p′-*Acetamido*-, m.p. 213° (0, 0), and p-p′-*amino*-*benzenesulphonamido*-*benzenesulphon*-β-*hydroxy*iso*butylamide*, m.p. 184—185° (0—1, 4). 3-*Acetamido*-4-*methoxybenzenesulphon*-*amide*, m.p. 225·5° (0, 0—1), and -β-*hydroxy*-*ethyl*-, m.p. 152—153° (0, 0), -n-*propyl*-, m.p. 146—147° (0, 0), and -iso*butyl*-*amide*, m.p. 125° (0, 0—1). 3-*Amino*-4-*methoxybenzenesulphon*-*amide*, m.p. 142—142·5° (0, 0), and -β-*hydroxy*-n-*propylamide*, m.p. 102° (0, 0). *p*-Propion-, m.p. 113°, -n-, m.p. 120—121°, and -iso*butyr*-, m.p. 131—132°, -n-, m.p. 115—116°, and -iso*valer*-, m.p. 120—121°, -*acetmethyl*-, m.p. 136—137°, -*acetethyl*-, m.p. 142—143°, and -*carbethoxy*-, m.p. 103°, -*amidobenzenesulphonyl chlorides* are prepared from the appropriate anilide and $ClSO_3H$.

II. Succinanil (modified prep.) and $ClSO_3H$ at 60—65° give a sulphonyl chloride, converted by 28% aq. NH_3 at 70° into N-*phenylsuccinamide*-p-*sulphonamide*, m.p. 234—238° (decomp.), or by the appropriate OH-amine (2 mols.) and 7% KOH (2·5 mols.) at 70° into N-*phenyl*-N′-β-*hydroxyethylsuccinamide*-p-*sulphon*-β-*hydroxyethylamide*, m.p. 137—142° (with less 5-*anilo*-2-*pyrrolidone*-4′-*sulphon*-β-*hydroxyethylamide*, m.p. 85—93°), and p-β-*carboxypropionamidobenzenesulphon*-β-*hydroxy*-n-*propylamide*, m.p. 179—192° (decomp.) (*Et* ester, m.p. 125—128°).

p-OMe·CH_2·CO·NH·C_6H_4·SO_2Cl and NH_2·$[CH_2]_2$·OH give p-*methoxyacetamidobenzenesulphon*-β-*hydroxyethylamide*, m.p. 125—127°. OAc·CHMe·COCl and *p*-NH_2·C_6H_4·SO_2·NH_2 in Et_2O or OAc·CHMe·CO·NHPh and $ClSO_3H$ (followed by aq. NH_3) give p-α-*acetoxy*-, m.p. 192·5°, and thence by 1·5N-NaOH at 50—55° p-α-*hydroxy*-*propionamidobenzenesulphonamide*, m.p. 196°. p-α-*Acetoxypropionamidobenzenesulphon*-β-*hydroxy*-n-*propylamide*, m.p. 97—103°, is similarly obtained. Treating the appropriate dianilide with $ClSO_3H$, followed by the appropriate OH-amine, gives *malon*-, m.p. 203—208° (decomp.), *succin*-, m.p. 243—250° (decomp.), and *glutar*-*anilide*-4 : 4′-*di*(*sulphon*-β-*hydroxyethylamide*), m.p. 196—198°, and *malon*-, m.p. 173—176° (decomp.), *succin*-, m.p. 265—270° (decomp.), and *glutar*-*anilide*-4 : 4′-*di*(*sulphon*-β-*hydroxy*-n-*propylamide*), m.p. 187—190°. 2 : 5-Diketo-1 : 4-diphenylpiperazine similarly yields its 4′ : 4″-*di*(*sulphon*-*amide*, m.p. 325° (decomp.), -β-*hydroxyethylamide*, m.p. 260—270° (decomp.), and -β-*hydroxy*-n-*propylamide*), m.p. 280—284° (decomp.). *p*-CH_2Cl·CO·NH·C_6H_4·SO_2Cl and OH·CHMe·CH_2·NH_2 give p-*chloroacetamidobenzenesulphon*-β-*hydroxy*-n-*propylamide*, m.p. 125—129°, converted by NH_4CNS in boiling EtOH into 2-*anilo*-4-*ketotetrahydrothiazole*-4′-*sulphon*-β-*hydroxy*-n-*propylamide* (I), m.p. 209—212°. *p*-CHMeBr·CO·NH·C_6H_4·SO_2Cl gives similarly *p*-α-bromopropionamidobenzenesulphon-β-hydroxy-*n*-propylamide, m.p. 140—143°, and thence the 5-*Me* derivative, m.p. 190—192°, of (I).

p-CH_2Cl·CO·NH·C_6H_4·SO_2·NH_2 and NH_4CNS yield (?) 3-*phenyl*-ψ-*thiohydantoin*-4′-*sulphonamide* [? 2-*imino*-3-*anilo*-4-*ketotetrahydrothiophen*-4′-*sulphon*-*amide*], m.p. 258° (decomp.; darkens from 238°). These products have little or no antistreptococcal activity. R. S. C.

Free radicals of the type of Wurster's salts. L. Michaelis, M. P. Schubert, and S. Granick (J. Amer. Chem. Soc., 1939, **61**, 1981—1992).—Stability of free radicals obtained by partial oxidation of *p*-diamines with Br in dil. solution [usually MeOH–0·005N-aq. AcOH (4 : 1)] at the optimum p_H (mostly ~3) is best judged by the rate of decomp. (as determined by colour changes and the nature of the electrometric titration curves), and is differentiated from effects due to the instability of the di-imines partly by being unaffected by increasing the concn. of the diamine. By 33 examples it is shown that stability is (*a*) decreased by Me *o*- to NHMe or NMe_2 (2 *o*-Me have enormous effect) or by OMe, Cl, or SO_3H in the ring, (*b*) increased by *N*-Me if there is no Me in the ring, and (*c*) unaffected by Me in the ring if the N are unmethylated (occasionally a slight decrease). Absorption spectra of the radicals are recorded. Results are explained as due to resonance of different forms of the radical. R. S. C.

Reactivity of the aromatic nucleus. I. Karrer's theory of coupling. W. J. Hickinbottom and E. W. Lambert (J.C.S., 1939, 1383—1386).—Karrer's observation (A., 1915, i, 1073) that $NPh(C_5H_{11}\text{-}iso)_2$ (I) or $NPhBu^{\alpha}_2$ in aq. AcOH with diazotised *p*-NH_2·C_6H_4·SO_3H (II) gives NHR·C_6H_4·N_2·C_6H_4·SO_3H (R = Bu^{α} or *iso*-C_5H_{11}), with elimination of R, is not confirmed (cf. Reilly *et al.*, J.C.S., 1918, **113**, 99); the product is NR_2·C_6H_4·N_2·C_6H_4·SO_3H. The product from (I) and (II) (+ KOH) is *K* 4-*diisoamylaminoazobenzene*-4′-*sulphonate*, reduced by $Na_2S_2O_4$ to p-*aminodiisoamylaniline* (*dihydrochloride*; p-*benzamidodiisoamylaniline*, m.p. 101°). With *p*-NO_2·C_6H_4·N_2Cl (III), (I) gives 4′-*nitro*-4-*diisoamylaminoazobenzene*, m.p. 120°. NHPh·C_5H_{11}-*iso* (IV) and (II) give *K* 4′-iso*amyl*-*aminoazobenzene*-4-*sulphonate*, reduced ($Na_2S_2O_4$) to p-*amino*iso*amylaniline* (*dihydrochloride*); (III) and (IV) give 4′-*nitro*-N-iso*amyldiazoaminobenzene*, m.p. 72—73°. $NPhBu^{\beta}_2$ and (II) give *K* 4′-*diiso*butyl-*aminoazobenzene*-4-*sulphonate*, reduced ($Na_2S_2O_4$) to

p-aminodi*iso*butylaniline [*dihydrochloride*, m.p. 223—224° (darkens ~210°); *p-benzamidodiisobutylaniline*, m.p. 111°], also obtained by reducing the *hydrochloride* of p-*nitrosodiisobutylaniline*, m.p. 62—63°. $NPhBu^{\beta}_2$ and (III) give 4′-*nitro*-4-*diisobutylaminoazobenzene*, m.p. 122—123°; 4′-*nitro*-4-*methyl*-tert.-*butylaminoazobenzene*, m.p. 133—134°, 4′-*nitro*-N-tert.-*butyldiazoaminobenzene*, m.p. 142—143°, 4′-*nitro*-4-*di*-n-*octylaminoazobenzene*, m.p. 66—67°, 4′-*nitro*-N-n-*octylaminodiazoaminobenzene*, m.p. 61—62°, 4′-*nitro*-4-*dicetylaminoazobenzene*, m.p. 70—71°, and 4-*nitro*-N-*cetyldiazoaminobenzene*, m.p. 77°, are similarly prepared. *N*-Dialkylarylamines are purified through their picrates, which are less sol. than those of the corresponding *sec.* amines. The following are prepared: (I), b.p. 166—168°/18 mm. (*picrate*, m.p. 146°); $NPhBu^{\beta}_2$, b.p. 142—144°/21 mm. (*picrate*, m.p. 141°); 1 : 4 : 2- and 1 : 3 : 2-$C_6H_3Me_2$·NMe_2, b.p. 82—82·5°/18 mm. (*picrate*, m.p. 154—155°); *o*-C_6H_4Cl·NMe_2, b.p. 101—103°/28 mm. (*picrate*, m.p. 133—134°). *Dicetylaniline*, m.p. 30°, is obtained from $C_{16}H_{33}$·NHPh and $C_{16}H_{33}I$ at 110°. E. W. W.

Effect of vitamin-*C* on enzymic oxidation of a monophenol. F. Wyss-Chodat and F. Chodat (Arch. Sci. Phys. nat., 1939, [v], **21**, Suppl., 53—58).—Tyrosinase and aq. *p*-cresol give first a yellow and then a brown solution, but not in presence of ascorbic acid (I), although the O_2 uptake is much increased with (I). (I) is without effect on the brown solution and inhibits the reaction between tyrosinase, *p*-cresol, and glycine. The extent of the O_2 uptake depends on the amount of (I) present and the rapidity of uptake on the amount of *p*-cresol. J. L. D.

Condensation products of phenols and ketones. IV. *o*-Cresol and acetone. W. Baker and D. M. Besly (J.C.S., 1939, 1421—1424).—The condensation product from *o*-cresol (I) and $COMe_2$ regarded by Niederl *et al.* (A., 1929, 551; cf. also A., 1932, 842) as $CO(CH_2·CMe_2·C_6H_3Me·OH)_2$ is identical with that regarded by Süközd (Acta Lit. Sci. Univ. Hung. Franc.-Joseph., 1932, **2**, 230) as OH·$C_6HMe(CMe_2)_3C_6HMe$·OH, and is 6 : 6′-*dihydroxy*-3 : 3 : 5 : 3′ : 3′ : 5′-*hexamethylbis*-1 : 1′-spiro*hydrindene*, m.p. 245—246°. It is prepared (cf. Sökösd, *loc. cit.*) from (I), $COMe_2$, and conc. HCl at 100° (bath) for 60 hr. (purifying through the *diacetate*, m.p. 266—267°) and also from (4 : 3 : 1-OH·$C_6H_3Me)_2CMe_2$ and AcOH–conc. HCl. It gives a *dibenzoate*, m.p., α-form, 170—171°, solidifying to β-form, m.p. 201°, *di*-p-*nitrobenzoate*, m.p. 247—248°, *Me*$_2$ *ether*, dimorphous, m.p. 158—159°, and 7 : 7′-Br_2-derivative, m.p. 224°, is oxidised ($KMnO_4$–AcOH) to give some phoronic anhydride, and nitrated (hot conc. HNO_3–AcOH) to NO_2-compounds, m.p. 233—234° (decomp.), and ~225°, which are probably degradation products. E. W. W.

Reaction of *p*-fluorophenol with benzene and aluminium chloride. A. W. Weston and C. M. Suter (J. Amer. Chem. Soc., 1939, **61**, 2556—2557).—The by-product formed during de-ethylation of *p*-C_6H_4F·OEt by $AlCl_3$ in C_6H_6 (A., 1939, II, 109) is *p*-C_6H_4Ph·OH and is obtained also from *p*-C_6H_4F·OH, C_6H_6, and $AlCl_3$. *p*-C_6H_4Cl·OH does not react with C_6H_6–$AlCl_3$, nor does *p*-C_6H_4F·OH with PhMe or PhCl. R. S. C.

Synthesis of 2-*n*-butyl-α-naphthol. Y. F. Chi (J. Amer. Chem. Soc., 1939, **61**, 2487—2488).—α-$C_{10}H_7$·OH, Pr^nCO_2H, and $ZnCl_2$ give 2-n-*butyryl*-α-*naphthol*, m.p. 85—86°, b.p. 145—152°/1 mm. (*oxime*, m.p. 119°; *semicarbazone*, m.p. 201—202°; *Me*, m.p. 80—81°, b.p. 155—157°/1 mm., and *Et ether*, m.p 79—81°, b.p. 158—159°/1 mm.) (with some α-$C_{10}H_7$ n-*butyrate*, m.p. 95·5—96·5°, b.p. 125—130°/1 mm.), reduced by Zn–Hg–HCl to 2-n-*butyl*-α-*naphthol*, m.p. 73—74°, b.p. 140—149°/1 mm. R. S. C.

Structure of fluorene. W. C. Lothrop (J. Amer. Chem. Soc., 1939, **61**, 2115—2119).—Pyrolysis of allyloxyfluorene derivatives indicates that little or no fixation of the ethylenic linkings occurs, other reactions notwithstanding. Fluorene is considered to be benzenoid rather than naphthoid. 2-Hydroxyfluorene, CH_2:CH·CH_2Br, and anhyd. K_2CO_3 in boiling $COMe_2$ give 2-*allyloxyfluorene* (99%), m.p. 95—96°, which at 235—238° gives a mixture, separable with difficulty into 2-*hydroxy*-3- (~60%), m.p. 87—88°, and -1-*allylfluorene* (~25%), m.p. 111—112°. These products give *allyl ethers*, m.p. 44—45° and 82—83°, respectively, pyrolysis of which yields in both cases 2-*hydroxy*-1 : 3-*diallylfluorene*, m.p. 58°, b.p. 170°/3 mm. Crude 3-methoxyfluoren-9-one, red P, and HI in boiling AcOH give 3-*hydroxyfluorene*, m.p. 136—137° (*benzoate*, m.p. 128°), the allyl ether of which gives a gum when pyrolised. *o*-COCl·C_6H_4·NH·SO_2·C_6H_4Me-*p*, 1 : 4 : 2-$C_6H_3Me_2$·OMe, and $AlCl_3$ in CS_2 give 2′-p-*toluenesulphonamido*-4-*methoxy*-2 : 5-*dimethylbenzophenone*, m.p. 140—141° (N-*Me* derivative, m.p. 168—169°, prepared by Me_2SO_4–alkali), slowly hydrolysed by conc. H_2SO_4 at room temp. to the NH_2-*ketone*, m.p. 102—104°. Diazotisation etc. then gives (84% yield under stated conditions) 3-*methoxy*-1 : 4-*dimethylfluorenone* (I), m.p. 140—141°, and a little 2′-*hydroxy*-4-*methoxy*-2 : 5-*dimethylbenzophenone*, m.p. 94—95° (*acetate*, m.p. 81—82). HI–red P–AcOH converts (I) into 3-*hydroxy*-1 : 4-*dimethylfluorene* (II), m.p. 180—181° (*acetate*, m.p. 100°; 2-*benzeneazo*-derivative, m.p. 183—184°), or (shorter heating) 3-*hydroxy*-1 : 4-*dimethylfluorenone*, m.p. 223—224° (*acetate*, m.p. 133—134°), obtained also by 48% HBr. The *allyl ether*, m.p. 54—55°, of (II) when heated at 215° in N_2 gives 3-*hydroxy*-1 : 4-*dimethyl*-2-*allylfluorene*, m.p. 150—151°. Improved prep. from *m*-cresol (118 g.) gives 1 : 2 : 3-$C_6H_3Me_2$·OMe (26·3 g.) (by way of 2 : 1 : 3-NH_2·C_6H_3Me·OMe and 1 : 2 : 3-C_6H_3MeBr·OMe), which by methods given above affords 2′-p-*toluenesulphonamido*-, m.p. 136—138°, 2′-p-*toluenesulphonmethylamido*-, m.p. 160°, 2′-*amino*-, m.p. 144—145°, and 2′-*hydroxy*-4-*methoxy*-2 : 3-*dimethylbenzophenone*, m.p. 135—136° (*acetate*, m.p. 97—98°), 3-*methoxy*-, m.p. 178—179°, and 3-*hydroxy*-1 : 2-*dimethylfluorenone*, m.p. 258—259° (decomp.) (*acetate*, m.p. 137—138°), 3-*hydroxy*-1 : 2-*dimethylfluorene*, m.p. 212—213° (decomp.) [*acetate*, m.p. 146—147°; *benzeneazo*-derivative, m.p. 201° (decomp.); *allyl ether*, m.p. 102—103°], and 3-*hydroxy*-1 : 2-*dimethyl*-4-*allylfluorene*, m.p. 135—136°. R. S. C.

Isomeric γδ-di-*p*-hydroxyphenyl-Δ$^{\beta}$-*n*-hexenes. F. VON WESSELY and A. KLEEDORFER (Naturwiss., 1939, **27**, 567—568; cf. A., 1939, II, 259, 312).—Dehydration of γδ-di-*p*-anisyl-*n*-hexan-γ-ol gives *trans*-(I) and impure *cis*-(*p*-OMe·C_6H_4·CEt:)$_2$ and isomeric *γδ-di*-p-*anisyl*-Δ$^{\beta}$-n-*hexenes*, m.p. 50° (II) and an oil (III). From (II) and (III) are obtained *γδ-di*-p-*hydroxyphenyl*-Δ$^{\beta}$-n-*hexenes*, m.p. 153° (IV) (*diacetate*, an oil; *dibenzoate*, m.p. 126°), and m.p. 143·5° (V) (*diacetate*, m.p. 74°; *dibenzoate*, m.p. 184°), respectively. (II) and (III) are converted by O_3 into ethyldeoxyanisoin, by I into (I), and by H_2–Pd into (*p*-OMe·C_6H_4·CHEt·)$_2$, m.p. 146°. Œstrogenic activity is (*p*-OH·C_6H_4·CHEt·)$_2$, m.p. 186° > (IV) > (*p*-OH·C_6H_4·CHEt·)$_2$, m.p. 130° (prep. by hydrogenation of diethylstilbœstrol) > (V). R. S. C.

Stereochemistry of diphenyls. XLVII. 2 : 5-Di-*m*-4′-xylylquinols and their derivatives. R. ADAMS and G. C. FINGER (J. Amer. Chem. Soc., 1939, **61**, 2182—2183; cf. A., 1939, II, 505).—Prep. of 2 : 5-di-*m*-4′-xylylquinol and its 3 : 6-Br_2-derivatives is modified and the yields are recalc. (cf. Browning *et al.*, A., 1930, 1588). Addition of 3 : 6-dibromo-2 : 5-di-*m*-4′-xylylbenzoquinone in EtOH to aq. NaOH at ≯ room temp. gives 3 : 6-*dihydroxy*-2 : 5-*di*-m-4′-*xylylbenzoquinone* (I), m.p. 282—284°, the *diacetate* (prepared by hot Ac_2O–C_5H_5N), m.p. 186—188°, of which is hydrolysed by HCl–AcOH to (I) and reduced by $SnCl_2$–EtOH to 3 : 6-*diacetoxy*-2 : 5-*di*-m-4′-*xylylquinol*, m.p. 213—215°. Acetylation, best by hot Ac_2O–C_5H_5N and a trace of $SnCl_2$, then yields 1 : 2 : 4 : 5-*tetra-acetoxy*-3 : 6-*di*-m-4′-*xylylbenzene*, m.p. 276—278°. In no case were diastereoisomeric forms obtained. R. S. C.

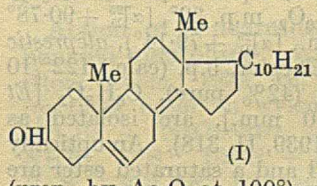
Synthesis of 6 : 7-dihydroxy-1 : 4-dimethylphenanthrene from *p*-xylylacetic acid and 6-nitroveratraldehyde by the Pschorr reaction. J. T. CASSADAY and M. T. BOGERT (J. Amer. Chem. Soc., 1939, **61**, 2461—2463).—6 : 3 : 4 : 1-NO_2·C_6H_2(OMe)$_2$·CHO (improved prep.), m.p. 132—133° (lit. 133·5—134·5°), and 1 : 4 : 2-$C_6H_3Me_2$·CH_2·CO_2H in Ac_2O at 105—110° give 6-*nitro*-3 : 4-*dimethoxy*-α-p-2′-*xylylcinnamic acid*, m.p. 226—227°, reduced by $FeSO_4$–aq. NH_3 to the 6-NH_2-*acid*, m.p. 191—192°, which with *iso*-C_5H_{11}·O·NO and H_2SO_4 in dioxan, followed by NaH_2PO_2 and Cu powder, gives 6 : 7-*dimethoxy*-1 : 4-*dimethylphenanthrene*-10-*carboxylic acid* (I), m.p. 215·5—216·5°. Boiling with basic Cu carbonate in quinaldine then gives 6 : 7-*dimethoxy*-, m.p. 175—176°, and thence (48% HBr) 6 : 7-*dihydroxy*-1 : 4-*dimethylphenanthrene* (35%), m.p. 164—164·5° (*diacetate*, m.p. 133—133·5°) [also obtained less well (10—15%) from (I) by HBr–AcOH], sol. in cold olive oil and appreciably sol. in H_2O. M.p. are corr. R. S. C.

Synthesis of vitamin-*A* methyl ether. F. B. KIPPING and F. WILD (Chem. and Ind., 1939, 802).—COMe·$[CH_2]_2$·OMe is converted by CH_2:CH·CH_2·MgCl into the carbinol, dehydrated to ζ-*methoxy*-δ-*methyl*-Δ$^{\alpha\gamma}$-*hexadiene*, which with Br followed by KOH affords α-*bromo*-ζ-*methoxy*-δ-*methyl*-Δ$^{\beta\delta}$-*hexadiene*. The Li derivative therefrom with β-ionone gives a *tert.*-alcohol dehydrated to *vitamin*-A *Me ether*. No details are given. R. S. C.

Organic peroxides. VI. Cyclane peroxides. N. A. MILAS, S. A. HARRIS, and P. C. PANAGIOTAKOS (J. Amer. Chem. Soc., 1939, **61**, 2430—2432; cf. A., 1938, II, 469).—*cyclo*Pentanone (I) and 0·6M-H_2O_2–Et_2O give 1-*hydroxy*cyclo*pentyl H peroxide* (II) or *di*-(1-*hydroxy*cyclo*pentyl*) *peroxide* (III), oils. When kept, (II) gives its *solvate*, +0·5H_2O_2, m.p. 73—75° (gas at 105°), also obtained from (I) by 30% H_2O_2 and converted in hot Et_2O or 1 : 1 Et_2O–light petroleum into *dicyclopentylidene peroxide*, $\left([CH_2]_4C<\begin{matrix}O\cdot\\O\cdot\end{matrix}\right)_2$, m.p. 160° (decomp.). When kept, (III) gives an insol. *polymeride*, $\left([CH_2]_4>C<\begin{matrix}O\cdot\\O\cdot\end{matrix}\right)_x$, m.p. 166° (decomp.). Similarly are prepared 1-*hydroxy*-cyclo*hexyl*, m.p. 76—78°, -3- (also +0·5H_2O_2, m.p. 120—121°), -2-, and -4-*methyl*cyclo*hexyl H peroxide*, oils, *di*-(1-*hydroxy*cyclo*hexyl*), m.p. 68—70° *di*-(1-*hydroxy*-3-, -2-, and -4-*methyl*cyclo*hexyl*), and *di*-(1-*hydroxy*cyclo*octyl*) *peroxide*, oils, and 1-*hydroxy*-cyclo-*heptyl*, m.p. 92—94°, and *-octyl H peroxide*, an oil. R. S. C.

αβ-Diarylacetylene glycols. II. An enediol from hexaethylbenzil. R. C. FUSON, J. CORSE, and C. H. MCKEEVER (J. Amer. Chem. Soc., 1939, **61**, 2010—2012; cf. A., 1939, II, 260).—2 : 4 : 6-$C_6H_2Et_3$·COCl (prep. in 85% yield from the acid by $SOCl_2$ or less well by PCl_5), b.p. 108—110°/2 mm., with Mg + MgI_2 in Et_2O–C_6H_6–N_2 gives αβ-*dihydroxy*-αβ-*di*-2 : 4 : 6-*triethylphenylethylene* (I), m.p. 149—151° (decomp.; in air), 154—155·5° (in N_2), (2 : 4 : 6-$C_6H_2Et_3$·CO)$_2$ (II), and some 2 : 4 : 6-$C_6H_2Et_3$·CO_2H. (I) is stable in air, insol. in 40% aq. NaOH, reduces Tollens' reagent, $FeCl_3$, and Cu(OAc)$_2$ at 0°, gives a positive 2 : 6-dichlorobenzeneone-indophenol test, and is oxidised to (II). Catalytic hydrogenation of (II) in Ac_2O yields a cis-*diacetate*, m.p. 133·5—134°, of (I); a trans-*diacetate*, m.p. 188—190°, is obtained from (I) by boiling Ac_2O. BzCl–C_5H_5N converts (I) into *dibenzoates*, m.p. 235—236° and 124—124·5°. Hot HCl–MeOH converts (I) into 2 : 4 : 6 : 2′ : 4′ : 6′-*hexaethylbenzoin*, m.p. 64—65·5°, but the compounds are not interconvertible. The non-acidity of (I) indicates that C:C·OH is acidic only if a neighbouring group is negative (*e.g.*, CO); absorption max. at 2·78 and 2·83 μ. are characteristic of acidic OH. R. S. C.

Sitosterol complex. Structure of α$_1$-sitosterol. S. BERNSTEIN and E. S. WALLIS (J. Amer. Chem. Soc., 1939, **61**, 2308—2313).—α$_1$-Sitosterol is probably (I), in which the OH is *cis* to the Me on $C_{(10)}$. The absorption spectrum and failure of α$_1$-sitosteryl acetate (II) (prep. by Ac_2O at 100°), m.p. 137—138°, to react with maleic anhydride indicate non-conjugation of the ethylenic linkings. H_2–PtO_2 in AcOH at room temp. or 60° reduces (II) (by 5 : 6-addition) to α$_1$-*dihydrositosteryl acetate* (III), m.p. 108·5—110·5°, $[\alpha]_D^{25}$ +35·1° in $CHCl_3$ (hydrolysed by 5% KOH–EtOH to α$_1$-*dihydrositosterol*, m.p. 152—154°, $[\alpha]_D^{20}$ +10·9° in $CHCl_3$), but in presence of a little conc. HCl at



(I)

65—70° gives α_1-*sitostanyl acetate* (IV), m.p. 147—148°, $[\alpha]_D^{19}$ +39·4° in $CHCl_3$, hydrolysed to α_1-*sitostanol*, m.p. 185—186°, $[\alpha]_D^{25}$ + 27·0° in $CHCl_3$. Dry HCl–$CHCl_3$ at 0° converts (III) (by migration of the double linking from 8 : 14 to 14 : 15) into α_1-iso*dihydrositosteryl acetate* (V), m.p. 137·5—138·5°, $[\alpha]_D^{20}$ +42·0° in $CHCl_3$, hydrolysed to α_1-iso*dihydrositosterol*, m.p. 152—154°, $[\alpha]_D^{20}$ +31·0° in $CHCl_3$, and hydrogenated in AcOH to (IV). With BzO_2H in $CHCl_3$, (V) gives the 14 : 15-*oxide*, m.p. 152—154°, converted by a little H_2SO_4 in AcOH at 100° into $\Delta^{8:9,14:15}$-*sitostadienyl acetate*, m.p. 121·5—122°.

R. S. C.

α_3-Sitosterol, $C_{29}H_{48}O$, m.p. 142°, $[\alpha]_D^{25}$ +1·65° in $CHCl_3$, and its benzoate, m.p. 167·5—168°, $[\alpha]_D^{28}$ +14·85° in $CHCl_3$, and *m*-dinitrobenzoate, m.p. 202·5—203°, $[\alpha]_D^{27}$ +15·35° in $CHCl_3$.—See A., 1939, III, 950.

Sugar-cane wax. IV. Diol derivatives of sugar-cane sitosterol and stigmasterol. V. Oxidation of sugar-cane sitostanyl acetate. T. Mitui (J. Agric. Chem. Soc. Japan, 1939, **15**, 795—804, 805—808).—IV. Sugar-cane sitosterol (I) is probably identical with 22-dihydrostigmasterol and contains the side-chain ·CHMe·CH_2·CH_2·CHEtPr^β (cf. A., 1938, II, 232). The syntheses of *sitostane*-3 : 6-, m.p. 215°, and -3 : 7-*diol*, m.p. 176°, and *stigmastane*-3 : 6-, m.p. 213°, and -3 : 7-*diol*, m.p. 174°, from (I) and stigmasterol are described; α-saccharostanediol (A., 1939, II, 421) differs from these and the 3 : 4-diols.

V. Oxidation of sugar-cane sitostanyl acetate with CrO_3 gives *trans*-androsterone, 3-hydroxynor*allo*cholanic acid, and 3-hydroxyætio*allo*bilianic acid [Me_2 ester, m.p. 78° (sinters at 74°)]. J. N. A.

Constitution of cholesterol. XVI. Oxidation by peracetic acid. F. Pirrone and R. Vannucchi (Gazzetta, 1939, **69**, 470—478).—A dil. solution of cholesterol in aq. H_2O_2–AcOH gives (*a*) in sunlight, the diacetate of cholestane-3 : 5 : 6-triol (I) (cf. Dunn *et al.*, A., 1934, 1347); (*b*) at the b.p., (I) and a *substance*, $C_{24}H_{40}O_4$ (II), m.p. 115—116° (turbid, clear at 121—122°); (*c*) at 100° (bath), traces of (II) and of a substance, m.p. 63—65°. E. W. W.

Alepric, aleprylic, aleprestic, and aleprolic acids, new homologues of chaulmoogric acid. H. I. Cole and H. T. Cardoso (J. Amer. Chem. Soc., 1939, **61**, 2349—2351).—Alepric, $C_{14}H_{24}O_2$, m.p. 48°, $[\alpha]_D^{25}$ +77·12° (*Et* ester, b.p. 174°/10 mm., $[\alpha]_D^{25}$ +66·54°), aleprylic, $C_{12}H_{20}O_2$, m.p. 32°, $[\alpha]_D^{25}$ +90·78° (*Et* ester, b.p. 148°/10 mm., $[\alpha]_D^{25}$ +79·14°), *aleprestic* (70·5% pure), $C_{10}H_{16}O_2$ [*Et* ester, b.p. (calc.) 122°/10 mm.], and *aleprolic acid* (42% pure), $C_6H_8O_2$ [*Et* ester, b.p. (calc.) 70°/10 mm.], are isolated as previously described (A., 1939, II, 318). An optically inactive, monounsaturated and a saturated ester are probably also present in *Hydnocarpus wightiana* oil.

R. S. C.

Arylation of oils and fats. II. Crystalline derivatives of phenylstearic acid. Syntheses of the *S*-benzylthiuronium salt, *p*-substituted phenacyl esters, and *p*-xenylamide of phenylstearic acid. W. Kimura and H. Taniguchi (J. Soc. Chem. Ind. Japan, 1939, **42**, 234—235B).—ι-Phenylstearic acid (I) is converted into the S-*benzylthiuronium* salt (II), m.p. 134—135°, p-*xenylamide* (III), m.p. 91—92°, p-*iodophenacyl*, m.p. 34—35°, and p-*phenylphenacyl* (crude), m.p. ~35—40°, ester; 2-ι-*phenylheptadecylbenziminazole* is an oil. (II) and particularly (III) are suitable for the identification of (I). H. W.

Relation between chemical constitution and local anæsthetic activity. III. Substituted cinnamic esters of dialkylamino-alcohols. IV. Local anæsthetics containing an ephedrine-like nucleus. W. A. Lott and W. G. Christiansen (J. Amer. Pharm. Assoc., 1939, **28**, 499—502, 502—506).—III. α- and β-Alkylcinnamic acids (prepared by Claisen condensation and Reformatsky synthesis, respectively) are converted through the chlorides or Na salts into the following ester hydrochlorides: β-*diethylaminoethyl* α-*methyl*-, m.p. 133—134·5°, α-*ethyl*-, m.p. 145°, α-n-*propyl*-, m.p. 125—126°, α-iso*propyl*-, m.p. 152—153°, α-n-*butyl*-, m.p. 105·5—106·5°, α-n-*amyl*-, m.p. 83—85°, and γ-*diethylaminopropyl* α-*ethyl-cinnamate hydrochloride*, m.p. 143·8—144·4°; β-*diethylaminoethyl* o-*chloro*-, m.p. 127·5—128°, and p-*dimethylamino*-α-*ethylcinnamate hydrochloride*, m.p. 170—171°; γ-*diethylaminopropyl* p-, m.p. 191—192°, and o-*amino*-α-*ethylcinnamate dihydrochloride*, m.p. 170—170·5°; β-*diethylaminoethyl* β-*methyl*-, m.p. 141—142°, and β-*propyl-cinnamate hydrochloride*. CHPh:CAlk·COCl and NH_2·$[CH_2]_2$·NMe_2 in an inert solvent give N-(β-*diethylaminoethyl*)-α-*methyl*-, m.p. 111—112·5°, -α-*ethyl*-, m.p. 163—164°, -α-n-*propyl*-, m.p. 134·2—134·9°, -α-n-*butyl*-, m.p. 124·5°, and -α-*amyl-cinnamamide hydrochloride*, m.p. 92—95°. All the compounds possess pronounced local anæsthetic activity.

IV. The following substances were prepared (cf. Cherbuliez *et al.*, A., 1931, 350); all possessed local anæsthetic, but no significant vasopressor, activity: β-*diethylamino*-γ-*hydroxy*-γ-*phenylpropyl benzoate*, m.p. 181—181·5°, α-*ethylcinnamate*, m.p. 149—150°, *phenylcarbamate*, m.p. 203—204°, and p-*ethoxybenzoate*, m.p. 177—178°, *hydrochloride*; β-*diethylamino*-γ-*methoxy*-γ-*phenylpropyl phenylcarbamate hydrochloride*, m.p. 198—199·5°; β-*dimethylamino*-γ-*hydroxy*-γ-*phenylpropyl benzoate hydrochloride*, m.p. 215—216°. F. O. H.

Synthesis of *dl*-β-*cyclo*hexylalanine. D. Shemin and R. M. Herbst (J. Amer. Chem. Soc., 1939, **61**, 2471—2472).—In presence of freshly prepared PtO_2, H_2 reduces CHPh:C(NHAc)·CO_2H in AcOH to N-*acetyl*-β-dl-cyclo*hexylalanine*, m.p. 178°, hydrolysed by HCl to dl-β-cyclo*hexylalanine*, cryst. (*Bz* derivative, m.p. 182—182·5°), which with PhNCO yields α-*phenylcarbamido*-β-cyclo*hexylpropionic acid*, m.p. 177·5° (decomp.), and thence (HCl–EtOH) 3-*phenyl*-5-cyclo*hexylmethylhydantoin*, m.p. 172·5°. M.p. are corr. R. S. C.

α-Naphthacetylamino-acids.—See B., 1939, 1025.

Analogue of thyroxine. M. Bovarnick, K. Bloch, and G. L. Foster (J. Amer. Chem. Soc., 1939, **61**, 2472—2474).—3 : 5-Di-iodo-4-*p*-anisyloxybenzenediazonium chloride in AcOH–H_2O–H_2SO_4 at 100—110° gives 3 : 5-*di-iodo*-4-*hydroxyphenyl* p-*anisyl ether*, m.p. 160—163°, converted by 3 : 4 : 5 : 1-

$C_6H_2I_3{\cdot}NO_2$ and anhyd. K_2CO_3 in boiling COMeEt into 2 : 6 : 3′ : 5′-*tetraiodo*-4-*nitro*-4′-p-*anisyloxydiphenyl ether*, m.p. 190—192°, reduced by $SnCl_2$–HCl–AcOH to the 4-NH_2-*ether*, m.p. 185—187° (hydrochloride, unstable). The diazonium compound (prep. by OEt·NO in AcOH) therefrom with $KCu(CN)_2$ gives 2 : 6 : 3′ : 5′-*tetraiodo*-4-*cyano*-4′-p-*anisyloxydiphenyl ether*, m.p. 225—226°, converted by HCl–$SnCl_2$–Et_2O–$CHCl_3$ into the 4-*aldehyde*, m.p. 196—198°. With $NHAc{\cdot}CH_2{\cdot}CO_2H$ and NaOAc in boiling Ac_2O this gives *α-acetamido*-β-3 : 5 : 3′ : 5′-*tetraiodo*-4′-p″-*anisyloxy*-p-*phenoxyphenylacrylic azlactone*, m.p. 264—265°, which is reduced by red P–HI–Ac_2O to β-3 : 5 : 3′ : 5′-*tetraiodo*-4′-p″-*hydroxyphenoxy*-p-*phenoxyphenylalanine* [*thyroxine* p-*hydroxyphenyl ether*] (I), m.p. 267—268° (decomp.), converted by I in NH_3–MeOH–H_2O into the 3 : 5 : 3′ : 5′ : 3″ : 5″-I_6-compound (II), decomp. from 210°. (I) and (II) are physiologically inactive. R. S. C.

Mohler's test for benzoic acid. E. T. Illing (Analyst, 1939, **64**, 586; cf. A., 1932, 632).—The rapid fading of the colour due to $C_6H_3(NH_2)_2{\cdot}CO_2H$ is prevented by diluting with a solution obtained by successive treatment of aq. H_2SO_4–KNO_3 with aq. NH_3 and aq. NH_2OH,HCl. E. C. S.

Preparation of 5-fluoroacetylsalicylic acid. C. M. Suter and A. W. Weston (J. Amer. Chem. Soc., 1939, **61**, 2317—2318).—2 : 5 : 1-OEt·$C_6H_3F{\cdot}MgBr$ (prep. with aid of EtBr) and CO_2 in Et_2O give 5-*fluoro*-2-*ethoxybenzoic acid*, m.p. 65·5—66·5°, hydrolysed by HI (*d* 1·7) to 5-*fluorosalicylic acid*, m.p. 178·5—179·5°. The F increases the toxicity to mice of this and its O-*Ac* derivative, m.p. 130—131°. R. S. C.

Stereochemistry of diphenyls. XLVI. 2-Substituted diphenyls. R. Adams and T. L. Cairns (J. Amer. Chem. Soc., 1939, **61**, 2179—2181; cf. A., 1938, II, 337).—*o*-$C_6H_4Br{\cdot}NO_2$, *m*-$C_6H_4I{\cdot}CO_2Et$, and activated Cu-bronze, first at 215° and then at 235—250°, give an ester, hydrolysed to 2-*nitrodiphenyl*-3′-*carboxylic acid*, m.p. 207—208°, the *Et* ester (prepared by $SOCl_2$ and then EtOH), m.p. 63—65°, b.p. 215°/11 mm., of which in 95% EtOH is boiled with Raney Ni and then reduced by H_2–PtO_2 at 3—3·5 atm., yielding *Et* 2-*aminodiphenyl*-3′-*carboxylate* (I), m.p. 75—76°. A diazo-reaction then affords 2-*iododiphenyl*-3′-*carboxylic acid*, m.p. 168—170°, which gives a homogeneous *quinine* salt, m.p. 184—187°, $[\alpha]_D^{16\cdot2}$ —106° in MeOH. The *Ac* derivative, m.p. 111—111·5°, of (I) with Na and Me_2SO_4 in C_6H_6 gives homogeneous 2-*acetmethylamido*- (II), m.p. 228—239°, and a little 2-*acetamido-diphenyl*-3′-*carboxylic acid*, m.p. 183—188°. Resolution of (II) failed; *quinine* salts, m.p. 173—182°, $[\alpha]_D^{27}$ —129°, and m.p. 172·5—173·5°, $[\alpha]_D^{28}$—140° in $CHCl_3$, were obtained, but did not mutarotate and gave the same inactive acid. M.p. are corr. R. S. C.

2 : 3-Hydroxynaphthoic acid.—See B., 1939, 1021.

Relation between resonance-stabilised chelate rings and acidity. R. T. Arnold and J. Sprung (J. Amer. Chem. Soc., 1939, **61**, 2475—2476; cf. A., 1938, II, 280).—Among cyano-, aldehydo-, and nitro-naphthols and some analogous C_6H_6 derivatives, "fixation" of the ethylenic linkings leads to increasing stability of the chelate rings and thus decreasing acidity. 2 : 1-CN·$C_{10}H_6{\cdot}SO_3Na$ and KOH in glycerol at 140° give 2-*cyano*-α-*naphthol*, m.p. 178—179° (*acetate*, m.p. 87°). 4 : 1-OAc·$C_{10}H_6{\cdot}CHO$ (prep. from the OH-aldehyde by NaOAc–Ac_2O–AcOH), m.p. 103—105°, NH_2OH,HCl, NaOAc, and $NaHCO_3$ in boiling, aq. MeOH give 4-*hydroxy*-1-*naphthaldoxime*, decomp. 150°, the N-*Ac* derivative, decomp. 155°, of which with C_5H_5N in hot EtOH gives 4-*cyano*-α-*naphthol*, m.p. 176—176·5°, also obtained from 4 : 1-CN·$C_{10}H_6{\cdot}N_2{\cdot}BF_4$. R. S. C.

Hydrolysis of arylamides used as dye intermediates. I. V. Hopper, J. H. MacGregor, and F. J. Wilson (J. Soc. Dyers and Col., 1939, **55**, 449—453).—Derivatives of the Naphtol AS series are hydrolysed by boiling KOH–EtOH, $(CH_2{\cdot}NH_2)_2$, or mono-, di-, or tri-ethanolamine, to give the parent arylamine and acid (except where the acid component is $CH_2Ac{\cdot}CO_2H$, $CH_2Bz{\cdot}CO_2H$, or terephthaloyldiacetic acid, when it is destroyed). Naphtol AS-LC is the 4-chloro-2 : 5-dimethoxyanilide of 2 : 3-OH·$C_{10}H_6{\cdot}CO_2H$ (I), and Naphtol AS-L4G, m.p. 200°, is 1-*acetoacetamido*-5-*ethoxybenzthiazole*. Constitutions are confirmed by synthesis from the appropriate acid, arylamine, and PCl_3 in PhMe or xylene, or in C_5H_5N at 115°. The following are also synthesised: the 2 : 4-*dimethoxyanilide*, m.p. 155°, 2-*chloro*-4-*anisidide*, m.p. 228°, 5-*chloro*-, m.p. 211°, and 5-*bromo*-2-*anisidide*, m.p. 216—217°, and 2-*methoxy*-5-*diethylaminosulphonylanilide*, m.p. 209—210° (3-*amino*-4-*methoxybenzenesulphondiethylamide* has m.p. 105°), of (I); the anilide, m.p. 183°, o-*toluidide*, m.p. 164°, α-, m.p. 190—191°, and β-naphthylamide, new m.p. 202°, 2 : 5-dimethoxyanilide, m.p. 147—148°, 2-*chloro*-4-*anisidide*, m.p. 182°, 4-*chloro*-2 : 5-*dimethoxyanilide*, m.p. 192°, and 2-*methoxy*-5-*diethylaminosulphonylanilide*, m.p. 183—184°, of 5 : 6 : 7 : 8-tetrahydro-2-hydroxy-3-naphthoic acid (the Ac derivative of the parent acid has new m.p. 147°); the 4-*methoxy*-2-*methylanilide*, m.p. 243—244°, 2 : 5-*dimethoxyanilide*, m.p. 285°, 4-*chloro*-2 : 5-, m.p. 237°, and 5-*chloro*-2 : 4-*dimethoxyanilide*, m.p. 272°, and 2-*methoxy*-5-*diethylaminosulphonylanilide*, m.p. 245°, of 2-hydroxyanthracene-3-carboxylic acid; 1-benzoylacetamido-5-ethoxybenzthiazole, new m.p. 208°; and the *bis*-4-*chloro*-2 : 5-*dimethoxyanilide*, m.p. 255—256°, of terephthaloyldiacetic acid. A. T. P.

Action of benzamide and acetamide on dibenzoyl disulphide. L. Szperl and L. Rakowski (Rocz. Chem., 1939, **19**, 409—412).—The following reactions occur in xylene at the b.p.: Bz_2S_2 + NH_2Bz → NHBz·SBz + BzSH; NHBz·SBz → $NHBz_2$ + S; BzSH + NH_2Bz → $NHBz_2$ + H_2S: Bz_2S_2 + NH_2Ac → NHAc·SBz + BzSH; NHAc·SBz → NHBzAc + S; BzSH + NH_2Ac → NHBzAc + H_2S; NHBzAc + BzSH → $NHBz_2$ + AcSH. R. T.

Oxidisability of thioarylhydrazides to disulphides. H. Wuyts and A. Lacourt (Bull. Soc. chim. Belg., 1939, **48**, 193—200).—NHPh·NH·CSPh (I) is oxidised by air or by I + $NaHCO_3$ to the corresponding *disulphide* (II), $(NHPh{\cdot}N{:}CPh{\cdot}S)_2$,

m.p. 149°, which is insol. in alkali, contains two active H, and yields a Ac_2 derivative. Similar *disulphides*, m.p. 165° (III) and —, are formed from NHPh·NH·CS·$C_{10}H_7$-α and NPhMe·NH·CS·C_6H_{11} whereas *o*-C_6H_4Me·NH·N:C(SMe)·C_6H_4Me-*p* resists oxidation. Reduction of the disulphides by $SnCl_2$ and HCl regenerates the thiohydrazides. With MgMeI the reaction $(NHPh·N:CPh·S)_2$ + MgMeI = NHPh·N:CPh·SMe + NHPh·N:CPh·SMgI is quant. The product, m.p. 187°, derived from (I) is also obtained from (II) by the action of EtOH, CH_2O, and HCl. Similarly (III) yields a substance, m.p. 198°. H. W.

Polyhydric alcohol–polybasic acid reactions. III. Glycerol–phthalic anhydride reaction. IV. Glyceryl phthalate from phthalic acid. R. H. Kienle, P. A. van der Meulen, and F. E. Petke (J. Amer. Chem. Soc., 1939, **61**, 2258—2268, 2268—2271; cf. A., 1930, 1434).—III. Interaction of glycerol (2 mols.) and *o*-$C_6H_4(CO)_2O$ (3 mols.) at ~200° is at first rapid and exothermic, owing to formation of glyceryl H phthalates, but then becomes slower. Periodic determination of H_2O evolved and of the acid and sap. val., mol. wt., analysis, and physical properties of the product show that the later reaction is mainly formation of large mols. by interesterification with smaller amounts of intra-esterification and anhydride-formation. Gelation occurs at fairly low mol. wts. and is dependent on the three-dimensional nature of the intertwining mols. Apparatus is described.

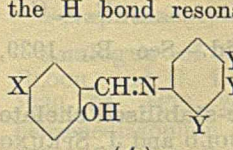
IV. Reaction of glycerol with *o*-$C_6H_4(CO_2H)_2$ is essentially similar to the later stages of that with *o*-$C_6H_4(CO)_2O$, but differences in the early stages are noted. R. S. C.

Derivatives of phthalylcarbamide. C. S. Smith and C. J. Cavallito (J. Amer. Chem. Soc., 1939, **61**, 2218—2221).—Figures in brackets below indicate relative hypnotic activity (all low) when injected (0·5 g. per kg. body-wt.; suspended in aq. glucose–glycerol) intraperitoneally into rats. Heating the appropriate acid anhydrides and carbamide derivatives, first at 124° and then with $POCl_3$ at 100°, gives "phthalylcarbamide," *o*-$C_6H_4(CO·NH)_2CO$ (35%) [0], m.p. 207—207·5°, and its N-*Me* (40%) [0], m.p. 190—192°, N-*allyl* (30%), m.p. 135—?, N-*Ph* (48%) [1], m.p. partly 164—165°, remainder 194°, N-o- (18%) [1], m.p. 190° (decomp., rapid), 200·5° (slow heating), N-m- (38%) [1], m.p. 139°, and N-p-*tolyl* (21%) [3], m.p. 155—160°, N-o- (17%) [1], m.p. 220°, and N-p-*phenetyl* (42%) [2], m.p. 196—198°, N-o- (20%) [1], m.p. 218°, and N-p-*anisyl* derivatives (12%) [2], m.p. 199°, *phthalylthiocarbamide* (49%), m.p. 181—181·5°, Δ²-*tetrahydro*- (19%) [0], m.p. 270°, 3- (57%) [4], m.p. 190° (decomp.), and 4-*nitro-phthalylcarbamide* (61%), m.p. 206—207°, 3-*nitro*-N- or -N′-p-*tolyl*- (38%) [3], m.p. 189—190°, and -p-*phenetyl-carbamide* (35%), m.p. 191—195°. R. S. C.

Preparation of *N*-substituted phthalimides. G. Wanag (Latvij. Univ. Raksti, 1939, **4**, 405—421).—*N*-Substituted phthalimides are rapidly and quantitatively obtained from *o*-$C_6H_4(CO)_2O$ (I) and primary aromatic amines in boiling, glacial AcOH; the disappearance of the amine is established by the colour test with bindone. The reactant ratio 1 : 1 is satisfactory since eventual *o*-$C_6H_4(CO_2H)_2$, formed from the liberated H_2O and (I), reacts almost as rapidly as (I). Amine salts react slowly and incompletely but, with the exception of the nitrates, they can be employed if NaOAc is also added. Substituted anilines do not differ greatly from NH_2Ph in rapidity and completeness of reaction. The change can be extended to fatty and fatty-aromatic primary amines; the corresponding salts are nearly inactive unless NaOAc is present. Since *sec.* and *tert.* amines are not reactive they can be separated from primary amines by this method. (I) can be replaced by 3-nitrophthalic, succinic, or naphthalic anhydride. Dilution of AcOH is unwise. The following *-phthalimides* are described: phenyl-, m.p. 208°; o-, m.p. 183°, m-, m.p. 176°, and p-, m.p. 204°, *-tolyl-*; o-, m.p. 137°, and p-, m.p. 177°, *-ethylphenyl-*; 2 : 4-, m.p. 155°, 2 : 5-, m.p. 163°, 2 : 6-, m.p. 204°, and 3 : 5-, m.p. 135°, *-dimethylphenyl-*; 2 : 4 : 6-, m.p. 171°, and 2 : 4 : 5-, m.p. 147°, *trimethylphenyl-*; o-, m.p. 165°, m-, m.p. 154°, and p-, m.p. 285°, *-diphenylyl-*; p-*triphenylmethylphenyl-*, m.p. 247°; 1-, m.p. 181°, and 2-, m.p. 216°, *-naphthyl-*; 1-*tetrahydronaphthyl-*, m.p. 142°; 2-*fluorenyl-*, m.p. 288°; p-*acetamidophenyl*, m.p. 283°; p-*anilinophenyl-*, m.p. 270°; p-*dimethylaminophenyl-*, m.p. 260°; methyl-, m.p. 134°; ethyl-, m.p. 78°; *iso*propyl-, m.p. 86°; *n*-butyl-, m.p. 34°; *iso*butyl-, m.p. 93°; n-*heptyl-*, m.p. 40°; n-*heptadecyl-*, m.p. 63°; allyl-, m.p. 70°; benzyl-, m.p. 115°; α-, m.p. 43—44°, and β-, m.p. 130°, *-phenylethyl-*; benzhydryl-, m.p. 225° (this compound is possibly 1 : 4-*diketo*-3 : 3-*diphenyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline); 2-*tetrahydronaphthyl-*, m.p. 128°; cyclo*hexyl-*, m.p. 168°; *camphyl-*, m.p. 55°. H. W.

Δ²·⁴-Cholestadiene-3-acetic acid, m.p. 226°.—See B., 1939, 1077.

Phototropy of anils and of solutions of the leuco-cyanides of malachite- and brilliant-greens. V. de Gaouck and R. J. W. Le Fèvre (J.C.S., 1939, 1457—1465).—Phototropy among anils appears to occur only in the solid state; in solution, no such changes of colour or other properties can be produced by illumination. Salicylidene-*m*-toluidine (I), one of the most phototropic anils, is examined in C_6H_6, CCl_4, or $CHCl_3$, spectrophotometrically, and dielectrically (diagrams of apparatus). Absorption spectra of 11 other anils are examined. *X*-Ray examination of the two forms of (I) shows that, except for the colour, no other crystallographical property is changed by light. Phototropic mechanism must thus depend on intermol. resonance in the crystal lattice (diagrams given and mechanism discussed). Such mechanism should be influenced by factors tending to modify the H bond resonance, *e.g.*, phototropic *o*- or *p*-hydroxyanils should lose this property if the H of the OH is methylated; methylation does destroy phototropy. Substituents in the aryl nuclei should have a great effect. Results with a no. of anils (type *A*; X = Me, Cl, Br, NO_2, Y = H;

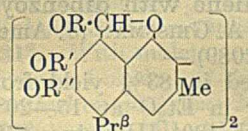


(*A*.)

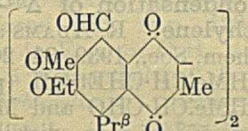
X = Me, 4-Y = NO_2; X = NO_2, 4-Y = Me; X = H, 4-Y = H, Me, Cl, Br, NO_2; X = H, 2- or 3-Y = Me) show that phototropy does not occur if X is other than H; influence of Y is marked, as although (I) and salicylidene-aniline (II) and -*p*-bromoaniline show phototropy, the corresponding -*o*- and -*p*-toluidine and -*p*-chloroaniline undergo no apparent colour change. (II) shows little colour development in sunlight, but if the light is first passed through a blue filter, a strong colour change is induced in the anil. The leuco-cyanides of malachite- and brilliant-green show phototropy in EtOH (owing to induced ionisation), but not in C_6H_6; their dipole moments, and that of leuco-malachite-green, illustrate facilitation of mesomerism by the NR_2 group. A. T. P.

Structure and absorption spectrum of *o*-phthalaldehydic acid.—See A., 1939, I, 507.

Structure of gossypol. XXII. Gossypol ethers and their reduction products. R. Adams and W. R. Dial (J. Amer. Chem. Soc., 1939, **61**, 2077—2082; cf. A., 1939, II, 320).—Gossypol ethers and some reactions thereof are described. Addition of 20% KOH–EtOH to gossypol Me_4 ether (I) and Et_2SO_4 in warm C_6H_6 gives the *Me_4 Et_2 ether* (II) (*A*; R = R′ = Me; R″ = Et), m.p. 271—272° or 228—229° [with AcOH–NHPh·NH_2 gives the *phenylhydrazone* (III), m.p. 268—269°, of gossypol Me_2 Et_2

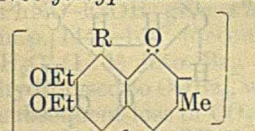


(*A*.)

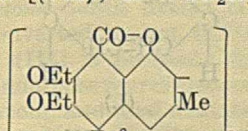


(V.)

ether], also obtained from gossypol Et_2 ether (IV) (*phenylhydrazone*, m.p. 260—261°) by Me_2SO_4–KOH–MeOH. With a little H_2SO_4 in AcOH at 100°, (II) gives (IV). HCl–MeOH reconverts (III) into (II), and HCl–EtOH gives a *Me_2 Et_4 ether* (*A*; R′ = Me; R = R″ = Et), m.p. 241—242°. Dil. HNO_3 oxidises (II) to *norgossic acid Me Et ether* [6-*carboxy*-5-*methoxy*-4-*ethoxy*-3-iso*propylphthalic anhydride*], m.p. 178—179°. CrO_3–AcOH oxidises (II) to *gossypolone Me_2 Et_2 ether* (V), m.p. 185—186°. Gossypol Et_6 ether (VI) gives the *Et_4 ether phenylhydrazone*, m.p. 241—242°, converted by HCl–MeOH into the *Me_2 Et_4 ether* (*A*; R = Me; R′ = R″ = Et), m.p. 206—207°. With conc. HNO_3–H_2O (1 : 4 by vol.), (VI) gives *gossypolonic acid Et_4 ether* [(VII); R = CO_2H],

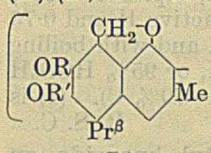


(VII.)



(VIII.)

m.p. 272—273°, and with CrO_3–AcOH gives *gossypolone Et_4 ether* [(VII); R = CHO], m.p. 146—147°, and *gossylic acid lactone Et_4 ether* (VIII), m.p. 244—245° [$(NO_2)_2$-derivative, m.p. 266—267°]. H_2–PtO_2 in AcOH (not EtOH or EtOAc) at 50°/3 atm. reduces gossypol Me_6 ether (IX) to *deoxygossypol Me_4 ether* (X) (*B*; R = R′ = Me), m.p. 261—263° (decomp.).



(*B*.)

PhN_2HSO_4 couples with gossylic acid Me_4 ether, but not with (IX) or (X); 2 : 4 : 1-$(NO_2)_2C_6H_3$·N_2HSO_4 couples with all three compounds. With HNO_3, (X) gives gossic acid, and with CrO_3 in boiling AcOH gives gossypolone Me_4 ether. Hydrogenation of (*A*; R = Et; R′ = R″ = Me) gives (*B*; R = R′ = Me), but that of (*A*; R = R′ = Me; R″ = Et) gives *deoxygossypol Me_2 Et_2 ether* (*B*; R = Me; R′ = Et), m.p. 240—242°; that of (I) [= (*A*; R = R′ = Me; R″ = H)] gives an indefinite product, whence (*B*; R = R′ = Me) or (R = Me; R′ = Et) were obtained. M.p. are corr. R. S. C.

Reactions of bromomagnesium enolates of mesityl ketones. II. Condensation. R. C. Fuson, W. O. Fugate, and C. H. Fisher (J. Amer. Chem. Soc., 1939, **61**, 2362—2365; cf. A., 1939, II, 373).—The MgBr derivative (I) of acetomesitylene reacts as 2 : 4 : 6-$C_6H_2Me_3$·CO·CH_2·MgBr. With 0·5 mol. of RCOCl it yields 2 : 4 : 6-$C_6H_2Me_3$·CO·CH_2·COR [R = Me (II) or Ph], but with more RCOCl yields 2 : 4 : 6-$C_6H_2Me_3$·CO·CH$(COR)_2$. With 2 : 4 : 6-$C_6H_2R_3$·COCl (R = Me or Et), it gives only 2 : 4 : 6 : 2′ : 4′ : 6′-hexamethyl- (*Cu* derivative) and 2 : 4 : 6-*trimethyl*-2′ : 4′ : 6′-*triethyl-dibenzoylmethane*, b.p. 188—190°/2 mm. (*Cu* derivative, m.p. 287°). With EtOAc, (I) gives 26% of (II), and with HCO_2Et gives 33% of *ω-hydroxymethyleneacetomesitylene*, b.p. 108—110°/3 mm. (*Cu* derivative). The appropriate MgBr derivative with CO_2 in Et_2O gives β-*keto*-β-*mesitylpropionic*, m.p. 104—105°, α-2 : 4 : 6-*trimethylbenzoyl-propionic*, m.p. 111·5—112·5°, and -iso*butyric*, m.p. 86—87°, and α-3 : 5-*dibromo*-2 : 4 : 6-*trimethylbenzoyl*isobutyric *acid*, m.p. 108—110°. With PhCHO, (I) gives *γ-keto*-α-*phenyl*-γ-*mesityl*-n-*propyl alcohol* (47%), m.p. 77—77·5°, and 26% of 2 : 4 : 6-$C_6H_2Me_3$·CO·CH:CHPh. 2 : 1-OMe·$C_{10}H_6$·CHO and (I) in C_6H_6–Et_2O give 82% of *mesityl* β-2-*methoxy*-1-*naphthylvinyl ketone*, m.p. 107—108° (*dibromide*, m.p. 148—149°). With COPhMe, (I) gives 2 : 4 : 6-$C_6H_2Me_3$·CO·CH:CPhMe, m.p. 85·5—87° (lit. 84°), and with $COPh_2$ gives 2 : 4 : 6-$C_6H_2Me_3$·CO·CH_2·CPh_2·OH, m.p. 74—75°. Br converts (I) only into 2 : 4 : 6-$C_6H_2Me_3$·CO·CH_2Br, but anhyd. CuCl in hot Et_2O gives a little (2 : 4 : 6-$C_6H_2Me_3$·CO·CH_2·)$_2$. 2 : 4 : 6-$C_6H_2Me_3$·CO·CH:CH_2 and (I) give 82% of (2 : 4 : 6-$C_6H_2Me_3$·CO·$CH_2)_2CH_2$. R. S. C.

Lignin and related compounds. XLV. Synthesis and properties of α-hydroxypropiovanillone. A. B. Cramer and H. Hibbert (J. Amer. Chem. Soc., 1939, **61**, 2204—2206).—*o*-$C_6H_4(OMe)_2$, CHMeBr·COBr, and $AlCl_3$ in CS_2 at room temp. give *α-bromopropiovanillone* (35%), m.p. 105—106°, unstable (prolonged heating) in solvents in which it is only slightly sol., which with Ac_2O–NaOAc at 100° gives *α-acetoxypropiovanillone acetate* (84%), m.p. 122—123°, hydrolysed by hot KOH–MeOH to *α-hydroxypropiovanillone* (I) (92%), m.p. 109—110°. With 0·5% dry HCl–EtOH this gives *α-ethoxypropiovanillone*, b.p. 125—140°/0·005 mm., with CH_2N_2–

Et_2O gives *α-hydroxypropioveratrone*, b.p. 130—150°/0·01 mm., with MgMeI shows 1·75 active H and 0·75 CO (low vals. due to OH *p*- to CO), and with boiling 5% aq. H_2SO_4, 5% dry HCl–MeOH, or 95% HCO_2H gives brown, amorphous products (~70% C). (I) is a possible precursor of lignin. R. S. C.

Action of magnesium *iso*butyl bromide on 3 : 4 : 5-trimethoxybenzonitrile. H. L. Haller and P. S. Schaffer (J. Amer. Chem. Soc., 1939, **61**, 2175—2177).—3 : 5 : 1-$(OMe)_2C_6H_3$·CO·NH_2 with PCl_5 gives a *product*, $C_9H_8O_2NCl$, m.p. 124—125°, but with P_2O_5 gives 3 : 5-*dimethoxybenzonitrile*, m.p. 87—88°, which with $MgBu^{\beta}Br$ in Et_2O gives 45—50% of 3 : 5 : 1-$(OMe)_2C_6H_3$·$COBu^{\beta}$, b.p. 143—145°/2 mm. (*semicarbazone*, m.p. 195—196°). This ketone resists H_2–Pd–C and gives unsatisfactory products with Na–EtOH or Zn–Hg–HCl. 3 : 4 : 5 : 1-$(OMe)_3C_6H_2$·CN (prepared from the amide by PCl_5) and $MgBu^{\beta}Br$ in Et_2O–PhMe give 3 : 4 : 5-*trimethoxyphenyl Bu*$^{\beta}$ *ketone*, b.p. 147—150°/1 mm. (*semicarbazone*, m.p. 205°), ? 4-*hydroxy*-3 : 5-*dimethoxyphenyl Bu*$^{\beta}$ *ketone*, m.p. 94° (faint green $FeCl_3$ reaction; *semicarbazone*, m.p. 162·5°; *oxime*, m.p. 110°; *benzoate*, m.p. 111°), and ? 3 : 5-*dimethoxy*-4-*butylphenyl Bu*$^{\beta}$ *ketone*, b.p. 128—130°/0·35 mm. (*semicarbazone*, m.p. 184°). R. S. C.

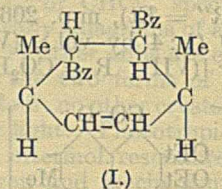
Methylation of β-ketonitriles. R. C. Fuson and D. E. Wolf (J. Amer. Chem. Soc., 1939, **61**, 1940—1942).—*p*-C_6H_4Br·CO·CH_2·CN (prep. from *p*-C_6H_3Br·CO·CH_2Br by conc., aq. KCN in EtOH) with Me_2SO_4 and aq. KOH at 70—130° (bath) gives only the O-*Me ether*, m.p. 58·5—59·5°, of the enol, but with boiling MeI–NaOEt–EtOH gives only p-*bromo-α-cyanopropiophenone*, m.p. 74·4—75·5°, obtained also from *p*-C_6H_4Br·CO_2Et, EtCN, and NaOEt, first at 80° and then at 110—120°. 2 : 4 : 6-$C_6H_2Me_3$·CO·CH_2·CN with MeI–NaOEt–EtOH undergoes approx. equal amounts of *O*- and *C*-methylation (cf. A., 1938, II, 279). M.p. are corr. R. S. C.

Acyloins from *tert.*-butylglyoxal. R. C. Fuson, H. Gray, and J. J. Gouza (J. Amer. Chem. Soc., 1939, **61**, 1937—1940).—Bu^{γ}CO·CHO (prep. from $COMeBu^{\gamma}$ by SeO_2 in MeOH–H_2O), b.p. 114—115°, $+0·5H_2O$, m.p. 91—92° (softens at 85°; lit., m.p. 85°) (2 : 4-*dinitrophenylhydrazone*, m.p. 171—172°; *phenylhydrazone*, m.p. 119—120°; osazone, m.p. 119·5—120°; *semicarbazone*, m.p. 134—135°; dioxime, m.p. 100·5—101·5°; gives 6- or 7-*nitro*-2-*tert.*-*butylquinoxaline*, m.p. 134·5—135°), with 25% aq. NaOH at room temp. gives OH·CHBu$^{\gamma}$·CO_2H, and with $AlCl_3$ and C_6H_6 gives *phenylpivalylcarbinol* [β-*keto*-α-*phenyl*-γγ-*dimethyl*-n-*butan*-α-*ol*], m.p. 46—47°, b.p. 90—102°/2 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 174—175°; *benzoate*, m.p. 96—97°). Similarly are obtained p-*tolyl*-, m.p. 48—49°, m-*xylyl*-(*A*), b.p. 133—135°/4 mm., and *mesityl-pivalylcarbinol*, m.p. 118—118·5°. Conc. HNO_3 at 100° converts the acyloins into *Ph* (I), b.p. 75—76°/1 mm., p-*tolyl* (II), b.p. 97—97·5°/1 mm., m-*xylyl* (III), b.p. 103—104°/1 mm., and mesityl Bu^{γ} diketone (IV) (isolated by further heating as 3-NO_2-derivative, m.p. 58—59°). (I) and (II) give *quinoxaline* derivatives, m.p. 108—109° and 109—110°, respectively, but (III) and (IV) do not react with *o*-$C_6H_4(NH_2)_2$. Some *di*-m-*xylylpivalylmethane* [αα-*di*-m-*xylyl*-γγ-*dimethyl*-n-*butan*-β-*one*], m.p. 111·5—112°, accompanies (*A*). HNO_3–H_2SO_4 at 0° converts (III) into 3 : 5 : 2 : 4 : 1-$(NO_2)_2C_6HMe_2$·CO_2H, new m.p. 202—203°. KOH–aq. EtOH converts (I) into βββ-*trimethylatrolactic* [α-*hydroxy*-α-*phenyl*-ββ-*dimethyl*-n-*butyric*] *acid*, m.p. 105—106°. Na, followed by BzCl, converts (I) in PhMe–N_2 into αβ-*dibenzoyloxy*-α-*phenyl*-γγ-*dimethyl*-Δ^{α}-n-*butene*, m.p. 138—139°. R. S. C.

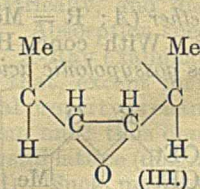
Two isomeric 2-acetyldecahydronaphthalenes. G. Cauquil (Compt. rend., 1939, **209**, 441—443).—Chlorination of a mixture of *cis*- and *trans*-decahydronaphthalene (obtained from $C_{10}H_8$–Ni–H_2) gives a mixture, b.p. 115°/18 mm., of *cis*- and *trans*-β-chlorodecahydronaphthalene, the Mg derivative of which with MeCHO gives 2-*decahydronaphthylmethylcarbinol*, b.p. 136—138°/14 mm., oxidised (CrO_3–AcOH) to a mixture b.p. 128—132°/13 mm., of 2-acetyldecahydronaphthalenes, separated through the semicarbazones into the trans-, b.p. 142—143°/22 mm. (*oxime*, m.p. 104°; *semicarbazone*, m.p. 242°), and cis-*isomerides*, b.p. 138°/22 mm. (oxime, an oil; *semicarbazone*, m.p. 196°). J. L. D.

Structure and absorption spectrum of phthalonic acid.—See A., 1939, I, 507.

Structure of gossypol. XXIII. Attempts to prepare des*apo*gossypolone tetramethyl ether. Condensation of $\Delta^{\beta\delta}$-hexadiene with dibenzoylethylene. R. Adams and T. A. Geissman (J. Amer. Chem. Soc., 1939, **61**, 2083—2089).—CHMe:CH·CHEt·OH (prepared in 83% yield from CHMe:CH·CHO and MgEtBr in Et_2O at 15—20°), b.p. 55°/15 mm., distilled with 48% HBr gives 67% of $(CHMe{:}CH)_2$, which (41 g.) with *trans*-$(CHBz{:})_2$ (60 g.) in PhMe (75 c.c.) gives 1 : 2-*dibenzoyl*-3 : 6-*dimethyl*-Δ^4-cyclo*hexene* (I) (53 g.), m.p. 136—137°, with a *stereoisomeride* (6·5 g.), m.p. 86—88° [*dibromide*, m.p. 152° (decomp.)]. Oxidation of (I) by many reagents gives indefinite results, the CH·CO reacting as well as the C:C; its *dibromide* (II), m.p. 169—170°, with NaOAc–AcOH–Ac_2O gives an isomeric *dibromide*, m.p. 202·5—203° (decomp.). With *o*-$CO_2H·C_6H_4·CO_3H$ (1 mol.) in $CHCl_3$–Et_2O at 0°, (I) gives *oxides*, (III), m.p. 187·5—188°, and (IV), m.p. 154—155°. If the Bz are *trans*, (I) thus has the structure shown. With hot 25% H_2SO_4–$COMe_2$ (1 : 4),



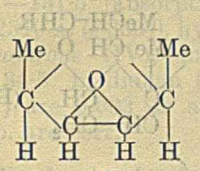
(I.)



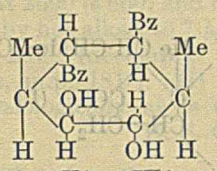
(III.)

(III) gives mainly 4 : 5-*dibenzoyl*-3 : 6-*dimethyl*cyclo*hexane*-1 : 2-*diol* (V), m.p. 173—175°, with less of the isomeric *diol* (VI), m.p. 212—213°; (IV) gives similarly mainly (VI) with some (V), but an impure specimen yielded also a *substance* [? (VII)], $C_{25}H_{28}O_4$, m.p. 187—188° (no CO reactions; gives no CHI_3 in dioxan). With HIO_4–AcOH (no oxidation occurs) at room temp. or 25% H_2SO_4–AcOH (1 : 3) at 100°, (IV) gives 4 : 5-*dibenzoyl*-2-*acetoxy*-3 : 6-*dimethyl*cyclo-

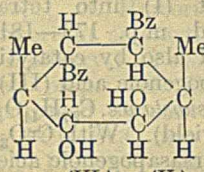
hexan-1-*ol*, m.p. 207°, hydrolysed by hot NaOMe–MeOH to (VI). With M-aq. HIO_4 in boiling $COMe_2$,



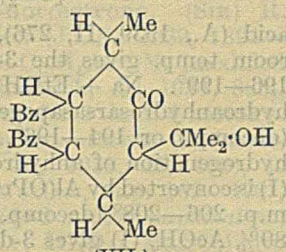
(IV.)



(V.) or (VI.)



(VI.) or (V.)



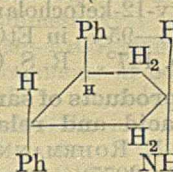
(VII.)

(IV) gives a *product*, $C_{24}H_{26}O_5$, m.p. 177—178° (decomp.). $Pb(OAc)_4$ in AcOH converts (VI) into a *product*, m.p. 170—170·5° (decomp.). A trace of 85% H_3PO_4 in boiling AcOH–Ac_2O dehydrates (I), yielding 1 : 2-*diphenyl*-3 : 6-*dimethyl*-3 : 6-*dihydro*iso*benzfuran* (VIII), m.p. 114—115°; the 4 : 5-*dibromide* (IX), m.p. 168—170° (decomp.), thereof is obtained therefrom or by a little H_2SO_4 in AcCl from (II), and with boiling C_5H_5N (not NaOAc–AcOH) gives 1 : 2-*diphenyl*-3 : 6-*dimethyl*iso*benzfuran* (X), m.p. 129—131°. With maleic anhydride in Et_2O or C_6H_6, (X) gives 1 : 4-*oxido*-1 : 4-*diphenyl*-5 : 8-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-2 : 3-*dicarboxylic anhydride* (70%), m.p. 310—312° (decomp.). (II) and C_5H_5N at 100° give 2 : 3-*dibenzoyl*-p-*xylene*, m.p. 144—145° [and (I)], obtained also from (VIII) by Br and NaOAc in boiling AcOH or, less well, from (I) by Br–C_5H_5N or (IX) by Br–NaOAc–AcOH, and reduced by Zn dust in NaOH–EtOH to 2 : 3-*di*-(α-*hydroxybenzyl*)-p-*xylene*, m.p. 149—151°. R. S. C.

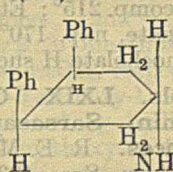
Reactive methylene groups and nitroso-compounds. Abnormal action of acids on 1 : 2 : 3-triketones. A. Schönberg and R. C. Azzam [with R. Michaelis] (J.C.S., 1939, 1428—1430; cf. A., 1937, II, 249).—CH_2PhBz and *p*-NO·C_6H_4·NMe_2–EtOH–piperidine at 100° (bath) give *benzil*-p-*dimethylaminoanil oxide* (I), m.p. 165—166°, and -*dimethylaminoanil* (II), m.p. 137—138° [the (II), m.p. 166°, of Skraup *et al.* (A., 1926, 722) is actually (I)]. (I) or (II) and H_2SO_4–H_2O (1 : 1) at 100° give Bz_2. CH_2Bz_2 and PhNO–EtOH give *Ph*$_2$ *triketone* β-*anil oxide* (III), m.p. 144—145° (decomp.), converted by hot H_2SO_4–H_2O (1 : 1) into Bz_2. Thus (III) is probably first hydrolysed to $COBz_2$, which undergoes rearrangement, subsequent loss of CO_2 to benzoin, and final oxidation (see below). CH_2Bz_2 and *p*-NO·C_6H_4·NMe_2–95% EtOH–Na_2CO_3 at 50—55° give *Ph*$_2$ *triketone* β-p-*dimethylaminoanil oxide*, m.p. 183—185° (decomp.). CH_2Bz·CO·C_6H_4Me-*p* and PhNO–EtOH give a mixture of isomeric (probably geometrical) *Ph* p-*tolyl triketone* β-*anil oxides*, m.p. 141—143° and 132—134°. $COBz_2$ with boiling H_3PO_4 (*d* 1·7) gives benzoin, but H_2SO_4–H_2O (1 : 1), or $AlCl_3$ at 100°, affords Bz_2. Benzoin and H_2SO_4–H_2O (1 : 1) also give Bz_2. Triketohydrindene hydrate and boiling H_2SO_4–H_2O (1 : 1) give bisindanedione, m.p. ~297°. A. T. P.

1-Hydrindone. C. C. Price and F. M. Lewis (J. Amer. Chem. Soc., 1939, **61**, 2553—2554).—Ph·$[CH_2]_2$·CO_2H and, best, 5% oleum at 140° (5 min.) give 27% of 1-hydrindone. Addition of BF_3 or $AlCl_3$ lowers the yield. R. S. C.

Anionotropic and prototropic changes in cyclic systems. VII. Structure of the chlorodiphenyl*cyclo*pentenone obtained by action of hydrogen chloride on anhydroacetonebenzil. H. Burton and C. W. Shoppee (J.C.S., 1939, 1408—1415).—Further evidence (cf. A., 1934, 409) is presented for formulating the compound (I), m.p. 129°, from anhydroacetonebenzil and EtOH–HCl as 2-chloro-3 : 4-diphenyl-Δ^2-*cyclo*pentenone (II). The argument of Allen *et al.* (A., 1937, II, 457) that structure (II) must be assigned to the compound (III), m.p. 142°, obtained from $POCl_3$ and 2-hydroxy-3 : 4-diphenyl-Δ^2-*cyclo*pentenone (IV), an enolic form of 3 : 4-diphenyl*cyclo*pentane-1 : 2-dione (V) is invalid, since (V) can also enolise to 2-hydroxy-4 : 5-diphenyl-Δ^2-*cyclo*pentenone (VI). Further, either (III) [improved prep.; also obtained from 2 : 3-diphenyl*cyclo*pentenone (VII) and SO_2Cl_2 in C_6H_6 at 15°] or (IV, VI) is reduced by P–HI–AcOH to (VII), which is hydrogenated (cf. A., 1939, II, 269) to *trans*-2 : 3-diphenyl*cyclo*pentanone (VIII), also obtainable by direct hydrogenation (PtO_2 with NaOAc,$3H_2O$ in EtOH; Pt-black with NaOAc and NH_2OH,HCl in EtOH) of (III). Therefore CO in (III) is unsymmetrical to the Ph groups, and (III) is regarded as a 2-*chloro*-4 : 5-*diphenyl*cyclo*pentenone* (IX), derived from (VI), not (IV). In contrast, (I) with P–HI–AcOH gives 3 : 4-diphenyl-Δ^3-*cyclo*pentenone (X), and this [or (I)] is catalytically reduced to *cis*-3 : 4-diphenyl*cyclo*pentanone. (I) gives an almost quant. yield of its *oxime* (XI), m.p. 172°; with NH_2OH at ≮40° the only product from (III) is a dimeric *oxime*, $C_{34}H_{26}O_2N_2$, m.p. 258—259° (decomp.). With piperonal–HCl, (I) forms a *piperonylidene* derivative, m.p. 165°, but (III) gives a *compound* (dimeric?), m.p. 188—189° (decomp. 210—215°). The formation of desylacetic acid (XII) from (III) and O_3 in AcOH (Allen *et al.*, *loc. cit.*) is not confirmed; the only identifiable product from this reaction (or from oxidation by $KMnO_4$ in 90% $COMe_2$ at −15° in presence of $MgSO_4$, or by CrO_3 in 90% AcOH at 43°) is BzOH. Oxidation of (I) by $KMnO_4$ in $COMe_2$ at 15° to (XII) (cf. A., 1934, 409) is confirmed. Possible tautomerism of (IX), which is best regarded as a mixture of interchangeable isomerides, is considered. Reduction (best catalytic) of (XI) in AcOH gives



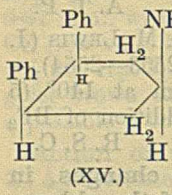
(XIII.)



(XIV.)

trans-3 : 4-*diphenyl*cyclo*pentylamine*, m.p. 119—120° [*picrate*, m.p. 232° (decomp.); *Ac* derivative (XIII), m.p. 119°]. *trans*- and *cis*-3 : 4-Diphenyl*cyclo*-

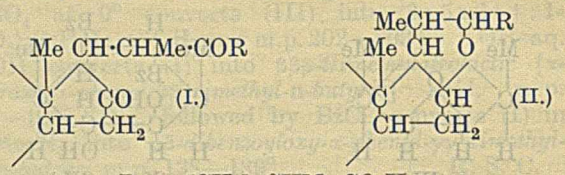
pentanoneoxime are reduced (Na in EtOH) respectively to (XIII) and a mixture of two cis-3 : 4-*diphenylcyclopentylamines* [*Ac* derivatives (XIV) or (XV), m.p. 133—134°, and (XV) or (XIV), m.p. 128°]. The *oxime*, m.p. 179°, of (X) is reduced and then acetylated to (XIII). The oxime of (VIII) is reduced and acetylated to two 1-*acetamido*-2 : 3-*diphenylcyclopentanes*, m.p. 187° and 170—171° (both slight previous sintering), also obtained by reducing the oxime of (VII). γδ-Diphenyl-Δ^{α}-pentenoic acid (cf. A., 1937, II, 247; a liquid isomeride is simultaneously formed) (*anilide*, m.p. 129—130°) is hydrogenated to γδ-diphenyl-*n*-valeric acid (*anilide*, m.p. 111—112°). An attempt to use its *Me* ester, b.p. 206—208°/15 mm., to synthesise (VIII) by the Dieckmann reaction was unsuccessful; a semi-solid product, yielding a *semicarbazone* (?), m.p. 237° (decomp.), was formed. E. W. W.



(XV.)

Wolff–Kishner reduction of steroid ketones. J. D. Dutcher and O. Wintersteiner (J. Amer. Chem. Soc., 1939, **61**, 1992—2000).—With 7 steroid ketones it is shown that NaOEt at 180° reduces a C:N·NH·CO·NH_2 at position 3 mainly to CH·OH (mixed epimerides; mostly that with the OH *trans* to the H on $C_{(5)}$), but that a similar group at position 7 or 12 gives only CH_2, and that presence of the latter reduces the amount of OH formed at $C_{(3)}$. Cholestenonesemicarbazone gives Δ^4-cholestene, αβ-unsaturated and saturated alcohols. Hydrazones and ketazines react similarly. With any derivative an added excess of N_2H_4,H_2O greatly suppresses formation of CH·OH. Time of heating (4·5—22 hr.), presence of H_2O, or exclusion of O_2 has little effect. Increase of temp. from 180° to 200° slightly favours formation of CH_2 from cholestanonesemicarbazone. It is considered that the semicarbazones give the hydrazones, which are either reduced to hydrocarbons or hydrolysed to ketones, which with NaOEt give the alcohols and MeCHO. The alcohols are separated from hydrocarbons as H succinates or, less well, H phthalates. The following are described. Cholestanone-, sinters at 227°, decomp. 238°, coprostanone-, sinters at 178°, decomp. 192°, cholestenone-, m.p. 215—235° (decomp.), and *dehydrolithocholic acid semicarbazone*, m.p. 230° (decomp.); *β-cholestanyl H phthalate*, m.p. 160°, and *succinate*, m.p. 171°; *α-coprostanyl H phthalate*, m.p. 218—220°; *cholestanone-hydrazone*, softens at 230°, m.p. 248° (decomp.), and *-ketazine*, decomp. ~200°; *cholestenoneketazine*, decomp. >190°; *dehydrodeoxycholic acid disemicarbazone*, discolours at 190°, decomp. 215°; Et α-3-hydroxy-12-ketocholanate H succinate, m.p. 170°, $[\alpha]_D$ +96·3—95·7° in EtOH; Et α-lithocholate H succinate, m.p. 147°. R. S. C.

Sterols. LXIX. Oxidation products of sarsasapogenin. Sarsasapogenoic acid and related substances. R. E. Marker and E. Rohrmann (J. Amer. Chem. Soc., 1939, **61**, 2072—2077).—Sarsasapogenoic acid (I) probably contains the grouping shown. It is reduced by H_2–PtO_2 in AcOH at 25°/3 atm. to anhydrotetrahydrosarsasapogenoic acid (II) (Fieser *et al.*, A., 1939, II, 31), m.p. 183—187° [*Me* ester, m.p. 125—127° (benzoate, m.p. 140—141·5°)], which appears to be identical with sarsasapogentic



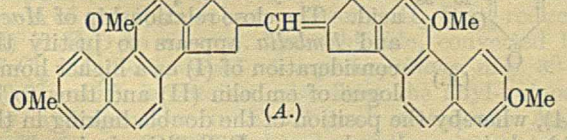
R = ·$[CH_2]_2$·CHMe·CO_2H

acid (A., 1939, II, 276), and with CrO_3–AcOH at room temp. gives the 3-dehydroanhydro-acid, m.p. 196—199°. Na + EtOH convert (I) into tetrahydroanhydrosarsasapogenoic acid, m.p. 179—181° (decomp.) or 194—196°, obtained also by catalytic hydrogenation of anhydrosarsasapogenoic acid (III); (I) is converted by $Al(OPr^{\beta})_3$ into a *substance*, $C_{27}H_{44}O_5$, m.p. 206—208° (decomp.) (poor yield). With CrO_3–80% AcOH, (I) gives 3-dehydrosarsasapogenoic acid, m.p. 163—164° (cf. Jacobs and Simpson's acid, m.p. 162°; A., 1935, 864) (*Me* ester, m.p. 125°), which gives a 4-*Br*-derivative, m.p. 188·5—191°, and thence by hot C_5H_5N 3-*dehydro*-$\Delta^{4:5}$-*sarsasapogenoic acid*, m.p. 199—201°. When (I) (as 3-acetate) is oxidised by CrO_3 in 80% AcOH at 80—85°, no neutral fraction is obtained, but 5% of the acid, $C_{22}H_{34}O_4$, m.p. 287° (decomp.) (A., 1939, II, 322), is isolated. KOH in aq. EtOH converts (I) into (III), m.p. 242—244° (decomp.) [no semicarbazone; unaffected by $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$], but Fieser and Jacobsen's method (A., 1938, II, 108) gives also an isomeric *acid*, m.p. 181—184° (decomp.), converted into (III) by hot NaOH–aq. EtOH. Analysis of (III) and derivatives shows that it is $C_{27}H_{40}O_4$ (not H_{42}). Its structure is discussed. The dibasic acid (*loc. cit.*) [Me_2 ester, m.p. 161—162° (*acetate*, m.p. 158—160°)] of Fieser *et al.* is $C_{27}H_{40}O_7$. The neutral acetate, m.p. 162—164°, obtained from sarsasapogenin acetate by CrO_3, is hydrolysed to a 3-OH-compound, $C_{27}H_{42-44}O_5$, m.p. 215—217°, gives a *semicarbazone*, m.p. 249—251° (decomp.), with H_2–PtO_2 in AcOH–EtOH (10 : 3) (not in EtOH) at 25°/3 atm., followed by KOH–EtOH, gives a *substance*, $C_{27}H_{46-48}O_4$, m.p. 215—217°, and with Zn–Hg–HCl–EtOH gives tetrahydrosarsasapogenin. R. S. C.

Œstrogens with oxygen in ring B. I. 7-Keto- and 7-hydroxy-œstrone. W. H. Pearlman and O. Wintersteiner (J. Biol. Chem., 1939, **130**, 35—45).—7 : 8-Dihydroxyœstrone (prep. from equilin acetate by OsO_4, followed by Na_2SO_3), *forms*, m.p. 253—254° and 210—216° (variable), $[\alpha]_D^{23}$ +135—139° in dioxan (cf. A., 1938, II, 102), when distilled at 205—210°/0·003 mm., gives 7-*ketoœstrone* (I), m.p. 212—212·5° (decomp.), $[\alpha]_D^{22}$ +167° in dioxan [spectrum identical with that of œstrone (II); *dioxime*, decomp. 252—253°; *enol diacetate* (III), m.p. 171—171·5°, showing absorption max. at 2680 (ε 9680) and min. at 2415 A. (ε 4320) indicating conjugation of C:C with the aromatic ring], unstable to alkali. The *disemicarbazone*, m.p. >295°, of (I) and NaOEt–EtOH at 185° give the same 7-deoxoœstrone, new m.p. 135·5—137·5°, $[\alpha]_D^{22}$ +72° in EtOH (benzoate, new m.p. 172·5°), as is obtained from œstrone, which proves the stereochemical configuration of (I). H_2–

Pd in AcOH rapidly converts (III) into 7-*hydroxy-œstrone diacetate*, dimorphic, m.p. 122—123° and 131—131·5° [absorption max. at 2690 (ε 660) and min. at 2510 A. (ε 350)], hydrolysed by hot alkali to 7-*hydroxyœstrone* (IV), m.p. 265—267° (decomp.), $[\alpha]_D^{25}$ +134·5° in dioxan (3-*benzoate*, m.p. 181°). (I) and (IV) are 0·003 as active physiologically as is (II). M.p. are corr. R. S. C.

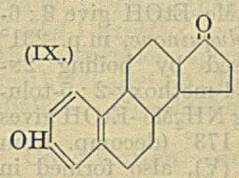
Synthesis of substances related to the sterols. XXVII. Synthesis of *x*-norœstrone. (SIR) R. ROBINSON and H. N. RYDON (J.C.S., 1939, 1394—1405).—The structure of 2 : 6-$C_{10}H_6$Ac·OMe (modified prep.; cf. Haworth and Sheldrick, A., 1934, 885), important as starting material for 3′-keto-4-acetoxy-7-methoxy-1 : 2-*cyclo*pentenophenanthrene (I) (modified prep.; cf. Robinson, A., 1938, II, 496), is confirmed by converting its *oxime*, m.p. 169—170°, by PCl_5–Et_2O into 6-*acetamido*-2-*methoxynaphthalene*, m.p. 162—163°, and this (HCl; HNO_2; Me_2SO_4) into 2 : 6-$C_{10}H_6(OMe)_2$. Conversion of compounds of the type of (I) into hydro-derivatives related to œstrone cannot be effected by direct hydrogenation. Thus, H_2–PtO_2 in AcOH at 70° and (I) give small amounts of 4 : 3′-*dihydroxy*-7-*methoxy*-, m.p. 139—140°, and 3′-*hydroxy*-4-*acetoxy*-7-*methoxy*-1 : 2-cyclo*pentenophenanthrene*, m.p. 145°, with non-cryst. products. Hydrolysis (KOH–MeOH) of the crude hydrogenation product from (I) yields 4-*hydroxy*-7-*methoxy*-1 : 2 : 3 : 4-*tetrahydro*-1 : 2-cyclo*pentenophenanthrene*, m.p. 141—142° (p-*nitrobenzoate*, m.p. 214—216°; *digitonide*) (stable to CrO_3–AcOH), and two oily fractions. Dehydrogenation (Pd–C) of that of lower b.p. gives 1 : 2-*cyclo*pentenophenanthrene (II); of the higher, (II) and 7-methoxy-1 : 2-*cyclo*pentenophenanthrene. Formation of the last indicates preferential deoxygenation in the 4-position in the hydrogenation of 4 : 7-dihydroxyphenanthrene derivatives. To obtain 3′-keto-compounds, it was decided to open the 5-membered ring before hydrogenation. 3′-Keto-4 : 7-dimethoxy-1 : 2-*cyclo*pentenophenanthrene (III) [prep. from (I) and NaOH–EtOH; Me_2SO_4] [2′-*oximino*-derivative, m.p. 248—249° (decomp.), from (III), KOBu^t, and *iso*-C_5H_{11}·O·NO] with HCO_2Et–NaOEt–EtOH in C_5H_5N, followed by AcOH, gives its 2′-*formyl* derivative, decomp. 195°, which with AcOH–NH_2OH,HCl at 70° yields the 2′-*CN*-derivative. The last is hydrolysed (aq. KOH–EtOH) to 4 : 7-*di-*



(*A*.)

methoxyphenanthrene-1-β-*propionic*-2-*carboxylic acid* (IV), m.p. 285° (decomp.), with the condensation *product* (*A*), m.p. 301—302°, also obtained (solely) from (III) and KOBu^t–Bu^{t}OH (under N_2) and $HCO_2C_5H_{11}$-*iso*. The *Me*$_2$ ester, m.p. 115°, from (IV) and MeOH–H_2SO_4, purified chromatographically (Al_2O_3), is hydrogenated (PtO_2 in AcOH at 70°) and then hydrolysed (aq. MeOH–KOH) to three acids, regarded as 4 : 7-*dimethoxy*-9 : 10-*dihydro*- (V), m.p. 208—209°, and -1 : 2 : 3 : 4-*tetrahydro*- (VI), m.p. 138—140°, and (main product) 7-*methoxy*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydrophenanthrene*-1-β-*propionic*-2-*carboxylic acid* (VII), m.p. 142—143°. The Pb salt of (VII) heated at 0·25 mm. gives the *Me ether* (VIII), m.p. 142—143°, demethylated (AcOH–HI at 140°) to x-*norœstrone* [7-*hydroxy*-3′-*keto*-

(IX.)



1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydro*-1 : 2-cyclo*pentenophenanthrene*] (IX), m.p. 222° (*acetate*, m.p. 145—146°), in which *x* denotes indeterminate (probably *cis-cis*) configuration. The Pb salt of (V) similarly gives 3′-*keto*-4 : 7-*dimethoxy*-9 : 10-*dihydro*-1 : 2-cyclo*pentenophenanthrene*, m.p. 143° [depressed by admixed (VIII)] (2 : 4-*dinitrophenylhydrazone*, m.p. 242—243°); the reaction fails with (VI).

4-Hydroxy-3′-keto-7-methoxy-1 : 2-*cyclo*pentenophenanthrene [*oxime* (+H_2O), m.p. 268°] in EtOH with Et_2SO_4 in aq. NaOH gives the -7-*methoxy*-4-*ethoxy*-compound, m.p. 194°, which, as before, gives via the 2′-formyl the 2′-*CN*-derivative, hydrolysed to 7-*methoxy*-4-*ethoxyphenanthrene*-1-β-*propionic*-2-*carboxylic acid*, m.p. 268—269°, the *Me*$_2$ ester, m.p. 118° (purified as before), of which is hydrogenated to 7-*methoxy*-4-*ethoxy*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-1-β-*propionic*-2-*carboxylic acid*, m.p. 160° (no other product isolated).

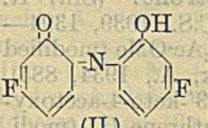
γζ-Diketo-ζ-(6-methoxy-2-naphthyl)heptoic acid (A., 1938, II, 496) is demethylated (AcOH–HCl) to the 6-*OH-acid*, m.p. 171—172°, which with hot aq. KOH gives 3-(6′-*hydroxy*-β-*naphthyl*)-Δ^2-cyclo-*pentenone*-2-*acetic acid*, m.p. 221—222°, cyclised (Ac_2O) to the *Ac*$_2$ derivative, m.p. 196—197° (decomp.), of 4 : 7-*dihydroxy*-3′-*keto*-1 : 2-cyclo*pentenophenanthrene*, m.p. 338° (decomp.), methylated to (III).

With the product from Et *cyclo*pentanone-2-carboxylate and K in C_6H_6, *m*-OMe·C_6H_4·$[CH_2]_2$·CH_2I (improved prep.) gives *Et* 2-(γ-m-*anisylpropyl*)cyclo*pentanone*-2-*carboxylate*, b.p. 187—190°/0·5 mm. [*semicarbazone* (+2MeOH)], which on hydrolysis and heating with Ac_2O at 260—270°/100 mm. gives 2-(γ-m-*anisylpropyl*)cyclo*pentanone*, b.p. 173—177°/0·8 mm. [*semicarbazone*, (+EtOH) m.p. 180°; 2 : 4-*dinitrophenylhydrazone*, m.p. 103—104°]. E. W. W.

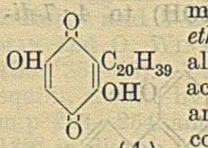
Action of alcoholic monomethylamine on derivatives of benzoquinone and toluquinone. I. Methoxy- and hydroxy-methoxy-derivatives. W. K. ANSLOW and H. RAISTRICK (J.C.S., 1939, 1446—1457; cf. A., 1938, III, 443).—*p*-Benzoquinone and excess of NH_2Me in EtOH at room temp., then at 0° for 3 days, give 2 : 5-*bismethylamino*-1 : 4-*benzoquinone* (I), m.p. 284—286° (decomp.). Methoxy- or 2 : 5-dimethoxy-1 : 4-benzoquinone and boiling NH_2Me–EtOH give (I). 2 : 6- or 2 : 3-Dimethoxy-1 : 4-benzoquinone in boiling or cold EtOH, respectively, affords 2 : 5-*bismethylamino*-3-*methoxy*-1 : 4-*benzoquinone* (II), m.p. 234°, hydrolysed by boiling 5N-H_2SO_4 to 2 : 5-dihydroxy-3-methoxy-1 : 4-benzoquinone (III), m.p. 159—160° (*diacetate*, m.p. 77°). *p*-Toluquinone or its 3- or 6-OMe- or 3 : 6-$(OMe)_2$-derivative gives 3 : 6-bismethylamino-2 : 5-toluquinone, new m.p. 231° (cf. Fichter, A., 1908, i, 658). 4-Methoxy-2 : 5-toluquinone acts abnormally

and affords (I) (mechanism suggested), converted by boiling 2N-NaOH into 2 : 5-dihydroxy-1 : 4-benzoquinone (IV), and thence by aq. $Na_2S_2O_4$ into 1 : 2 : 4 : 5-$C_6H_2(OH)_4$, new m.p. 232—233° (some decomp. from 200°) (cf. Nietzki *et al.*, A., 1888, 1181). 3 : 4-Dimethoxy- or 3 : 4 : 6-*trimethoxy*-2 : 5-*toluquinone* (V), m.p. 80°, and NH_2Me–EtOH give 3 : 6-*bismethylamino*-4-*methoxy*-2 : 5-*toluquinone*, m.p. 231° (partial sublimation), hydrolysed by boiling 2N-H_2SO_4 to 3 : 6-dihydroxy-4-methoxy-2 : 5-toluquinone [spinulosin] (VI) [boiling NH_2Me–EtOH gives only the $(NH_2Me)_2$ salt, m.p. 173° (decomp. from 164°)]. (VI) and CH_2N_2 give (V), also formed in smaller yield using Me_2SO_4–K_2CO_3–$COMe_2$. 4 : 6-Dimethoxy-2 : 5-toluquinone acts abnormally with NH_2Me, giving (II) (mechanism suggested). (V) and aq. $Na_2S_2O_4$ give 2 : 5-*dihydroxy*-3 : 4 : 6-*trimethoxytoluene*, m.p. 82—83°. 1 : 2 : 4 : 5-$C_6H_2(OAc)_3$·OMe and boiling H_2SO_4–MeOH (in N_2) give the quinol, oxidised (air at p_H 8) to 2-*hydroxy*-5-*methoxy*-1 : 4-*benzoquinone* (VII), m.p. 179° (decomp.) (darkens and softens from 171°) (2-*acetate*, m.p. 124°), converted by aq. $Na_2S_2O_4$ into 1 : 2 : 4-*trihydroxy*-5-*methoxybenzene*, m.p. 133°. (VII) and boiling NH_2Me–EtOH, then at room temp., give (I) and (?) 4 : 5-*bismethylamino*-1 : 2-*benzoquinone*, m.p. >360°, hydrolysed by 2N-NaOH to (IV). (VII) reacts possibly in the *o*-quinonoid form. 2 : 3-Dimethoxy-quinol and aq. $FeCl_3$ give the -quinone, converted by Ac_2O–H_2SO_4 into 2 : 3 : 1 : 4 : 5-$(OMe)_2C_6H(OAc)_3$, and thence [as for (VII)] into 5-*hydroxy*-2 : 3-*dimethoxy*-1 : 4-*benzoquinone*, m.p. 125—126° (softens at 115°) (1 : 4 : 5-*trihydroxy*-2 : 3-*dimethoxybenzene* has m.p. 157—158°). The latter and cold NH_2Me–EtOH give the NH_2Me salt, m.p. 228—230° (decomp.), of 2-*methylamino*-5-*hydroxy*-3-*methoxy*-1 : 4-*benzoquinone* [0·1N-HCl gives the free *quinone*, m.p. 179° (decomp.)], hydrolysed by boiling 5N-H_2SO_4 to (III). 2 : 5-Dihydroxy-3-methoxy-1 : 4-benzoquinone and cold NH_2Me–EtOH give the $(NH_2Me)_2$ salt, m.p. 214° (decomp.). 3-(fumigatin) or 6-hydroxy-4-methoxy-2 : 5-toluquinone (acts in *o*-quinonoid form) gives 6-*methylamino*-3-*hydroxy*-4-*methoxy*-2 : 5-, m.p. 213—214°, or (?) 5 : 6-*bismethylamino*-4-*methoxy*-2 : 3-*toluquinone*, m.p. 228°, respectively, both being hydrolysed by boiling aq. H_2SO_4 to (VI). 3-Methoxy-2 : 5-toluquinone and Ac_2O–H_2SO_4 give 2 : 5 : 6-*triacetoxy*-3-*methoxytoluene*, m.p. 155°, and thence [as for (VII)] 6-*hydroxy*-3-*methoxy*-2 : 5-*toluquinone*, m.p. 155—156° [6-*acetate*, m.p. 109°; 3 : 6-dimethoxytoluquinone, new m.p. 112° (cf. A., 1938, II, 237); 2 : 5 : 6-*trihydroxy*-3-*methoxytoluene*, m.p. 102—103°], converted by NH_2Me–EtOH (warm) into 3-*methylamino*-6-*hydroxy*-2 : 5-*toluquinone*, m.p. 252—254° (fumes from 220°), which is hydrolysed by boiling 2N-NaOH to 3 : 6-dihydroxy-2 : 5-toluquinone. 3 : 4-Dimethoxy-2 : 5-toluquinone and Ac_2O–H_2SO_4, and then H_2SO_4–MeOH (in N_2), give 2 : 5 : 6-trihydroxy-3 : 4-dimethoxytoluene, oxidised (air) to 6-*hydroxy*-3 : 4-*dimethoxy*-2 : 5-*toluquinone*, m.p. 105° (2 : 5 : 6-*trihydroxy*-3 : 4-*dimethoxytoluene*, m.p. 110—111°), which affords 3-*methylamino*-6-*hydroxy*-4-*methoxy*-2 : 5-*toluquinone*, m.p. 212—213°, hydrolysed by 2N-H_2SO_4 to (VI). No pure compound is isolated from 4-hydroxy-6-methoxy-2 : 5-toluquinone. In the cases where 2 OMe are replaced by 2 NHMe, yields were ~100%, where 1 OMe is replaced, 50%, and with *p*-benzo- and tolu-quinone, 33%. A. T. P.

Nitrosation of phenols. XVI. *m*-Fluorophenol. A new red indophenol. H. H. Hodgson and D. E. Nicholson (J.C.S., 1939, 1405—1408).—*m*-C_6H_4F·OH (I) does not give a NO-compound (cf. A., 1930, 1281), but in 50% aq. AcOH with aq. $NaNO_2$ (or in aq. NaOH–$NaNO_2$ followed by dil. H_2SO_4) gives red-brown mm'-*difluoro*-o-*indophenol* (II), no. m.p., which gives no steam-volatile org. products when boiled with alkalis, $KMnO_4$, $K_3Fe(CN)_6$, or HNO_3, and is sol. in cold aq. Na_2CO_3, and in conc. H_2SO_4 to a red solution. Other colour reactions supporting structure (II) include the formation of a red product from 2 : 5 : 1-NO·C_6H_3(OMe)·OH (III) and (I), and reduction of (II) (Zn–AcOH) to a leuco-compound, converted (O_2 + HCl) into a blue solution (oxazine) turned red by $FeCl_3$ [cf. indophenols from (III) and *p*-cresol or *p*-C_6H_4Cl·OH]. The reaction of (I) and HNO_2 probably consists of slow 6-nitrosation (in this position because of powerful negative inductive effect of F on the 4-position), with some nitration [some 2 : 5 : 1-NO_2·C_6H_3F·OH is always formed with (II)], followed by rapid condensation of the product with (I) (cf. Schoutissen, A., 1922, i, 135). E. W. W.


(II.)

Maesaquinone, a pigment from the fruits of *Maesa japonica*. M. Hiramoto (Proc. Imp. Acad. Tokyo, 1939, **15**, 220—222).—Extraction of the fruits with EtOH gives the orange-red *maesaquinone* (I), $C_{26}H_{42}O_4$, m.p. 122°, which is optically inactive and free from OMe but contains 2 OH since it yields a liquid Me_2 *ether* which solidifies when cooled and a *diacetate*, m.p. 45°. (I) dissolves in dil. alkali to a violet solution from which cryst. alkali salts are obtained. Zn and HCl in EtOH decolorise (I) but the colour returns on exposure to air. Reductive acetylation (Zn dust–Ac_2O) of (I) gives *leucomaesaquinone tetra-acetate*, m.p. 101·5°, catalytically hydrogenated to its H_2-compound, m.p. 121°, thus establishing the presence of a double linking in the side-chain. Under similar conditions (I) absorbs 2 H_2 and the quinol thus produced becomes coloured on exposure to air with formation of *dihydromaesaquinone*, m.p. 134° (*diacetate*, m.p. 90°; Me_2 *ether*, m.p. 75°), oxidised by H_2O_2 and alkali or by $KMnO_4$ to heneicosanoic acid. The close relationship of *Maesa* and *Embelia* appears to justify the consideration of (I) as a higher homologue of embelin (II) and thus to be (*A*), whereby the position of the double linking in the side-chain remains obscure. Difficulties in interpreting the course of the oxidation of (II) are discussed. H. W.


(*A*.)

Synthesis of phthiocol. R. J. Anderson and M. M. Creighton (J. Biol. Chem., 1939, **130**, 429—430).—2-$C_{10}H_7Me$ is treated successively with CrO_3, aq. $Ca(OCl)_2$, and 25% (vol.) H_2SO_4 at 100°, thus giving 57% of phthiocol. R. S. C.

Syntheses of hydroxydroserone (the pigment of *Drosera whittakeri*), phthiocol (the pigment of

human tubercle bacillus), and naphthapurpurin ; studies of related compounds. C. Kuroda (Proc. Imp. Acad. Tokyo, 1939, **15**, 226—229).—Naphthazarin (I) and all naphthaquinones which do not contain OH in the β position of the quinone ring do not react with $NaHCO_3$ whereas naphthapurpurin (II) and naphthaquinones containing β-OH react with $NaHCO_3$ and with the Na salts of certain weak acids, *e.g.*, AcOH. This behaviour is useful in separating compounds of the two classes. Na_3 derivatives of 2 : 5 : 8-trihydroxy- (III), ? 2 : 5 : 8-trihydroxy-6- or -7-methyl- (IV), 2 : 5 : 8-trihydroxy-3-methyl- (V), and 2-hydroxy-1 : 4-naphthaquinone are described. (II) is obtained by heating a solution of (I) in 0·5% aq. NaOH at 100° in contact with air, using a mechanical stirrer, and is separated from any unchanged (I) by $NaHCO_3$. The H of the OH in β position of the quinone ring can be replaced by Me by MeOH–HCl; thus are obtained the 2-*Me ethers*, m.p. 178° and —, of (III) and (IV); (V) does not react. Rapanone similarly gives a *Na* compound and a Me_1 *ether*, m.p. 95°, whereas a Me_2 ether is produced with CH_2N_2. 5 : 8-Dihydroxy-2-methyl-1 : 4-naphthaquinone, obtained from maleic acid and toluquinol, or from citraconic acid and quinol, is transformed by air and 0·5% NaOH into (V) (hydroxydroserone), m.p. 198° (Ac derivative, m.p. 152°). 2-$C_{10}H_7Me$ is oxidised by CrO_3 to 2-methyl-1 : 4-naphthaquinone, which is converted by 0·5% NaOH into phthiocol, m.p. 173° (Ac_1 derivative, m.p. 106°), transformed by Zn, Ac_2O, and NaOAc into $C_{10}H_4Me(OAc)_3$, m.p. 158°. Maleic anhydride, 1 : 4 : 2 : 3-$(OH)_2C_6H_2(OMe)_2$, $AlCl_3$, and NaCl give 2 : 3 : 5 : 8-*tetrahydroxy*-1 : 4-*naphthaquinone*, m.p. 270°. Citraconic anhydride and 2 : 1 : 4-$C_6H_3Me(OH)_2$ yield ? 5 : 8-*dihydroxy*-2 : 6- and -2 : 7-*dimethyl*-1 : 4-*naphthaquinone*, m.p. 127° and 215°.

H. W.

Synthesis of quinones related to vitamins-K_1 and -K_2. L. F. Fieser, W. P. Campbell, and E. M. Fry (J. Amer. Chem. Soc., 1939, **61**, 2206—2218).—Partly a detailed account of work already reported (A., 1939, II, 432). The structural arguments are expanded and the biological results modified in view of unreliability of the rapid Ansbacher technique (-*K*-activity) for pure substances. The following are new. 4 : 2 : 1-*p*-$SO_3H{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_5(OH){\cdot}CH_2{\cdot}CH{:}CH_2$ and $Na_2S_2O_4$ etc. give 4-*amino*-2-*allyl*-1-*naphthol hydrochloride* (I). 2-Allyl-1 : 4-naphthaquinone (colour reactions described) with H_2O_2–KOH–aq. EtOH gives 2-hydroxy-1 : 4-naphthaquinone, this fission being the basis of the Dam colour reaction. H_2–PtO_2 reduces (I) in H_2O to a cryst. hydrochloride, converted by $FeCl_3$ into 2-n-*propyl*-1 : 4-*naphthaquinone*, m.p. 39—39·5°, which is obtained also from the allyl-quinone by hydrogenation in EtOH and subsequent Ag_2O oxidation. 2 : 3-Diallyl-1 : 4-naphthaquinone and KOH–EtOH–H_2O give 2-hydroxy-3-allyl-1 : 4-naphthaquinone. Quinol diallyl ether in boiling kerosene (N_2) gives 2 : 3-, m.p. 87—90°, and 2 : 5-*diallylquinol* (29%), m.p. 129·5—131°, oxidised (Ag_2O) to the *quinones*, an oil and m.p. 16°, respectively. *p*-$O{:}C_6H_4{:}O$ and $(CH_2{:}CMe)_2$ in C_6H_6 give a substance, m.p. 113—115°, isomerised by N-alkali in N_2 to 1 : 4-dihydroxy-6 : 7-dimethyl-5 : 8-dihydronaphthalene, m.p. 232—238°, which with CrO_3 affords first a *product*, $(C_{12}H_{11}O_2)_x$, m.p. 120—126° (decomp.), and then the 6 : 7-dimethyl-1 : 4-naphthaquinone. 6 : 7-Dimethyl-2 : 3-diallyl-5 : 8-dihydro-1 : 4-naphthaquinol, m.p. 156·5—159°, and CrO_3 at 60° similarly give a *compound*, $(C_{18}H_{19}O_2)_x$, m.p. 54—56° after sintering, and thence at 80—100° 6 : 7-dimethyl-2 : 3-diallyl-1 : 4-naphthaquinone. 4-*Amino*-3 : 7-*dimethyl*-2-*allyl*-1-*naphthol hydrochloride*, $+3H_2O$, cryst., and the absorption spectra of 2 : 3-dimethyl-, 2 : 6-dimethyl-3-allyl-, 6 : 7-dimethyl-2 : 3-diallyl-, and 2 : 3-diallyl-1 : 4-naphthaquinone are described.

R. S. C.

Constitution and synthesis of vitamin-K_1. S. B. Binkley, L. C. Cheney, W. F. Holcomb, R. W. McKee, S. A. Thayer, D. W. McCorquodale, and E. A. Doisy (J. Amer. Chem. Soc., 1939, **61**, 2558—2559).—ζκξ-Trimethylpentadecan-β-one, obtained (A., 1939, II, 433) from vitamin-K_1, is identified by mixed m.p. The quinone-acid (*loc. cit.*) thought to be 2-ethyl-, is shown to be 2-methyl-1 : 4-naphthaquinonyl-3-acetic acid (I) (*Me* ester, m.p. 121·5—122·5°). Dihydrovitamin-K_1 diacetate (II) and CrO_3 give 1 : 4-*diacetoxy*-2-*methyl*-3-*naphthylacetic acid*, m.p. 205° (*Me* ester, m.p. 127·5—128·5°, synthesised), further oxidised to (I). The Na_1 salt of 2 : 1 : 4-$C_{10}H_5Me(OH)_2$ and phytyl bromide in C_6H_6 give a quinol, oxidised by air to a quinone [purified by adsorption and distillation (high vac.)], reductive acetylation of which affords (II). -K_1 is thus 2-methyl-3-phytyl-1 : 4-naphthaquinone.

R. S. C.

(A) **Synthetic approach to vitamin-K_1.** L. F. Fieser, W. P. Campbell, E. M. Fry, and M. D. Gates, jun. (B) **Synthesis of 2-methyl-3-phytyl-1 : 4-naphthaquinone.** (C) **Identity of synthetic 2-methyl-3-phytyl-1 : 4-naphthaquinone and vitamin-K_1.** L. F. Fieser (J. Amer. Chem. Soc., 1939, **61**, 2559, 2559—2561, 2561).—(A) In presence of anhyd. $H_2C_2O_4$, 2 : 1 : 4-$C_{10}H_5Me(OH)_2$ condenses (in boiling dioxan) with β-unsaturated alcohols or dienes. With $(CH_2{:}CMe)_2$ it gives 1 : 4-*dihydroxy*-2-*methyl*-3-β*γ*-*dimethyl*-Δ^{β}-*butenylnaphthalene* (I) (29%) [*diacetate* (II), m.p. 119—120°], and a *substance* (13%), m.p. 73—73·5°, of tocopherol type. Oxidation of (I) gives 2-*methyl*-3-β*γ*-*dimethyl*-Δ^{β}-*butenyl*-1 : 4-*naphthaquinone*, m.p. 95—95·5°, reduced by Zn dust in C_5H_5N–Ac_2O to (II). $CHPh{:}CH{\cdot}CH_2{\cdot}OH$ similarly gives a quinol (*diacetate*, m.p. 167·5—168°) and a *quinone*, m.p. 127—127·5°. Phytol (as above or at 140°) affords probably the *tocopherol*. An *acetoxyquinone*, $C_{23}H_{28}O_4$, was obtained in the geranyl series by a similar reaction, followed by $Pb(OAc)_4$-oxidation. Addition of Grignard reagents to 2-alkyl-1 : 4-naphthaquinone oxides (prep. by H_2O_2 in Na_2CO_3–EtOH–H_2O) is not promising. 2 : 6-*Dimethyl*-1 : 4-*naphthaquinone oxide*, m.p. 97—98°, with $CH_2{:}CH{\cdot}CH_2{\cdot}MgBr$ or $MgBr_2$ in Et_2O gives a *bromohydrin*, m.p. 146—148° (derived *bromodimethylnaphthaquinone*, m.p. 114—114·7°).

(B) 2 : 1 : 4-$C_{10}H_5Me(OH)_2$ and phytol in dioxan with $H_2C_2O_4$ or $CCl_3{\cdot}CO_2H$ at 75° give a quinol, oxidised to 2-*methyl*-3-*phytyl*-1 : 4-*naphthaquinone* (III), an oil, which has the absorption spectrum and physiological activity of vitamin-K_1 and gives similar derivatives (quinol diacetate and *dibenzoate*, m.p. 85—86°). 2 : 6-Dimethyl-3-phytyl- and 2-methyl-3-

geranyl-1 : 4-naphthaquinone have been similarly prepared.

(c) Identity of (III) and -K_1 is established by direct comparison of chemical, physical, and biological properties. R. S. C.

Photo-reactions. IV. Photo-reaction between phenanthraquinone and aromatic aldehydes. A new passage from phenanthraquinone to fluorenone. A. Schönberg and R. Moubacher (J.C.S., 1939, 1430—1432; cf. A., 1936, 437).—Phenanthraquinone (I) and PhCHO or *p*-C_6H_4Cl·CHO in sunlight give 9 : 10-*dihydroxyphenanthrene α-hydroxybenzylidene* (II), m.p. 177—178°, or *α-hydroxy-p-chlorobenzylidene ether* (III), m.p. ~ 222° (decomp.), respectively (cf. Klinger, A., 1889, 405); *p*-OMe·C_6H_4·CHO reacts similarly. (II) is converted by HNO_3 (*d* 1·3) at 90° into (I). (II) and (III) are methylated (CH_2N_2) to the *α-OMe*-derivatives, m.p. 80° (IV) and 170°, respectively. The latter is hydrolysed (20% aq. NaOH at 40°) to *p*-C_6H_4Cl·CO_2Me and 9 : 10-dihydroxyphenanthrene [aëration gives (I)]; (IV) similarly gives (I). Pyrolysis of (II) at 200° in vac. affords fluorenone (probably via diphenyleneketen) and BzOH, with some (I) and PhCHO. Similar decomp. of α-stilbenediol diacetate (modified prep.) at 165° gives Bz_2. A. T. P.

Derivatives of 1 : 2-benzanthraquinone-4′-sulphonic acid. A. Sempronj (Gazzetta, 1939, **69**, 448—453).—Sulphonation (method : Heller *et al.*, A., 1908, i, 994) of 1 : 2-benzanthraquinone gives the 4′-sulphonic acid; the K salt (I), with KOH at 260° gives BzOH and 5 : 2-OH·$C_{10}H_6$·CO_2H. The 4′-sulphonyl chloride, m.p. 263°, at 275° yields 4′-chloro-1 : 2-benzanthraquinone (cf. Johnson *et al.*, A., 1932, 1030), also obtained from (I) and $NaClO_3$ in conc. HCl at the b.p. Reduction (Zn–aq. NH_3) of (I) gives 1 : 2-benzanthracene-4′-sulphonic acid (II) (*chloride*, m.p. 193°; *Et* ester, m.p. 157°), which with KOH at 300° yields 4′-*hydroxy*-1 : 2-*benzanthracene*, m.p. 230° (*Me ether*, m.p. 163°). The corresponding 4′-*acetoxy*-derivative, m.p. 193—194°, is oxidised ($K_2Cr_2O_7$–AcOH) to 4′-*acetoxy*-1 : 2-*benzanthraquinone*, m.p. 202—203°, hydrolysed to the 4′-*OH*-compound, m.p. 224—225°. The *K* salt of (II) distilled with KCN gives 1 : 2-benzanthracene. E. W. W.

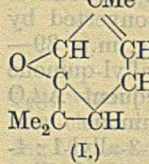
1-Nitrosomenthoneoxime and its decomposition. J. C. Earl, D. Johnson, and J. G. McKean (J. Proc. Roy. Soc. New South Wales, 1939, **72**, 109—112).—Piperitone hydroxylamino-oxime is oxidised by yellow HgO in boiling $CHCl_3$ to 1-nitrosomenthoneoxime, m.p. 124—125° to a blue liquid; this passes when kept or heated into N_2O and piperitoneoxime. H. W.

Addition of oxygen to double linkings. S. Tanaka (Mem. Coll. Sci. Kyoto, 1939, **22**, A, 97—197).—Δ^3-*p*-Menthene (I) and BzO_2H or AcO_2H in $CHCl_3$ or Et_2O give *menthene* 3 : 4-*oxide* (II), b.p. 74—75°/14 mm., probably by decomp. of an intermediate unstable ester. (II) and 10% aq. H_2SO_4 at 0° give the 3 : 4-*glycol*, m.p. 75—76°, converted by 10% aq. H_2SO_4 at 100° into *i*-menthone, also obtained by passing (II) over Al_2O_3 at 250°. (I) and HOCl or HOI give the chloro- or iodo-hydrin (III), respectively, converted by KOH into (II), also obtained from (III) and AgOBz or AgOAc in 80% EtOH at 100°. Stilbene and AcO_2H give the oxide; in $CHCl_3$, 94% of α- and 6% of β-oxide in 19·5 hr.; in Et_2O, 100% of α in 200 hr. The mechanism of oxidation of PhCHO and MeCHO, by BzO_2H or AcO_2H, involving formation of intermediate additive compound, is discussed. Oxidation velocities of (I), βζ-dimethyl-Δ^ζ-octene, styrene, heptaldehyde, and PhCHO with AcO_2H are compared; the speed with C:C is > with C:O derivatives. The biological connexion of the results is discussed. A. T. P.

Catalytic action of Japanese acid clay on terpene compounds. VI. Hydration of limonene with acetic acid. T. Kuwata (J. Soc. Chem. Ind. Japan, 1939, **42**, 247B).—In presence of activated Japanese acid clay, an equimol. mixture of *d*-limonene (I) and AcOH gives 35—40% of *d*-α-terpinyl acetate. When reaction is effected at 15—25° the proportion of polymerised substances is small, most of the unused (I) being recovered unchanged. H. W.

Phellandrene nitrosites. II. α- and β-Nitrosite of *d*-α-phellandrene. P. A. Berry, A. K. Macbeth, and T. B. Swanson (J.C.S., 1939, 1418—1421).—d-α-*Phellandrene* α-, m.p. 119°, $[\alpha]_D^{20}$ −133·8° in $CHCl_3$, and β-*nitrosite*, m.p. 100°, $[\alpha]_D^{20}$ +198·3° in $CHCl_3$, have been prepared (cf. A., 1939, II, 220). The mutarotations of the compounds and transmutation of the β- into the α-nitrosite have been examined. F. R. S.

***l*-Δ^3-Carene 5 : 6-epoxide, a constituent of the oil from *Zieria Smithii*.** A. R. Penfold, G. R. Ramage, and J. L. Simonsen (J.C.S., 1939, 1496—1504).—From the oil there have been isolated linalool (*xenylurethane*, m.p. 83—85°), an alcohol, $C_{10}H_{14}O$ (3 : 5-*dinitrobenzoate*, m.p. 119°), and l-Δ^3-*carene* 5 : 6-*epoxide* (I), $C_{10}H_{14}O$, b.p. 83—85°/14 mm., $[\alpha]_{5461}$ −88°. Ozonolysis of (I) gives *cis*-homocaronic acid (*di*-p-*phenacyl* ester, m.p. 147—149°), with some $COMe_2$, CH_2O, and *trans*-caronic acid (?). With hot aq. KOH, (I) affords geranic acid, but with cold EtOH–KOH, a mixture is obtained, from which can be separated an *acid*, $C_{10}H_{16}O_2$, m.p. 83° (an active Δ^2-*cyclo*geranic acid ?). The action of HCl and HBr on (I) yields respectively dl-1 : 8-*dichloro*-, decomp. 72°, and -*dibromo*-p-*menthan*-3-*one* (II), decomp. 74°, which is hydrogenated (Pd–C) to *dl*-menthone (2 : 4-*dinitrophenylhydrazone*, m.p. 141—142°). The foregoing reactions are in accord with the suggested structure.



(I.)

When (I) is heated at 160—165°, an oil is formed which gives a 2 : 4-*dinitrophenylhydrazone*, m.p. 218—220°, and a mixture of semicarbazones, from which an α-, decomp. 221—222°, and β-*semicarbazone*, decomp. 183—185°, can be separated. Certain observations do not eliminate the possibility that (I) is a dicyclic ketone with a somewhat inert CO. Semicarbazide acetate and (I) in the cold for several days afford a *semicarbazone*, m.p. 192°, $[\alpha]_{546}$, −95° in C_5H_5N, derived from $C_{10}H_{14}O$, but not homogeneous; it is hydrogenated to a mixture from which can be separated a *semicarbazone*, m.p. 212°, and is hydro-

lysed [steam-*o*-$C_6H_4(CO_2H)_2$] to a mixture containing a fraction, $C_7H_{10}O$, b.p. 87°/15 mm., $[\alpha]_{5461}$ +26·3° (2 : 4-*dinitrophenylhydrazone*, m.p. 176°, not identical with the corresponding *derivative* from 2-methyl-Δ^2-*cyclo*hexenone, m.p. 202—203°, or the 3-Me compound), and a fraction, b.p. 127—130°/13 mm., $[\alpha]_{5461}$ +6·52° (a mixture containing $\Delta^{1:4(8)}$-*p*-menthadien-3-one). These results do not agree with a ketonic structure for (I). Alcoholic 2 : 4-dinitrophenylhydrazine sulphate with (I) gives an α-, m.p. 192—193°, and β-2 : 4-*dinitrophenylhydrazone*, $C_{18}H_{24}O_5N_4$, m.p. 165—166°, whilst the aq. reagent affords a 2 : 4-*dinitrophenylhydrazone*, $C_{16}H_{20}O_5N_4$, m.p. 145—147°. NaOAc–AcOH and (II) give $\Delta^{1:4(8)}$-p-*menthadien*-3-*one*, b.p. 120—122°/14 mm., $[\alpha]_{5461}$ −0·1° (2 : 4-*dinitrophenylhydrazone*, α-form, m.p. 187°, β-form, m.p. 125—127°), which on ozonolysis affords $COMe_2$, lævulic acid, an oil (*semicarbazone*, decomp. 232—233°), and β-*methyl*-Δ^{α}-*butene*-αδ-*dicarboxylic acid*, m.p. 140—141°, the latter reduced to β-methyladipic acid (*di*-p-*phenylphenacyl ester*, m.p. 124—125°). F. R. S.

Thujone series. III. Sabina ketone. A. G. Short and J. Read (J.C.S., 1939, 1415—1418).—Oxidation of sabinene with $KMnO_4$ gives crude *l*-sabina ketone (I), which is reduced (Na–EtOH) to a mixture of ketols, b.p. 96—101°/15 mm., α_D^{15} +65·00° ($l = 1$) and b.p. 126—132°/0·5 mm., α_D^{15} +50·50° ($l = 1$). The former fraction and *p*-NO_2·C_6H_4·COCl afford d-α-*sabinaketyl* p-*nitrobenzoate*, m.p. 89·5°, $[\alpha]_D^{18}$ +94·5° in $CHCl_3$, hydrolysed to *d*-α-sabina ketol, b.p. 100°/16 mm., α_D^{15} +88·84° ($l = 1$), $[\alpha]_D^{15}$ +90·6° in EtOH. Oxidation (CrO_3) of this ketol yields pure (I), b.p. 97·5°/17 mm., $[\alpha]_D^{15}$ −34·2° in EtOH (2 : 4-*dinitrophenylhydrazone*, m.p. 124·5°, $[\alpha]_D^{15}$ +135·2° in $CHCl_3$). Amination (HCO_2NH_4) of crude (I) gives a ketylamine, b.p. 63—64°/19·5 mm., α_D^{18} +43·8° ($l = 1$), probably a mixture, and *disabinaketylamine*, b.p. 166—167°/9·5 mm. $[\alpha]_D^{19}$ +60·6° in $CHCl_3$; from the mixture a p-*nitrobenzoylsabinaketylamine*, m.p. 141°, $[\alpha]_D^{18}$ +84·0° in $CHCl_3$, has been prepared. Some of the structural and stereochemical relationships of (I) are discussed. F. R. S.

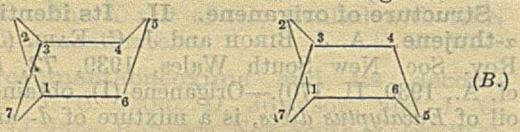
Terpenoid amines. I. Isomeric thujylamines. H. L. Dickison and A. W. Ingersoll (J. Amer. Chem. Soc., 1939, **61**, 2477—2482).—Thujylamines are named by reference (α, β) to the thujone to which they are related and by assigning the prefix *iso* to that member of a pair having the higher numerical α. The most characteristic salts are marked * below. When impure α-thujone (from *Thuja occidentalis*), α_D^{25} −18°, and HCO_2NH_4 are heated with separation of the aq. $(NH_4)_2CO_3$ formed and are then heated at 175—185°, there are formed (+)-β- (I), b.p. 199·6°/750 mm., 77·0°/12 mm., α +27·8° (homogeneous), $[\alpha]$ +51·27° in EtOH, +35·31° in C_6H_6 [*Bz* derivative, m.p. 73—75°, $[\alpha]$ +91·44° in MeOH; *sulphate**, m.p. 242° (decomp.), $[\alpha]$ +42·77°; p-*toluenesulphonate**, m.p. 194·7°, $[\alpha]$ +27·91°; *H oxalate*, $+H_2O$, $[\alpha]$ +36·10° (anhyd.); *nitrate*, $+0·5H_2O$, m.p. 105°, $[\alpha]$ +35·97°; d-, $+2H_2O$, m.p. 80—113°, $[\alpha]$ +82·59°, and l-*mandelate*, $+H_2O$, m.p. 120—128°, $[\alpha]$ −29·52°], (+)-iso-β- (II), b.p. 193·4°/737 mm., 76·8°/11 mm., α +94·94° (homogeneous), $[\alpha]$ +107·9° in EtOH, +108·4° in C_6H_6 [*Bz* derivative, m.p. 131·5°, $[\alpha]$ +87·74° in MeOH, +90·5° in $CHCl_3$; *H sulphate*, $+H_2O$, m.p. 153° (decomp.), $[\alpha]$ +55·25°; p-*toluenesulphonate*, m.p. 170—171°, $[\alpha]$ +41·6°; *H oxalate**, $+H_2O$, m.p. 167°, $[\alpha]$ +62·50° (anhyd.); *nitrate**, m.p. 176·9°, $[\alpha]$ +70·48°; ?-*malate*, m.p. 160°, $[\alpha]$ +49·84°; *perchlorate*, m.p. 168°, $[\alpha]$ +55·47°], (−)-α- (II), b.p. 196·7°/756 mm., 77·6°/12 mm., α −14·15° (homogeneous), $[\alpha]$ −1·41° in EtOH, −13·25° in C_6H_6 [*Bz* derivative, m.p. 94·5°, $[\alpha]$ −12·16° in C_6H_6; *sulphate**, $+4H_2O$, m.p. 243° (decomp.), $[\alpha]$ +3·47° (anhyd.); p-*toluenesulphonate*, a glass; *oxalate**, m.p. 200—201°; *nitrate*, m.p. 150°, $[\alpha]$ +2·60°; *H* dl-*malate*, m.p. 148·5°, $[\alpha]$ +1·73°; d-*mandelate*, $+H_2O$, m.p. 99·5°, $[\alpha]$ +65·23°], (−)-iso-α-*thujylamine* (IV), b.p. 202·2°/748 mm., 81·1°/12 mm., α_D^{27} −22·07° (homogeneous), $[\alpha]_D^{26}$ −23·29° in EtOH, −26·92° in C_6H_6 [*Bz*, a glass, and p-*nitrobenzoyl* derivative, m.p. 146·5°, $[\alpha]$ −51·25° in $CHCl_3$; *sulphate**, $+H_2O$, m.p. 263° (decomp.), $[\alpha]$ −16·66° (anhyd.); p-*toluenesulphonate*, m.p. 198·6°, $[\alpha]$ −10·40°; *oxalate*, m.p. 235° (decomp.), $[\alpha]$ −12·37°; *nitrate*, m.p. 159—160°, $[\alpha]$ −15·18°; *H* l-*malate*, m.p. 186—187°, $[\alpha]$ −14·73°], and (+)-*fenchylamine* (from the fenchone present in the ketone), b.p. 195·3°/730 mm., 73·4°/11·5 mm., α_D^{27} +22·19° (homogeneous), $[\alpha]_D^{26}$ +25·89° in EtOH, +19·11° in C_6H_6 [*Bz* derivative, m.p. 90·2°, $[\alpha]$ +24·43° in MeOH; *sulphate*; p-*toluenesulphonate*, $+H_2O$, m.p. 188—189°, $[\alpha]$ +2·60° (anhyd.); *H oxalate*, m.p. 165°, $[\alpha]$ +3·11°; *nitrate*, $+0·5H_2O$, m.p. 190° (decomp.), $[\alpha]$ +3·41° (anhyd.); *H* l-*malate**, m.p. 191—193°, $[\alpha]$ 0; d-*mandelate**, m.p. 190·3°, $[\alpha]$ +60·8°]. β-Thujoneoxime, m.p. 53° $[\alpha]$ +105·3° in MeOH, and Na–EtOH give 83·7% of (II), 6% of (I), 4% of (IV), and a trace of (III) [cf. Short *et al.*, A., 1939, II, 79; *d-iso*thujylamine = (II); their *l*-thujylamine = (IV)]. *dl*-Mandelic acid is readily resolved by (I), (III), or (V), and *dl*-malic acid by (IV) or (V). Unless otherwise stated, $[\alpha]$ are $[\alpha]_D^{25}$ in H_2O (for the salts, including any H_2O of crystallisation). R. S. C.

Structure of origanene. II. Its identity with α-thujene. A. J. Birch and J. C. Earl (J. Proc. Roy. Soc. New South Wales, 1939, **72**, 55—61; cf. A., 1939, II, 170).—Origanene (I), obtained from oil of *Eucalyptus dives*, is a mixture of *d*- and *dl*-α-thujene. The latter gives a characteristic nitrosochloride apparently identical with that obtained from (I). Oxidation of (I) by $KMnO_4$ in $COMe_2$ yields the cryst. α-thujaketonic acid (II), m.p. 75—76°, $[\alpha]_D$ −200° in H_2O, and a liquid acid, probably mainly *dl*-α-thujaketonic acid (III), which yields a semicarbazone, m.p. 196—197°; a little *d*-pinonic acid appears to be present. Distillation of (II) or (III) under reduced pressure affords β-thujaketonic acid, identified by comparison with an authentic specimen and by oxidation to β-tanacetogendicarboxylic acid. The identity of (I) with α-thujene is confirmed by the conversion of the dibromide into *p*-cymene by C_5H_5N and by the production of terpinene dihydrochloride by the action of HCl in AcOH. H. W.

Oximino-α-thujene. A. J. Birch (J. Proc. Roy. Soc. New South Wales, 1939, **72**, 106—108).—α-Thujene nitrosochloride is transformed by hot aq. C_5H_5N into *oximino-α-thujene* (I), which could not be cryst. or distilled. This is transformed into 1 : 3 : 2-$C_6H_3MePr^{\beta}$·NH·OH (II) (*hydrochloride*, m.p. 149°) by the short action of cold, conc. HCl. (I) or (II) is converted by hot conc. HCl into 1 : 3 : 5 : 2-$C_6H_2MePr^{\beta}Cl$·NH_2 (III) and by 50% H_2SO_4 into *p*-aminothymol. This can be obtained exactly similarly from carvoxime but it has not been found possible to prepare (III) by the action of conc. HCl on the latter since hydrolysis occurs with ultimate formation of carvacrol. H. W.

Action of acetic acid on camphene in the presence of boric acid or boric trioxide. Action of acetic acid on camphene in the presence of boric acid. M. Imoto (J. Soc. Chem. Ind. Japan, 1939, **42**, 230—232B; cf. A., 1938, II, 416).—When heated at 110—120° for about 46 hr. camphene (I) and glacial AcOH give only 12·4% of ester. (I), AcOH, and H_3BO_3 afford 1·6% of ester in 7 hr. at 95—98° and 3·4% in 8 hr. at 110—120°; addition of H_2O to the mixture has little effect. (I), AcOH, and B_2O_3 give little ester at room temp. or at 50—60°; the yield is 32·0% when the reactant ratio is 1·5 : 2 : 0·67 (32 hr.) and 20·7% with 1 : 1·5 : 0·1 (24 hr.); the ester produced is *iso*bornyl acetate (II), b.p. 95°/15 mm., $[\alpha]_D^{34}$ −7·25°. Between (I), Ac_2O, and H_3BO_3 the reactions are: $3Ac_2O + H_3BO_3 = 3AcOH + B(OAc)_3$ and $3C_{10}H_{16} + 3AcOH = 3C_{10}H_{17}$·OAc; the results obtained are better than those with α-pinene (*loc. cit.*). In both cases abrupt heating causes an explosive reaction so that it is necessary to drop the Ac_2O into the heated mixture of (I) and H_3BO_3. The max. recorded yield of ester is 65·1%. The existence of an equilibrium (I) + $Ac_2O \rightleftharpoons$ (II) is established. H. W.

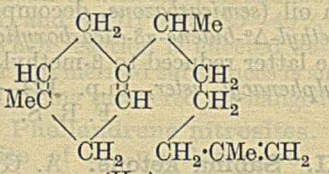
Stereochemistry of pinane and its derivatives. K. Ganapathi (J. Indian Inst. Sci., 1939, **22**, A, 155—169).—The norpinane (I) ring system can exist in the strainless forms (*A*) and (*B*). On the basis of these formulæ detailed consideration is given to the



phenomena of isomerism between (I) and nopinane, among compounds substituted at $C_{(4)}$ or $C_{(5)}$, those substituted at two of the atoms 4, 5, or 6, those substituted at $C_{(2)}$ or $C_{(3)}$, and those with double linkings. The bearing of the space configuration on the stability of pinane and its derivatives, the isomerisation of β- to α-pinene, and on ring fission and isomerisation is discussed. H. W.

Constituents of some Indian essential oils. XXVI. Structures of *l*-α- and -β-curcumenes. F. D. Carter, F. C. Copp, B. S. Rao, J. L. Simonsen, and (in part) K. S. Subramaniam (J.C.S., 1939, 1504—1509).—*l*-α-Curcurmene (I) (cf. A., 1928, 1253) with Se gives cadalene together with an azulene. *l-Dihydro-α-curcumenylamine*, b.p. 153—154°/14 mm. (*Ac* derivative, m.p. 109°), is converted by AcOH–$NaNO_2$ into (I). Oxidation of (I) with MnO_2 affords a mixture containing *p*-C_6H_4Me·CO_2H, *p*-$C_6H_4(CO_2H)_2$, and 1 : 2 : 4-$C_6H_3(CO_2H)_3$, and with O_3 yields $COMe_2$, CH_2O, *l*-δ-p-*tolylamyl Me ketone*, b.p. 154°/15 mm., $[\alpha]_{5461}$ −30·8° (*semicarbazone*, m.p. 138—139°), γ-*p*-tolylvaleraldehyde (2 : 4-*dinitrophenylhydrazone*, m.p. 94—95°), and *l*-γ-p-*tolyl*-n-*valeric acid*, b.p. 180°/17 mm., $[\alpha]_{5461}$ −13·82° in EtOH (p-*phenylphenacyl* ester, m.p. 73—74°). These results indicate that (I) is a mixture of *l*-ζ-p-*tolyl*-β-*methyl*-Δ^{β}-*heptene* and -Δ^{α}-*heptene*, the Δ^{β}-compound predominating in the natural hydrocarbon, with approx. equal quantities of Δ^{α}- and Δ^{β}-compounds in the hydrocarbon liberated from the hydrochloride.

l-β-Curcumene (II) has been shown to be a mixture of two hydrocarbons (II*a* and *b*). Ozonolysis of (II)



gives CH_2O, $COMe_2$, a diketone, $C_9H_{16}O_2$ (*di*-2 : 4-*dinitrophenylhydrazone*, m.p. 178—180°), together with small amounts of lævulic acid and the degradation products of (I). Oxidation of (II) with SeO_2 affords *l*-β-*curcumenal*, $C_{15}H_{22}O$, b.p. 149—150°/3 mm., $[\alpha]_{5461}$ −74·1° (*semicarbazone*, m.p. 159°, $[\alpha]_D$ −77·8° in $CHCl_3$; 2 : 4-*dinitrophenylhydrazone*, m.p. 139°, $[\alpha]_D$ −145·4° in $CHCl_3$; *nitroguanylhydrazone*, m.p. 151°, $[\alpha]_D$ −86·1° in $CHCl_3$; *oxime*, b.p. 170—175°/4 mm., $[\alpha]_D$ −67°; β-*curcumenonitrile*, b.p. 178—182°/17 mm., and its *anilide*, m.p. 87°; *Me* ester, b.p. ~180—182°/16 mm., of β-curcumenylic acid), and *l*-β-curcumenol, b.p. 175°/17 mm., $[\alpha]_D$ −39° (p-*xenylurethane*, m.p. 79—80°). Ozonolysis of a mixture of (I) and (II) gives a keto-acid, oxidised (NaOBr) to α-methylglutaric acid.

From the lower-boiling hydrocarbon fraction of the oil from *C. aromatica*, there has also been isolated a hydrocarbon which contains a conjugated system, and from the higher-boiling fractions a black picrate, m.p. 120° (*s*-guajazulene picrate ?). F. R. S.

Lignin and related compounds. XLI. Detection, isolation, and determination of the syringyl radical in plant products. M. J. Hunter and H. Hibbert. **XLII. Isolation of a bisulphite-soluble "extracted lignin."** W. H. Steeves and H. Hibbert. **XLIII. Absence of the piperonyl group in the lignin structure.** M. J. Hunter and H. Hibbert. **XLIV. Ethanolysis of maple wood. Separation and identification of the water-soluble aldehyde constituents.** J. J. Pyle, L. Brickman, and H. Hibbert (J. Amer. Chem. Soc., 1939, **61**, 2190—2194, 2194—2195, 2196—2198, 2198—2203; cf. A., 1939, II, 382).—XLI. Syringyl, admixed with guaiacyl, derivatives containing CO *p*-to the OH are determined by pptg. the K salt of the former by KOAc in EtOH. Other less effective reagents are KOAc–EtOH–Et_2O > NH_3–EtOH > NH_3–Et_2O > KOH–EtOH. NH_3 in dry Et_2O ppts. salts of

both series. The phenolic fraction obtained by ethanolysis of maple wood is thus shown to contain 53% of 4 : 3 : 5 : 1-$OH{\cdot}C_6H_2(OMe)_2{\cdot}CO{\cdot}CHMe{\cdot}OEt$. Clemmensen reduction of propiosyringone gives 26·6% of 1 : 3 : 5 : 4-$C_6H_2Pr^a(OMe)_2{\cdot}OH$. 4 : 3 : 5 : 1-$OH{\cdot}C_6H_2(OMe)_2{\cdot}CO{\cdot}CHMe{\cdot}OAc$ and KOH–MeOH give 98% of a K salt, converted by AcOH into *α-hydroxypropiosyringone*, m.p. 126—127°.

XLII. Red oak meal is extracted successively with EtOH–C_6H_6, H_2O, 5% NaOH–N_2, H_2O, 1% AcOH, H_2O, and MeOH, and acetylated with Ac_2O–AcOH–H_2SO_4 at 15—30°. The product is purified to OMe 11·1% by fractional pptn. and then hydrolysed by NaOH in aq. $COMe_2$ to give a lignin (OMe 20·8%), which is sol. in aq. $NaHSO_3$ and is partly reacetylated by Ac_2O–C_5H_5N. Fructose and hydroxymethylfurfuraldehyde give cryst. acetylated products, which produce no lignin when hydrolysed.

XLIII. The CH_2O-producing component of maple and sassafras lignin is almost entirely removed by heating with 95% HCO_2H and largely so by hot 2% HCl–EtOH, whereas piperonal is only slightly affected. It is concluded that lignin contains no CH_2O_2:C_6H_3 and that the CH_2O is derived from unsaturated side-chains of aromatic compounds.

XLIV. The H_2O-sol. aldehyde fraction obtained by ethanolysis of maple wood contains ~ equal amounts of *syringoylacetaldehyde* (I), m.p. 74—74·5°, 4 : 3 : 5 : 1-$OH{\cdot}C_6H_2(OMe)_2{\cdot}CHO$ (II), 4 : 3 : 1-$OH{\cdot}C_6H_3(OMe){\cdot}CHO$, and 4 : 3 : 1-$OH{\cdot}C_6H_3(OMe){\cdot}CO{\cdot}CH_2{\cdot}CHO$. The structure of (I) follows from failure of the CHI_3 reaction, reduction of ammoniacal $AgNO_3$, formation of a *disemicarbazone*, m.p. 239°, and, rapidly in 3N-HCl, of a *monosemicarbazone*, m.p. 210—210·5°, oxidation by H_2O_2 to syringic acid (III), and cleavage by alkali to (III) and by aq. $NaHSO_3$ at 110° in N_2 containing O_2 to 4 : 3 : 5 : 1-$OH{\cdot}C_6H_2(OMe)_2{\cdot}COMe$ [with, in one experiment, some (III)] [formed by oxidation to $OH{\cdot}C_6H_2(OMe)_2{\cdot}CO{\cdot}CH_2{\cdot}CO_2H$ and subsequent fission]. Condensation of (I) with polyhydric phenols to give anthocyanidins and flavones is discussed.

R. S. C.

Tea tannin and its fermentation products.—See A., 1939, III, 951.

Conversion of *l*- into a *d*-abietic acid. T. Hasselstrom and J. D. McPherson (J. Amer. Chem. Soc., 1939, **61**, 2247).—When gum rosin is boiled in AcOH, saturated with HCl at 0°, and kept at room temp. for 2 weeks, the same dichlorodihydroabietic acid (I), m.p. 190·5° (decomp.; corr.), $[\alpha]_D$ −10° to −8·1° in EtOH, is obtained as from pure abietic acid. With boiling NaOEt–EtOH, (I) gives a d-*abietic acid*, m.p. 142—143° (corr.), $[\alpha]_D$ +20° in EtOH [$NH(C_5H_{11}\text{-}n)_2$ salt, m.p. 119—119·5° (corr.), $[\alpha]_D$ +3·3° in EtOH], with a small amount of (?) dihydroabietic acid.

R. S. C.

Hydroxy- and amino-derivatives of dehydroabietic acid and dehydroabietinol. L. F. Fieser and W. P. Campbell (J. Amer. Chem. Soc., 1939, **61**, 2528—2534).—Prep. of dehydroabietic acid is modified to give a 43% yield from crude Na abietate. Me 6-acetyldehydroabietate (I) is accompanied in the Friedel–Crafts product by a 1 : 1 mol. *compound*, m.p. 119·5—120°, of (I) and the 8-*Ac* ester (II), dimorphic, m.p. 137° or 153—153·5°, $[\alpha]$ +40°, best resolved by converting (I) into its *oxime* (III), m.p. 121·5—122·5°, $[\alpha]$ +76°. (II) gives no oxime. The structure of (II) is proved by HNO_3-oxidation to 1 : 2 : 3 : 4-$C_6H_2(CO_2H)_4$. With Ac_2O and HCl in warm AcOH, (III) gives a mixture, which by partial hydrolysis etc. yields *Me* 6-*aminodehydroabietate* (IV) (62%), m.p. 137—137·5°, $[\alpha]$ +81° [*hydrochloride*, m.p. (+H_2O) 250—260° (decomp.; sinters at ~160°) or (anhyd.) >290° (vac.)], 6-*aminodehydroabietic acid* (24%), m.p. 214—215° (vac.), $[\alpha]$ +82° (*hydrochloride*, m.p. >295°; *Ac* derivative, m.p. 255—256°, $[\alpha]$ +80°), and 6-*carboxylmethylamidodehydroabietic acid* (6%), m.p. 254—255°, $[\alpha]$ +82°, hydrolysed by boiling KOH–Bu^{a}OH to 6-*carboxydehydroabietic acid*, +H_2O, m.p. >280°, $[\alpha]$ +71° in 80% EtOH. (IV) gives a Ac_2, m.p. 150—151°, $[\alpha]$ +75°, and Ac_1 derivative, cryst., $[\alpha]$ +79°. A diazo-reaction converts (IV) into *Me* 6-*hydroxydehydroabietate* (68%) (V), m.p. 157—157·5°, $[\alpha]$ +71°. H_2–Cu chromite reduces Me dehydroabietate in dioxan at 250°/87—71 atm. to *dehydroabietinol*, b.p. 177°/1 mm., $[\alpha]$ +53° (3 : 5-*dinitrobenzoate*, m.p. 123—124°), and (IV) to 6-*aminodehydroabietinol* (VI), m.p. 139·5—140°, $[\alpha]$ +72° (*hydrochloride*, cryst., $[\alpha]$ +63°). Ag_2O–MeI, followed by NH_4I, converts (VI) into a methiodide, m.p. 152—152·5° (decomp.), which at 140°/1—2 mm. yields 6-*dimethylaminodehydroabietinol Me ether* [*hydrochloride*, m.p. 226—227° (decomp.; vac.), $[\alpha]$ +78°]. 6-*Hydroxydehydroabietinol*, m.p. 180—181·5°, $[\alpha]$ +72°, is œstrogenic; it is obtained from (VI) by a diazo-reaction, but not by hydrogenation of (V). M.p. are corr. $[\alpha]$ are $[\alpha]_D^{25}$ in EtOH, unless otherwise stated.

R. S. C.

Saponins and sapogenins. XI. Neotigogenin, a steroid sapogenin. L. H. Goodson and C. R. Noller. **XII. Product of direct oxidation of echinocystic acid with dichromic acid.** R. N. Jones, D. Todd, and C. R. Noller (J. Amer. Chem. Soc., 1939, **21**, 2420—2421, 2421—2423).—XI. From *Chlorogalum pomeridianum* are isolated small amounts of *neotigogenin* (I), +*x*EtOH, m.p. 202—203°, $C_{27}H_{44}O_3$, $[\alpha]_D^{26}$ −64·9° in $CHCl_3$, as *acetate*, m.p. 174—176°, $[\alpha]_D^{25}$ −73·4° in $CHCl_3$. CrO_3 oxidises (I) to *neotigogenone*, $C_{27}H_{42}O_3$, m.p. 211—214°, $[\alpha]_D^{25}$ −60·6° in $CHCl_3$ [*oxime*, m.p. 231—232° (decomp.)]. HCl–EtOH converts tigogenin into a product, m.p. 189·5—194·5°, which probably contains no (I).

XII. Norechinocystenone and norechinocystenedione (II) (A., 1939, II, 333) show weak absorption max. at 2900—3000 (due to CO) and 2450—2500 A. CO·C:C is thus absent. *iso*Norechinocystenedione (III) shows no CO absorption in Et_2O and only an inflexion in EtOH, although the CO max. (2930 A.) is developed by NaOH in moist EtOH. Hot KOH–EtOH converts (III) into (II). *Norechinocystenone-oxime*, m.p. 253—253·5°, *norechinocystenedionedioxime*, m.p. 248—249°, and "iso*norechinocystenedionemono-oxime*," m.p. 254—257° (preheated at 240°), are prepared. A cyclic semiacetal structure is suggested for (III).

R. S. C.

Derivatives of tetronic acid. F. Reuter and R. B. Welch (J. Proc. Roy. Soc. New South Wales,

1939, 72, 120—128).—The yield of tetronic acid (I) obtained by the reduction of α-bromotetronic acid in presence of Pd–C can be increased to 48% by addition of solid $Ba(OH)_2$ to the reaction mixture. In the prep. of (I) $Ba(OH)_2$ is superior to NaOH for the hydrolysis of α-carbethoxytetronic acid (II). The product obtained by heating $CH_2Br{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$ (III) at 120°/25—30 mm. is a mixture of (I) with a bromotetronic acid. In a variety of solvents (III) and NaOEt afford Et_2 2 : 5-diketo*cyclo*hexane-1 : 4-dicarboxylate. $OEt{\cdot}CHMe{\cdot}COCl$ and $CHNa(CO_2Et)_2$ condense to *r*-α-carbethoxy-γ-methyltetronic acid, which could not be resolved into its optical antipodes by strychnine in EtOH. (II) and $NHPh{\cdot}NH_2$ afford the *phenylhydrazone*, $C_{13}H_{14}O_4N_2$, m.p. 157° (decomp.). Treatment of Et_2 acetosuccinate with Br in $CHCl_3$ followed by removal of solvent and HBr in a vac. and prolonged heating of the residue at 95—100°/20—30 mm. gives α-carbethoxymethyltetronic acid, m.p. 93—94°, in considerably improved yield; it is hydrolysed to *α-carboxymethyltetronic acid*, m.p. 173°. Similarly Et_2 α-bromoacetylglutarate is cyclised to *α-β′-carbethoxyethyltetronic acid*, m.p. 78—79°, hydrolysed to *α-β′-carboxyethyltetronic acid*, m.p. 175°. Successive bromination and cyclisation of Et_2 propionylsuccinate gives non-cryst. *γ-methyl-α-carbethoxymethyltetronic acid*, b.p. 172°/0·5 mm. (*γ-methyl-α-carboxymethyltetronic acid*, m.p. 164°). Et_2 α-propionylglutarate is converted into the very hygroscopic *γ-methyl-α-β′-carboxyethyltetronic acid*, b.p. 190°/0·45 mm. (corresponding *acid*, m.p. 134°). (II) is transformed by successive treatments with Na and AcCl in dioxan into *α-carbethoxy-α-acetyltetronic acid*, m.p. 95°, hydrolysed by $Ba(OH)_2$ at 60° to α-acetyltetronic acid, m.p. 79°. H. W.

2-Furfuryl bromide. J. E. Zanetti and J. T. Bashour (J. Amer. Chem. Soc., 1939, 61, 2249—2251).—Evaporating the Et_2O solution at 10 mm. gives 2-furfuryl bromide, b.p. 32·5—34·5°, which is very unstable and explodes if the HBr formed by decomp. accumulates. R. S. C.

Hydroxymethylfurfuraldehyde derivatives of high mol. wt. T. Iseki and T. Sugiura (J. Biochem. Japan, 1939, 30, 113—118).—2 : 2′-Di(furylmethyl) ether 5 : 5′-dialdehyde is reduced by Ag_2O–aq. NH_3 to 5 : 5′-dicarboxy-2 : 2′-di(furylmethyl) ether, m.p. 209—210° (cf. A., 1933, 719) [*Me*$_1$, m.p. 144—146°, *Me*$_2$, m.p. 154°, and *Et*$_2$ ester, m.p. 71°; *chloride* (I), m.p. 98—99°; *CH*$_2$*Cl·CH*$_2$ ester, m.p. 78—79°]. (I) with C_5H_5N condenses to *tetra-(2 : 2′-dimethyl-5 : 5′-furoic anhydride) ether*, $C_{48}H_{32}O_{24}$, m.p. 165—167°. F. O. H.

Sugar–amino-acid compounds. T. Iseki and T. Sugiura (J. Biochem. Japan, 1939, 30, 119—123; cf. A., 1933, 719).—5 : 5′-Dicarboxy-2 : 2′-di-(furylmethyl) ether chloride with NH_3 or the appropriate amine gives the corresponding *carbamyl*, m.p. 204°, *carbanilyl*, m.p. 169°, *carbo-o-hydroxyanilyl*, m.p. 329° (239°?), and *carboxymethylcarbamyl* derivative, m.p. 223° (*Et* ester, m.p. 107°). 2 : 2′-Di(furylmethyl) ether 5 : 5′-dialdehyde with 2-furoic acid and NH_2Ph in EtOH at the b.p. gives 2 : 2′-*di(furylmethyl) ether* 5 : 5′-*di-(2-cinchonic acid)*, m.p. 251°. F. O. H.

Derivatives of coumaran. IV. Structure of tectorigenin. V. Synthesis of 4-hydroxycoumaran-3-one. R. L. Shriner, E. J. Matson, and R. E. Damshroder. V. R. L. Shriner and M. Witte (J. Amer. Chem. Soc., 1939, 61, 2322—2327, 2328—2329; cf. A., 1938, II, 333).—IV. The *iso*flavone structure of tectorigenin (isolation described), m.p. 230° (Me_2 ether, m.p. 188°; Me_3 ether unobtainable), is confirmed by synthesis of isomeric coumaranone derivatives. Iretol, $CH_2Cl{\cdot}CN$, and dry HCl–Et_2O give *α-chloro-2 : 4 : 6-trihydroxy-3-methoxyacetophenone-imine hydrochloride*, decomp. 164—165°. With hot H_2O this undergoes hydrolysis and ring-closure, yielding 3 : 5-*dihydroxy*-4- (I), m.p. 208·5—209·5°, and -6-*methoxycoumaran-2-one* (II), m.p. 177—178°. With CH_2N_2, (I) gives 3 : 4 : 5-*trimethoxycoumar-2-one* (III), m.p. 142·5—143·5°, and with *p*-$OH{\cdot}C_6H_4{\cdot}CHO$ in abs. EtOH at 65—70° gives the very unstable 1-p-*hydroxybenzylidene* derivative, decomp. 291° (block), reduced (H_2–PtO_2; EtOH; 3 atm.) to the impure, unstable 1-*p*-hydroxybenzyl derivative, m.p. 114—117° (decomp.). (III) yields the 1-p-*anisylidene*, m.p. 148—149°, and thence the 1-p-*anisyl* derivative, m.p. 93—94°. Similarly are obtained from (II) 3 : 5 : 6-*trimethoxy*- (IV), m.p. 153·5—154·5°, 3 : 5-*dihydroxy*-6-*methoxy*-1-p-*hydroxybenzylidene*-, decomp. 282° (block), unstable, and -1-p-*anisyl*-, m.p. (impure) ~155—170° (decomp.), and 3 : 5 : 6-*trimethoxy*-1-p-*anisylidene*-, m.p. 195—196°, and -1-p-*anisyl*-, m.p. 116°, -*coumaran-2-one*. Antiarol (modified prep.), $CH_3Cl{\cdot}CN$, $ZnCl_2$, and HCl in Et_2O give an imine, hydrolysed to *α-chloro-6-hydroxy-2 : 3 : 4-trimethoxyacetophenone*, m.p. 107—107·5°, which with NaOAc–EtOH yields (III). 2 : 5 : 1 : 4-$(OMe)_2C_6H_2(OH)_2$, $CH_2Cl{\cdot}CN$, and HCl in Et_2O give *α-chloro-2 : 4-dihydroxy-3 : 6-dimethoxyacetophenone*, m.p. 150·5—151·5°, converted by NaOAc–EtOH into 5-*hydroxy*-3 : 6-*dimethoxycoumaran-2-one*, m.p. 180—181° (decomp.), and thence by CH_2N_2 into (IV).

V. 2 : 6 : 1-$C_6H_3(OH)_2{\cdot}COMe$ and boiling Ac_2O give 2 : 6-*diacetoxyacetophenone*, m.p. 60°, which with Br in CS_2 gives the *α-Br-* (I), m.p. 112°, and in AcOH the *αα-Br*$_2$-derivative, m.p. 113°. 40% HBr (20 c.c.) and a trace of $Na_2S_2O_4$ in boiling 60% EtOH (80 c.c.) give *α-bromo-2 : 6-dihydroxyacetophenone*, m.p. 143°, converted by NaOAc and a trace of $Na_2S_2O_4$ in aq. EtOH into 3-*hydroxycoumaran-2-one*, m.p. 120° (sublimes from 85°) (converted by BzCl–Na_2CO_3–aq. $COMe_2$ into 2 : 3-*dibenzoyloxybenzfuran*, m.p. 183°), the volatility and unusual solubility of which indicate chelation of the OH and CO. M.p. are corr. R. S. C.

Vitamin-*E*. XVII. Oxidation products of α-tocopherol and of related 6-hydroxychromans. L. I. Smith, W. B. Irwin, and H. E. Ungnade (J. Amer. Chem. Soc., 1939, 61, 2424—2429).—The red compound (I), m.p. 109—110°, obtained from 6-hydroxy-2 : 2 : 5 : 7 : 8-pentamethylchroman by $AgNO_3$–EtOH–HNO_3, is 2 : 2 : 7 : 8-*tetramethylchroman-5 : 6-quinone*; the gummy product from *dl*-α-tocopherol (oily, fluorescent phenazine derivative) is also a 5 : 6-quinone. The *phenazine*, m.p. 151—151·5°, and *tetramethylphenazine* derivative (impure), m.p. 204—205°, of (I) fluoresce, particularly in ultraviolet light. H_2–PtO_2 reduces the former to a colour-

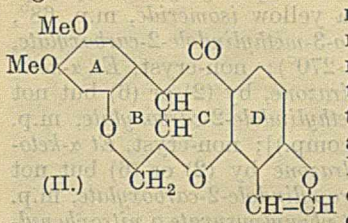
less substance, oxidised by air. $NaHSO_3$ reduces (I) to a colourless substance, very rapidly oxidised in air. 2 : 3 : 1 : 4-$C_6H_2Me_2(OH)_2$, isoprene, and $ZnCl_2$ give 6-hydroxy-2 : 2 : 7 : 8-tetramethyl-5-γ-methyl-Δ^{β}-*n*-butenylchroman and 2 : 2 : 2′ : 2′ : 7 : 8-hexamethyl-3′ : 4′-dihydropyrano-5′ : 6′-5 : 6-chroman, oils, which with $AgNO_3$–EtOH–HNO_3 give (I). Structures are supported by absorption spectra. Formation of the red compounds occurs only in alcohols (MeOH > EtOH > $Pr^{\beta}OH$ > $Bu^{\gamma}OH$ > mesitol), and the simultaneous production of aldehydes may be significant. R. S. C.

7-Hydroxy-3-benzoylflavone. S. Rangaswami and T. R. Seshadri (Proc. Indian Acad. Sci., 1939, **10**, A, 6—8).—Resacetophenone, Bz_2O, and NaOBz at 180—190° give a mixture, converted by short treatment with 10% KOH–EtOH into 7-hydroxy- and 7-*hydroxy*-3-*benzoyl-flavone*, m.p. 264—265°. The latter product is hydrolysed by boiling 5% Na_2CO_3 to 7-hydroxyflavone and BzOH. The method of Robinson *et al.* (A., 1926, 1149) usually gives large amounts of 3-Bz compound, which can often be separated from the 7-OBz-compound by utilising the varying rates of hydrolysis of *C*- and *O*-Bz. R. S. C.

Phenolhomophthalein. B. Hoï (Compt. rend., 1939, **209**, 321—324).—Equimol. amounts of homophthalic anhydride (I) with PhOH and $SnCl_4$ at 125° afford 3-p-*hydroxyphenyl*iso*coumarin* (II), m.p. 227° (*acetate*, m.p. 161°), also obtained by cyclisation of 4′-hydroxydeoxybenzoin-2-carboxylic acid (III) (cf. A., 1939, II, 429). *Phenolhomophthalein*, m.p. 160—170°, is also formed, has properties like those of phenolphthalein, and exists in three tautomeric forms. In NaOH (II) gives an intense yellow solution which fades when the Na salt of (III) is formed. (III), also formed from (I) and PhOH in presence of conc. H_2SO_4, melts at about 211°, being converted into (II). (II) or (III) with N_2H_4 and NH_2OH affords a *homophthalazone*, m.p. 243° (decomp.), and a *lactazone*, m.p. 258°, respectively. J. L. D.

Yellow pigment of *Papaver nudicaule*. I. J. R. Price, (Sir) R. Robinson, and (in part) R. Scott-Moncrieff (J.C.S., 1939, 1465—1468).—Nudicaulin chloride (I) has been isolated as a yellow amorphous powder; a formula of the order $C_{30}H_{38}O_{15}NCl$ containing 0·3 OMe is indicated. Hydrolysis affords glucose in amount > the theoretical for a monoglucoside but considerably < that required for a diglucoside; this is possibly due to condensation of the aglycone with glucose. The presence of *p*-OH·C_6H_4· and of NH_2 is indicated. After methylation and oxidation ($KMnO_4$), anisic acid is obtained. The formation of a ψ-base is the chief reason for suspecting the presence of a flavylium salt structure, but this is not decisive. F. R. S.

Active principles of leguminous fish-poison plants. III. Structure of elliptone. S. H. Harper (J.C.S., 1939, 1424—1427).—During the prep. of dehydroelliptone (I) from *l*-elliptone (II), O-*acetylelliptolone*, m.p. 175·5°, hydrolysed to *elliptolone*, m.p. 228°, is obtained. Zn and KOH with (I) give *elliptic acid*, m.p. 190° (*Me* ester, m.p. 143°), which is oxidised (H_2O_2) to derric acid. It follows that the degradation has taken the same course as with rotenone and *iso*-rotenone, and therefore rings A, B, and C of these are identical with those in (II). Degradation of (I) with KOH–EtOH affords 4-*hydroxy-coumarone*-5-*carboxylic acid*, m.p. 221° (*Me* ester, m.p. 105°), also obtained by carboxylation of 4-hydroxycoumarone. This confirms the structure assigned to (II). The isomerism of the α- and β-oximes of rotenone is due to dimorphism. F. R. S.



Absorption spectra of some sulphur compounds.—See A., 1939, I, 507.

Oxidation products of pyrrole amines. III. T. Ajello (Gazzetta, 1939, **69**, 453—459).—Zn, Fe, or Cu and AcOH, etc., which with oximinophenylmethylpyrrole (I) give amorphous products, reduce 3-oximino-2 : 5-diphenylpyrrole (II) to aminodiphenylpyrrole (III). Cu powder in AcOH at room temp., however, reduces (II) slowly to *azoxydiphenylpyrrole* (IV), m.p. 170—172° [*picrate*, m.p. 180° (decomp.)], also obtained by oxidation of (III) by H_2O_2–AcOH, by CrO_3–AcOH, or by $FeCl_3$. (IV) is readily reduced to (III). $FeSO_4$ or CuCl and (I) yield benzoylmethyl-*iso*oxazole. E. W. W.

Oximinopyrroles. XII. Transformation of the pyrrole into the pyrimidine nucleus. T. Ajello (Gazzetta, 1939, **69**, 460—470).—4-Oximino-2 : 3 : 5-triphenylpyrrole (I) when steam-distilled gives HCN, PhCHO, NH_3, and an amorphous product. With HCl in $CHCl_3$, (I) and 3-oximino-2 : 5-diphenylpyrrole (II) give only their hydrochlorides. With PCl_5 in $CHCl_3$, (I) gives 4-hydroxy-2 : 3 : 6-triphenylpyrimidine (III), and a substance, m.p. 228°, converted by boiling AcOH into (III). Similarly (II) gives 4-hydroxy-2 : 6-diphenylpyrimidine. E. W. W.

Mixed platinum hydroxylamine tetrammines.—See A., 1939, I, 533.

2′-Aminopyridide of *p*-nitrobenzenesulphinic acid.—See B., 1939, 1077.

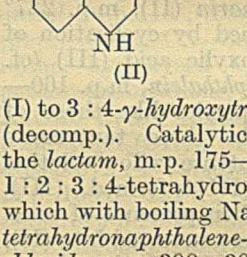
Indoles. VII. Derivatives of 7-nitroindole. G. K. Hughes, F. Lions, and E. Ritchie (J. Proc. Roy. Soc. New South Wales, 1939, **72**, 209—220).—*o*-Nitrophenylhydrazones of α-CO esters are obtained by adding KOH to a well-stirred solution of the ester in EtOH at 0° followed immediately by the diazo-solution from *o*-NO_2·C_6H_4·NH_2. The following methods of cyclisation are used: (1) the *o*-nitrophenylhydrazone (I) is boiled with glacial AcOH for several hr.; (I) is kept in conc. H_2SO_4 (2) or HCl–EtOH (3); (I) is heated under reflux with (1 : 10) H_2SO_4 (4) or conc. HCl (5); (I) is heated with $ZnCl_2$ in cumene (6) or EtOH (7); (I) is boiled with a solution of HBr in AcOH (8). The following transitions are described, the figures in parentheses indicating the methods of cyclisation used: *Et pyruvate o-nitrophenylhydrazone*, m.p. 106° (by 5 but not by 1, 2, or 3), to *7-nitroindole-2-carboxylic acid*, m.p. 231°, which is not reduced by $FeSO_4$–NH_3 to the NH_2-compound but is decarb-

oxylated in glycerol at 220° to 7-*nitroindole*, m.p. 113°; *Et* α-*ketobutyrate* o-*nitrophenylhydrazone*, m.p. 94°, by (1) and (3) to a yellow *isomeride*, m.p. 68°, and by (2) to *Et* 7-*nitro*-3-*methylindole*-2-*carboxylate*, m.p. 115° (*acid*, m.p. >270°); non-cryst. *Et* α-*ketovalerate* o-*nitrophenylhydrazone*, by (2) or (6) but not by (1) to *Et* 7-*nitro*-3-*ethylindole*-2-*carboxylate*, m.p. 85° [*acid*, m.p. 245° (decomp.)]; non-cryst. *Et* α-*ketohexoate* o-*nitrophenylhydrazone* by (2) or (6) but not by (1) to *Et* 7-*nitro*-3-*propylindole*-2-*carboxylate*, m.p. 70° (*acid*, m.p. 196°); *Et phenylpyruvate* o-*nitrophenylhydrazone*, m.p. 68°, by (3) or (8) but not by (1), (2), (4), (5), or (6) to *Et* 7-*nitro*-3-*phenylindole*-2-*carboxylate*, m.p. 112°; *Et H ketopimelate* o-*nitrophenylhydrazone*, m.p. 122°, by (5) but not by (2) or (6) to γ-7-*nitro*-2-*carboxyindolylbutyric acid*, m.p. 171°, and by (7) to 7-*nitro*-γ-2-*carbethoxyindolylbutyric acid*, m.p. 184°. Acetone-*o*-nitrophenylhydrazone, m.p. 70°, could not be cyclised by (5) or (6); Et_2 ketone *o*-nitrophenylhydrazone, m.p. 60°, by (5) but not by (1) to 7-*nitro*-3-*methyl*-2-*ethylindole*, m.p. 104°; iso*butaldehyde*-o-*nitrophenylhydrazone*, m.p. 59°, by (5) to (?) 2 : 2′-iso*butylidenedi*-(7-*nitro*-3 : 3′-*dimethylindolenine*), m.p. 154°; cyclo*pentanone*-o-*nitrophenylhydrazone*, m.p. 64°, not converted into an indole by (2), (4), or (5); acetophenone-*o*-nitrophenylhydrazone, m.p. 138°, not cyclised by (2), (5), or (6); *propiophenone*-o-*nitrophenylhydrazone*, m.p. 120°, not cyclised by (5) but giving by (6) a mixture of red and orange crystals, m.p. ~70°; *deoxybenzoin*-o-*nitrophenylhydrazone*, m.p. 125°, not cyclised by (5) or (6); 3-*acetylpyridine*-o-*nitrophenylhydrazone*, m.p. 144°, not cyclised by (5) or (6). H. W.

Indoles. VIII. 3-Hydroxymethylindole-2-carboxylactone. R. H. Harradence and F. Lions (J. Proc. Roy. Soc. New South Wales, 1939, **72**, 221—227).—Addition of PhN_2Cl to acetobutyrolactone in 2·5% NaOH gives α-*ketobutyrolactonephenylhydrazone* (I), m.p. 220°, which could not be converted into an indole by saturated HCl–EtOH, EtOH–H_2SO_4, conc. HCl, conc. H_2SO_4, glacial AcOH, or HBr in AcOH. Gradual addition of conc. HCl to a solution of (I) in hot AcOH followed by short boiling gives a small yield of 3-*hydroxymethylindole*-2-*carboxylactone* (II), m.p. 209°, which is insol. in boiling Na_2CO_3 or cold NaOH but is sol. in boiling NaOH. 3-*Hydroxymethylindole*-2-*carboxylic acid* has m.p. 244—245° (decomp.). (II) is transformed by N_2H_4,H_2O in boiling H_2O into the *hydrazide* of 3-*hydroxymethylindole*-2-*carboxylic acid*, m.p. 195—200° (vigorous gas evolution) when rapidly heated, which passes when heated at 180—200° into the *compound*, $C_{10}H_9ON_3$, m.p. 285°, and affords a :*CHPh* derivative, m.p. 235°. 3-*Hydroxymethylindole*-2-*carboxylic acid phenylhydrazide* has m.p. 196°. (I) could not be caused to react satisfactorily with KCN. H. W.

Identification reactions on isaceen [diacetyldihydroxyphenylisatin]. M. J. Schulte (Pharm. Weekblad, 1939, **76**, 1256—1257).—Diacetyldihydroxyphenylisatin (I) (10 mg.) is boiled with EtOH (1 c.c.) and 0·1N-NaOH (1 c.c.); a violet colour develops, which becomes deep blue on cooling and adding 0·5N-Br (1 drop). The blue colour is extracted with $CHCl_3$. An orange-red colour is produced with Ehrlich's diazo-reagent, NaOH, and $NaNO_2$; when the solution is acidified (H_2SO_4) and boiled the colour changes to yellow and EtOAc is formed. (I) gives a purple colour in H_2SO_4. S. C.

Preparation of trimethyleneindole derivatives. R. G. Gould, jun., and W. A. Jacobs (J. Biol. Chem., 1939, **130**, 407—414).—3-*Amino*-1-*naphthoic acid nitrate*, m.p. 225—230° (decomp.), and conc. H_2SO_4 at −30° to −40° give (?) 5- (I), m.p. 303—308° (decomp.), and 8-*nitro*-3-*amino*-1-*naphthoic acid*, m.p. 230—231° (decomp.) [*Ac* derivative, m.p. 274—276° (decomp.)]. $Fe(OH)_2$ reduces (I) to 3 : (?)5-*diamino*-1-*naphthoic acid*, unstable [Ac_2 derivative, m.p. 323—330° (decomp.)], but (II) thus yields 3-*aminonaphthostyril*, m.p. 238—240° [*picrate*, m.p. 245—250° (decomp.); *Ac* derivative, m.p. 300—302° (decomp.); obtained also with difficulty from 3 : 8 : 1-$(NH_2)_2C_{10}H_5{\cdot}CO_2H$], reduced by Na–BuOH to (*inter alia*) 3 : 4-β-*aminotrimethyleneindole*, a gum [*picrate*, m.p. 242—248° (decomp.); *hydrochloride*, m.p. 215—222° (decomp.), hygroscopic]. 1 : 4-$C_{10}H_6(CO_2H)_2$ and HNO_3 (*d* 1·58) at 0° give the 5-NO_2-derivative, m.p. (crude) 270—274° (decomp.), reduced by $Fe(OH)_2$ to *naphthostyril*-4-*carboxylic acid* (I), m.p. >350°, the NH_4 salt of which with Na–BuOH yields 3 : 4-γ-*carboxytrimethyleneindole* (II), m.p. 142—144° [*Me* ester, m.p. 82—84°; *picrate*, m.p. 168—170° decomp.)]. Na–BuOH reduces the *Me*, m.p. 260—261°, or *Et* ester (III), m.p. 217—218°, of (I) to 3 : 4-γ-*hydroxytrimethyleneindole*, m.p. 147—150° (decomp.). Catalytic hydrogenation of (III) yields the *lactam*, m.p. 175—177°, of 8-amino-4-carbethoxy-1 : 2 : 3 : 4-tetrahydronaphthalene-1-carboxylic acid, which with boiling NaOH affords 8-*amino*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-1 : 4-*dicarboxylic acid* [*hydrochloride*, m.p. 300—309° (decomp.)]. R. S. C.



(II)

Synthesis of peptide-like derivatives of aminohydrocarbostyril. Amyostatic poisons. T. Sasaki and T. Hashimoto (Proc. Imp. Acad. Tokyo, 1939, **15**, 233—238).—Gradual alternate addition of $NaHCO_3$ and CHMeBr·COBr to *dl*-3-aminohydrocarbostyryl hydrochloride (I) and $NaHCO_3$ at 0° yields dl-3-α-*bromopropionamido*-dl-*hydrocarbostyril* (II), m.p. 228—229° (decomp.), transformed by NH_3–EtOH at 100° into dl-3-(dl-α-*alanylamido*)*hydrocarbostyril* (III), $C_9H_9ON_2{\cdot}CO{\cdot}CHMe{\cdot}NH_2$, m.p. 180—182° [*hydrochloride*, m.p. 245—246° (decomp.)]. Treatment of (II) with the requisite amine leads to dl-3-(dl-N-*methyl*-α-*alanylamido*)-, m.p. 187—188° [*hydrochloride*, m.p. 261—262° (decomp.)], -(dl-N-*dimethyl*-α-*alanylamido*)-, m.p. 163—164° [*hydrochloride*, m.p. 248—249° (decomp.)], -(dl-N-*ethyl*-2-*alanylamido*)- [*hydrochloride*, m.p. 270—271° (decomp.)], and -(dl-N-*diethyl*-α-*alanylamido*)-, m.p. 140—141° [*hydrochloride*, m.p. 385—386° (decomp.)], -*hydrocarbostyril*. $CH_2Cl{\cdot}CH_2{\cdot}COCl$ and (I) afford dl-3-(-β-*chloropropionamido*)*hydrocarbostyril*, m.p. 226—227° (decomp.), converted into dl-3-(β-*alanylamido*)*hydrocarbostyril* (IV), m.p. 227—228° (decomp.) [*hydrochloride*, m.p. 265—266° (decomp.)], which affords N-Me_1 [*hydrochloride* (+$2H_2O$)], N-Me_2, m.p. 176—177° [*hydrochloride*, m.p. 305—306°

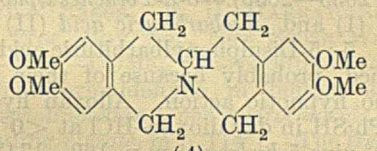
(decomp.)], N-*Et*$_1$, m.p. 177—178° [*hydrochloride*, m.p. 236—237° (decomp.)], and N-*Et*$_2$, m.p. 156—157° [*hydrochloride*, m.p. 308—309° (decomp.)], derivatives. CHEtBr·COBr and (I) yield dl-3-(dl-α-*bromobutyramido*)*hydrocarbostyril*, m.p. 220—221° (decomp.), whence dl-3-(dl-α-*aminobutyramido*)*hydrocarbostyril* (V), m.p. 169—170° (*hydrochloride*) (+1H_2O)]. dl-3-(dl-α-*Bromoisovaleramido*)-, m.p. 239—240° (decomp.), is transformed into dl-3-(dl-α-*amino*isovaleramido)-*hydrocarbostyril* (VI), m.p. 269—270° [*hydrochloride*, m.p. 295—296° (decomp.)]. Similarly, dl-3-(dl-α-*bromohexoamido*-, m.p. 190—192°, affords dl-3-(dl-*leucylamido*)-*hydrocarbostyril* (VII), m.p. 255—257° [*hydrochloride*, m.p. 304—305° (decomp.)]. The amyostatic activity of the bases decreases in the sequence (III), (IV), (V), (VI), (VII) parallel with their solubility in acid. H. W.

Synthesis of diaminohydrocarbostyril by the diketopiperazine method. Amyostatic poisons. IV. T. Sasaki and H. Ueda (Proc. Imp. Acad. Tokyo, 1939, **15**, 239—242).—Diacetylglycine anhydride (I), 2 : 4-$(NO_2)_2C_6H_3$·CHO, anhyd. NaOAc, and C_5H_5N in PhMe at 130—135° give *di*-2 : 4-*dinitrobenzylidenediketopiperazine*, converted by red P and boiling HI (*d* 1·7) into 3 : 7-*diaminohydrocarbostyril*, m.p. 207° [*dihydrochloride*; *Bz*$_2$, m.p. 285—286°, and *Ac*$_2$, m.p. 293° (decomp.), derivatives]. Similarly, (I), 2 : 6-$(NO_2)_2C_6H_3$·CHO, and $NHEt_2$ in PhMe at 130—140° afford *di*-2 : 6-*dinitrobenzylidenediketopiperazine*, converted into 3 : 5-*diaminohydrocarbostyril* (dihydrochloride; *Ac*$_2$ derivative, decomp. ~325°). The amyostatic action of 3-aminohydrocarbostyril is nullified by the introduction of NH_2 at $C_{(5)}$ or $C_{(7)}$. H. W.

Co-ordination compounds with 8-aminoquinoline as a chelate group. G. J. Burrows and E. Ritchie (J. Proc. Roy. Soc. New South Wales, 1939, **72**, 113—117).—If the four valencies of a quadricovalent metal are planar, *cis*- and *trans*-forms of their compounds with 8-aminoquinoline (I) should exist but if the valencies are tetrahedrally disposed optically active forms should be obtainable. In all cases investigated the complex compound appears to be homogeneous and no sign of *cis–trans* isomerism has been detected. The following *compounds* are obtained by mixing conc. solutions of the metallic salt in H_2O and of (I) in EtOH; after 30 min. the ppt. is collected and dried in air: $[Cu(C_9H_8N_2)_2]SO_4,7H_2O$; $[Cu(C_9H_8N_2)]SO_4,5H_2O$; $[Cu(C_9H_8N_2)_2]Cl_2,5H_2O$; $[Cu(C_9H_8N_2)]Cl_2,H_2O$; $[Cu(C_9H_8N_2)_2](NO_3)_2,6H_2O$; $[Fe(C_9H_8N_2)]SO_4,6H_2O$; $[Ni(C_9H_8N_2)_2]Cl_2,2H_2O$; $[Ni(C_9H_8N_2)]Cl_2,16H_2O$; $[Ni(C_9H_8N_2)_2](NO_3)_2,4H_2O$; $[Ni(C_9H_8N)](NO_3)_2,10H_2O$; $[Co(C_9H_8N_2)_2]Cl_2,H_2O$. H. W.

Identification of 4-nitroacridone-1-carboxylic acid [by conversion into] 4-aminoacridine. K. Matsumura (J. Amer. Chem. Soc., 1939, **61**, 2247—2248).—The identity of 4-nitroacridone-1-carboxylic acid (A., 1938, II, 246) is confirmed by conversion of the derived aminoacridone by Na–Hg in 33% aq. EtOH into 4-aminoacridine, new m.p. 178° (uncorr.), 182·3° (corr.) [hydrochloride, new m.p. 285° (decomp.)] (cf. Lehmstedt, *ibid*, 419). New m.p. 218° (uncorr.) [223·5° (corr.)] and 328—329° (decomp.) are recorded for 2-aminoacridine and its hydrochloride. R. S. C.

Synthesis of dibenzopyridocoline derivatives. III. Synthesis of 3′ : 4′ : 3″ : 4″-tetramethoxy-1 : 4 : 5 : 8-tetrahydro-(1′ : 6′ : 2 : 3 : 1″ : 6″ : 6 : 7-dibenzopyridocoline). S. Sugasawa, K. Kakemi, and H. Kazumi (Proc. Imp. Acad. Tokyo, 1939, **15**, 223—225; cf. A., 1938, II, 378; 1939, II, 343).—*Dihomoveratryl ketone*, m.p. 99—101° (*oxime*, m.p. 108—111°), is not obtained by the thermal decomp. of the alkaline-earth homoveratrates but is prepared in 45—50% yield from the Pb salt. It is transformed by Leuckart's method into *formdihomoveratrylmethylamide*, m.p. 129—130°, which is converted by $POCl_3$ in dry xylene into the non-cryst. 6 : 7-*dimethoxy*-3-3′ : 4′-*dimethoxybenzyl*-3 : 4-*dihydro*isoquinoline (I) (*perchlorate*, m.p. 230—232°). The *hydrochloride* of the base is reduced catalytically to 6 : 7-dimethoxy-3-3′ : 4′-dimethoxybenzyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline (*hydrochloride*, m.p. 206°). (I) is readily converted by HCl and CH_2O at 100° into 3′ : 4′ : 3″ : 4″-*tetramethoxy*-1 : 4 : 5 : 8-*tetrahydro*-(1′ : 6′ : 2 : 3 : 1″ : 6″ : 6 : 7-*dibenzopyridocoline* (*A*) [*hydrochloride* (+0·5H_2O), decomp. 271—272°].



(*A*)

H. W.

Synthesis of coloured derivatives of nirvanol. II. *N*-Benzylazo-compounds. S. P. Lingo [with H. R. Henze] (J. Amer. Chem. Soc., 1939, **61**, 2029—2032; cf. A., 1939, II, 344).—5-Phenyl-5-ethylhydantoin, *p*-NO_2·C_6H_4·CH_2Cl, and NaOMe in hot MeOH give 5-*phenyl*-3-p-*nitrobenzyl*-5-*ethylhydantoin*, m.p. 177—177·5°, reduced by H_2–Raney Ni at 100°/20 atm. to the 3-p-NH_2·C_6H_4·CH_2 derivative (I), m.p. 171·7°. $NaNO_2$–HCl, followed by $CO(NH_2)_2$, gives the diazonium salt, which by coupling yields 5-*phenyl*-3-β-*dimethylaniline*-, m.p. 228·5—229°, -3-β-*naphthylamine*- (II) m.p. (crude) ~120° (decomp. from 100°) [reduced by Zn–HCl–AcOH to (I); pyrolysis and subsequent reduction give (I) and 1 : 2-$C_{10}H_6(NH_2)_2$], -3-*phenol*-, m.p. 245—247° (later decomp.), -3-α-, m.p. ~120—148°, decomp. ~150°, and -3-β-*naphthol*- (III), m.p. 212—213°, -3-1′ : 5′-*dihydroxynaphthalene*-, decomp. 196° (sinters at 194°), and -3-4′-*hydroxy*-3′-*carboxybenzene*-, darkens at ~125°, m.p. 133—134°, -*azobenzyl*-5-*ethylhydantoin*; these products, except (II) and (III) which are too insol., dye wool and silk. M.p. are corr. R. S. C.

Colour in relation to chemical constitution of organic and inorganic salts of oximino-pyrazolones and -*iso*oxazolones. S. Dutt and (Miss) I. N. D. Dass (Proc. Indian Acad. Sci., 1939, **10**, A, 55—64).—CH_2Bz·CO_2Et and NH_2OH,HCl in boiling AcOH give 3-phenyl*iso*oxazolone, m.p. 174° [:N·OH derivative (I), m.p. 130° (lit., 120°)]. OH·N:CAc·CO_2Et (improved prep.) and NH_2OH,HCl in AcOH at 100° give 4-oximino-3-methyl*iso*oxazolone (II), m.p. 150°. Prep. of 3-phenyl-, m.p. 235°

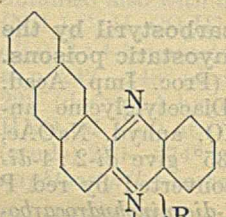
[:N·OH derivative (III), m.p. 188°], and 4-oximino-3-methylpyrazolone (IV), m.p. 217° (lit., 130°), is modified. Salts of (I) and (II) are purple or deep magenta in solution (absorption max. at ~5800 A.), existing as $\overset{N}{}\!\!<\!\!\overset{CR\cdot C(NO)}{O}\!\!>\!\!C\cdot OH$, which contains the highly strained NO (cf. A., 1938, II, 507). However, the corresponding salts of (III) and (IV) exist as $\overset{N}{}\!\!<\!\!\overset{CR\cdot C(N\cdot OH)}{N}\!\!>\!\!C\cdot OH$, do not contain NO, and are thus only orange (absorption max. at ~4800 A.). The salts dissociate in H_2O and develop their full colour in, *e.g.*, $COMe_2$ only if a little H_2O is present. The following *salts* of (I), (II), (III), and (IV), respectively, are described: NH_2Me, m.p. 122°, 107°, 155°, 167°; NH_2Et, m.p. 112°, 108°, 170°, 135°; $NHMe_2$, m.p. 102°, 102°, 185°, 161°; $NHEt_2$, m.p. 103°, 87°, 193°, 173°; NMe_3, m.p. 110°, 72°, 185°, 169°; NH_2Bu^{α}, m.p. 82°, 112°, 176°, 134°; piperidine, m.p. 121°, —, 211°, 158°; Na, m.p. 110°, 210°, —, —; K, m.p. 122°, —, 239°, 273°; NH_4, m.p. 86°, 96°, 184°, 214° (all m.p. with decomp.). R. S. C.

5-Sulphonylbarbituric acids. E. L. D'Ouville, F. J. Myers, and R. Connor (J. Amer. Chem. Soc., 1939, **61**, 2033—2036).—5-p-*Toluenesulphonyl*-5-*ethylbarbituric* (I) and *-thiobarbituric acid* (II) are rather unstable. 5 : 5-Disulphonylbarbituric acids could not be obtained, probably because of their instability. (I) has no hypnotic action. Alloxan hydrate (III) and $CH_2Ph\cdot SH$ in dry dioxan–HCl at <0° or AcOH–Ac_2O at 0° give 5-*hydroxy-*, m.p. 169—174° (decomp.) [with $(CH_2Ph\cdot S)_2$, formed by reduction of (III)], and 5-*acetoxy*-5-*benzylthiolbarbituric acid*, m.p. 210—235° (decomp.; pink at 190°), respectively. *p*-$C_6H_4Me\cdot SH$ does not condense with (III). 5 : 5-Dibromobarbituric acid and *p*-$C_6H_4Me\cdot SO_2Na,2H_2O$ (IV) in abs. MeOH at room temp. give 40% of Na 5-bromobarbiturate and *p*-$C_6H_4Me\cdot SO_2Br$, the latter product reacting with more (IV) to give (*p*-$C_6H_4Me\cdot SO_2)_2$ (V). 5-Bromo-5-ethylbarbituric acid and (IV) in abs. MeOH at room temp. give 20% (8% at 64°) of (I), m.p. 200·5—203·5° (decomp.), *p*-$C_6H_4Me\cdot SO_2\cdot CHEt\cdot CO\cdot NH_2$ [due to fission of (I)], and 18% of (V). 5-Bromo-5-ethylthiobarbituric acid similarly (at 5°) gives 20% of (II), m.p. 179·9—180°, unstable when kept. R. S. C.

Desmotropism of xanthine derivatives. T. B. Johnson and J. C. Ambelang (J. Amer. Chem. Soc., 1939, **61**, 2483—2485).—No purine could be obtained from alloxan by $CH_2(NH_2)_2$ or $(CH_2\cdot NH_2)_2$ or from alloxan-4-imine-5-oxime by *o*-$C_6H_4(NH_2)_2$. $(CH_2\cdot NH_2)_2$ in HCl–H_2O or –EtOH gives the "*anil-hydrate*," $CO\!<\!\overset{NH\cdot CO}{NH\cdot CO}\!>\!C(OH)\cdot NH\cdot[CH_2]_2\cdot NH_2$, m.p. ~214° (decomp.) [*hydrochloride*, $+H_2O$, m.p. 225—230° (decomp.)]. R. S. C.

Quinazolines. VIII. Methyl esters of 1 : 3-dimethylbenzoylenecarbamide-5-carboxylic acid and 2 : 4-dimethoxyquinazoline-5-carboxylic acid. N. A. Lange, D. C. Chisholm, and J. L. Szabo (J. Amer. Chem. Soc., 1939, **61**, 2170—2171; cf. A., 1935, 99).—Contrary to Scott *et al.* (J.C.S., 1921, **119**, 664), 2 : 4-diketo-1 : 2 : 3 : 4-tetrahydroquinazoline-5-carboxylic acid (I), new m.p. 346° (block), with Me_2SO_4–alkali gives the 1 : 3-Me_2 derivative, m.p. 318°. The Me ester (II), new m.p. 307—309°, of (I) is obtained by HCl–MeOH or, best, by $SOCl_2$ [gives the *chloride*, m.p. 331—332° (decomp.)], followed by MeOH, and with Me_2SO_4–KOH–H_2O gives *Me* 2 : 4-*diketo*-1 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinazoline*-5-*carboxylate*, new m.p. 144·4—145·5° (corr.), obtained less well by the method of Scott *et al.*, who misinterpreted its nature. With PCl_5–$POCl_3$, followed by NaOMe–MeOH, (I) gives *Me* 2 : 4-*dimethoxyquinazoline*-5-*carboxylate*, m.p. 134·5—135·5° (corr.), hydrolysed by boiling, dil. HCl to (II). The *Et*, m.p. 297—299°, and CH_2Ph ester, m.p. 257—261°, and *amide*, m.p. 359°, of (I) are described. R. S. C.

Flavinduline derivatives. X. K. Yamada and I. Ikoma (J. Soc. Chem. Ind. Japan, 1939, **42**, 228—229B; cf. A., 1938, II, 380).—The solubility, colour reactions, dyeing properties, and fastness of the *dyes* (*A*, R = Cl + 0·5$ZnCl_2$, m.p. 240—242°; R = Br, m.p. 213—215°; R = I, m.p. 143—145°) derived from anthra-1 : 2-quinone and *o*-$NH_2\cdot C_6H_4\cdot NHPh$, are described.



(*A.*)

H. W.

Synthesis of 1-6′-amino-2′-methyl-5′-pyrimidylmethyl-2-methyl-3-β-hydroxyethylpyridinium bromide hydrobromide. F. C. Schmelkes and R. R. Joiner (J. Amer. Chem. Soc., 1939, **61**, 2562—2563).—Synthesis of the following is reported without details by the methods indicated in parentheses: 3-nitro-6-hydroxy- (from 3-nitro-6-amino-2-methylpyridine), 6-chloro-3-nitro- (by PCl_5), 3-*amino*- (by H_2–Pd), m.p. 113°, 3-*cyano*- (Sandmeyer), m.p. 58°, and 3-*acetyl*-, b.p. 75—78°/2 mm., -2-*methylpyridine*; 2-*methyl*-3-β-*hydroxyethylpyridine* (successive reactions with Br, KOAc–EtOH, and then reduction), b.p. 125°/3 mm. (*picrate*, m.p. 125°; *acetate*, b.p. 90—92°/3 mm.). With 6-amino-2-methyl-5-bromomethylpyrimidine hydrobromide this gives 1-6′-*amino*-2′-*methyl*-5′-*pyrimidylmethyl*-2-*methyl*-3-β-*hydroxyethylpyridinium bromide hydrobromide*, m.p. 247°. 2-*Methyl*-5-β-*hydroxyethylpyridine*, b.p. 103°/2 mm., and 1-6′-*amino*-2′-*methyl*-5′-*pyrimidylmethyl*-2-*methyl*-5-β-*hydroxyethylpyridinium bromide hydrobromide*, m.p. (?) 245°, are also reported. R. S. C.

Bilichrysins. New type of bile pigment. R. Lemberg and W. H. Lockwood (J. Proc. Roy. Soc. New South Wales, 1939, **72**, 69—74).—Gradual addition of 0·1N-I (≡2 atoms) in EtOH to mesobiliverdin and $Zn(OAc)_2$ in MeOH containing NH_3 gives mesobiliviolin II, which passes when kept in $CHCl_3$ into mesobiliviolin III (I) and *mesobilichrysin* (II), $C_{33}H_{38}O_7N_4$, m.p. 240° (decomp.) when rapidly heated or m.p. 231° after changing in colour from 170° to 215° when slowly heated. (II) shows a band at 416 mμ. in ammoniacal solution. Addition of $Zn(OAc)_2$ to (II) in EtOH causes an immediate deepening of colour but no further change if the solution is kept in a vac. On exposure to air oxidation to (I) occurs. The colour of an alkaline solution of (II) is discharged by Na–Hg and the leuco-compound

thus produced is quickly oxidised by air and gives a urobilinoid pigment which shows an intense green fluorescence with $Zn(OAc)_2$; the absorption spectrum displays a band in the blue-green; mesobilinogen behaves similarly. Biliverdin is oxidised analogously to *bilichrysin*. The chrysins may be distinguished from the urobilinoid pigments immediately by the absorption spectra and by the Zn reaction; from the rubins by the Gmelin and by the Zn reaction; from dihydromesobilirubin by the diazo-reaction; from hydroxylated as well as from non-hydroxylated dipyrromethenes by the Zn reaction (the former do not yield fluorescent Zn salts, the latter afford Zn salts somewhat similar to urobilinoid pigments). H. W.

Syntheses of *iso*oxazole derivatives by means of fulminic acid. I. A. Quilico and G. Speroni (Gazzetta, 1939, **69**, 508—523).—Aq. NaO·N:C in $COMe_2$ containing H_2SO_4 and saturated with C_2H_2 gives 5-iso*propenyl*isoo*xazole* (I), b.p. 151·5—152°, which with Br in CS_2 forms 5-αβ-*dibromo*iso*propyl*iso*oxazole*, b.p. 130—135°/12 mm. With $K_2Cr_2O_7$–H_2SO_4, (I) gives *iso*oxazole-5-carboxylic acid; with $KMnO_4$–H_2SO_4, 5-acetyl*iso*oxazole, which with MgMeI gives 5-iso*oxazolyldimethylcarbinol*, b.p. 90—105°/15 mm., reconverted by P_2O_5 into (I). $[R]_D$ of (I) and other *iso*oxazoles is tabulated. E. W. W.

***iso*Oxazole group. VII. Primary alcohols and aldehydes.** A. Quilico and L. Panizzi (Gazzetta, 1939, **69**, 536—546).—3-Methyl*iso*oxazolyl-5-methylamine hydrochloride and $NaNO_2$ give 3-*methyl*iso*oxazolyl*-5-*carbinol*, b.p. 140°/25 mm. (*Bz*, m.p. 53—54·5°, and p-NO_2·C_6H_4·*CO*, m.p. 82—83°, derivatives). This is oxidised by $K_2Cr_2O_7$–H_2SO_4 to the acid, but when dissolved in dil. $K_2Cr_2O_7$ and dropped into boiling dil. H_2SO_4 through which steam is passing, gives 3-*methyl*iso*oxazole*-5-*aldehyde* (I), m.p. 47—48°, b.p. 70—75°/30 mm. [*peroxide*, $[R·CH(OH)·O]_2$, m.p. 100—102° (decomp.), obtained by extracting (I) with Et_2O containing peroxide] [p-*nitrophenylhydrazone*, m.p. 258—259° (decomp.); *semicarbazone*, m.p. 225—226° (decomp.); *oxime*, m.p. 96·5—98°]. With CH_2N_2, (I) gives 5-acetyl-3-methyl-*iso*oxazole (p-*nitrophenylhydrazone*, m.p. 222—223°; *semicarbazone*, m.p. 203—204°; *oxime*, m.p. 114—115°). Similarly 5-*methyl*iso*oxazolyl*-3-*carbinol*, b.p. 134·5—135·5°/30 mm. (*Bz*, m.p. 62—63°, and p-NO_2·C_6H_4·*CO*, m.p. 92—93°, derivatives), is oxidised to 5-*methyl*iso*oxazole*-3-*aldehyde*, b.p. 65—75°/30 mm. [p-*nitrophenylhydrazone*, m.p. 228—229° (decomp.); *semicarbazone*, m.p. 202—203° (decomp.); *oxime*, m.p. 113—114°] (further oxidised to the acid), which with CH_2N_2 gives 3-acetyl-5-methyl*iso*oxazole (new prep. from the 3-nitrile and MgMeI). Both aldehydes in 20% KOH undergo the Cannizzaro reaction. Certain derivatives of the above position-isomerides give no depression of m.p. when mixed. E. W. W.

Morpholine condensations. C. B. Kremer, M. Meltsner, and L. Greenstein (J. Amer. Chem. Soc., 1939, **61**, 2552).—Morpholine, $C_6H_4Cl·NO_2$, and anhyd. Na_2CO_3 give 1-*o*-, m.p. 40—41°, and 1-*p*-nitrophenylmorpholine, m.p. 149—150° (also obtained from 1-phenylmorpholine by HNO_3–H_2SO_4). $SnCl_2$ then yields 1-*p*- and 1-*o*-*aminophenylmorpholine*, m.p. 98—98·5°. R. S. C.

Orientation of nuclear methylation in phenols and naphthols. W. T. Caldwell and T. R. Thompson (J. Amer. Chem. Soc., 1939, **61**, 2354—2357).—Contrary to general assumptions, $CH_2·NR_2$ introduced by CH_2O and NHR_2 into a phenol may enter the position *o*- or *p*- to the OH according to rules not yet understood. Structures of the products are proved by hydrogenating-fission to PhMe derivatives. The following are prepared (many m.p. are new): 3-1′-piperidinomethyl-*p*-, m.p. 44·5—45°, and 4-1′-piperidinomethyl-*m*-cresol, an oil; 4-1′-piperidinomethyl-*s*-*m*-xylenol, m.p. 99°; 6-1′-piperidinomethyl-4-*iso*propyl-*m*-cresol, m.p. 152—153°; 2-1′-piperidinomethyl-α-naphthol, m.p. 137°; 1-1′-piperidinomethyl-β-naphthol, m.p. 93—94°; 4-1′-piperidinomethyl-2 : 5-dimethylphenol, m.p. 130—131°; *x*-1′-piperidinomethylcarvacrol, m.p. 184—185°; 3 : 5 *di*-1′-*morpholinomethylpyrocatechol*, m.p. 173—174°; 4-1′-*morpholinomethyl*-s-m-*xylenol*, m.p. 96·5—97°; 6-1′-*morpholinomethyl*-2 : 3 : 5-*trimethylphenol*, m.p. 78°; *x*-*methylcarvacrol*, b.p. 244—246°. It is established that $CH_2·NR_2$ enters the 2 and 5 positions of quinol and *p*- to the OH of thymol. R. S. C.

Use of morpholine for the production of "Mannich" bases. R. H. Harradence and F. Lions (J. Proc. Roy. Soc. New South Wales, 1939, **72**, 233—248).—$COMe_2$, morpholine hydrochloride (I), and paraformaldehyde in boiling abs. EtOH give α-*morpholinobutan*-γ-*one hydrochloride*, m.p. 149° (corresponding *picrate*, m.p. 114°). The free *base* (II), b.p. 116°/20 mm. (considerable decomp.), is reduced by Al–Hg in moist Et_2O to α-*morpholinobutan*-γ-*ol* (III), b.p. 95—100°/2·5 mm. (*picrate*, m.p. 142—144°). (III) is converted by BzCl in $CHCl_3$ into α-*morpholino*-γ-*benzoyloxybutane hydrochloride*, m.p. 152° (corresponding *picrate*, m.p. 147°). α-*Morpholino*-γ-p-*nitrobenzoyloxybutane hydrochloride*, m.p. 199°, and the corresponding *picrate*, m.p. 211°, are described. Successive treatments of (II) with MeI and $CHNa(CO_2Et)_2$ lead to *Et* δ-*keto*-α-*carbethoxyhexoate*, b.p. 162—164°/26 mm. (*semicarbazone*, m.p. 118°; *dinitrophenylhydrazone*, m.p. 55°), which does not give a colour with $FeCl_3$ and is hydrolysed and decarboxylated to γ-acetylbutyric acid; the ester is not cyclised by NaOEt–EtOH. *cyclo*Hexanone, (I), and 40% CH_2O readily yield 2-*morpholinomethyl*cyclo*hexanone hydrochloride*, m.p. 128° (corresponding *picrate*, m.p. 135°); the free *base*, b.p. 145—147°/5·5 mm., is reduced [$Al(OPr^{\beta})_3$ in $Pr^{\beta}OH$] to 2-*morpholinomethyl*cyclo*hexanol*, b.p. 120—128°/1·8 mm., probably a mixture of stereoisomerides, which gives a non-cryst. picrate. 2-*Morpholinomethyl*-1-*benzoyloxy*cyclo*hexane hydrochloride*, m.p. 211°, and the corresponding p-*nitrobenzoyl* compound, m.p. 233°, are described. Analogously, 4-methyl*cyclo*hexanone yields 4-*methyl*-2-*morpholinomethyl*cyclo*hexanone*, b.p. 131—132°/2·2 mm. (*hydrochloride*, m.p. 145°; *picrate*, m.p. 139°), and -2-*morpholinomethyl*cyclo*hexanol*, b.p. 135—137°/2 mm. (no picrate; *hydrochlorides*, m.p. 228—230° and 242—244° respectively, of the *Bz* and p-*nitrobenzoyl* derivatives). 2-Methyl*cyclo*hexanone gives 2-*methyl*-6-*morpholinomethyl*cyclo*hexanone*, b.p. 130°/1·8 mm., m.p. 48—50° (*picrate*, m.p. 118°), and 2-*methyl*-6-*morpholinomethyl*cyclo*hexanol*, b.p. 137—138°/2·3 mm.

(non-cryst. *benzoate hydrochloride*; p-*nitrobenzoate hydrochloride*, m.p. 237°). *cyclo*Pentanone yields 2-*morpholinomethylcyclopentanone*, b.p. 115—118°/2 mm. (*hydrochloride*, m.p. 137°; *picrate*, m.p. 130°), reduced by Ponndorff's method to a liquid which yields morpholine when distilled in a vac. or, under other conditions, 2 : 5-*dimorpholinomethylcyclopentanone dihydrochloride*, m.p. 195° (corresponding *dipicrate*, m.p. 152°. COPhMe gives *Ph* β-*morpholinoethyl ketone* (*hydrochloride*, m.p. 177°; *picrate*, m.p. 194°), transformed by $NHPh{\cdot}NH_2$ into 1 : 3-diphenylpyrazoline, m.p. 153°. 2-Acetylthiophen affords non-cryst. 2-*thienyl* β-*morpholinoethyl ketone* (*hydrochloride*, m.p. 194°; *picrate*, m.p. 189—190°), converted by $NHPh{\cdot}NH_2$ into 1-*phenyl*-3 : 2-*thienylpyrazoline*, m.p. 103°. Acetoveratrone forms 3 : 4-*dimethoxyphenyl* β-*morpholinoethyl ketone*, m.p. 129° (*hydrochloride*, m.p. 192°; *picrate*, m.p. 165°), which yields 1-*phenyl*-3-3′ : 4′-*dimethoxyphenylpyrazoline*, m.p. 130°. *Morpholinomethylantipyrine*, m.p. 131°, and its *picrate*, m.p. 190°, are described. H. W.

New method of introducing the cyano-group into compounds containing methylene with mobile hydrogen. C. Musante (Gazzetta, 1939, **69**, 523—535).—$CO_2Et{\cdot}CCl{:}N{\cdot}OH$ (I) and compounds of type $CHNa(COR)_2$ etc. give esters of *iso*oxazole acids which lose CO_2 with ring-opening to form compounds of type $CN{\cdot}CH(COR)_2$ etc. Thus (I) and $CHAc_2Na$ give a product (II) which on hydrolysis by EtOH–KOH and acidification yields $CHAc_2{\cdot}CN$. The product from (II) and 10% aq. KOH when acidified and treated with $NHPh{\cdot}NH_2$ forms 3′-*keto*-2′-*phenyl*-5 : 6′-*dimethyl*-2′ : 3′-*dihydropyridazino*-4′ : 5′ : 3 : 4-iso*oxazole*, $\begin{matrix}N{:}CMe{-}CH{\cdot}CMe\\ NPh{\cdot}CO{\cdot}C{=}{=}N\end{matrix}>O$ (?), m.p. 178—179°. Similarly CHBzAcNa with (I) gives $CHBzAc{\cdot}CN$; CHBzNa gives $CHBz_2{\cdot}CN$; $CHBzNa{\cdot}CO_2Et$ gives $CH_2Bz{\cdot}CN$. $CN{\cdot}CHNa{\cdot}CO_2Et$ (III) and (I) in MeOH give a product which with aq. KOH and acid forms *carbomethoxycyanoacetamide*, m.p. 119° (decomp.) [p-*nitrobenzeneazo*-derivative, m.p. 207—209° (sinters 190°)]. (III) and (I) in EtOH give a product hydrolysed to *carbethoxycyanoacetamide*, m.p. 162°, also obtained from $CN{\cdot}CHNa{\cdot}CO{\cdot}NH_2$ and $ClCO_2Et$. At 180° these substances decompose to products, m.p. ≮270°. E. W. W.

Derivatives of chromanone. R. H. Harradence, G. K. Hughes, and F. Lions (J. Proc. Roy. Soc. New South Wales, 1939, **72**, 273—283).—Chromanone (I) and $NHPh{\cdot}NH_2$ at 100° give the very unstable *chromanonephenylhydrazone* (II), m.p. 84° (*hydrochloride*, decomposes when heated), which could not be cyclised to a chromenoindole by conc. HCl, HCl–EtOH, 10% H_2SO_4, or AcOH, the product being usually a dark, red-brown oil. *Chromanonedinitrophenylhydrazone* has m.p. 244°. *Chromanoneketazine*, m.p. 176°, is completely hydrolysed to (I) by boiling HCl (1 : 1) and could not be converted into a pyrrole derivative by the method of Perkin and Plant. The failure of (II) to effect an indole ring-closure is not due to lack of reactivity of CH_2 vicinal to CO since (I) readily condenses with *o*-$NO_2{\cdot}C_6H_4{\cdot}CHO$ to 3-*o*-*nitrobenzylidenechromanone*, m.p. 142°, which can be reduced to *chromeno*-3′ : 4′ : 2 : 3-*quinoline*, m.p. 124° (*picrate*, m.p. 229°), more readily obtained by the action of NaOH on (I) and *o*-$NH_2{\cdot}C_6H_4{\cdot}CHO$ in boiling EtOH. In the Mannich reaction (I) behaves as a normal ketone, reacting with morpholine hydrochloride and paraformaldehyde in abs. EtOH to give 3-*morpholinomethyl*-4-*chromanone* (II), m.p. 93° (*hydrochloride*, m.p. 171—172°; *picrate*, m.p. 172°), and a *by-product*, $C_{20}H_{18}O_5$, m.p. 167° (*dinitrophenylhydrazone*, m.p. 221°). Reduction of (II) with $Al(OPr^{\beta})_3$ and $Pr^{\beta}OH$ gives the non-cryst. 3-*morpholinomethyl*-4-*chromanol*, b.p. 175—180°/0·8 mm. (*benzoate hydrochloride*, m.p. 177°; p-*nitrobenzoate hydrochloride*, m.p. 195°). 3-*Morpholinomethyl*-4-*chromanone methiodide*, m.p. 149—150°, from the components in boiling EtOH, and $CHAcNa{\cdot}CO_2Et$ in boiling EtOH afford (I) and 9-*keto*-7 : 8 : 9 : 12-*tetrahydrodibenzpyran*, m.p. 128—130° [*dinitrophenylhydrazone*, m.p. 250—251° (decomp.)], which gives an amorphous powder when reduced (Clemmensen). $NHEt_2$,HCl, paraformaldehyde, and (I) in boiling EtOH yield 3-*diethylaminomethylchromanone hydrochloride*, m.p. 124°. 3-N-*Piperidinomethylchromanone* is a liquid, b.p. 116—117°/1 mm. H. W.

Thiazoles. XXIII. Synthesis of benzthiazoles structurally related to quinoline antimalarials. H. H. Fox and M. T. Bogert (J. Amer. Chem. Soc., 1939, **61**, 2013—2017; cf. A., 1936, 869). —$OMe{\cdot}C_6H_3{\ll}\begin{matrix}SCl\\ N\end{matrix}{>}S$ (modified prep. from *p*-$OMe{\cdot}C_6H_4{\cdot}NH_2$ and S_2Cl_2) with NaOH–$Na_2S_2O_4$ gives 4 : 1 : 2-$OMe{\cdot}C_6H_3(NH_2){\cdot}SNa$ (I), converted by dil. AcOH, followed by HCl–Et_2O, into 2-*thiol*-p-*anisidine hydrochloride* ($NH_2 = 1$) (II), m.p. 210—211° (decomp.); the Zn salt with air and aq. NH_3 gives *di*-2-*amino*-5-*methoxyphenyl disulphide*, m.p. 73—73·5°, and with boiling HCO_2H containing a little AcOH and Zn gives 5-*methoxybenzthiazole* (III), m.p. 72·5—73°, also obtained less well from (II) by HCO_2H. H_2SO_4–HNO_3 (*d* 1·45) or fuming HNO_3–H_3PO_4 converts (III) into the 6-NO_2-derivative (IV), m.p. 202—203·5°; fuming HNO_3–H_2SO_4 at 45° gives a (?) 5 : 7-$(NO_2)_2$-derivative, m.p. 161—162·5°. Fe–HCl reduces (IV) to 6-*amino*-5-*methoxybenzthiazole*, m.p. 130·5—131·5° [*hydrochloride*, m.p. 223—224° (decomp. after darkening; sealed tube)], and thence converted by $Cl{\cdot}[CH_2]_2{\cdot}NEt_2$,HCl in abs. EtOH at 110° into 6-β-*diethylaminoethylamino*-5-*methoxybenzthiazole*, b.p. 140—145°/0·0001 mm. BzCl–NaOH and (I) give 4 : 1 : 2-$OMe{\cdot}C_6H_3(NHBz){\cdot}SBz$, m.p. 162—163°, converted by Ac_2O–NaOAc into 5-methoxy-1-phenylbenzthiazole (V), m.p. 114—114·5°, the 6-NO_2-derivative (VI), m.p. 210—211°, of which, prepared by AcOH–HNO_3 (*d* 1·4) at 60°, is also obtained from (IV) by BzCl–NaOH. Boiling 48% HBr hydrolyses (V) to 5-hydroxy-1-phenylbenzthiazole, m.p. 227—227·5° [(? 5 : 7-)$(NO_2)_2$-derivative, m.p. 194·5—196°], the 6-NO_2-derivative, m.p. 171°, of which (prep. by warm HNO_3–AcOH) is also obtained from (VI) by boiling 10% NaOH. 1-*Chloro*-4-*nitro*-6-*methoxy*iso-*benz*-1 : 2 : 3-*dithiazole*, $\begin{matrix}OMe\\ NO_2\end{matrix}{>}C_6H_2{\ll}\begin{matrix}SCl\\ N\end{matrix}{>}S$, m.p. 220° (decomp. after darkening; slow heating) or

>190° (decomp.; rapid heating), is hydrolysed by H_2O to the 1-*OH*-compound, decomp. 162·5°, which yields 1 : 3 : 4 : 5-OMe·$C_6H_2(NO_2)(NH_2)$·SNa (VII) and thence the corresponding Zn salt. The thiol is obtained from (VII) by HCl, but rapidly oxidises in air to *di*-3-*nitro*-2-*amino*-5-*methoxyphenyl disulphide*, m.p. 171°. Addition of HCO_2H–Ac_2O to crude (VII) in H_2O gives 3-nitro-5-methoxybenzthiazole, m.p. 150—152° (lit., 149—150°), reduced by Fe–HCl to the 3-NH_2-compound, m.p. 145·5—146° (lit., 151°) [hydrochloride, m.p. 207—209° (lit., 206—208°)], and thence giving 3-β-*diethylaminoethylamino*-5-*methoxybenzthiazole*, b.p. 215—217°/5—6 mm. Warm Ac_2O converts (VII) into 3-nitro-5-methoxy-1-methylbenzthiazole, m.p. 147° (lit., 149—150°). M.p. are corr. R. S. C.

Sulphanilamido-derivatives of heterocyclic amines. R. J. Fosbinder and L. A. Walter (J. Amer. Chem. Soc., 1939, **61**, 2032—2033).—2 : 6-Diaminopyridine and *p*-NO_2·C_6H_4·SO_2Cl in EtOAc at room temp. give 2-*amino*-6-p-*nitrobenzenesulphonamidopyridine*, m.p. 228—230°, reduced by Sn–HCl to 2-*amino*-6-p-*sulphanilamidopyridine**, m.p. 204—206°, which is also obtained from 2-*amino*-6-N^4-*acetylsulphanilamidopyridine*, double m.p. 194—196° and 237—239° (decomp.), by hot 5—10% NaOH (10% HCl gives mainly *p*-NH_2·C_6H_4·SO_3H). Similarly are obtained 2-p-*nitrobenzenesulphonamido*-4-*methylthiazole*, m.p. 197—199°, 2-N^4-*acetylsulphanilamido-thiazole*, m.p. 256—257°, and -4-*methylthiazole*, m.p. 259—260°, and 2-*sulphanilamido-thiazole**, m.p. 194—196°, and -4-*methylthiazole**, m.p. 236—238°. Compounds marked * are effective against strepto- and pneumo-cocci in mice. R. S. C.

Ergot alkaloids. XVIII. Production of a base from lysergic acid. Its comparison with synthetic 6 : 8-dimethylergoline. W. A. Jacobs and R. G. Gould, jun. (J. Biol. Chem., 1939, **130**, 399—405; cf. A., 1938, II, 396).—The lactam obtained from dihydrolysergic acid (A., 1938, II, 384) is catalytically hydrogenated to, among other products, 6 : 8-*dimethylergoline*, m.p. 205—212° (*hydrochloride*, +2H_2O, $[\alpha]_D^{27}$ −30° in H_2O), the inactive *form* (I) of which is synthesised and gives no depression of the m.p. on admixture.

1 : 3-CO_2H·$C_{10}H_6$·NH_2,H_2SO_4, OH·CMe$(CH_2$·$OEt)_2$, $PhNO_2$, and H_2SO_4 at 130—140° give 3-*methylbenz*-2′ : 1′-5 : 6-*quinoline*-7-*carboxylic acid*, m.p. 320—324° (decomp.) (*hydrochloride*; *Et* ester, m.p. 85—86°), converted by HNO_3 (*d* 1·4) boiling or (*d* 1·58) at room temp. mainly into the 3′-NO_2-derivative, m.p. 320—324° (decomp.). $Fe(OH)_2$ reduces this to the *lactam*, m.p. 288—289°, of the NH_2-acid, the *methiodide*, m.p. 294—296° (decomp.), of which gives the *methochloride*, m.p. 290—295° (decomp.), and thence (H_2–PtO_2) the 1 : 2 : 3 : 4-H_4-*lactam*, m.p. 249—250° (decomp.). Na–BuOH then gives (I), m.p. 222—223° (*hydrochloride*, anhyd.). 2-Methyl-5 : 6-benzquinoline-7-carboxylic acid similarly gives a crude NO_2-acid and thence the *lactam*, m.p. 319—320° (decomp.), of the 3′-NH_2-acid. R. S. C.

Alkaloids of *Nuphar luteum*. O. Achmatowicz and M. Mollówna (Rocz. Chem., 1939, **19**, 493—506).—The rhizomes were extracted with aq. tartaric acid, and the alkaloids pptd. with NH_3 were subjected to fractional vac. distillation. In this way were obtained α-*nupharidine* (I), $C_{15}H_{23}ON$, b.p. 121—121·5°/2 mm., $[\alpha]_D^{18}$ −112·1° (*hydrochloride*, m.p. 258—259°; *hydriodide*, m.p. 301—302°; *methiodide*, m.p. 185—187°; *picrate*, m.p. 165—167°; *platinichloride*, m.p. 245—247°; O-*benzoate*, an oil), and β-*nupharidine*, $C_{15}H_{23}ON$, b.p. 127—128°/2·5 mm. (*hydrochloride*, m.p. 269—270°; *hydriodide*, m.p. 273—275°; *picrate*, m.p. 152—153°; *platinichloride*, m.p. 230—232°). The alkaloids do not contain OMe or NMe; they contain one OH, a ternary N, and a double linking. With H_2 (Pt or Pd–C catalyst) they yield *dihydro*-α-, an oil (*hydrochloride*, m.p. 240—242°; *hydriodide*, m.p. 301—302°; *picrate*, m.p. 190—192°), and -β-*nupharidine*, an oil (*hydriodide*, m.p. 279—280°). R. T.

Organo-selenium compounds. I. Selenium diphenyl dihydroxides and diphenylselenides. C. K. Banks and C. S. Hamilton (J. Amer. Chem. Soc., 1939, **61**, 2306—2308).—PhOR (R = OH·$[CH_2]_2$, OH·$[CH_2]_3$, OH·CHMe·CH_2, and Me) with $SeOCl_2$ gives *Se di*-4-β-*hydroxyethylphenyl*, m.p. 172°, *di*-4-γ-, m.p. 159°, and -β-*hydroxy*-n-*propoxyphenyl*, m.p. 147°, and *di*-p-*anisyl*, m.p. 163°, *dichloride*, hydrolysed by hot, aq. Na_2CO_3 to the *dihydroxides*, m.p. 99°, 140°, 56°, and 134°, respectively. A large excess of HNO_3 (*d* 1·5) at 0° then affords *Se* 3-*nitro*-4-*methoxy*-, m.p. 203°, -4-β-*hydroxyethoxy*-, m.p. 175°, -4-γ-*hydroxy*-n-*propoxy*-, m.p. 117°, and -4-β-*hydroxy*-n-*propoxyphenyl dihydroxide*, m.p. 128°, reduced by H_2–Raney Ni in EtOH at room temp./2·67 atm. to *di*-3-*amino*-4-*methoxy*-, m.p. 112° (*dihydrochloride*, m.p. >250°), -4-β-*hydroxyethoxy*-, m.p. 132°, -4-γ-, m.p. 104°, and -4-β-*hydroxy*-n-*propoxy*-, m.p. 128°, -*phenyl selenide*. The $(OH)_2$-dihydroxides form dinitrates. NHPhAc and $SeOCl_2$ in Et_2O give a 2 : 1 additive *compound*, m.p. 135°; in $CHCl_3$ they give *Se di*-4-*acetanilide dihydroxide*, m.p. 223°, reduced to *di*-4-*acetamidophenyl selenide*, double m.p. 176° and 216°, which with boiling 20% HCl gives *di*-p-*aminophenyl selenide*, m.p. 117°. R. S. C.

Structure of the protein molecule. D. L. Talmud (Acta Physicochim., 1939, **10**, 753—774).—A review of work on the structure of the protein mol. is given. Wrinch's theory (A., 1937, II, 475; III, 296) of "globular" proteins has been tested experimentally. In the "cyclol" structure, all the "openings" in the faces of a globular mol. make up a space enclosed by 12 hexagons. The side groups may reduce this opening to the size of a C_6H_6 ring. Foreign mols. in a solution of a globular protein of cross-section < that of the C_6H_6 ring will diffuse through the mol. If a reaction then occurs which is accompanied by an increase in the size of the foreign mol., then that portion of the reaction products originating inside the globular mol. will be enclosed within the mol. This has been shown to occur by converting NH_2·CH_2·CO_2Et into 2 : 5-diketopiperazine (I) in aq. solutions of cryst. egg-albumin and pepsin. The vol. of (I) enclosed in the globular protein mols. was almost equal to the total vol. of the protein globules. It is shown that (I) is neither adsorbed nor enclosed in the form of solution. Heavy

pepsin mols. "full of" (I) have been isolated in the cryst. form. The rate of formation of (I) is accelerated by the presence of the globular structure. A hypothesis on the nature of this catalysis is put forward, the globular protein mol. being compared with an elementary biological cell. The intra-globular osmotic pressure is considered. A. J. M.

Keto-enol tautomerism of proteins. I. Tautomerism of gelatin: potentiometric titration data. II. Tautomerism of peptides and diketopiperazines. A. P. KONIKOV and L. M. NAZAROVA (Arch. sci. biol. U.S.S.R., 1935, **39**, 497—504, 505—521).—I. Diminution in p_H of gelatin solution on treatment with alkali is reversible and depends on formation of $H^{\cdot}$ by enolisation of peptide linkings in polypeptides and diketopiperazines.

II. The mechanism of the enolisation of peptide linkings is examined. The process is associated with a lactam–lactim transformation and is accompanied by racemisation of NH_2-acids united in the polypeptide. CH. ABS. (*p*)

Mol. wt. of crystalline myogen.—See A., 1939, III, 938.

Preparation of thyroxine from casein treated with iodine. C. R. HARINGTON and E. V. PITT RIVERS (Nature, 1939, **144**, 205).—The results of Ludwig and Mutzenbecher (A., 1939, II, 369) have been confirmed. Possible mechanisms by which thyroxine is formed in these experiments are discussed. L. S. T.

Dissociation of the hæmocyanin molecule. S. BROHULT and S. CLAESSON (Nature, 1939, **144**, 111—112).—The effects of different types of salts, *e.g.*, NaCl, NH_4Cl, Na_2SO_4, and $CaCl_2$, and of non-electrolytes, such as glucose and $CO(NH_2)_2$, investigated by means of the ultracentrifuge, on the dissociation of the hæmocyanin (I) mol. in 0·08M-OAc′ (p_H 5·2) and PO_4''' (p_H 6·0) buffers, are recorded. Well-defined sub-multiples of the original mol. are obtained. The dissociation effect increases with the valency of the ions. NaCl gives no components < half-mols., and the reaction ceases before all the whole mols. are dissociated. The effect is smaller with non-electrolytes. Complete reversibility can be obtained in all cases where the dissociation has given only half-mols. The dissociation of the (I) mol. is a general rather than a sp. reaction associated with a special type of compound. Certain mols. or groups have a stronger effect than others, but all types, whether charged or not, affect the dissociation of (I). L. S. T.

Reducing groups of ovalbumin. M. L. ANSON (Science, 1939, **90**, 142—143).—Oxidation of denatured ovalbumin by $Fe(CN)_6'''$ at p_H 6·8 in presence of Duponol PC occurs at a much lower [$Fe(CN)_6'''$] than in absence of Duponol, and the amount of $Fe(CN)_6''''$ formed is independent of time, temp., and concns. within wide limits. Reduction of $Fe(CN)_6'''$ does not occur when SH groups of the denatured ovalbumin are destroyed with CH_2O or $CH_2I{\cdot}CO{\cdot}NH_2$. $CO(NH_2)_2$ and guanidine promote the reaction with $Fe(CN)_6'''$, but are much less effective than Duponol. I and $CH_2I{\cdot}CO{\cdot}NH_2$, but not $Fe(CN)_6'''$, react with native ovalbumin. Reaction is not necessarily confined to SH groups. L. S. T.

Carbon and hydrogen determinations. Effect of pressure on lessening combustion and sweeping-out times. S. S. BRODIE (Ind. Eng. Chem. [Anal.], 1939, **11**, 517—518; cf. A., 1938, II, 517).—A procedure is described for the semi-micro-analysis of org. compounds under pressure (5—10 cm. of Hg) in 25 min. Halogen is absorbed by Ag supported on asbestos. J. L. D.

Qualitative test for oxygen in organic compounds. C. V. BOWEN, J. F. BOURLAND, and E. F. DEGERING (J. Chem. Educ., 1939, **16**, 295—296).—Vapours of the sample are passed through wood-C heated to dull redness, and any CO_2 formed is pptd. by aq. $Ba(OH)_2$. Air is first removed from the apparatus by heating PhMe or C_7H_{16} in it. L. S. T.

Determination of amido- and nitrile-nitrogen as ammonia. L. PALFRAY, S. SABETAY, and S. ROVIRA (Compt. rend., 1939, **209**, 483—485).—The substance is heated (to the b.p.) with KOH in $CH_2Ph{\cdot}OH$ during (usually) 1 hr.; the NH_3 is removed in N_2, absorbed in H_2O, and titrated with 0·1N-H_2SO_4 (methyl-orange). Good results are obtained. It is impracticable to determine the amount of KOH used. J. L. D.

Identification of flavouring constituents of commercial flavours. VIII. Semi-micro-determination of amino-nitrogen atom in semicarbazones. J. B. WILSON (J. Assoc. Off. Agric. Chem., 1939, **22**, 688—690).—A semi-micro-modification of Veibel's method (cf. A., 1937, II, 130) is detailed. E. C. S.

Semi-micro-determination of sulphur in organic substances. A. ANGELETTI (Annali Chim. Appl., 1939, **29**, 356—359).—The substance (0·02—0·03 g.) is heated in a closed tube with solid $KMnO_4$ and the SO_4'' produced is pptd. as $BaSO_4$ by excess of 0·05N-$BaCl_2$; standard aq. K_2CrO_4 is then added to ppt. Ba and excess of K_2CrO_4 determined iodometrically. F. O. H.

Micro-determination of selenium in organic compounds. S. UMEZAWA (Bull. Chem. Soc. Japan, 1939, **14**, 153—154; cf. A., 1929, 1323).—Se is determined in selenophen and selenophthen derivatives by catalytic oxidation (O_2–Pt) in a Pregl spiral. The products are dissolved in H_2O, boiled with HCl, and reduced with $NaHSO_3$, and the resulting Se is weighed. A. LI.

Qualitative organic analysis. II. Identification of alkyl halides, aromatic nitroso-compounds, aromatic hydrocarbons, and *cyclo*pentadiene compounds. (MISS) W. J. LEVY and N. CAMPBELL (J.C.S., 1939, 1442—1446; cf. A., 1937, II, 529).—The respective alkyl halide (bromide unless stated otherwise) and $CS(NH_2)_2$–EtOH, then picric acid, give: *S*-methyl- (I), m.p. 224° (from MeI), -ethyl- (II), m.p. 188° (from EtI), -propyl-, m.p. 177° (more readily from PrBr than from PrCl), -*iso*propyl-, m.p. 196°, -*n*-, m.p. 177° (readily from BuBr), -*iso*-, m.p. 167° (from $Bu^{\beta}I$), and -*sec*.-butyl-, m.p. 166° (from iodide; small yield); -*n*-, m.p. 154°,

-iso-, m.p. 173°, and *-sec.*-amyl-, m.p. 157°, *-n*-hexyl-, m.p. 157°, -n-*heptyl-*, m.p. 142°, -n-*octyl-*, m.p. 134°, *-cetyl-*, m.p. 137° (from RI), *-allyl-*, m.p. 155° (from RCl), -α-, m.p. 167°, and -β-*phenylethyl-*, m.p. 139° -o-, m.p. 222°, -m-, m.p. 205°, and -p-*bromobenzyl-*, m.p. 219° (from RCl), -o-, m.p. 213°, -m-, m.p. 200°, and -p-*chlorobenzyl*-iso*thiocarbamide picrate*, m.p. 194°. BuI or *iso*valeryl chloride gives (I) (using MeOH as solvent) or (II) (using EtOH). $ClCO_2Me$ or $ClCO_2Et$ gives (I) or (II), respectively. Similarly prepared from the respective dibromides are: *SS*-ethylene-, m.p. 260°, *-propylene-*, m.p. 232° (small yield), -iso*butylene-*, m.p. 223° (small yield), and *-trimethylene-di*isothiocarbamide *picrate*, m.p. 229°. The respective aromatic *C*-NO-compound and 2-phenylindole in EtOH–KOH give: 3-*anilo-*, m.p. 154°, -m-, m.p. 148°, and -p-*chloroanilo-*, m.p. 157°, -m-, m.p. 169°, and -p-*bromoanilo-*, m.p. 154°, -m-, m.p. 136°, and -p-*tolylimino*-2-*phenylindolenine*, m.p. 146°; p-$C_6H_4Me{\cdot}NO$ gives also a compound, m.p. 215° (cf. Reissert, A., 1909, i, 435). Most suitable for identification of *C*-NO-compounds are the azo-compounds from p-$C_6H_4Br{\cdot}NH_2$ (method: Ingold, A., 1925, i, 646): 2-, m.p. 110°, 3-, m.p. 119°, and 4-*chloro*-4′-*bromo-*, m.p. 190°, 2 : 4′-, m.p. 104°, 3 : 4′-, m.p. 126°, and 4 : 4′-*dibromo-*, m.p. 205°, 4′-*bromo*-3-, m.p. 82°, and -4-*methyl-azobenzene*, m.p. 152°, are described. 1 : 2 : 4 : 5-$C_6H_2Me(NO_2)_3$, (III) is not recommended as a reagent for NH_2Ar (cf. *loc. cit.*); 4 : 6-dinitro-*N*-phenyl-, m.p. 145°, *-m*-tolyl-, m.p. 150°, *-m*-xylyl-, m.p. 186°, and *p*-anisyl-*m*-toluidine, m.p. 139°, are recorded. 1 : 4 : 2 : 3 : 5-$C_6HMe_2(NO_2)_3$ (IV) is not so reactive as (III) with aliphatic amines. (IV) and NH_2Me give 3 : 5-*dinitro*-N-*methyl*-p-*xylidine*. Purification by chromatographic adsorption does not affect the fluorescence (ultra-violet) of $C_{10}H_8$, anthracene (V), or chrysene (all purple), pyrene (light green), or 1 : 2-(purple) or 2 : 3-benzanthracene (VI) (slight green) (cf. Dutt, A., 1930, 1345). (V) or (VI) gives also some dianthracene (not formed in dark) or 2 : 3-naphthaquinone (trace in dark), respectively. Hydrocarbons, highly purified or crude, viz., CH_2Ph_2, Ph_2, retene, fluorene, 9-phenyl-, or 1 : 2- or 3 : 4-benz-, or 1 : 2 : 5 : 6-dibenz-fluorene, phenanthrene, perylene, 1 : 2-benzanthracene, 9 : 10-benzphenanthrene, and fluoranthene, give characteristic colours with $CHPhCl_2$–H_2SO_4 in C_6H_6 (cf. Lippmann *et al.*, A., 1902, ii, 702). Benzopyrene, $(CH_2Ph)_2$, hydrindene, (VI), or truxene, gives no characteristic colour. Quinones do not react. p-$C_6H_4(NO_2)_2$ added to Vanscheidt's reagent (A., 1935, 74) gives a reagent which affords characteristic green or blue colours with *cyclo*pentadiene and derivatives, *e.g.*, di*cyclo*-pentadiene, indene, fluorene, 2-nitro-, 2-bromo-, 2 : 7-dibromo-, 7 : 2- or 2 : 3-bromonitro-, 1 : 2- or 3 : 4-benz-, or 1 : 2 : 5 : 6-dibenz-fluorene, and truxene (cf. Stobbe *et al.*, A., 1927, 347). 9-Phenylfluorene, CH_2Ph_2, $CHPh_3$, $CPh_3{\cdot}OH$, CPh:CH, or acenaphthene gives a negative test. 2 : 4 : 1-$(NO_2)_2C_6H_3{\cdot}CO_2H$ is best obtained by Storrie's method (A., 1937, II, 498). A. T. P.

Determination of alcoholic and phenolic groups. E. Raymond and E. Bouvetier (Compt. rend., 1939, **209**, 439—441; cf. Sabetay, A., 1937, II, 44).—The HCl liberated when the dry substance is treated with stearyl or palmityl chloride in gently boiling, dry CCl_4 or benzine is removed with dry air, collected in H_2O, and titrated with 0·5N-NaOH. The method is applied to a variety of alcohols and phenols but fails with those insol. in the above solvents. *tert.*-Alcohols and phenols react slowly. Amines interfere with the determination; CO_2H undergoes quant. reaction and its presence must be corr. for. J. L. D.

Determination of water in ether. R. Gaspart and G. Serrure (Bull. soc. chim. Belg., 1939, **48**, 283—292; cf. A., 1939, II, 195).—Extinction curves from 3400 to 3700 cm.$^{-1}$ for very dil. solutions of H_2O in Et_2O are recorded with a view to their use for the determination of H_2O in Et_2O. F. J. G.

Quantitative separation of unsaturated fatty acids in fats and phosphatides.—See A., 1939, III, 1020.

Okuda's iodine method for determination of cystine. M. Sato, T. Hirano, and T. Kan (J. Agric. Chem. Soc. Japan, 1939, **15**, 783—790).—Improvements in the method (A., 1926, 190; 1929, 1191) are described. For the quant. oxidation of cysteine by I the [HCl] must be 0·5—1N., the temp. of the solution 0—8°, and the [KI] 0·01—0·03M. When cystine is reduced there is a close relationship between the amounts of cystine, and Zn, concn. of acid, temp. during reduction, and time of reduction. 30 min. are sufficient for the reduction of 0·1 mg.-mol. of cystine at 20° using 2 g. of Zn and 60 c.c. of N-HCl. 0·5N-HCl is better than hot H_2O for washing after the reduction and decolorisation. J. N. A.

Micro-determination of threonine. R. J. Block and (Miss) D. Bolling (J. Biol. Chem., 1939, **130**, 365—374).—Threonine (I) (0·5—5 mg. in 10 mg. of NH_2-acids) is oxidised by $Pb(OAc)_4$ (1 g.) in AcOH. The MeCHO produced is removed in air and determined colorimetrically (560 mμ. filter) after reaction with p-$C_6H_4Ph{\cdot}OH$ in H_2SO_4. 15 NH_2-acids and 9 carbohydrates are shown not to interfere. If much *l*-hydroxyproline or *l*-tryptophan is present, more $Pb(OAc)_4$ must be used. Alanine and serine also yield MeCHO, but only in small amount, and do not interfere appreciably unless a large excess is present. By this method it is shown that casein yields ~3·5, serum-proteins ~6·0, and gelatin 0·5—1·1% of (I). R. S. C.

Diazo-reaction. I. Diazo-reaction in acid and alkaline media, and in alkaline medium subsequently acidified. II. Limits and significance of Gebauer-Fülnegg's modification of Pauly's diazo-reaction. III. Significance and limits of Hanke and Koessler's proposed modification in the determination of tyrosine and tyramine. M. Vialli and V. Erspamer (Arch. Fisiol., 1939, **39**, 1—19, 20—32, 33—41).—I. Colour reactions with p-$SO_3H{\cdot}C_6H_4{\cdot}N_2Cl$ (I) in acid and alkaline media, and in the latter subsequently acidified, are tabulated for 58 compounds of histological importance. Positive results are obtained with histidine, histamine, and

tryptophan; negative with cysteine and cystine. Purine derivatives react only at high concn. The product from ascorbic acid becomes colourless when acidified. Colour changes with $COMe_2$ and glucose are described.

II. The method of Gebauer-Fülnegg (A., 1930, 1605) is critically examined. Diazonium salts are coupled with 36 compounds in alkaline solution, and the product is extracted with $Bu^{\beta}OH$, $Bu^{\alpha}OH$, or other org. solvent. Generally, coloured products from acidic and basic substances are respectively slightly and easily sol. in $Bu^{\beta}OH$. The method is not suitable for distinguishing derivatives of glyoxaline from those of tyrosine (cf. *loc. cit.*).

III. The reaction of Hanke and Koessler (A., 1922, ii, 322), in which substances are treated with a diazonium salt, followed by NaOH and NH_2OH (which gives a bluish colour with certain compounds), is examined as a method for detecting phenols. The reaction is given, *inter alia*, by $CH_2R{\cdot}CH(NH_2){\cdot}CO_2H$ ($R = p$-$OH{\cdot}C_6H_4$), $CH_2R{\cdot}CHMe{\cdot}NHMe$, and $CH_2R{\cdot}CH(NH_2){\cdot}CH_2{\cdot}OH$ (and also by $COMe_2$), but not by $OH{\cdot}CHR{\cdot}CHMe{\cdot}NHMe$ or 3 : 4 : 1-$(OH)_2C_6H_3{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$. Its use in histochemistry is recommended. E. W. W.

Preparation of aniline derivatives. Hydrosulphoiodometric determination of azo-compounds. V. Indacochea Z. (Bol. Soc. Quím. Peru, 1939, **5**, 124—133).—Azo-compounds (0·1—0·5 g.) such as methyl-red can be determined by addition of 10 c.c. of 11% $NaHSO_3$ and 3 g. of Zn powder; after shaking, 1 c.c. of AcOH is added and then 5 g. of $NaHCO_3$. Excess of the $Na_2S_2O_4$ produced in the reaction is titrated with I and starch. F. R. G.

Determination of dehydrocholic acid. G. Saba (J. Biochem. Japan, 1939, **30**, 61—67).—Application of the alkaline m-$C_6H_4(NO_2)_2$ reagent of Kaziro and Shimada (A., 1937, II, 500) to the colorimetric determination of 0·25—1·5 mg. of dehydrocholic acid (pure or in tissue extracts) is described. F. O. H.

Precipitation reaction between the pyridine derivatives picoline, β-picoline, and collidine and phenol derivatives. H. Bergstermann, P. A. Nöcker, and B. Krauskopf (Arch. exp. Path. Pharm., 1938, **191**, 55—75).—The pptg. power of the series C_5H_5N, α- β-picoline, and collidine increases in that order (order of decreasing hydrophilism). The phenols fall into the same series as that observed by Labes (*ibid.*, **190**, 421) using other C_5H_5N derivatives. For reaction partners low in residual valency substituents the degree of hydrophobism is the governing factor. Hydrophilic substituents in the phenol, *e.g.*, NH_2, OH, or $CO{\cdot}NH_2$, weaken the reaction. J. H. B.

Precipitation reactions of quinoline and quinolinimide with phenol substitution products. R. Labes, B. Krauskopf, and H. Bergstermann (Arch. exp. Path. Pharm., 1939, **192**, 603—617).—Quinoline is a better precipitant than the C_5H_5N derivatives previously examined (cf. preceding abstract). The order of activity of the phenol substituents in promoting pptn. is approx. the same as with C_5H_5N, the methylpyridines, and the ethylpyridinecarboxylates. Dihydric phenols and salicylamide, however, show a sp. increase in activity. Quinolinimide gives no reaction except with NH_2-phenols. J. H. B.

Determination of 8-hydroxyquinoline in presence of sulphosalicylic acid. A. Castiglioni (Annali Chim. Appl., 1939, **29**, 315—316).—The ppt. from 8-hydroxyquinoline (*B*) and silicotungstic acid in dil. HCl solution is dried at 105° and weighed as $12WO_3,SiO_2,4B,4H_2O$ (factor 0·2039). F. O. H.

Ultramicro-determination of thiamine by fermentation.—See A., 1939, III, 920.

Boric acid colour reaction of flavone derivatives. C. W. Wilson (J. Amer. Chem. Soc., 1939, **61**, 2303—2306).—The yellow colour given by citrin with H_3BO_3 and anhyd. citric acid in $COMe_2$ is given also by quercitrin, kaempferol, 2 : 4-$(OH)_2C_6H_3{\cdot}CO{\cdot}CH(OH){\cdot}CO{\cdot}C_6H_3(OH)_2$-3 : 4, 5 : 2′ : 4′ : 6′-tetrahydroxy-4-methoxy- and 4 : 2′ : 4′ : 6′-tetrahydroxy-chalkone, but not by fisetin, naringenin, hesperetin, or cyanidin. Curcumin gives a pink colour. The nature of the necessary groups is discussed. R. S. C.

Determination of the barbiturates. R. F. Chatfield (Pharm. J., 1939, **143**, 346).—The work of Paget and Tilley (A., 1937, II, 268) on the reactions of ten substituted barbiturates with Millon's reagent is modified and a proposed separation table is given. J. D. R.

Silicotungstic acid determination of nicotine. Errors involved and a new technique for steam-distillation of nicotine. A. W. Avens and G. W. Pearce (Ind. Eng. Chem. [Anal.], 1939, **11**, 505—508).—The sample is suspended in H_2O made just alkaline [NaOH or $Ba(OH)_2$] to phenolphthalein and distilled in steam (30 min.) under pressure, the distillate being collected in aq. HCl. Silicotungstic acid (I) (12%) is added to an aliquot of the distillate, which is heated (steam-bath) for 15 min. and then left overnight at 0—10°. The ppt. is filtered off under standard conditions and nicotine (II) determined in the usual manner. Different filter-papers retain different amounts of (I) which introduces errors into abs. determinations of (II). Under standard conditions, the amount retained is const. J. L. D.

Colorimetric determination of hydroxyproline and its application to gelatin hydrolysates. W. D. McFarlane and G. H. Guest (Canad. J. Res., 1939, **17**, B, 139—142).—The solution is treated with $CuSO_4$, NaOH, and H_2O_2, followed by isatin and HCl, and the red colour is determined photo-electrically using a light filter. Moisture-free gelatin contains 14·65% of hydroxyproline. S. H. H.

Colorimetric determination of proline. G. H. Guest (Canad. J. Res., 1939, **17**, B, 143—144).—The proline (I) in casein (II) is determined by oxidation of (I) with PbO_2 and condensation of the product with p-$NMe_2{\cdot}C_6H_4{\cdot}CHO$ to give a red compound, estimated photo-electrically. (II) contains 7·94% of (I). The method fails in presence of hydroxyproline. S. H. H.