BRITISH CHEMICAL ABSTRACTS

A., II.—Organic Chemistry

DECEMBER, 1937.

Chain vibrations of isomeric paraffins and their identification in the Raman spectrum.—See A., I, 549.

Oxidation of propane.—See A., I, 621.

Paraffin hydrocarbons from crude synthetic *iso*octane [ββδ-trimethylpentane]. D. B. Brooks, R. B. Cleaton, and F. R. Carter (J. Res. Nat. Bur. Stand., 1937, **19**, 319—337).—The following hydrocarbons have been isolated from crude *iso*octane, partly by distillation and partly by crystallisation from CH_4: ββ- and βγ-dimethylbutane; β-methyl-, ββ-, βγ-, βδ-dimethyl-, βγγ- and βγδ-trimethylpentane; β-methyl-, βδ-, βε-, δε-dimethyl-, ββδ-, ββε-trimethyl-, γγδδ-tetramethyl-, and ββγγδ-pentamethyl-hexane; βδ-, γγ-dimethyl-, δ-ethyl-, ββζ-, ββδ-(or ββε-)trimethyl-heptane; βζ-dimethyloctane. The majority of these are present to the extent of <0·05%. F. L. U.

Reaction for unsaturated hydrocarbons or their peroxides. E. Lederer (Petroleum, 1937, **33**, No. 38, 9—13).—When treated with the heavy-metal salts of certain aliphatic, hydroaromatic, or aromatic carboxylic and sulphonic acids, *e.g.*, Mn or Co octoate or stearate, unsaturated hydrocarbons give a characteristic colour change, *e.g.*, from colourless to deep brown in the case of the Mn salts. Development of the colour forms a delicate test for the presence of unsaturated compounds, the test being carried out by treating 0·5—1 c.c. of the oil with 10 mg. of the Mn salt and heating the mixture for 10 min. on the steam bath. The reaction is dependent on the presence of a peroxide of the unsaturated compound. The reaction may be used to free the oil from peroxides. Colour changes occurring when certain (particularly polynuclear) hydrocarbons are treated with Ag salts are due to another type of reaction, viz., a reduction with separation of colloidal Ag. A. B. M.

Photochemical chlorination of ethylene compounds.—See A., I, 627.

Polymerisation of isoprene. W. H. Carmody and M. O. Carmody (J. Amer. Chem. Soc., 1937, **59**, 2073—2074).—Vapour-phase polymerisation of isoprene over $AlCl_3$ gives exclusively a sol. polymeride, the mol. wt. (1300 in C_6H_6) of which is approx. twice that of the product formed during liquid-phase polymerisation (A., 1932, 830). H. B.

Pyrolysis of *iso*butene at very low conversions. C. D. Hurd and F. H. Blunck (J. Amer. Chem. Soc., 1937, **59**, 1869—1871).—Decomp. of *iso*butene at 650° to the extent of 0·1—1% gives CH_4 (50—59), C_2H_4 (11—13·6), and C_3H_6 (29—36%) as the only gaseous products. The persistence of C_2H_4 emphasises the need for caution in interpreting the method of extrapolating products formed during such decomp. to their vals. at zero conversion. H. B.

βεε-Trimethyl-$\Delta^{\alpha\gamma}$-hexadiene and its hydrogen bromide additive product. K. N. Campbell (J. Amer. Chem. Soc., 1937, **59**, 1980—1983).—The ketol from $Bu^{\gamma}CHO$ (prep. from $MgBu^{\gamma}Cl$ and HCO_2Me) and $COMe_2$ in EtOH–NaOEt is dehydrated (distillation with I) to β-keto-εε-dimethyl-Δ^{γ}-hexene (I), b.p. 78—80°/40 mm. (2 : 4-dinitrophenylhydrazone, m.p. 159—161°; *semicarbazone*, m.p. 178°), which gives an unstable compound with dry HCl. The carbinol from (I) and MgMeCl is similarly dehydrated to βεε-trimethyl-$\Delta^{\alpha\gamma}$-hexadiene (II), b.p. 128°/732 mm., which is reduced catalytically to βεε-trimethylhexane and by Al–Hg in moist Et_2O to βεε-trimethyl-Δ^{β}-hexene (?), b.p. 72°/735 mm. (ozonolysis products, $COMe_2$ and $CH_2Bu^{\gamma}\cdot CHO$). (II) and HBr (1 mol.) in cold $CHCl_3$ give the not very stable β-bromo-βεε-trimethyl-Δ^{γ}-hexene (?), b.p. 75—77°/50 mm., oxidised by $KMnO_4$ and $Na_2Cr_2O_7$ (method: Farmer and Marshall, A., 1931, 460) to $OH\cdot CMe_2\cdot CO_2H$ and by O_3 (followed by Zn dust and H_2O) to $Bu^{\gamma}CHO$ and (polymeric) $OH\cdot CMe_2\cdot CHO$. αβ-Addition of HBr, with no rearrangement, thus occurs. H. B.

Peroxide effect in the addition of hydrogen bromide to ethylene compounds. XIV. Addition of hydrogen bromide to the higher alkenes. M. S. Kharasch and W. M. Potts (J. Org. Chem., 1937, **2**, 195—197).—Addition of HBr to Δ^{α}-nonene, -undecene, -tridecene, and -pentadecene, and to allylbenzene etc., gives primary bromides whenever peroxides are present, and *sec.* bromides in the presence of antioxidants. E. W. W.

Oxidation of unsaturated hydrocarbons by atmospheric oxygen. I. E. Afferni (Annali Chim. Appl., 1937, **27**, 366—372).—Oxidation of $Me\cdot[CH_2]_{13}\cdot CH{:}CH_2$ by air at 125—145°, for 40 days, produces a wt. increase of 16·5%, and yields CO and CO_2, the evolution of which increases to a max. and eventually ceases, a polymerised acid (30%), mol. wt. 730—800, forming an *Et* ester $C_{17}H_{34}O_2$, b.p. 117·5°/15 mm., and a highly polymerised unsaponifiable residue. No peroxides were detected. L. A. O'N.

Action of elementary fluorine on organic compounds. IV. Vapour-phase fluorination of ethane. J. D. Calfee and L. A. Bigelow (J. Amer. Chem. Soc., 1937, **59**, 2072—2073; cf. A., 1937, II, 81).—C_2H_6 and F_2 react in the vapour phase

over Cu gauze to give C_2F_6 and smaller amounts of CF_4, CHF_3, and $CMeF_3$ (?). H. B.

Kinetics of the pyrolysis of *n*-propyl iodide and *n*-butyl iodide.—See A., I, 621.

Allylic rearrangements. IV. Composition of butenyl bromides prepared from crotyl alcohol and methylvinylcarbinol. W. G. Young and J. F. Lane (J. Amer. Chem. Soc., 1937, **59**, 2051—2056).—Mixtures of $CHMe{:}CH{\cdot}CH_2Br$ (I) and $CH_2{:}CH{\cdot}CHMeBr$ (II) are obtained from either crotyl alcohol or methylvinylcarbinol by treatment with (i) 48% HBr at −15°, (ii) 48% HBr + conc. H_2SO_4 at −15°, (iii) saturated aq. HBr at 0°, (iv) dry HBr at −20°, (v) $PBr_3 + C_5H_5N$ at −15° or −75°. The composition (determined refractometrically and corr. for small amounts of inert impurities) of the mixtures varies with each reagent and with the alcohol used. Since known mixtures of (I) and (II) do not alter appreciably under the experimental conditions used, rearrangements must occur during the formation of the bromides from the alcohols. Considerable rearrangement of (II) into (I) occurs with 48% HBr at 20°. H. B.

Bouveault reaction for the preparation of unsaturated alcohols. G. Goethals (Natuurwetensch. Tijds., 1937, **19**, 184—188).—Reduction of Me Δ^{β}-pentenoate with Na in dry MeOH or EtOH gave a mixture of 25% of amyl alcohol and 75% of Δ^{β}-pentenol together with smaller quantities of β- or γ-methoxyvaleric acid, and a very small quantity of β- or γ-methoxy-*n*-amyl alcohol. S. C.

Derivatives of ββ'β'-trialkylethanols. R. V. Rice, G. L. Jenkins, and W. C. Harden (J. Amer. Chem. Soc., 1937, **59**, 2000).—The *H phthalates*, m.p. 70—71°, 68—69°, 44·5—45·5°, and 84—85°, *H tetrachlorophthalates*, m.p. 140—141°, 149·5—150·5°, 144—145°, and 138—139°, and *phenylcarbamates*, m.p. 99—100°, 80—81°, —, and 135—136°, of $CH_2Bu^{\gamma}{\cdot}OH$, $CMe_2Et{\cdot}CH_2{\cdot}OH$, $CMeEt_2{\cdot}CH_2{\cdot}OH$, and $CEt_3{\cdot}CH_2{\cdot}OH$, respectively, are described. The narcotic action of the alcohols is < that of $CBr_3{\cdot}CH_2{\cdot}OH$. H. B.

Esters derived from heptyl alcohol. M. Roger and F. Dvolaitzka (Recherches, Roure-Bertrand, 1937, 79—82).—The following *heptyl* esters have been examined particularly with regard to their possible use in perfumery: formate, b.p. 76—77°/25 mm.; acetate, b.p. 95—96°/28 mm.; propionate, b.p. 88°/10—12 mm.; butyrate, b.p. 105°/10—12 mm.; iso*butyrate* (I), b.p. 98°/10—12 mm.; iso*valerate*, b.p. 108°/10—12 mm.; hexoate (II), b.p. 121°/10—12 mm.; heptoate, b.p. 132—133°/10—12 mm.; octoate, b.p. 145°/10—12 mm.; *nonoate*, b.p. 162°/10—12 mm.; *decoate*, b.p. 170—172°/10—12 mm.; *undecoate*, b.p. 167·5—168·5°/3 mm.; *undecenoate* (III), b.p. 174—175°/10—12 mm.; *laurate*, b.p. 184°/10—12 mm.; *myristate*, b.p. 190—191°/3 mm.; *palmitate*, b.p. 205—206°/3 mm.; *stearate*, b.p. 215—217°/3 mm., m.p. 15°; *oleate*, b.p. 216—217°/3 mm.; *geranate* (IV), b.p. 149—151°/3 mm.; *citronellate*, b.p. 139—140°/3 mm.; *benzoate*, b.p. 150°/10—12 mm.; *phenylacetate*, b.p. 143°/10—12 mm.; *cinnamate*, b.p. 185°/10—12 mm.; *anisate*, b.p. 155—157°/3 mm.; *salicylate* (V), b.p. 160°/10—12 mm. In the ester series, as in that of the ethers, the same fruity, fatty and green odours, although less fugitive, accompany the heptyl radical. The odours of (I), (II), (III), (IV), and (V) appear original. H. W.

Alcohol, $C_{19}H_{40}O$, m.p. 62·5°, from oil of raspberries.—See A., III, 331.

Lipins of tubercle bacilli.—See A., III, 318.

Carbohydrates. IX. Introduction of copper into polyhydric alcohols. T. Lieser and R. Ebert (Annalen, 1937, **532**, 89—94; cf. A., 1937, II, 179).—The alcohol is usually dissolved in 5—10% NH_3 and shaken with excess of $Cu(OH)_2$; after filtration, MeOH is added to the filtrate followed, if necessary, by Et_2O, whereby the complex is pptd. Alternatively, the non-reducing oligosaccharide is dissolved in aq. $NEt_4{\cdot}OH$. *Complexes* are thus obtained with $(CH_2{\cdot}OH)_2$, glycerol, erythritol, adonitol, mannitol, sorbitol, dulcitol, methylxyloside, methyl- and phenyl-glucoside, glucose, galactose, fructose, β-glucosan, maltose, lactose, cellobioside, sucrose, inositol, and tartaric acid (structures suggested). With oligosaccharides the union with Cu is less complete than with monosaccharides, probably owing to the isolated position of certain OH groups. H. W.

Triphenylmethyl ethers of glycerol and glycerol derivatives. C. D. Hurd, C. O. Mack, E. M. Filachione, and J. C. Sowden (J. Amer. Chem. Soc., 1937, **59**, 1952—1954).—Glycerol α-CPh_3 ether (I) [βγ-Me_2 derivative, b.p. 210—212°/3 mm., m.p. 45—50°, from (I), MeI, and Ag_2O in C_6H_6] heated at 180—190° gives glycerol αγ-$(CPh_3)_2$ ether (II), which at 260° affords *glycerol* (CPh_3)$_3$ *ether*, m.p. 196—197° [also prepared from glycerol (III) and CPh_3Br in C_5H_5N]. (I) is obtained from (II) and excess of (III) at 205—215°. Decomp. of the βγ-dibenzoate of (I) at 260—300° gives $CHPh_3$, BzOH, and an unidentified unsaturated liquid. 2 : 2-*Dimethyl*-4-*triphenylmethoxymethyl*-1 : 3-*dioxolan* [αβ-iso*propylideneglycerol CPh*$_3$ *ether*], m.p. 71—73° (from the OH-compound and CPh_3Cl in C_5H_5N), heated at 310—328° affords $CHPh_3$, $COPh_2$, and $COMe_2$. H. B.

Characteristic reaction of yperite (ββ'-dichlorodiethyl sulphide). B. Telinek (Bull. Soc. chim., 1937, [v], **4**, 1813—1815).—In contact with a test paper impregnated with the Ag–NH_3 complex of isatin, $(CH_2Cl{\cdot}CH_2)_2S$ gives a yellow spot with a green halo, which, when treated with EtOH–AcOH, turns deep blue. J. D. R.

Parachors of alkyl thiosulphites. H. Stamm and H. Wintzer (Ber., 1937, **70**, [*B*], 2058—2060).—Measurements of the parachors of Me_2, Et_2, Pr^{α}_2, and Bu^{α}_2 thiosulphite show the impossibility of the presence of a true, homopolar double linking, but are not sufficiently accurate to permit a decision between $(\cdot S{\cdot}OAlk)_2$ and $S{:}S(OAlk)_2$. H. W.

Preparation of alkanesulphonyl chlorides from *iso*thiocarbamides. II. J. M. Sprague and T. B. Johnson (J. Amer. Chem. Soc., 1937, **59**, 1837—1840).—The following are prepared by the methods previously described (A., 1936, 974, 1229) unless stated otherwise: S-*dodecyliso*thiocarbamide *hydrochloride*, m.p. 132—135°, and *hydrobromide*, m.p. 112—114°; S-*hexadecyliso*thiocarbamide *hydro-*

chloride, m.p. 126—128°; S-cyclo*hexyl*iso*thiocarbamide hydrochloride* (I), m.p. 230—231° (modified prep.), *hydrobromide*, m.p. 202—203°, and *picrate*, m.p. 173—174°; S-sec.-*octyl*iso*thiocarbamide picrate*, m.p. 130—131°; S-tert.-*butyl*iso*thiocarbamide hydrochloride* (II), m.p. 162° [from $CS(NH_2)_2$ and $Bu^{\gamma}OH$–HCl], and *picrate*, m.p. 160—161°; S-iso-, m.p. 167—168°, and -sec.- (III), m.p. 164·5—165·5°, -*butyl*iso*thiocarbamide picrates*; S-p-*nitrobenzyl*-, m.p. 225—228°, and S-α-*naphthylmethyl*-, m.p. 238°, -iso*thiocarbamide hydrochlorides*; *dodecane*-, m.p. 42—43°, *hexadecane*-, m.p. 52—53°, α-*methylpropane*-, 89—90·5°/19 mm., α-*methylheptane*-, b.p. 110—111°/4 mm., cyclo*hexane*-, b.p. 123—124°/16 mm., and p-*nitrophenylmethane*-, m.p. 92—93°, -*sulphonyl chlorides*; *dodecane*-, m.p. 93—94°, *hexadecane*-, m.p. 96·5—97·5°, cyclo*hexane*-, m.p. 94—95°, and α-*naphthylmethane*-, m.p. 171—172°, -*sulphonamides*. Complete elimination of S as SO_4'' occurs when (II) is treated with Cl_2–H_2O; partial elimination takes place with (I) and (III) (as nitrate or hydrochloride). Data previously recorded (*loc. cit.*) for $Bu^{\alpha}SO_2Cl$ apply to $Bu^{\beta}SO_2Cl$. Further details are given for the prep. of $EtSO_2Cl$, $Bu^{\alpha}SO_2Cl$, and $CH_2Ph{\cdot}SO_2Cl$. H. B.

Agar. C. Neuberg and C. H. Schweitzer (Monatsh., 1937, **71**, 46—66).—Agar is separated by cold H_2O into a sol. fraction *A* containing S and an insol., S-free fraction *B*. *A* is further separated by pptn. with EtOH (A_1; 3·6% S), with $Pb(OAc)_2$ (A_2; 4·8% S), and with quinidine hydrochloride (A_3; 6% S). Agar is partly hydrolysed with 25% HBr (cold), and the Ba salt of a sol. acid with 4·3% S is isolated. The agar fraction A_3 is hydrolysed by "sulphatase" to yield H_2SO_4 and no reducing sugars, but similar hydrolysis of the HBr fission product yields both H_2SO_4 and reducing sugars. The S is present in agar in the form of polysaccharide sulphuric esters, and more of these groups are introduced by treatment with $ClSO_3H$ in C_5H_5N and $CHCl_3$. J. D. R.

Partial synthesis of muscle-adenylic acid. T. Jachimowicz (Biochem. Z., 1937, **292**, 356—359).—Phosphorylation of adenosine by Fischer's method (A., 1915, i, 296) affords a product identical (indicated by m.p., titration data, and deamination by muscle-deaminase) with muscle-adenylic acid. F. O. H.

Constitution of adenosinetriphosphoric acid. II. H. K. Barrenscheen and T. Jachimowicz (Biochem. Z., 1937, **292**, 350—355; cf. A., 1933, 1202).—The rate of deamination (Van Slyke) of the acid (I) by 30% $NaNO_2$ is < that of adenylic acid, whilst the rates are approx. equal with 60% $NaNO_2$ (cf. Lohmann, A., 1932, 1274). Bone-phosphatase (Martland and Robison, A., 1929, 603) liberates approx. ⅓ of the total P of (I) as inorg. PO_4'''; this PO_4''' originates from the difficultly hydrolysable fraction, the readily hydrolysable fraction being practically unaffected. These findings do not support Lohmann's conception (A., 1936, 53) of the constitution of (I). F. O. H.

Formation of a lævorotatory phosphoric ester from the Neuberg ester. M. G. Macfarlane and R. Robison (Enzymologia, 1937, **4**, Part II, 125—128).—Experiments are described, the results of which support the view that the varying rotations of the fructose monophosphates prepared by partial hydrolysis of hexose diphosphate are due to the formation of another lævorotatory ester, more resistant to hydrolysis than fructose 1-phosphate, from fructose 6-phosphate during heating by migration of the PO_4''' radical to some other C atom. Samples of the lævo-ester prepared by fractional crystallisation of the brucine salts and of the Ba salts after Br oxidation had $[\alpha]_{5461}$ −24·2° and −21·3°, respectively, but these probably are not absolutely pure and still contain some fructose 6-phosphate. P. W. C.

Lysolecithin and tosylglycerides.—See A., III, 456.

Biological uptake of deuterium by fatty acids and cholesterol.—See A., III, 470.

Ester formation and structural relationships. S. G. Toole and F. J. Sowa (J. Amer. Chem. Soc., 1937, **59**, 1971—1973).—The yields of Me esters from the following acids, MeOH, and Et_2O,BF_3 at 64±1° increase in the order: $EtCO_2H$, AcOH, $CH_2Cl{\cdot}CO_2H$ (I), $CHCl_2{\cdot}CO_2H$ (II), $CCl_3{\cdot}CO_2H$ (III), $CH_2Ph{\cdot}CO_2H$ (IV). The same order is found for (I)—(III) with MeOH–HCl and for (I)—(IV) with MeOH–H_2SO_4. The order is reversed for (I)—(III) with EtOH–HCl and when the amides of all the above acids are treated with MeOH + BF_3. There appears to be no direct relationship between the ionisation const. and yield of ester; the controlling factor in substituted acetic acids is probably the inductive effect of the substituent. H. B.

Preparation of [ethyl] esters [using toluene]. V. M. Mitschovitsch (Bull. Soc. chim., 1937, [v], **4**, 1661—1669).—Aliphatic acids, or aromatic acids with CO_2H in a side-chain, heated with EtOH, PhMe, and 1—2% of H_2SO_4 give almost quant. yields of their Et esters, H_2O being eliminated in a ternary azeotropic mixture with EtOH and PhMe. Aromatic acids with nuclear CO_2H are esterified similarly, using a larger proportion of H_2SO_4. E. W. W.

Re-esterification of carboxylic esters. I. F. Adickes, F. Plessmann, and P. Schmidt (Ber., 1937, **70**, [*B*], 2119—2128).—The Et ester (1 mol.) is heated with anhyd. MeOH (5—10 mols.) for 8 hr. at 100°; the mixture is fractionally distilled and tested for EtOH by the CHI_3 test. If positive, the process is repeated for a much shorter time. *Et* β-*bromo*-β-*diphenylenepyruvate* (I), m.p. 70—71°, is readily transformed into the Me ester (II), but the analogously constituted $CBr_3{\cdot}CO{\cdot}CO_2Et$, Et β-benzyl-β-diphenylenepyruvate, Et α-hydroxy-β-diphenyleneacrylate, and Et diphenyleneacetate are resistant towards EtOH. Et 2-bromo-1 : 3-diketohydrindene-2-carboxylate is readily transformed into the *Me* ester, m.p. 120—121°, and re-esterification of Et 1 : 3-diketohydrindene-2-carboxylate (corresponding *Me* ester, m.p. 132°) occurs with nearly equal readiness, whereas Et 2-chloro-1 : 3-diketohydrindene-2-carboxylate is unaffected. Replacement of the diketohydrindene group by a Bz residue appears to destroy activity in the cases of $CBr_2Bz{\cdot}CO_2Et$, $CMeBzBr{\cdot}CO_2Et$, and

$CHAcBz{\cdot}CO_2Et$. *Et α-bromo-α-trimethylacetylacetate* is also inactive. The possibility that change is due to eliminated HBr is excluded. $OH{\cdot}CHMe{\cdot}CO_2Et$, $SH{\cdot}CH_2{\cdot}CO_2Et$, $CCl_3{\cdot}CO_2Et$, $Et_2C_2O_4$, $CBr_2(CO_2Et)_2$, $CHPh{:}C(CO_2Et)_2$, $o\text{-}NH_2{\cdot}C_6H_4{\cdot}CO_2Et$, 2 : 4 : 6-$(NH_2)_3C_6H_2{\cdot}CO_2Et$, Et pyridine-2-carboxylate, and *Et* α-p-*toluenesulphonyldiphenylacetate* are unchanged, but slight reaction is observed with HCO_2Et, $COPh{\cdot}CO_2Et$, $(OH)_2C(CO_2Et)_2$, and $CO(CO_2Et)_2$. It appears, therefore, the CO α or β to CO_2Et is requisite for the ready re-esterification with MeOH, but the possible action of semiacetals as intermediates is excluded, although such compounds are readily produced. Thus crystallisation of (I) from EtOH gives the *Et semiacetal*, m.p. 113—117° (decomp.), and rapid treatment with warm MeOH yields the *Me semiacetal*, m.p. 98°. (II) gives a *Me*, m.p. 104° (decomp.), and *Et*, m.p. 102° (decomp.), *semiacetal*. H. W.

Thermal decomposition of lead formate and of formic acid at a lead surface.—See A., I, 628.

One-third basic aluminium acetate solution.—See A., I, 616.

Unsaturated lower fatty acids. Crystalline derivatives. S. Komori and S. Ueno (Bull. Chem. Soc., Japan, 1937, **12**, 433—435).—"Tohaku" (*Lindera obtusifolia*) oil yields, by the ester–Br method, obtusilic acid, b.p. 148—150°/13 mm. (p-*bromophenacyl* ester, m.p. 43·3°; shown to be Δ^{γ}-decenoic acid by oxidation of the Me ester by $KMnO_4$), and linderic acid, b.p. 170—172°/13 mm., m.p. 1—1·3° (p-*bromo*-, m.p. 47·5°, and p-*phenyl-phenacyl* ester, m.p. 42·5°; *S-benzylthiuronium* salt, m.p. 139°; *Me* ester *dibromide*, b.p. 178—182°/2 mm.; oxidised to dihydroxylauric acid, m.p. 102°), and from the residue tsuzuic acid, m.p. 18—18·5°, b.p. 185—188°/13 mm. [p-*phenyl*-, m.p. 54·5°, and p-*bromo-phenacyl* ester, m.p. 61·3°; with O_3 gives $(CH_2{\cdot}CO_2H)_2$]. R. S. C.

Δ^{γ}-Decenoic acid. Derivatives of *d*-galacturonic acid.—See A., III, 332.

Partial hydrogenation of fish oil. VIII. Constituents of [the] docosatrienoic acid produced by hydrogenating methyl clupanodonate. M. Takano (Bull. Chem. Soc., Japan, 1937, **12**, 395—401; cf. B., 1937, 1082).—Ozonolysis of that part of the Me docosatrienoate, produced by hydrogenating clupanodonic acid (I), which gives a tetrathiocyanate indicates that the ester is a mixture of mainly $\Delta^{\gamma\eta\delta}$- or $\Delta^{\gamma\eta\xi}$-, some $\Delta^{\gamma\eta\lambda}$-, and a small amount of $\Delta^{\gamma\eta\sigma}$-isomeride. (I) would then be a mixture of $\Delta^{\gamma\eta\lambda\sigma}$- and $\Delta^{\gamma\eta\lambda\xi\sigma}$-docosapentenoic acids; the latter is probably correct (cf. Inoue and Kato, A., 1935, 195), the Δ^{ν}-linking being formed by shift of the Δ^{ξ}-linking during hydrogenation. The $\Delta^{\gamma\eta}$-linkings, which absorb $(CNS)_2$, are harder to hydrogenate than the $\Delta^{\lambda\xi\sigma}$-linkings, which are indifferent to $(CNS)_2$. R. S. C.

Electrolytic reduction of glycollic acid and lactic acid. E. Baur (Z. Elektrochem., 1937, **43**, 821—822; cf. A., 1936, 943).—At high c.d. $OH{\cdot}CH_2{\cdot}CO_2H$ is reduced completely to MeOH, but with a lower c.d. HCO_2H can also be detected. It is concluded that the reaction proceeds through initial formation of MeOH and HCO_2H, the latter being reduced subsequently to CH_2O and then MeOH. On electrolytic reduction lactic acid yields EtOH and HCO_2H in stoicheiometric proportions. J. W. S.

Acetoacetic ester condensation. XI. Extent of condensation of monosubstituted acetic esters. D. C. Roberts and S. M. McElvain (J. Amer. Chem. Soc., 1937, **59**, 2007—2008).—The max. yields of $CH_2R{\cdot}CO{\cdot}CHR{\cdot}CO_2Et$ (I) obtained (method : A., 1934, 1091) from $CH_2R{\cdot}CO_2Et$ (6 mols.) and NaOEt (1 mol.) at 95° (78° when R = H) are : R = H 75—76, Me 46—47, Et 40—42, Pr^{α} 34—35, Pr^{β} 0, Bu^{γ} 0, Ph 53—55% (mol. ratio approx. 2 : 1); for R = *n*-alkyl, the extent of the condensation decreases and the time necessary for max. yields increases with the size of R. (I) are not formed from $Bu^{\beta}CO_2Et$ and $CH_2Bu^{\gamma}{\cdot}CO_2Et$ even when the reactions are carried out (cf. A., 1929, 1424) so that any EtOH formed is removed. H. B.

Magnesium mesityl bromide as a reagent in the acetoacetic ester condensation. M. A. Spielman and M. T. Schmidt (J. Amer. Chem. Soc., 1937, **59**, 2009—2010).—$Bu^{\beta}CO_2Et$, $CH_2Bu^{\gamma}{\cdot}CO_2Et$, and $Pr^{\beta}CO_2Et$ (none of which undergoes the acetoacetic ester condensation with NaOEt) are converted by Mg mesityl bromide (best added to ester) into Et α-*iso*valeryl*iso*valerate (I) (51%) [use of $MgPr^{\beta}Br$ (cf. Conant and Blatt, A., 1929, 675; Ivanov and Spasov, A., 1931, 726) gives 1·2%], *Et αγ-di*tert.-*butylacetoacetate* (II) (32%), b.p. 138—140°/32 mm., and Et α-*iso*butyryl*iso*butyrate (26·5%), respectively. The non-formation of these CO-esters with NaOEt is attributed to their inability to enolise; they do not give colours with $FeCl_3$. Et stearate is similarly converted into Et α-stearylstearate (27%), m.p. 48—49° (lit. 28—29°). (I) is hydrolysed (5% Na_2CO_3 at 225° in a steel bomb) to $COBu^{\beta}_2$. (II) is hydrolysed (aq. EtOH–KOH at 200°) to *dineopentyl ketone*, b.p. 185°/740 mm. (*semicarbazone*, m.p. 178—179°). H. B.

Condensations brought about by bases. I. Condensation of ethyl *iso*butyrate to ethyl *iso*butyryl*iso*butyrate. C. R. Hauser and W. B. Renfrow, jun. (J. Amer. Chem. Soc., 1937, **59**, 1823—1826).—In accordance with a mechanism discussed for the acetoacetic ester condensation, $Pr^{\beta}CO_2Et$ is converted by $CNaPh_3$ (a base sufficiently strong to form an enolate of the condensation product) in Et_2O into Et α-*iso*butyryl*iso*butyrate (I); the first stage appears to be the formation of the enolate $CMe_2{:}C(O){\cdot}OEt$, since treatment of this with $Pr^{\beta}COCl$ also gives (I). Hydrolysis (aq. KOH) of (I) affords $COPr^{\beta}_2$ [*semicarbazone*, m.p. 160° (corr.)], also prepared from $MgPr^{\beta}Br$ and $Pr^{\beta}CN$. H. B.

Preparation and rearrangement of dialkyl maleates. P. A. Shearer and A. M. Pardee (Proc. S. Dakota Acad. Sci., 1935, **15**, 24—26).—Rubber accelerates conversion into the corresponding fumarates; improved yields are accordingly obtained by using all-glass apparatus in the prep. Ch. Abs. (*r*)

Reaction between esters of organic acids and magnesium *iso*propyl chloride. IV. Experiments with ethyl β-phenylpropionate and ethyl succinate. A. Spassov (Bull. Soc. chim.,

1937, [v], **4**, 1658—1661).—$CH_2Ph{\cdot}CH_2{\cdot}CO_2Et$ and $MgPr^{\beta}Cl$ give C_3H_6, and, after hydrolysis, $CH_2Ph{\cdot}CH_2{\cdot}COPr^{\beta}$ (semicarbazone, new m.p. 118—119°; cf. A., 1931, 1050). $(CH_2{\cdot}CO_2Et)_2$ similarly gives C_3H_6, $Pr^{\beta}CO{\cdot}[CH_2]_2{\cdot}CO_2H$ (*semicarbazone*, m.p. 152°), and $\beta\eta$-*dimethyloctane-*$\gamma\zeta$*-dione*, b.p. 100—102°/9 mm. (*dioxime*, m.p. 173—174°). E. W. W.

Synthesis of higher dicarboxylic acids, $CO_2H{\cdot}[CH_2]_n{\cdot}CO_2H$, $CO_2H{\cdot}[CH_2]_{16}{\cdot}CO_2H$, and $CO_2H{\cdot}[CH_2]_{18}{\cdot}CO_2H$. S. Shiina (J. Soc. Chem. Ind. Japan, 1937, **40**, 324B).—By electrolysis of a solution of $CO_2K{\cdot}[CH_2]_8{\cdot}CO_2Et$, the ester $CO_2Et{\cdot}[CH_2]_{16}{\cdot}CO_2Et$ (I) is obtained which by reduction is converted into $OH{\cdot}[CH_2]_{18}{\cdot}OH$. The glycol gives, through the iodide, $(CH_2)_{18}(CO_2H)_2$. The following m.p. are recorded: $CO_2H{\cdot}[CH_2]_{16}{\cdot}CO_2H$, 124·2—124·6°; (I), 47·5—47·7°; $CO_2Me{\cdot}[CH_2]_{16}{\cdot}CO_2Me$, 58·9—59·2°; $CO_2H{\cdot}[CH_2]_{18}{\cdot}CO_2H$, 123·8—124·2° ($Et_2$, 54·6—54·8°, and Me_2, 65·2—65·4°, ester); $OH{\cdot}[CH_2]_{18}{\cdot}OH$, 97·5—97·8°, $OH{\cdot}[CH_2]_{20}{\cdot}OH$, 102·4—102·6°, and the corresponding iodides, m.p. 62·2—62·4° and 65·3—65·6°, respectively. F. R. S.

Condensation of acetaldehyde with ethyl malonate. A. Rœsch (Bull. Soc. chim., 1937, [v], **4**, 1643—1658).—MeCHO (I) and $CH_2(CO_2Et)_2$ (II) in aq. K_2CO_3 (KCN less satisfactory) give "*Et_2 ethanolmalonate*" (III), an oil [decomp. on distillation, giving (I), (II), etc.], which does not yield an Ac derivative or urethane, and is not dehydrated by H_3PO_4. KOH hydrolyses (III) to $CH_2(CO_2H)_2$; with AcCl (III) gives $CEtCl(CO_2Et)_2$. E. W. W.

Catalytic hydrogenation of saturated lactones. F. Wessely, A. Münster, and S. Wang (Monatsh., 1937, **71**, 27—29).—At room temp. and pressure, hydrogenation (Pd–H_2) of β-hydroxy*iso*propylmalonolactone is without effect, whilst β-phenyl-β-propiolactone-α-carboxylic acid yields PhMe and $CH_2(CO_2H)_2$ J. D. R.

Diazo-reaction of ascorbic acid. G. Barac (Compt. rend. Soc. Biol., 1937, **126**, 61—62).—The absorption of the diazo-colour in the visible region has been determined and the non-formation of azo-vitamin-*C* explained. H. G. R.

Preparation of methyl *d*-glucosonate. H. Ohle (Ber., 1937, **70**, [*B*], 2153).—A hot solution of K di*iso*propylideneglucosonate (33 g.) in 10 parts by vol. of MeOH is boiled with 20 c.c. of 5N-H_2SO_4. K_2SO_4 is filtered off and the filtrate is boiled for 3 hr. after addition of 10 c.c. of 12N-HCl. The yield of Me ester is about 90%. H. W.

Constitution of pectic substances. F. Just (Woch. Brau., 1937, **54**, 317—318).—A review of the work of Henglein, Schneider, and co-workers. I. A. P.

Nitroguanylhydrazones of aldehydes and ketones. G. B. L. Smith and E. P. Shoub (J. Amer. Chem. Soc., 1937, **59**, 2077—2078).—*Nitroguanylhydrazones* of the following are prepared (method: A., 1935, 769): MeCHO, m.p. 234°; PrCHO, m.p. 95°; heptaldehyde, m.p. 93°; octaldehyde, m.p. 118°; $CHMe{:}CH{\cdot}CHO$, m.p. 177·5°; veratraldehyde, m.p. 195°; hexone, m.p. 112·5°; Me *n*-amyl ketone, m.p. 109·5°; acetoacetanilide, m.p. 184°. H. B.

Kinetics of aldol condensation.—See A., I, 622.

Photolysis of *n*- and *iso*-butaldehyde.—See A., I, 627.

Addition of magnesium *n*-butyl bromide to acetone. G. Pierotti and T. D. Stewart (J. Amer. Chem. Soc., 1937, **59**, 1773—1775).—$MgBu^{a}Br$ and $COMe_2$ (slight excess) in Et_2O at 0° in complete absence of O_2 give $CMe_2Bu^{a}{\cdot}OH$ (I) and smaller amounts of C_4H_8, C_7H_{14} [from (I)], C_8H_{18}, $Pr^{\beta}OH$, and $(\cdot CMe_2{\cdot}OH)_2$ (II); in presence of atm. O_2 (either during prep. of $MgBu^{a}Br$ or during its reaction with $COMe_2$) $Bu^{a}OH$ and $CHMeBu^{a}{\cdot}OH$ (III) are also formed. (III) results from Et_2O peroxide which reacts as MeCHO. The ratios $Pr^{\beta}OH$: (II) and (I) : reduction products [$Pr^{\beta}OH$ + (II)] are approx. 3 : 1 and 6 : 1, respectively. H. B.

Preparation of ketones from higher fatty acids. III. Preparation of ketones from the fatty acids of hydrogenated sardine oils. IV. Preparation of ketones from the fatty acids of coconut oil and of hardened rape-seed and soya-bean oils. K. Kino (J. Soc. Chem. Ind. Japan, 1937, **40**, 311B, 311—312B).—III. By heating the fatty acids with Mg, ketones of various m.p. are obtained, the acids of higher m.p. giving ketones of higher m.p.

IV. The ketones of highest m.p. are obtained from acids with high m.p. and also from acids which are least unsaturated. F. R. S.

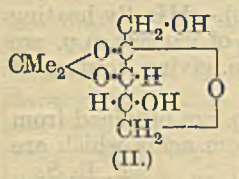
Combination of sugars with amino-acids. II. F. Lieben and B. Bauminger. **III. Experiments with animal charcoal.** J. Benek and F. Lieben (Biochem. Z., 1937, **292**, 371—375, 376—379; cf. A., 1937, II, 401).—II. The decomp. of glucose (I) in systems containing (I) and glycine (II) in O_2 at 70° is retarded by increase in either component above the optimum ratio of (I) : (II) = 1·5—2·0 : 1. In N_2, the presence of (II) is still necessary for the (much lower) decomp. of (I). Presence of methylene-blue increases the decomp. almost to the aërobic val.

III. Presence of C increases the decomp. of (I) and formation of CO_2 and lactic acid; (II), however, is also decomposed with formation of CO_2 and NH_3, a decomp. enhanced tenfold by the presence of (I). F. O. H.

Preparation of erythrose and some of its derivatives. G. E. Felton (Iowa State Coll. J. Sci., 1935, **10**, 79—81).—Ozonolysis of arabinal yields erythrose, $[\alpha]_D$ +11·5° (initial), +30·5° (equil.), isolated as iso*propylidenemethylerythroside*. *Acetobromoarabinose*, a *deoxypentose disaccharide tetra-acetate*, two forms, m.p. 167—169° and 185·5°, and *dihydroarabinal*, b.p. 83—85°/1 mm., $[\alpha]_D$ ±48·3°, are described. Ch. Abs. (*r*)

Structure of monoacetone-*d*-xylulose. P. A. Levene and R. S. Tipson (J. Biol. Chem., 1937, **120**, 607—618).—The *p*-$C_6H_4Me{\cdot}SO_2$ derivative and NaI method (A., 1932, 254; 1933, 1145) is applied to 2 : 3 : 4 : 5-*iso*propylidenefructose (I) and to *iso*propylidene-*d*-xylulose (II). The 1-p-*toluenesulphonyl*

derivative, m.p. 83°, $[\alpha]_D^{25}$ −25·9° in EtOH, of (I) is unaffected by NaI in $COMe_2$ at 100°. Similarly the 1 : 4-*di*-p-*toluenesulphonyl* derivative, m.p. 71—73°, $[\alpha]_D^{25}$ +6·3° in $COMe_2$, of (II) is not appreciably affected by NaI. This indicates that *p*-$C_6H_4Me{\cdot}SO_2$ is not attached in position 5. With MeI–Ag_2O–$COMe_2$, (II) gives its *Me*$_2$ derivative, b.p. 47°/0·1 mm., $[\alpha]_D^{24}$ −12·6° in $COMe_2$, which with 0·2N-$H_2C_2O_4$ at 65° gives *dimethylxylulose* (III), m.p. 48—49°, $[\alpha]_D^{26}$ in MeOH −26·7° → −16·3° after 30 min. The strongly reducing properties of (III) show that the reducing group at position 2 is protected by CMe_2 in the *iso*propylidene derivative, but free in the Me_2 sugar. With MeOH–HCl, followed by Ag_2CO_3, (III) gives *trimethyl-methylxyluloside* (α + β), b.p. 61—64°/0·25 mm., of which three successive fractions had $[\alpha]_D^{26}$ −18·6°, −7·0°, and +4·3° in $COMe_2$, showing partial separation into the α- and β-forms. Further methylation (MeI–Ag_2O) gives *trimethyl-methylxyluloside* (α + β) (IV), b.p. 52°/0·25 mm., hydrolysed ($H_2C_2O_4$) to *Me*$_3$ *xylulose* (V), b.p. 64°/0·25 mm., $[\alpha]_D^{25}$ −14·0° in MeOH. That (IV) is 1 : 3 : 4-*trimethyl-methylxylulofuranoside* is shown by oxidation (HNO_3, *d* 1·42, at 59—95°), which with (IV) or (V) gives crude *dimethylxylosonic acid* (VI), esterified to a mixture of the Me ester with its "methylglycoside," and some Me_2 *l*-dimethoxysuccinate. By complete methylation (Purdie) and treatment with NH_3–MeOH, dimethoxysuccindiamide is obtained. This shows that (II) is 2 : 3-iso*propylidene*-d-*xylulo*-*furanose*. With $Ba(MnO_4)_2$–H_2SO_4, (VI) gives a *product*, $C_6H_{10}O_6$, m.p. 151°, $[\alpha]_D^{26}$ −68·8° in H_2O.


(II.)

E. W. W.

Structure of β-chloralglucose. W. Freudenberg and A. M. Vajda (J. Amer. Chem. Soc., 1937, **59**, 1955—1957).—β-Chloralglucose [the β-glucochloralose of Coles *et al.* (A., 1929, 429)], m.p. 237·5—238°, $[\alpha]_D^{23}$ −17·2° in C_5H_5N, is 1 : 2-trichloroethylideneglucofuranose since it contains 3 active H (Zerevitinov), is oxidised by $Pb(OAc)_4$ in AcOH to CH_2O, is reduced (H_2, Ni, EtOH–NaOH) to (impure) *chloroethylideneglucofuranose*, m.p. 168—170° [hydrolysed (0·5N-HCl) to glucose and $CH_2Cl{\cdot}CHO$ (2 : 4-*dinitrophenylhydrazone*, m.p. 149—151°)], and is methylated (Me_2SO_4, CCl_4, 50% NaOH) to *trimethyl*-β-*chloralglucose* (I), m.p. 113—114°, $[\alpha]_D^{22}$ −28·7° in $CHCl_3$. Methylation (method: West and Holden, A., 1934, 636) of 1 : 2-*iso*propylideneglucofuranose gives the 3 : 5 : 6-*Me*$_3$ derivative, b.p. 117—119°/0·7 mm., hydrolysed (aq. EtOH–HCl) to 3 : 5 : 6-trimethylglucofuranose, which with $CCl_3{\cdot}CHO$ and conc. H_2SO_4 at 10—15° affords (I) (cf. White and Hixon, A., 1933, 810). H. B.

Reaction of 4 : 6-ethylidene-β-methylglucoside derivatives; 4 : 6-dimethylglucose. D. J. Bell and R. L. M. Synge (J.C.S., 1937, 1711—1718).—4 : 6-Ethylidene-β-methylglucoside with N_2O_5 in $CHCl_3$ yields 4 : 6-*ethylidene*-β-*methylglucoside* 2 : 3-*dinitrate* (I), m.p. 88—89°, $[\alpha]_D^{16}$ −21·0° in $CHCl_3$, converted by 0·1% H_2SO_4 in Ac_2O into 6-*acetyl*-4-α-*acetoxyethyl*-β-*methylglucoside* 2 : 3-*dinitrate* (II), m.p. 113—115°, $[\alpha]_D^{17}$ +22·7° in $CHCl_3$, which on hydrolysis ($COMe_2$–HCl) yields MeCHO and unidentified products, and on nitration (HNO_3–$CHCl_3$) gives MeCHO and β-*methylglucose* 2 : 3 : 4-*trinitrate* 6-*acetate*, m.p. 104—105°, $[\alpha]_D^{17\cdot5}$ −27·0° in $CHCl_3$, which is resistant to hydrolysis (NaOMe–$CHCl_3$) and to iodination (NaI–$COMe_2$). (II) with NaOMe in $CHCl_3$–MeOH yields β-*methylglucoside* 2 : 3-*dinitrate*, m.p. 96—98°, $[\alpha]_D^{20}$ −20·5° in $CHCl_3$–$COMe_2$, acetylated (Ac_2O–NaOAc or –C_5H_5N) to β-*methylglucoside* 2 : 3-*dinitrate* 4 : 6-*diacetate*, m.p. 138—140°, $[\alpha]_D^{18}$ −5·2° in $CHCl_3$, and methylated to 4 : 6-*dimethyl*-β-*methylglucoside* 2 : 3-*dinitrate*, m.p. 54—57°, $[\alpha]_D^{15}$ −13·4° in $CHCl_3$, which is hydrolysed (Na_2S) to 4 : 6-*dimethyl*-β-*methylglucoside* (III), b.p. 130—160°/0·4 mm., m.p. 50—52°, $[\alpha]_D^{18}$ −28·8° in $CHCl_3$ (2 : 3-*di*-p-*toluenesulphonate* (IV), m.p. 146—149°, $[\alpha]_D^{20}$ −14·8° in $CHCl_3$). Hydrolysis of 4 : 6-benzylidene-β-methylglucoside 2 : 3-di-*p*-toluenesulphonate (H_2SO_4 or HCl in $COMe_2$) yields β-methylglucoside 2 : 3-di-*p*-toluenesulphonate (a syrup), methylated (MeI–Ag_2O) to (IV). (III) is hydrolysed (HCl) to 4 : 6-dimethylglucose, m.p. 156—158°, identical with the dimethylglucose, m.p. 156—157°, of Haworth and Sedgwick (A., 1926, 1228). 4 : 6-Ethylidene-β-methylglucoside 2 : 3-diacetate (V) with Ac_2O–H_2SO_4 (0·1%) yields 4-α-*acetoxyethyl* β-*methylglucoside* 2 : 3 : 6-*triacetate* (a syrup), which with HNO_3–$CHCl_3$ gives β-*methylglucoside* 4-*nitrate* 2 : 3 : 6-*triacetate* (VI), m.p. 112—114°, $[\alpha]_D^{17\cdot5}$ −27·0° in $CHCl_3$, reduced (Fe–Zn–AcOH) to methylglucoside 2 : 3 : 6-triacetate, which is nitrated (HNO_3–$CHCl_3$) to yield (VI). Nitration (HNO_3–$CHCl_3$) of (I) affords β-*methylglucoside* 2 : 3 : 4 : 6-*tetranitrate*, m.p. 116—118°, $[\alpha]_D^{17}$ +9·35° in $CHCl_3$, whilst similar nitration of (V) yields β-*methylglucoside* 4 : 6-*dinitrate* 2 : 3-*diacetate*, m.p. 118—120°, $[\alpha]_D^{17}$ −7·3° in $CHCl_3$, hydrolysed (NaOMe) to β-*methylglucoside* 4 : 6-*dinitrate*, m.p. 147—149°, $[\alpha]_D^{17}$ −5·3 in MeOH, which is methylated (MeI–Ag_2O) to 2 : 3-dimethyl-β-methylglucoside 4 : 6-dinitrate. J. D. R.

Calcium chloride compound of α-*d*-galactose. R. M. Hann and C. S. Hudson (J. Amer. Chem. Soc., 1937, **59**, 2075).—The *compound*, $C_6H_{12}O_6,CaCl_2,3H_2O$, m.p. 129—130° (corr.), $[\alpha]_D^{20}$ (in H_2O) +75·82° (after 2·7 min.) → +42·68°, is described. H. B.

Reduction of the methyl ester of 2 : 3 : 4-trimethyl α-methyl-*d*-galacturonide to 2 : 3 : 4-trimethyl α-methyl-*d*-galactoside. P. A. Levene, R. S. Tipson, and L. C. Kreider (Science, 1937, **86**, 332—333).—Reduction has been effected in H_2 with a Cu chromite catalyst. Distillation gave a *product*, m.p. about 30°, $[\alpha]_D^{25}$ +198·4° in H_2O, which on hydrolysis yields 2 : 3 : 4-trimethyl-*d*-galactose. L. S. T.

Conversion of uronic acids into corresponding hexoses. I. Conversion of 2 : 3 : 4-trimethylmethyl-*d*-galacturonide methyl ester into 2 : 3 : 4-trimethylmethyl-*d*-galactoside. P. A. Levene and L. C. Kreider (J. Biol. Chem., 1937, **121**, 155—164; cf. A., 1937, II, 442).—2 : 3 : 4-*Trimethyl*-α-*methylgalacturonamide*, m.p. 153—153·5°, $[\alpha]_D^{22}$ +121·5° in $CHCl_3$ (from the Me ester and NH_3), with $SOCl_2$ yields the *nitrile*, m.p. 156—157°, $[\alpha]_D^{23}$ +177·6° in $CHCl_3$. The CN group of this could not be eliminated. $AgNO_3$ in aq. NH_3–MeOH followed by H_2S gave only the *thioamide*, m.p. 182—183°

(also prepared from the nitrile and H_2S in MeOH–NH_4OH); heating with conc. aq. NH_3 gave the amide, whilst Na + MeOH gave a *compound*, probably the Me iminogalacturonate, m.p. 65—65·5°, $[\alpha]_D^{24}$ +194° in $CHCl_3$. The nitrile is reduced (Raney's catalyst) to 6-*amino*-2 : 3 : 4-*trimethyl*-α-*methyl*-d-*galactoside*, b.p. 172°/25 mm., $[\alpha]_D^{25}$ +161·3° in $CHCl_3$, which with HNO_2 gives 2 : 3 : 4-trimethyl-α-methyl-*d*-galactoside, $[\alpha]_D^{28}$ +132·2° in MeOH. A. Li.

l-Sorbose. II. New acetyl and methyl derivatives of *l*-sorbose. Numerical relationships in the *l*-sorbose series. H. H. Schlubach and G. Graefe (Annalen, 1937, **532**, 211—227; cf. A., 1933, 1145).—*l*-Sorbose with Ac_2O in well-cooled C_5H_5N gives α-l-*sorbose tetra-acetate* (I), m.p. 100·8° (corr.), $[\alpha]_D^{20}$ −21·3° in $CHCl_3$, converted by Ac_2O and NaOAc at 100° into α-*sorbose penta-acetate* (II), m.p. 97·0°, $[\alpha]_D^{20}$ −56·5° in $CHCl_3$. (I) with PCl_5–$AlCl_3$ or with PCl_5 alone gives very unstable, partly halogenated products, whereas with anhyd. HCl at 0° α-*acetochlorosorbose* (III), m.p. 67·0°, $[\alpha]_D^{20}$ −83·3° in $CHCl_3$, is obtained in 72% yield; it is still less stable than the corresponding fructose compound, but can be preserved for a few weeks in abs. Et_2O at 0°. It is re-converted by $AgNO_3$ into (I). Treatment of (III) with AgOAc in boiling C_6H_6 does not lead to complete replacement of Cl, but in Ac_2O at 80° l-β-*sorbose penta-acetate* (IV), m.p. 113·8°, $[\alpha]_D^{20}$ +74·4° in $CHCl_3$, is obtained, a Walden inversion occurring as with the aldohalogenoses, but not with β-acetochlorofructose. Treatment of (III) with $AgNO_3$ and Ag_2CO_3 in MeOH yields β-*methylsorboside tetra-acetate*, m.p. 75·0°, $[\alpha]_D^{20}$ +79·8° in $CHCl_3$. The isomeric α-methylsorboside tetra-acetate has m.p. 89·5°, $[\alpha]_D^{20}$ −52·6° in $CHCl_3$. β-*Methylsorboside* (V), has m.p. 106·2°, $[\alpha]_D^{20}$ +39·0° in H_2O_2 +84·3° in MeOH, +97·1° in EtOH, +101·4° in EtOAc. Hydrolysis of (V), α-methylsorboside (VI), and β-methylfructoside, in contrast to that of the Me glucosides of the aldohexoses, occurs rapidly at 20°, and since they are all pyranose derivatives, the difference must be ascribed to that usually observed between a *sec.* and a *tert.* OH. The aldofuranosides are readily hydrolysed. The half-periods of inulin and sucrose are of the same order of magnitude as those of (V) and (VI). Generally, the differences in the rates of hydrolysis of ketopyranoses and ketofuranoses are not so great as those between the corresponding aldose compounds. The vals. of $[\alpha]_D$ for (II) and (IV) and (V) and (VI) enable the validity of Hudson's rules to be tested for ketoses on an extended basis. The observation that the increments for the different groups in the case of fructose are generally appreciably > those for similar groups in the aldose series cannot be generalised, since the α_x-vals. of *l*-sorbose are invariably considerably < those of *d*-fructose and vary irregularly around those of the aldoses. The only general differences between ketoses and aldoses are the greater reactivity of the former and the more pronounced tendency to form derivatives of the keto-form. Comparison of (V) and (VI) with the methylfructosides shows close resemblance between (V) and α- and (VI) and β-methylfructoside. The assignment of sorbose to the *l*-series and the designation of its derivatives therefrom in consonance with Hudson's rules are inappropriate. H. W.

Ring structure of α-methyl-*l*-sorboside. R. L. Whistler and R. M. Hixon (J. Amer. Chem. Soc., 1937, **59**, 2047—2048; cf. Arragon, A., 1936, 1234).—α-Methyl-*l*-sorboside (I) (tetra-acetate, m.p. 88°, $[\alpha]_D^{25}$ −52·4° in $CHCl_3$, unaffected by AcCl–HCl) is methylated (Me_2SO_4 followed by MeI–Ag_2O) to the Me, derivative (II), $[\alpha]_D^{32}$ −48·8° in $CHCl_3$, hydrolysed (2% HCl) to tetramethyl-*l*-sorbose (III), $[\alpha]_D^{28}$ −10·2° in $CHCl_3$, +4·95° in MeOH. Oxidation [HNO_3 (*d* 1·42) at 70—95°] of (III) gives *d*-dimethoxysuccinic acid, indicating that (I)—(III) possess pyranoid structures. H. B.

Fructose anhydrides. XXI. Synthetic difructose anhydrides. H. H. Schlubach and H. Knoop (Annalen, 1937, **532**, 207—210).—Repetition of the work of Schlubach and Elsner (A., 1929, 51) leads to the isolation of a hygroscopic, amorphous compound which does not reduce Fehling's solution. Its $COMe_2$ content (1·4%) and its properties in conjunction with the results of acetylation and methylation indicate that it is the difructose anhydride (I) obtained by Schlubach and Behre (A., 1934, 174) by the action of HCl on fructose, contaminated with a dextrorotatory, probably *iso*propylidene compound. A second substance (II) had $[\alpha]_D$ +44° in H_2O, +52° in MeOH, but higher vals. are occasionally observed. Its reducing power increases with the time of experiment and hence is due to causes other than the presence of reducing groups. It is slowly hydrolysed by N-H_2SO_4. When methylated it gives a *Me ether* (OMe = 45·3%), b.p. 141°/0·05 mm., $[\alpha]_D^{20}$ +55·1° in H_2O, +49·8° in $CHCl_3$, +47·8° in C_6H_6, +40·4° in CCl_4, hydrolysed to a trimethylfructose, b.p. 93°/0·05 mm., $[\alpha]_D^{20}$ +22·2° in H_2O, +15·5° in $CHCl_3$, ±0° in C_6H_6, −7·3° in CCl_4, which gives a non-cryst. *phenylosazone*. (II) appears therefore to be a difructose anhydride and unlike (I) to be a fructofuranose. The mol. wt. follows from the b.p. of the Me derivative. The simultaneous production of both types of anhydride is understandable since in solutions of fructose the furanose form is present in considerable proportion with the pyranose variety. From these forms under the influence of acids very varied difructose anhydrides result all of which are hydrolysed with great difficulty by acids and are very stable, saturated systems which show no tendency to polymerise. H. W.

***aldehydo*-Derivatives of *d*-α-galaheptose.** R. M. Hann and C. S. Hudson (J. Amer. Chem. Soc., 1937, **59**, 1898—1900).—*d*-α-Galaheptose [*oxime* (I), m.p. 179° (decomp.) (all m.p. except this are corr.), $[\alpha]_D^{20}$ (in H_2O) −5° → −1·6°] (as hydrate) and EtSH in conc. HCl give d-α-*galaheptose Et mercaptal*, m.p. 204—205°, $[\alpha]_D^{20}$ −9·7° in C_5H_5N, the *hexa-acetate*, m.p. 145—146°, $[\alpha]_D^{20}$ +5·6° in $CHCl_3$, of which with $HgCl_2$ + $CdCO_3$ in $COMe_2$ affords aldehydo-d-α-*galaheptose hexa-acetate* (II), m.p. 173—174°, $[\alpha]_D^{20}$ +27° in $CHCl_3$ [*oxime* (III), m.p. 130°, $[\alpha]_D^{20}$ +16·3° in $CHCl_3$], acetylated further (Ac_2O–AcOH–conc. H_2SO_4 at 20°) to the *octa-acetate*, m.p. 112°, $[\alpha]_D^{20}$ +19·8° in $CHCl_3$. Acetylation (Ac_2O, C_5H_5N) of (I) or (III) affords aldehydo-d-α-*galaheptoseoxime*

hepta-acetate, m.p. 125—126°, $[\alpha]_D^{20}$ +38·6° in $CHCl_3$, which when heated to 170° pases into d-α-*galaheptononitrile hexa-acetate*, m.p. 194°, $[\alpha]_D^{20}$ +31·7° in $CHCl_3$, also formed from (I) or (III) and Ac_2O–NaOAc. d-α-*Galaheptosesemicarbazone*, m.p. 136—137° $[\alpha]_D^{20}$ (in H_2O) −22° → +32·9°, is acetylated (Ac_2O, C_5H_5N) to the *semicarbazone*, m.p. 180°, $[\alpha]_D^{20}$ +16·7° in $CHCl_3$, of (II). There is no parallelism between the rotations of the above compounds and those of the corresponding derivatives of mannose. H. B.

Behaviour of glucosides when micro-sublimed. R. Fischer (Arch. Pharm., 1937, **275**, 516—526).—Micro-sublimation of æsculin, fraxin, daphnin, phloridizin, quercitrin, baptisin, arbutin, solanin, digitonin, hederin, and other saponins gives the aglucones, but syringin and salicin sublime unchanged. The aglucone is best obtained by moistening with HCl before sublimation; this allows identification of the glucosides in and characterisation of many natural products. Solanidine hydrochloride sublimes. R. S. C.

Strophanthin. J. Kraus (Naturwiss., 1937, **25**, 651).—From a technical strophanthin prep. after mild hydrolysis, a trisaccharide, *glucosidoglucosidocymarose*, $C_{19}H_{34}O_{14}$, m.p. 217—220°, has been isolated; it is not identical with the methylstrophanthobioside of Feist (A., 1898, i, 329). From the same strophanthin prep. after acetylation an *acetylstrophanthin*, m.p. 216—220°, was obtained. W. O. K.

Scoporin.—See A., III, 333.

Fructosides of Amaryllidaceæ. *Lycoris* and *Narcissus*.—See A., III, 503.

Fructose anhydrides. XX. Constitution of asphodelin. H. H. Schlubach and H. Lendzian (Annalen, 1937, **532**, 200—207).—Extraction of *Asphodelus* tubers (harvested in October) with H_2O, removal of proteins by basic Pb acetate, and pptn. with EtOH gives the crude carbohydrate, which is further purified by repeated fractional pptn. by EtOH from H_2O. The persistent presence of N in small amount shows that homogeneity is not reached by this method. The product is therefore acetylated in C_5H_5N and the *acetate* (I), $[\alpha]_D^{20}$ −16·6° in $CHCl_3$, after repeated pptn. from C_6H_6 by light petroleum is deacetylated (Zemplén) to asphodelin (II), $[\alpha]_D^{20}$ −30·9° in H_2O. For a polyfructosan it is remarkably stable to heat. The reducing val. (Bertrand) is 0·35%, the aldose val. 0·4%. During hydrolysis the aldose val. increases to 11·1%. Methylation of (I) in $COMe_2$ affords *methylasphodelin*, $[\alpha]_D^{20}$ −33·3° in C_6H_6, which on hydrolysis gives 1 : 3 : 4 : 6-tetramethylfructose, a mixture of trimethyl-fructose and -glucose, and a dimethylfructose, $[\alpha]_D^{20}$ +19·6° in $CHCl_3$, apparently identical with that derived from methylirisin and methylgraminin. The ratio of the amounts of tetra-, tri-, and di-methylhexoses, calc. as fructose, is nearly 1 : 5 : 1. (II) must therefore contain at least six hexose residues; this is roughly confirmed by cryoscopic determinations of the mol. wt. The aldose val. of the trimethylhexose fractions points to the presence of at least one glucose unit in five hexose units. Whether the glucose is an integral component of (II) or the product of the fission of an accompanying glucose anhydride remains undecided. The latter possibility is supported by the behaviour of the material obtained from tubers collected in January. The type of structure of (II) resembles that of sinistrin. H. W.

Fructose anhydrides. XIX. Constitution of asparagosin. H. H. Schlubach and H. Böe (Annalen, 1937, **532**, 191—200).—The fresh asparagus roots are extracted with H_2O, proteins are removed with basic Pb acetate, and the crude carbohydrate is purified by systematic fractional pptn. by EtOH from H_2O. Thus obtained, *asparagosin* (I) has m.p. 197—198° after softening at 170° and swelling at 193°, $[\alpha]_D^{20}$ −32·4°. It is acetylated in C_5H_5N–H_2O to an Ac_2 derivative, which in anhyd. C_5H_5N passes into the *triacetate* (II), m.p. 93° after softening at 80°, $[\alpha]_D^{20}$ −20·1° in $CHCl_3$, which when deacetylated (Zemplén) affords (I) with $[\alpha]_D^{20}$ −32·6° in H_2O. It does not react with Fehling's solution. The mol. wt., determined cryoscopically in H_2O, corresponds with the presence of 9—10 fructose units. Acid hydrolysis causes 92·2% fission as a max. (measured by the reducing val. according to Bertrand). According to the method of Auerbach and Bodländer aldoses are absent so that (I) is composed entirely of fructose units. Treatment of (II) with Me_2SO_4 and alkali followed by MeI–Ag_2O gives *trimethylasparagosin*, $[\alpha]_D^{20}$ −47·8° in $CHCl_3$. This is hydrolysed by alcoholic $H_2C_2O_4$ followed by 0·25% HCl to a tetramethylfructose, $[\alpha]_D^{20}$ +21·1° to +15·3° in $CHCl_3$, 3 : 4 : 6-trimethylfructose, $[\alpha]_D^{20}$ +26·1° to +23·0° in $CHCl_3$ (phenylosazone, forms, m.p. 126—127° and 78—79°, respectively), identical with that derived from inulin, and a dimethylfructose, $[\alpha]_D^{20}$ +14·0° to +21·0° in $CHCl_3$, identical with that derived from irisin and graminin (III). The ratio of the amounts of these products, calc. as fructose, is almost exactly 1 : 8 : 1. (I) is therefore a polyfructosan $(C_6H_{10}O_5)_{10}$. In its special structure it is allied most closely to inulin, of which it may be regarded as a model to scale 1 : 3. Since the presence of an open chain in (I) is impossible and that of a large ring must be assumed for the same reasons as in the cases of (III), sinistrin, and triticin the existence of (I) is a further argument for the presence of a large ring in inulin. H. W.

Constitution of galactogen. I. H. H. Schlubach and W. Loop [with H. Schmidt] (Annalen, 1937, **532**, 228—235).—Galactogen (I) is separated as the Cu compound from its mixture with glycogen (II) in the vineyard snail (cf. May, A., 1934, 1251) and, after regeneration, is treated with malt disatase until further action does not occur. It has then $[\alpha]_D^{20}$ −17·6° in H_2O. The half-period of acid hydrolysis of (I) is somewhat < that of (II). May's explanation that the difference in the galactose (III) content of the hydrolysate according as it is calc. from the reducing power or optical activity is due to a peculiar variety of (III) is unnecessary; the phenomenon is probably due to varying amounts of reversion products depending on the conditions of reaction. Direct methylation of (I) by KOH and Me_2SO_4 is difficult. It is therefore treated with aq. C_5H_5N and Ac_2O followed by anhyd. C_5H_5N and Ac_2O and the *acetate* is treated with Me_2SO_4–KOH in $COMe_2$, then with Na and MeI in liquid NH_3–anisole, and finally with Ag_2O–MeI,

thereby yielding *methylgalactogen* (44·7% OMe; calc. 45·6%), $[\alpha]_D^{20}$ −71·1° in $CHCl_3$. This is hydrolysed completely by 40% HCl to a mixture of tetramethyl- and dimethyl-methylgalactosides without apparent formation of trimethyl-methylgalactoside. The components are therefore present in the ratio 1 : 1. The structure of (I) resembles therefore that of irisin and differs completely from that of (II) which gives mainly a trimethylglucose when hydrolysed. H. W.

So-called "soluble starch." W. S. Reich and P. Trpinac (Bull. Soc. chim., 1937, [v], **4**, 1921—1923).—"Sol starch," prepared from potato starch by hydrolysis with glycerol at 220°, is benzoylated (BzCl–C_5H_5N) to a *tribenzoate* of "amylone" (a non-reducing sugar with 3 free OH per glucose unit), and a different *tribenzoate*, $[\alpha]_D^{24}$ +64·7° in $CHCl_3$. By prolonging the time, or increasing the temp. of hydrolysis of the starch, a non-reducing sugar with 4 free OH per glucose unit is formed (*octabenzoate*, $[\alpha]_D^{23}$ +70·6° in $CHCl_3$). J. D. R.

Hydrolysis of starch paste by β-amylase and by heating under pressure.—See A., III, 430.

Application of cleavage type of oxidation by periodic acid to starch and cellulose. E. L. Jackson and C. S. Hudson (J. Amer. Chem. Soc., 1937, **59**, 2049—2050).—Maize starch (I) is oxidised by aq. HIO_4 (1 mol. consumed per $C_6H_{10}O_5$ during 24 hr.) at 21—22° to a product, $[\alpha]_D^{20}$ +9° in H_2O, which reduces Fehling's solution, gives an immediate ppt. with NHPh·NH_2, and shows no colour with I. Similar products, $[\alpha]_D^{20}$ (in H_2O) −25° and −29°, respectively, are formed [more slowly than from (I)] from cotton and filter-paper; the amount of HIO_4 consumed is >1 mol. probably owing to further oxidation during prolonged contact. Hydrolysis (0·1N-HCl at 99—100°) of all the products gives (−)-solutions having approx. the equilibrium val. for *d*-erythrose. H. B.

Carbohydrates. X. Viscosity of solutions of cellulose. T. Lieser and R. Ebert (Annalen, 1937, **532**, 94—103; cf. A., 1937, II, 179).—In agreement with Staudinger the sp. viscosity of solutions of cellulose (I) in NH_3–$Cu(OH)_2$ is found to be independent of temp. and concn. η_{sp} of the same sample of (I) dissolved in NEt_4·OH and diluted with 0·7N-NaOH is about thrice as great and dependent on temp. and concn. Similar results are obtained in NEt_4·OH alone, in NMe_3, *p*-cresol diluted with NaOH, and in PEt_4·OH diluted with NaOH. The state of dissolution of (I) is not regarded as essentially different in the two sets of experiments; this view is supported by the observation that η_{sp} of (I) in $(CH_2{\cdot}NH_2)_2$ is similar to that in org. bases. It appears impossible to regard the interaction of (I) and $Cu(OH)_2$–NH_3 otherwise than as a pseudostoicheiometric, micellary surface change regulated by the ratio, micelle surface : micelle content. This ratio appears to be true also in the cases of mercerisation, xanthate reaction, addition of $HClO_4$, and production of the primary Knecht compound. Permutoid introduction of Cu into (I) dissolved in strong org. bases is possible if the temp. is kept sufficiently low. The dissolution of (I) in such bases of sufficiently high mol. wt. and concn. occurs since they force apart the main valency chains at the surface of the micelle, conquering the micellary forces until they penetrate to the thread mols. situated within the micelles; these become solvatised with production of mol. compounds. Low temp. favour the production of these as of all mol. compounds, whereas at higher temp. they become dissociated. Apart from hydrolytic influences, similar conditions maintain in solutions of (I) in conc. inorg. acids. These agents have a unique position as solvents of (I). Mild solvents, *e.g.*, Schweitzer's solution, are incapable of overcoming the micellary forces of highly polymerised (I). The differences of η_{sp} in org. bases or inorg. acids and in $Cu(OH)_2$–NH_3 lead to the hypothesis that, other things being equal, micellary and mol. solutions of (I) have nearly the same sp. η. It is therefore impossible to distinguish by measurements of viscosity between the micellary and mol. condition. H. W.

Highly polymerised compounds. CLXXV. K_m constants of cellulose acetates. H. Staudinger and A. E. Werner (Ber., 1937, **70**, [*B*], 2140—2148).—In consequence of the gradual alteration of K_m in cellulose derivatives of lower mol. wt. the viscosity of dil. solutions of tetra-acetylglucose laurate and stearate, *ditetra-acetylglucose adipate*, m.p. 163·5°, *dihepta-acetylcellobiose adipate*, m.p. 225—226°, and *sebacate*, m.p. 234—235°, has been determined. After making allowance for the viscosity of the aliphatic chain K_m for the glucose acetate residue shows a progression. In explanation it is assumed that the ratio of diameter to length of mol. must be very high for exact fulfilment of the laws of η. With short-chained, irregularly formed mols. a group which increases the diameter at any point causes increase in η. The simpler glucose derivatives have unbranched, extended thread mols. Since the K_m consts. of cellulose acetates can be calc. from those of these products, it follows that the macromols. of meso- and eucolloidal cellulose acetates and of cellulose itself must be constructed of long, unbranched glucose chains. The mols. of starch are extended but branched, whereas glycogen and its derivatives are composed of spherical mols. The K_m consts. of *cetyl triacetylgallate*, m.p. 88°, and *ditriacetylgalloyloxydecane*, m.p. 122·5—123°, in $COMe_2$, $CHCl_3$, and dioxan are almost identical with those of the corresponding glucose triacetate derivatives. For glucose pentabenzoate and penta-acetate and maltose octa-acetate η_{sp}/c is const. over a large region of concn. as expected for compounds with spherical mols. H. W.

[Reaction of] monochloroamine with organolithium and -zinc compounds. G. H. Coleman, J. L. Hermanson, and H. L. Johnson (J. Amer. Chem. Soc., 1937, **59**, 1896—1897).—NH_2Cl and ZnR_2 (R = Et, Pr^{α}) in Et_2O–light petroleum at −30° give NH_2R (46—57%) and NH_3 (41—47%); NH_2R (8—17%), NHR_2 (5—8%), NH_3 (27—38%), and N_2 are formed using NCl_3. LiR (R = Me, Bu^{α}, Ph, *p*-tolyl) added to NH_2Cl at about −50° gives max. yields (33—39%) of NH_2R; NH_3 is also formed. H. B.

Addition of butylamine to butyl *iso*cyanide. T. L. Davis and W. E. Yelland (J. Amer. Chem. Soc., 1937, **59**, 1998—1999).—*Bu*$^{\alpha}$ iso*cyanide* (I),

b.p. 124—125°/761·5 mm. (from Bu$^{\alpha}$I and AgCN at 125—130°), with NH_2Bu^{α} and $ZnCl_2$ at 105—110° gives 18·4% of *NN'*-di-*n*-butylformamidine (II) [*picrate*, m.p. 114·5—116·5°, which when heated > m.p. or fused with NaOH affords (I)]. (II) is also produced [with (I) and tarry products] from NH_2Bu and $CHCl_3$ (or $CHBr_3$), preferably in presence of $ZnCl_2$. (II) is also synthesised from HCO·NHBu$^{\alpha}$, b.p. 124—126°, NH_2Bu^{α},HCl, and $POCl_3$. H. B.

Compounds of carbonyl chloride with hexamethylenetetramine, *m*-toluidine, and ethylenediamine. N. A. Pushin and R. V. Mitić (Annalen, 1937, **532**, 300—301).—Even when an excess of $COCl_2$ in $CHCl_3$ is employed, the compound $COCl_2,2C_6H_{12}N_4$ is obtained from $(CH_2)_6N_4$. $COCl_2$ and *m*-$C_6H_4Me{\cdot}NH_2$ afford *di*-m-*tolylcarbamide hydrochloride*, m.p. 162°. *Ethylenecarbamide hydrochloride*, $CO<^{NH\cdot CH_2}_{NH\cdot CH_2}$, HCl, is derived from $(CH_2{\cdot}NH_2)_2$. H. W.

Onium compounds. XVII. Thioethers of formocholine and their sulphones. R. R. Renshaw and D. E. Searle (J. Amer. Chem. Soc., 1937, **59**, 2056—2058).—SAlk·$CH_2{\cdot}NMe_2$ (from $NHMe_2$, 40% CH_2O, and AlkSH) with MeI in PhMe afford *trimethyl(alkylthiolmethyl)ammonium iodides*, of which the following are described: Alk = *Me*, m.p. 136—137°, *Et*, m.p. 119—120°, *Pr*$^{\alpha}$, m.p. 111—113°, *Pr*$^{\beta}$, m.p. 143—145°, *Bu*$^{\alpha}$, m.p. 123—126°, *Bu*$^{\beta}$, m.p. 153—154°. The corresponding sulphates are oxidised (5% $KMnO_4$ in neutral solution) to *trimethyl(alkanesulphonylmethyl)ammonium sulphates*, $[AlkSO_2{\cdot}CH_2{\cdot}NMe_3]_2SO_4$; the following are described: Alk = *Et*, decomp. 178°, *Pr*$^{\alpha}$, decomp. 190°, *Pr*$^{\beta}$, decomp. 190°, *Bu*$^{\alpha}$, decomp. 190°, *Bu*$^{\beta}$, decomp. 197°. The following *triethyl(alkylthiolmethyl)ammonium iodides* are similarly prepared from SAlk·$CH_2{\cdot}NEt_2$ and EtI: Alk = *Me*, m.p. 134—136°, *Et*, m.p. 102—103·5°, *Pr*$^{\alpha}$, m.p. 81—85°, *Pr*$^{\beta}$, m.p. 132—133°, *Bu*$^{\beta}$, m.p. 100—101°. M.p. are corr. Pharmacological properties are discussed (cf. A., 1932, 540). H. B.

Acetylcarnitine. R. Krimberg and V. Vitants (Acta Univ. Latviensis, Med. Fak. Ser., 1933, **1**, 297—303).—Carnitine and AcCl yield *acetylcarnitine chloride*, m.p. 181°, $[\alpha]_D^{20}$ −26·91°, which, with moist Ag_2O, yields acetylcarnitine, m.p. 145°, $[\alpha]_D^{20}$ −19·52° (*Au*, m.p. 128°, and *Pt*, m.p. 187°, salts); this with $Ba(MnO_4)_2$ gives the same acetobetaine as does carnitine, thus showing that the OH is in the β-position. Ch. Abs. (*r*)

Preparation of the simpler α-alkylaminoacids. I, II. W. Cocker (J.C.S., 1937, 1693—1695, 1695—1696).—I. An improved prep. of sarcosine (I) (cf. A., 1931, 1402) is described. Interaction of $PhSO_2{\cdot}NH{\cdot}CH_2{\cdot}CO_2H$ with EtI and NaOH, followed by hydrolysis (H_2SO_4), yields $NHEt{\cdot}CH_2{\cdot}CO_2H$ (II), m.p. 180—182° [lit. 160° (decomp.)] (*phenylhydantoin*, m.p. 110°). *N*-Propylglycine, m.p. 196—198° (*Bz* derivative, m.p. 89—90°), is similarly formed using PrI. *N*-Benzenesulphonylalanine is methylated (Me_2SO_4) to N-*benzenesulphonyl*-N-*methylalanine*, m.p. 96—97°, hydrolysed (H_2SO_4) to *N*-methylalanine, m.p. 315—317° (decomp.) [lit. 260° (decomp.)] (*Bz* derivative, m.p. 129—129·5°; *phenylhydantoin*, m.p. 145—146°). Hydrolysis of *N*-benzenesulphonyl-*N*-benzylglycine with H_2SO_4 yields glycine (III), and with conc. HI, CH_2PhI and PhSH.

II. 2 : 1-OMe·$C_{10}H_6{\cdot}SO_2Cl$ and (III) in C_6H_6–NaOH afford N-2-*methoxynaphthalene*-1-*sulphonylglycine*, m.p 184·5°, methylated (Me_2SO_4) to N-2-*methoxynaphthalene*-1-*sulphonylsarcosine*, m.p. 145°, hydrolysed (60% H_2SO_4) to β-$C_{10}H_7{\cdot}$OMe and a little (I). Similarly, *mesitylenesulphonylglycine*, m.p. 154·5°, is prepared from mesitylenesulphonyl chloride and (III) is methylated (Me_2SO_4) to *mesitylenesulphonylsarcosine*, m.p. 164—165°, and hydrolysed (60% H_2SO_4) to (I). *m*-Xylene-4-sulphonyl chloride and (III) yield N-m-*xylene*-4-*sulphonylglycine* (IV) (*hydrate*, m.p. 76°; *anhyd.*, m.p. 110—110·5°), methylated (Me_2SO_4) to N-m-*xylene*-4-*sulphonylsarcosine*, m.p. 104·5—105°, also hydrolysed by H_2SO_4 to (I). (IV) heated with *p*-$C_6H_4Me{\cdot}SO_3Et$ and NaOH yields N-m-*xylene*-4-*sulphonyl*-N-*ethylglycine*, m.p. 108—109°, hydrolysed by H_2SO_4 to (II). J. D. R.

Infra-red absorption spectra of the stereoisomerides of cystine. N. Wright (J. Biol. Chem., 1937, **120**, 641—646).—Determination of the infra-red absorption spectra of *l*- (I), *d*-, *dl*-, and *meso*-cystine shows that *dl*-cystine obtained by crystallisation is a compound. (I) from protein and cystinuric urine have identical spectra. A. L.

Multivalent amino-acids and peptides. IX. Synthesis of *l*-cystinyl-*l*-cystine. J. P. Greenstein (J. Biol. Chem., 1937, **121**, 9—17).—l-*Cysteinyl*-l-*cysteine hydrochloride*, m.p. 166°, $[\alpha]_D^{22}$ +35° in 0·2N-HCl [from anhydrocysteinylcysteine (A., 1937, II, 262) with cold conc. HCl for 4 days], is oxidised by air in aq. NH_3 at p_H 8·5 to l-*cystinyl*-l-*cystine* (I), $[\alpha]_D^{22}$ −60° in N-HCl (*dihydrochloride*), hydrolysed by dil. HCl to cystine having the same [α] as the initial material. The mol. wt. of (I) and of the Me_2 ester, m.p. 257° (decomp.), of its NN'-Bz_2 derivative, m.p. 220° (decomp.), indicate the formula $[S{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO{\cdot}NH{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}S]_2$. A. Li.

Synthesis of substances related to capsaicin. P. C. Mitter and S. C. Ray (J. Indian Chem. Soc., 1937, **14**, 421—424).—The following iso*butylamides*, in order of decreasing pungency, are described: Δ$^{\alpha}$-*hepteno*-, b.p. 140°/4 mm., Δ$^{\alpha}$-*noneno*-, b.p. 170°/7 mm., n-*hepto*-, b.p. 130°/7 mm., benzo-, *cinnamo*-, m.p. 114°, n-*hexo*-, b.p. 136°/9 mm., Δ$^{\alpha}$-*hexeno*-, b.p. 138°/4 mm., n-*octo*-, b.p. 155°/8 mm., Δ$^{\alpha}$-*octeno*-, b.p. 150°/4 mm., Δ$^{\beta}$-*deceno*-, b.p. 155°/4 mm., Δ$^{\omega}$-*undeceno*-, b.p. 175°/5 mm., *aniso*-, m.p. 105—106°. A. Li.

Stability and toxicity of a complex salt of silver chloride and thiocarbamide. W. M. Lauter and A. M. Stauff (J. Amer. Pharm. Assoc., 1937, **26**, 724—726).—The complex $AgCl,5CS(NH_2)_2$ is unstable in H_2O, $AgCl,2CS(NH_2)_2$ being formed. $AgCl,7CS(NH_2)_2$ is stable in H_2O and has a toxicity of approx. 0·3 mg. per g. in rats. F. O. H.

Carbamide series. XIV. Structure of the guanidonium ion; evidence from electrolysis. T. L. Davis, W. E. Yelland, and C. C. Ma (J. Amer. Chem. Soc., 1937, **59**, 1993—1997).—Dil. NH_4 amalgams appear to be formed when guanidine salts

are electrolysed in H_2O or org. solvents using a Hg cathode. Evidence is discussed to show that the guanidonium ion is $^+C(NH_2)_3$; electrolysis results in the production of $[\cdot C(NH_2)_3]_2$, which decomposes to NH_3 and $(CN)_2$ [subsequently reacting with part of the NH_3 to give NH_4CN and $CO(NH_2)_2$ (via NH_4CNO)]. H. B.

Reduction of nitroguanidine. IX. Reduction of nitrosoguanidine to aminoguanidine. E. Lieber and G. B. L. Smith (J. Amer. Chem. Soc., 1937, **59**, 1834—1835).—Aminoguanidine (I) is best prepared from nitrosoguanidine (II) by reduction with H_2 and Raney Ni in MeOH at 25°. The effects of catalyst, temp., and solvent are investigated. The yields of (I) from (II) are generally > those from nitroguanidine (cf. A., 1937, II, 10), except for PtO_2 in 15% AcOH [in which solvent (II) is unstable]. H. B.

Cacodylates of zinc. R. Thiollais and H. Perdreau (Bull. Soc. chim., 1937, [vi], **4**, 1896—1898).—ZnO and $AsMe_2O_2H$ yield *Zn cacodylate monohydrate* and *heptahydrate*, also obtained from $ZnSO_4$ and Ba cacodylate. J. D. R.

Complex compounds of mercury halides with the halides of the aliphatic amines.—See A., I, 628.

Ring fission in complex platinum compounds.—See A., I, 630.

Ethylene compounds of platinum.—See A., I, 630.

Dipole moment of *n*-propyl*cyclo*propane.—See A., I, 499.

Synthesis of *cyclo*pentane*spirocyclo*pentane. N. Chatterjee (Sci. and Cult., 1936, **1**, 478).—Et 1-cyano*cyclo*pentane-1-cyanoacetate (from *cyclo*pentanone cyanohydrin and $CN\cdot CH_2\cdot CO_2Et$) with $CH_2Cl\cdot CH_2\cdot CO_2Et$ gives *Et* 1-*cyano*cyclo*pentane*-1-α-*cyanoglutarate*, b.p. 210—213°/8 mm., hydrolysed and decarboxylated to cyclo*pentane*-1-*carboxylic*-1-α-*glutaric acid*, m.p. 131—132°. The Et_2 ester, b.p. 162—165°/4 mm., of this, with Na in C_6H_6, yields Et_2 1-*keto*-[0 : 4 : 4]-dicyclo*nonane*-2 : 4-*dicarboxylate*, b.p. 168°/4 mm., hydrolysed and decarboxylated to 1-*keto*-[0 : 4 : 4]-dicyclo*nonane*-4-*carboxylic acid*, m.p. 67°; this is reduced (Clemmensen) and the product decarboxylated to [0 : 4 : 4]-dicyclo*nonane* (*cyclo*pentane*spirocyclo*pentane). Ch. Abs. (*r*)

Action of N_2O_3 on $\Delta^{1:3}$-*cyclo*hexadiene. A. S. Onischtschenko (Bull. Acad. Sci. U.R.S.S., Sér. Chim., 1937, 539—546).—$\Delta^{1:3}$-*cyclo*Hexadiene (I) in AcOH, $C_5H_{11}\cdot NO_2$, and 10% HCl in EtOH at −10° yield the *nitrosochloride*, m.p. 123°, of (I). (I) in Et_2O and N_2O_3 at −5° yield a *ψ-nitrosite* (impure), which is reduced (Sn and HCl) to 1 : 4-diamino-Δ^2-*cyclo*hexene, +2HCl [*platinochloride*, *aurichloride*, both m.p. ≮250°; *di*-N-*benzoyl* derivative, m.p. 278—280° (decomp.)], and 1-*hydroxy*-4-*amino*-Δ^2-cyclo*hexene*, +HCl [*platinochloride*, $+2H_2O$, decomp. at 222—223°; *aurichloride*, $+H_2O$, m.p. 187—190° (decomp.)]. R. T.

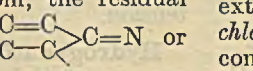
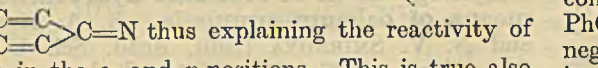
Sulphonaphthenic acids. S. von Pilat and M. Turkiewicz (Petroleum, 1937, **33**, No. 41, 1—4).—Several chlorinated naphthenic acids and their derivatives were prepared and their properties and behaviour towards alkalis examined. Na sulphonaphthenates were obtained from the Cl_2-compounds by decomp. with Na_2SO_3, and the corresponding esters from esters of chloronaphthenic acids. The course of this reaction was examined with regard to the formation of lactones and hydroxy- and olefinecarboxylic acids. The Na salts behave as salts of a strong acid, changing the colours of Me-orange and Congo-red. A study of the saponification products of monochloronaphthenic acids indicates that the Cl is mainly (65%) in the α-position with regard to the CO_2H. The interfacial tension between C_6H_6 and solutions of naphthenates, chloro- and sulpho-naphthenates was measured. The first-named cause the greatest mol. lowering of tension. H. C. R.

Hydrogenation of aromatic hydrocarbons by means of calcium–ammonia. B. A. Kazanski and N. V. Smirnova (Bull. Acad. Sci. U.R.S.S., Sér. Chim., 1937, 547—554).—H_4-derivatives are obtained by passing C_6H_6, PhMe, $C_{10}H_8$, or $\Delta^{1:3}$-*cyclo*hexadiene through a layer of Ca–NH_3 at 0°. R. T.

Friedel–Crafts synthesis. N. O. Calloway (Chem. Rev., 1935, **17**, 327—392).—A general summary. Ch. Abs. (*r*)

Preparation of bromomesitylene. F. Duke, H. Lewis, and R. E. Dunbar (Proc. S. Dakota Acad. Sci., 1935, **15**, 21—23).—Mn is superior to Fe as catalyst in the direct bromination of mesitylene. Ch. Abs. (*r*)

Halogenation of aromatic and aliphatic compounds. R. Oda and K. Tamura (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1937, **33**, 129—208).—Halogenation is usually effected by addition of Br or Cl_2 in AcOH to the org. compounds in AcOH, less frequently in *n*-C_6H_{14} or H_2O; excess of halogen is determined periodically by addition of KI and titration with $Na_2S_2O_3$. The velocity coeffs., calc. for a bimol. reaction, invariably increase or decrease with time. When bromination occurs instantaneously the reaction is followed by the combined use of KI and Br. These react momentarily and quantitatively, $Br_2 + KI = KBr + IBr$, but in presence of a very rapidly reacting org. compound some of the Br is utilised thereby and less IBr (which does not react with org. compounds) is produced. The amount of it produced therefore indicates the activity of the org. compound. The following general conclusions are reached. C_6H_6, halogenobenzene (I), $PhNO_2$, BzOH, $COPh_2$, and, probably, PhCHO are scarcely brominated. (I) directs towards the *o*- and *p*-, the others towards the *m*-position. PhMe, xylene, $C_{10}H_8$, and 1 : 2 : 3 : 4-tetrahydronaphthalene (II) are brominated with moderate rapidity and Me directs to the *o*- and *p*-positions. Anthracene and phenanthrene are brominated very rapidly but the change can be followed iodometrically. Bromination of aromatic NH_2- and OH-compounds and of true aliphatic, unsaturated compounds such as $CHPh{:}CH_2$ and *cyclo*hexene takes place instantaneously and too rapidly to be followed iodometrically; OH and NH_2 direct to the *o*- and *p*-positions. The theory of alternating polarity is

regarded as incapable of explaining these observations but the electromeric displacement hypothesis accounts for the unusual reactivity of NH_2Ph and PhOH and the disturbing influence of NO_2, halogen, or CO. The coupling theory of Schmidt is false since it fails to explain the unusual turgidity of $PhNO_2$ although it appears valid for the directive influence of NO_2. Schmidt's double linking rule explains satisfactorily the general influence of Me. Thus in PhMe a quantum-mechanical union exists between C of Me and C of the C_6H_6 nucleus united therewith, and hence reactivity is apparent in the *o*- and *p*-positions; this is also the cause of the reactivity of PhMe and (II). Similarly the reactivity of PhOH and NH_2Ph can be explained. If the unshared electron of the N of NH_2Ph is coupled with the *p*-electron of the $C_{(6)}$ atom, the residual nucleus must assume the form  or  thus explaining the reactivity of NH_2Ph in the *o*- and *p*-positions. This is true also for PhOH. H. W.

Direct conversion of iodic acid and aromatic hydrocarbons into iodonium compounds. I. Masson and E. Race (J.C.S., 1937, 1718—1723; cf. A., 1936, 61).—HIO_3 in H_2SO_4 with PhX (X = H, Me, Cl, Br, or I) yields mainly iodonium radicals $(C_6H_4X)_2I^{\cdot}$, some p-C_6H_4XI, and unidentified aliphatic degradation products of PhX. The reaction may be used for the detection of aromatic impurity in aliphatic hydrocarbons. With PhOMe and other highly reactive or easily oxidisable derivatives, decomp. takes place, and when X is a *m*-directing substituent (*e.g.*, NO_2) the reaction is almost entirely inhibited. The iodonium salts may be isolated from the reaction by SO_2, or NaI, or both, to yield diaryliodonium iodides, or by dilution with H_2O to yield the acid sulphates. Since I_2O_5 and H_2SO_4 with PhX afford only pure iodonium compounds in quant. yield, the following mechanism of reaction is suggested: primary deoxidation of HIO_3 to HIO_2 by PhX (which is oxidised to aliphatic substances) followed by $HO{\cdot}IO + 2PhX \rightarrow (C_6H_4{\cdot}X)_2{\cdot}I{\cdot}OH + H_2O$.

$(p\text{-}C_6H_4Cl)_2I{\cdot}HSO_4$ is converted by H_2O into $[(p\text{-}C_6H_4Cl)_2I]_2SO_4$, the change being reversed by H_2SO_4. The normal and acid sulphates are in equilibrium in 6N-H_2SO_4. J. D. R.

Aryl iododihalides as halogenating agents. B. S. Garvey, jun., L. F. Halley, and C. F. H. Allen (J. Amer. Chem. Soc., 1937, **59**, 1827—1829; cf. Bockemüller, A., 1931, 611).—Various unsaturated compounds [COPh·CH:CHPh, (:CHPh)$_2$, CO(CH:CHPh)$_2$, *trans*-(:CHBz)$_2$, Δ^{β}-pentene (the only aliphatic hydrocarbon to give a satisfactory product)] add Cl when heated with $PhICl_2$ in $C_2H_4Cl_2$, the reaction being less vigorous than with Cl_2; CHPh:CH·CO_2H and C_6H_6 are unattacked. $PhIF_2$ (from PhIO and 46% HF in AcOH) with simple olefines and (:CHPh)$_2$ in $CHCl_3$ gives mixtures; rubber similarly yields an impure F_1-derivative. Fluorination and/or coupling occurs with some aromatic hydrocarbons. Thus, acenaphthene affords *diacenaphthenyl*, m.p. 174°; pyrene yields *fluoropyrene*, m.p. 113°, and *dipyrenyl* (?), softens about 250°, molten at 300°; anthrone gives (in one case only) *dianthronyl*, m.p. 360°; anthracene furnishes 9-*fluoroanthracene*, m.p. 110° (oxidised to anthraquinone); benzanthrone affords Bz-2(or 3)-*fluorobenzanthrone*, m.p. 186° (oxidised to anthraquinone-1-carboxylic acid). No reaction occurs between $PhIF_2$ and various compounds (*e.g.*, $C_{10}H_8$, phenanthrene, αδ-diphenylbutadiene, PhOMe, NHAcPh, anthraquinone). H. B.

Decomposition of iodonium salts. R. B. Sandin, M. Kulka, and R. McCready (J. Amer. Chem. Soc., 1937, **59**, 2014—2015; cf. Lucas *et al.*, A., 1936, 323).—PhIO, p-OMe·C_6H_4·IO_2, and moist Ag_2O are triturated with a little $CHCl_3$; the aq. extract with KHal affords *phenylanisyliodonium chloride* (I), *bromide* (II), and *iodide*. Thermal decomp. of (I) and (II) gives mainly p-C_6H_4I·OMe with PhCl and PhBr, respectively, *i.e.*, the more electronegative anisyl radical remains attached to I. The I in p-C_6H_4I·OMe (not PhI) is eliminated by $SnCl_2$ in 40% HBr + approx. 75% AcOH; a quant. procedure is detailed. H. B.

Mechanism of sulphonation of aromatic compounds, and the hydrolysis of their sulphonic acids. V. Ufimtzev (Prom. Org. Chim., 1937, **4**, 157—161).—Theoretical. The stability to hydrolysis of sulphonic acids falls with rise of temp., time of heating, and $[H_2SO_4]$; as a result, at a given temp., a mixture of isomeric acids is formed, in which the proportion of the acid most resistant to hydrolysis rises with time. The reactions of sulphonation or hydrolysis are not of the first or second order. R. T.

Salts of nitro-compounds. I. Preparation, alkylation, and acylation of salts of phenylnitroacetonitrile. J. T. Thurston and R. L. Shriner (J. Org. Chem., 1937, **2**, 183—194).—$CH_2Ph{\cdot}CN$, KOEt, and *dl*-, *d*-, or *l*-octyl nitrate give the optically inactive *K* salt (I) of CN·CHPh·NO_2, considered to have a conjugated *aci*-structure. Neither (I) nor the Na salt (II) gives alkyl derivatives with alkyl halides; (II) and Me_2SO_4 yield CN·CPh:CPh·CN. The Ag salt (III), however, with MeI forms *aciphenylnitroacetonitrile Me ester*, CN·CPh:N  , m.p. 41—42°, decomp. on keeping, of which the *O*-alkyl structure is established by reduction (PtO_2–Ac_2O–H_2) to NHAc·CHPh·CH_2·NHAc (IV), new m.p. 155—155·5° (also synthesised via NH_2·CHPh·CN). With CH_2PhCl, (III) gives CN·CPh:N·OH, [reduced to (IV)], and PhCHO, by decomp. of an unstable CH_2Ph ester. With BzCl, (II), or better (III), gives a compound, m.p. 116° (decomp.), which is *O-benzoylphenylnitroacetonitrile*, and not the *C*-Bz compound, Ph ω-nitro-ω-cyanobenzyl ketone (A., 1933, 1163), since reduction (PtO_2–Ac_2O–H_2) gives (IV) and BzOH. E. W. W.

Halogenation of acenaphthene. M. Daschevski and A. Karischin (Prom. Org. Chim., 1937, **4**, 109—113).—Acenaphthene in EtOH (at the b.p.) and Cl_2 (2 mols.) give chiefly 4 : 5-dichloroacenaphthene (I) in 55% yield, together with 4-chloro- and traces of trichloro-acenaphthene. (I) in AcOH and $K_2Cr_2O_7$

yield 4 : 5-dichloroacenaphthenequinone and 4 : 5-dichloronaphthalic acid. R. T.

[Pyrene syntheses.] W. Quist (Annalen, 1937, **532**, 302).—Syntheses of pyrene (cf. Vollmann *et al.*, A., 1937, II, 450) from 2 : 6 : 2′ : 6′-tetramethyl- and 2 : 6′-diethyl-diphenyl and from phenanthrene and C_2H_4 have been described by Mattsson (Diss., Helsingfors, 1905). H. W.

Derivatives of 1 : 2-benzpyrene. A. Windaus and S. Rennhak (Z. physiol. Chem., 1937, **249**, 256—266).—1 : 2-Benzpyrene in CS_2 with Br at 5° gives the Br_3-derivative (I), m.p. 298—298·5°; in AcOH with conc. HNO_3 at room temp. a NO_2-derivative (II), m.p. 250·5—251°; with conc. HNO_3 at approx. 100° a $(NO_2)_2$-derivative (III), m.p. 286·5° (decomp.); with conc. H_2SO_4 and Ac_2O a *monosulphonic acid* (IV), m.p. 146—148° (*Me* ester, m.p. 206°; *K* and *Na* salts); and with Ac_2O and $AlCl_3$ *acetylbenzpyrene*, m.p. 186—186·5°, which, in dioxan, with aq. NaOH and conc. I in aq. KI at ≯60° followed by treatment with CH_2N_2 yields the *Me* ester, m.p. 151—151·5°, of the corresponding carboxylic acid. (II) boiled with NHPh·NH_2 for 5 hr. gives the corresponding NH_2-compound (V), m.p. 231° (decomp.) [*Ac* derivative, m.p. 217·5°; *picrate*, m.p. 180° (decomp.)]. The compounds (I)—(V) are not carcinogenic. W. McC.

Pharmaceutically important arsenic compounds. II. K. Brand and E. Rosenkranz (Pharm. Zentr., 1937, **78**, 685—691; cf. B., 1932, 1104).—The preps. of the following are described: NH_4 meta-arsenite, NH_4AsO_2, cyclo*hexylammonium meta-arsenite* and its $HAsO_2$ additive *compound*, $C_6H_{11}\cdot NH_3\cdot AsO_2$, $HAsO_2$, and NH_4Cl,As_2O_3. E. H. S.

Rearrangement of *N*-chloroacetanilide. R. S. Halford and J. C. Hornel (J. Amer. Chem. Soc., 1937, **59**, 1613—1615).—The rearrangement to *o*- and *p*-chloroacetanilide in aq. EtOH containing H_2SO_4 has been reinvestigated kinetically, using radioactive Cl′ as catalyst (cf. A., 1937, II, 87). Equal amounts of *o*- and *p*-compound are produced. The change in radioactivity of Cl′ in solution during the progress of the reaction rules out the possibility of an intramol. mechanism. A Cl′-intermediate mechanism is proposed. E. S. H.

Action of primary amines on dibromodiethylenediamine cobaltibromide. A. Ablov (Bull. Soc. chim., 1937, [v], **4**, 1783—1793).—Interaction of dibromodiethylenediamine cobaltibromide, [Co en_2Br_2]Br, and the appropriate amine in aq. EtOH yields pentamminocobalti-*compounds* of the structure [Co en_2(R)Br]Br_2 (other salts prepared are indicated in parentheses) where R is NH_2Ph, *m*-$C_6H_4Me\cdot NH_2$ (*dinitrate*, *di-iodide*), *p*-$C_6H_4Me\cdot NH_2$ (*di-iodide*), *o*-$NH_2\cdot C_6H_4\cdot OMe$ (*di-iodide*, *dinitrate*), *o*-$NH_2\cdot C_6H_4\cdot OEt$ (*di-iodide*, *dinitrate*), *m*-$C_6H_4Cl\cdot NH_2$ (*di-iodide*), *p*-$C_6H_4Cl\cdot NH_2$, *m*-$C_6H_4Br\cdot NH_2$ (*di-iodide*), *p*-$C_6H_4Br\cdot NH_2$, *p*-$C_6H_4I\cdot NH_2$, β-$C_{10}H_7\cdot NH_2$, NH_2Et (*di-iodide*, *dinitrate*). With α-$C_{10}H_7\cdot NH_2$ and *o*-$C_6H_4Me\cdot NH_2$, [Co en_3]Br_3 is formed; *o*-$C_6H_4Cl\cdot NH_2$ does not give a derivative, and with *o*-phenanthroline [Co $en_2(C_{12}H_8N_2)$]Br_3 results. T. D. R.

Anilides and phenylhydrazides of alanine, glycine, and leucine derivatives.—See A., III, 393.

Relative hypnotic effects of some carbamides of varied types. A. M. Hjort, E. J. de Beer, J. S. Buck, W. S. Ide, and D. W. Fassett (J. Pharm. Exp. Ther., 1937, **61**, 175—181).—The following carbamides have been prepared: ββ*β-tribromoethyl-*, m.p. 174°; ββ*-dibromopropyl-*, m.p. 110°; ββ*γ-tribromopropyl-*, m.p. 139°; as-m-*chlorophenylmethyl-*, m.p. 98—99°; as-p-*bromophenylmethyl-*, m.p. 110°; p-*dimethylaminophenyl-*, m.p. 181°; as-p-*dimethylaminophenyl*-n-*propyl-*, m.p. 125°; as-p-*hydroxyphenyl*-n-*propyl-*, m.p. 191°; as-m-*carboxyphenylethyl-*, m.p. 210°; as-o-, m.p. 110°, and -p-*ethylphenyl*iso*propyl-*, m.p. 104°; as-α-*naphthylmethyl-*, m.p. 119°; as-α-*naphthylethyl-*, m.p. 141°; as-β-*naphthylmethyl-*, m.p. 110°; as-β-*naphthylethyl-*, m.p. 99°; o- and p-*phenylenedi-*; bis-*pentamethylene-* (I), m.p. 104°; Δ^2-cyclo*hexenyl-*, m.p. 197°; N-p-*anisyl*-N-s-*diethyl*iso*thio-* (hydrochloride) (II), m.p. 150°. The hypnotic action of carbamide derivatives is increased by the introduction of halogen atoms. (I), from piperidine, is less potent than the Δ^2-*cyclo*hexenyl- and phenyl-carbamides. The introduction of OH or CO_2H into the ring of arylcarbamides much decreases their activity. (II) is a convulsant and relatively toxic. W. O. K.

Constitution and reactions of thiocarbonyl tetrachloride. IV. Reaction with secondary and tertiary amines. C. S. Argyle and G. M. Dyson (J.C.S., 1937, 1629—1634; cf. A., 1937, II, 375, 411).—*sec.*-Dialkyl- and arylalkyl-amines and $CCl_3\cdot SCl$ (I) give unstable compounds, $CCl_3\cdot S\cdot NRR'$; diarylamines give $CHPh_3$ dyes and substances containing at least one NRR′·C; *tert.* amines give dyes of the crystal-violet type by way of substances, $NR_2\cdot C_6H_4\cdot S\cdot CCl_3$, the CCl_3 of which provides the *tert.* C of the $CHPh_3$ series. The appropriate *sec.* amine and (I) in Et_2O–aq. NaOH at 30° give S-*dimethyl-*, b.p. 74°/15 mm., *-diethyl-*, b.p. 96°/15 mm., *-diisobutyl-*, b.p. 127°/15 mm. (decomp.), *-methylanilino-*, and *-methyl*-p-*toluidino-aminotrichloromethylthiol*; the arylalkyl compounds decompose when distilled and others of this type, although prepared, were very unstable. These thiols with HCl in ligroin regenerate the amine and (I), are reduced by Zn–AcOH to MeSH, are hydrolysed slowly by hot H_2O and rapidly by 20% aq. alkali to RCN and RCNS, and with an excess of an arylamine in ligroin give triarylguanidines in varying yield. $NHPh_2$ with $CSCl_2$ or (I) gives *NN′N″*-triphenylpararosaniline hydrochloride (II) and a red *compound* (III), (?) $NPh_2\cdot C(C_6H_4\cdot NHPh){:}C_6H_4{:}NHPhCl$. The structure of (III) is based on its conversion by H_2SO_4 at 70° into a sulphate and monosulphonic acid, by fuming HNO_3–AcOH at 100° into $NO\cdot N(C_6H_4\cdot NO_2\text{-}p)_2$ [with NH_2Ph at 120° gives $NH(C_6H_4\cdot NO_2)_2$], by $KMnO_4$ into PhNC (in alkali) or $NHPh_2$ (in acid), and by dry distillation into $NHPh_2$; AcCl–Ac_2O reacts with (III), but no Ac derivative could be isolated. Both (II) and (III) are also obtained from $NHPh_2$ with $CCl_3\cdot NO_2$, $CCl_3\cdot SO_2Cl$, or *p*-$C_6H_4Me\cdot S\cdot CCl_3$ at 150°. Reaction probably proceeds by way of $CS(NPh_2)_2$ which suffers *p*-rearrangement of the semidine–

benzidine type to NPh_2·CS·C_6H_4·NHPh and thence to (II). $NPhMe_2$ and (I) at <20° give S-p-*dimethylaminophenyltrichloromethylthiol* (IV), NMe_2·C_6H_4·S·CCl_3, m.p. 71° [$(NO_2)_2$-, m.p. 123°, and *Br*-derivative, m.p. 146° (decomp.); *hydrochloride*, m.p. 129—130° (decomp.)], with $CH(C_6H_4$·NMe_2-$p)_3$ and crystal-violet. The p-*di-ethyl-*, m.p. 44°, -n-*propyl-*, -n-*butyl-*, and p-*methylethyl-thiols*, oils, were similarly prepared. (IV) is hydrolysed by H_2O to *p*-NMe_2·C_6H_4·SH (V) (*Pb* salt), which is oxidised by air to *bis*-p-*dimethylaminophenyl sulphide*, m.p. 118°, also obtained from S_2Cl_2 and $NPhMe_2$. With NH_2Ph in EtOH (IV) and its analogues give S-p-*di-methyl-* (VI), m.p. 175°, *-ethyl-*, m.p. 128°, and -n-*propylaminophenyl*-NN′-*diphenyl*isothiocarbamide, NR_2·C_6H_4·S·C(NPh)·NHPh, m.p. 125°; with other arylamines (IV) gives S-p-*dimethylaminophenyl*-NN′-*di*-p-*tolyl-*, m.p. 142°, -p-*chlorophenyl-*, m.p. 157°, and -p-*bromophenyl*-isothiocarbamide, m.p. 167°. With NH_2–EtOH at 120° (VI) gives (V) and NH:C$(NHPh)_2$, and with NH_2Ph at 170° (V) and NPh:C$(NHPh)_2$; with $CHCl_3$–KOH it gives PhNC, and with Sn–HCl NH_2Ph, but it is unaffected by <80% KOH; it is also obtained from NPh:CCl·NHPh and NMe_2·C_6H_4·SK in hot EtOH. $NPhMe_2$, (IV), and $AlCl_3$ at 100° give *p*-C_6H_4Me·SH and crystal-violet, and $NHPh_2$ reacts similarly. NPh_2Me and (I) at 100—130° give NN′N″-*triphenyl*-NN′N″-*trimethyl-pararosaniline hydrochloride*; NPh_3 at 180° gives *hexaphenylpararosaniline hydrochloride*, converted into the *carbinol*; aryldialkylamines react with partial dealkylation and $N(CH_2Ph)_3$ similarly gives CH_2PhCl and $CSCl_2$. R. S. C.

Phenylthiocarbamides. The triad –N·C·S–. IV. Action of silver nitrate on phenylthiocarbamide. V. Action of nitrous acid on *N*-phenyl-*N*-methylthiocarbamide. K. B. Lal and H. Krall (J. Indian Chem. Soc., 1937, **14**, 474—477, 478—485).—IV. $AgNO_3$ and NHPh·CS·NH_2 (I) in acid solution give several complexes. With excess of aq. $AgNO_3$, the *compound* NHPh·CS·NH_2,$AgNO_3$, decomp. 132—134° (which takes up further $AgNO_3$), is formed, which with KSCN (II) yields a *compound* NHPh·CS·NH_2,AgSCN. Thus by Volhard's method (II) can be determined in presence of (I), provided (I) is < equiv. to (II), with which it is equimolecularly pptd.

V. NPhMe·CS·NH_2 (III) and HNO_2 in strongly acid solution give *phenylmethylformamidine disulphide*, [NPhMe·C(:NH)S]$_2$ (*perchlorate*, m.p. 143°; *picrate*, m.p. 140°), and NO; in presence of AcOH, compounds, m.p. 199° (decomp.), and 205—210°, and N_2, are formed, apparently by way of NPhMe·CS·OH. Acids presumably facilitate the change NPhMe·CS·NH_2 → NPhMe·C(NH)·SH. No diazothiol is formed in the reaction between (III) and HNO_2. E. W. W.

Some nuclear alkyl derivatives of β-phenylethylamine. J. H. Speer and A. J. Hill (J. Org. Chem., 1937, **2**, 139—147).—The following are prepared (h. = hydrochloride; p. = picrate): β-o-*tolylethylmethylamine*, b.p. 99°/12 mm. (*h.*, m.p. 167°; *p.*, m.p. 114—115°), β-*m-*, new b.p. 98—99°/12 mm. (cf. A., 1926, 512) (h., new m.p. 143°), and β-*p*-tolylethylmethylamine (*loc. cit.*); β-o-, b.p. 120·5°/14 mm. (*h.*, m.p. 147·5; *p.*, m.p. 110°), β-m-, b.p. 120°/15 mm. (*h.*, m.p. 148°; *p.*, m.p. 95°), and β-p-*tolyltriethylamine*, b.p. 119°/14 mm. (*h.*, m.p. 115—116°; *p.*, m.p. 132°); β-m-, b.p. 100°/9 mm. (*h.*, m.p. 161—162°; *p.*, m.p. 133°), and β-p-*tolyldiethylamine*, b.p. 107°/12 mm. (*h.*, m.p. 203—204°; *p.*, m.p. 126°); *benzyl-*, b.p. 165—167°/4 mm. (*h.*, m.p. 232—234°; *p.*, m.p. 125°), and *diphenylmethyl*-β-p-*tolylethylamine*, m.p. 73·5°, b.p. 193—195°/2·5 mm. (*h.*, m.p. 256°; *p.*, m.p. 155°); β-*diethylamino*-β′-*tolyldiethylamine*, b.p. 131—134°/3 mm. (*dihydrochloride*, m.p. 124—125°); β-p-*tolylethyldi*-n-*butylamine*, m.p. 120—122°/2·5 mm. (*h.*, m.p. 93°; *p.*, m.p. 62—63°); 1-β-p-*tolylethylpiperidine*, b.p. 118°/4 mm. (*h.*, m.p. 212°; *p.*, m.p. 144°); β-p-*ethylphenyl-*, b.p. 97°/8 mm. (*h.*, m.p. 208°; *p.*, m.p. 168°), and *methyl*-β-p-*ethylphenyl-ethylamine*, b.p. 90—91°/4·5 mm. (*h.*, m.p. 192—193°; *p.*, an oil); β-o-, b.p. 155°/4 mm. (*h.*, m.p. 169—170°; *p.*, m.p. 178—179°), and β-p-*benzylphenylethylamine*, b.p. 178—181°/8 mm. (*h.*, m.p. 222—224°; *p.*, m.p. 154—155°); β-o-, b.p. 146—148°/3 mm. (*h.*, m.p. 180°; *p.*, m.p. 169—171°), and β-p-*benzylphenylethylmethylamine*, b.p. 145—146°/3 mm. (*h.*, m.p. 192°; *p.*, m.p. 93—94°); β-o-, b.p. 157°/3 mm. (*h.*, m.p. 122°; *p.*, m.p. 143—144°), and β-p-*benzylphenyltriethylamine*, b.p. 169—170°/3 mm. (*h.*, m.p. 136·5°; *p.*, oil); and β-p-(β′-*phenylethyl*)-, m.p. 49°, b.p. 160°/2 mm. (*h.*, m.p. 213—215°; *p.*, m.p. 135°), and *methyl*-β-p-(β′-*phenylethyl*)-*phenylethylamine*, b.p. 152—155°/2·5 mm. (*h.*, m.p. 197°; *p.*, m.p. 115—116°).

The amines are obtained from the substituted phenylethyl bromides, prepared (PBr_3) from the alcohols which result from action of $(CH_2)_2O$ on the Mg derivatives of substituted bromobenzenes. The following intermediates are also described: *p*-C_6H_4Br·CO·CH_2Ph (I) (A., 1932, 158), b.p. 165°/3 mm. (*oxime*, m.p. 137°); p-*bromodiphenylmethane*, b.p. 162°/13 mm. (from COPh·C_6H_4Br, HI, and P); p-*bromo*-s-*diphenylethane*, m.p. 32°, b.p. 143°/3 mm. [obtained with $(CH_2Ph)_2$ from (I)]; β-p-*ethyl-*, b.p. 98—101°/4 mm. (*phenylurethane*, m.p. 104·5°), β-o-, b.p. 162°/3 mm. (*phenylurethane*, m.p. 124°), and β-p-*benzyl-* (II), b.p. 172°/4·5 mm. (*phenylurethane*, m.p. 93°), and β-p-β′-*phenylethyl-phenylethyl alcohol* (III), m.p. 67—68°, b.p. 172°/3 mm. (*phenylurethane*, m.p. 107°). As by-products with (II) and (III), pp′-*dibenzyl-*, m.p. 113°, b.p. 190—215°/5 mm., and pp′-*di*-β-*phenylethyl-diphenyl*, m.p. 146°, are obtained. 1-*Ethyl*-4-β-*bromoethylbenzene* has b.p. 84—86°/3 mm. As a by-product of the action of PBr_3 on (III), the *acid phosphite*, no m.p. <300°, of (III) is obtained. $C_6H_4(CO)_2NK$ and *p*-C_6H_4Me·CH_2·CH_2Br give β-p-*tolylethylphthalimide*, m.p. 117°, hydrolysed to the β-p-*tolylethylmonoamide*, m.p. 150°, of phthalic acid, and to the amine. E. W. W.

2-Methyl-α-naphthylamine-4-sulphonic acid. H. E. Fierz-David and E. Mannhart (Helv. Chim. Acta, 1937, **20**, 1024—1040).—1-Nitro-2-methylnaphthalene, b.p. 185—186°/18 mm., m.p. 80—81°, is obtained in 60% yield by gradual addition of fuming HNO_3 to 2-$C_{10}H_7Me$ in AcOH at 0° to 5° and subsequent gradual heating to 80° or from 2-

$C_{10}H_7Me$ and conc. HNO_3 at 70—75°. It is reduced by Fe in neutral solution or by $SnCl_2$–HCl in AcOH to 2-methyl-α-naphthylamine, b.p. 165°/12 mm. (Ac derivative, m.p. 188°). A hydrazo-derivative is not obtained in alkaline solution. Gradual addition of the base to 50% H_2SO_4 at 110—140° gives the *H sulphate*, which passes at 180°/vac. into 2-*methyl*-α-*naphthylamine*-4-*sulphonic acid*. This can be diazotised in the usual manner and converted into *azodyes* with α-$C_{10}H_7$·OH, *R* acid, chromotropic acid, 1 : 5-OH·$C_{10}H_6$·SO_3H, Schäffer and Neville–Winther acid, SS-acid, acetyl-H-acid, phenylmethylpyrazolone, and *p*-sulphophenylmethylpyrazolone. The dyes are somewhat yellower than those derived from 1 : 4-NH_2·C_6H_4·SO_3H, are more even, and usually somewhat faster to light. Unlike the latter, they are unaffected by CrO_3, since the presence of Me prevents the formation of OH *ortho* to N_2 which is essential to after-chroming. This view is confirmed by treatment of the dye from 1 : 4-NH_2·$C_{10}H_6$·SO_3H and 1 : 5-OH·$C_{10}H_6$·SO_3H in substance with CrO_3 and reduction of the product to 1 : 2 : 4-NH_2·C_6H_5(OH)·SO_3H; the hypothesis of Rosenhauer (A., 1930, 81) is thus established. H. W.

Aromatic nitro-derivatives. XIII. Substituted α-naphthylamines. A. Mangini (Atti R. Accad. Lincei, 1937, [vi], **25**, 387—391).—Reaction products from 1 : 2 : 4-$C_{10}H_5Cl(NO_2)_2$ and amines are described, as follows: N-2 : 4-*dinitro*-1-*naphthylethyl*-, m.p. 165·5—166·5°, and -*allyl*-*amine*, m.p. 146—147°, and -*piperidine*, m.p. 135—136°; N-*m*-*hydroxyphenyl*-2′ : 4′-*dinitronaphthylamine*, m.p. 176—177°; o-, m.p. 260° (decomp.) (*Et* ester, m.p. 185—186°), and m-2′ : 4′-*dinitro*-1′-*naphthylaminobenzoic acid*, m.p. 250° (decomp.) (*Et* ester, m.p. 152·5—153·5°); N-2′ : 4′-*dinitro*-1′-*naphthylsulphanilic acid*, m.p. 190° (decomp.); p-2′ : 4′-dinitro-1′-naphthylamino-acetophenone, new m.p. 170—171° (cf. A., 1936, 75) [*p*-*nitrophenylhydrazone*, m.p. 255° (decomp.)], and -*benzophenone*, m.p. 200—201° (decomp.), and 2-2′ : 4′-*dinitro*-1′-*naphthylaminopyridine*, m.p. 189—190° (decomp.). E. W. W.

[*C*-Alkyl] aniline derivatives.—See B., 1937, 1023.

Mononitroalkylanilines, nitroalkylacylanilines, and derivatives thereof.—See B., 1937, 1023.

Arylnaphthylamines.—See B., 1937, 1023.

Amidines. II. Diamidines from di-imidochlorides derived from diamines. H. K. S. Rao and T. S. Wheeler (J.C.S., 1937, 1643—1645).—(*p*-NHBz·C_6H_4)$_2$ and PCl_5 in $PhNO_2$ give *dibenzbenzidi*-*dedi*-*imidochloride*, (*p*-CPhCl:N·C_6H_4)$_2$, m.p. 212°, which with NH_3–MeOH gives NN′-*di*-(α-*aminobenzylidene*)*benzidine*, m.p. 252°, with KCN–MeOH gives NN′-*di*-(α-*cyanobenzylidene*)*benzidine*, m.p. 252°, with the appropriate base in $NPhEt_2$ at 100° gives NN′-*di*-(α-o-*chloroanilino*-, m.p. 234° [*picrate*, m.p. 229—230° (decomp.)], -*methylanilino*-, m.p. 234° [*picrate*, m.p. 248° (decomp.)], -*ethylanilino*-, m.p. 203° [*picrate*, m.p. 235° (decomp.)], -*benzylanilino*-, m.p. 174° [*picrate*, m.p. 185° (decomp.)], -*diphenylamino*-, m.p. 262° (*picrate*, m.p. 234°), -*ethyl*-o-*toluidino*-, m.p. 200° (*picrate*, an oil), and -*ethyl*-p-*toluidino*-

benzylidene)*benzidine*, m.p. 221° (*picrate*, an oil). *p*-$C_6H_4(NH_2)_2$ gives similarly *dibenz*-p-*phenylenediamidedi*-*imidochloride*, m.p. 176°, NN′-*di*-(α-*methylanilino*-, m.p. 264° [*picrate*, m.p. 243° (decomp.)], -*benzylanilino*-, m.p. 203° [*picrate*, m.p. 220° (decomp.), -*methyl*-o-*toluidino*-, m.p. 227° [*picrate*, m.p. 236° (decomp.)], -*ethyl*-o-*toluidino*-, m.p. 186° [*picrate*, m.p. 237° (decomp.)], and NN′-*di*-(α-*cyano*-*benzylidene*)-p-*phenylenediamine*, m.p. 236°. *m*-$C_6H_4(NH_2)_2$ and PCl_5 alone, when heated, give *dibenz*-m-*phenylenediamidedi*-*imidochloride*, m.p. 86°, and thence *di*-(α-*benzylanilinobenzylidene*)-m-*phenylenediamine*, m.p. 129—130° (*picrate*, a paste). R. S. C.

Pyrolytic products of azobenzene. L. F. Boullion and A. M. Pardee (Proc. S. Dakota Acad. Sci., 1935, **15**, 27—28).—The decomp. temp. is 460°; C_6H_6, NH_2Ph, Ph_2, $NHPh_2$, anthracene, phenanthrene, HCN, NH_3, and N_2 are formed.

Ch. Abs. (*r*)

Chloroamines. I. Azobenzene-*p*-sulphonic acid and certain of its derivatives. A. Chrząszczewska and C. Dobrowolski (Rocz. Chem., 1937, **17**, 411—422).—(NPh:)$_2$ and oleum at ≯80° yield azobenzene-*p*-sulphonic acid, +3H_2O (I) (*K*, +2H_2O, and *Na* salts), differing from that described by Janovski (A., 1882, 834) in that it decomposes at 130°, in giving a cryst. chloride, m.p. 124·4—125° (lit., m.p. 82°), and in giving an amide (II), m.p. 224·8—225·5° (cf. Skandarov, J. Russ. Phys. Chem. Soc., 1870, 643). (II) and aq. NaOCl yield the *Na* salt of *azobenzene*-p-*sulphonchloroamide*, +3H_2O, whilst when AcOH is added to (II) in presence of excess of NaOCl the product is *azobenzene*-p-*sulphondichloroamide*, m.p. 111·6—112·4°. (I) is possibly a stereoisomeride of Janovski's acid. R. T.

Crystalline liquid combinations of *p*-azocinnamic esters with *p*-azophenol derivatives. Processes of association. D. Vorländer [with R. Wilke, U. Haberland, and K. Ost] (Ber., 1937, **70**, [*B*], 2096—2108).—Combinations with cinnamic esters are peculiarly adapted to the development of > two cryst. liquid phases or forms. Comparison with benzoic esters shows that this may be due to ·C:C· in conjunction with the other associates, the C_6H_6 nucleus, ·N:N·, ·CH:N·, ·CO·, etc. Derivatives of β-phenylpropionic esters are less suitable. The cryst. liquid properties are related to the complete mol. and all its parts. Polymorphous cryst. liquid phenomena can depend stepwise on definite individual parts of the mol. which with falling temp. become successively operative until the whole mol. comes into action and co-operation subsequently exists. As the temp. rises the formation of the cryst. liquid occurs with the distribution over the complete mol. of the many at. linkings in the solid crystal. With the liberation of definite individual portions of the field of union, a second cryst. liquid form can result and so forth until previously to the passage into the amorphous state the remnants of the regions of union become disrupted. According to röntgenographic observations mol. association and union does not cease with the incidence of the amorphous state. The thermostable arrangement of the active portions of the mol. in the cryst. solid as in the cryst. liquid

phase passes in the amorphous material into a condition of max. disorder, since the points of union between the mols. can vary at every temp. and time so that there are no defined transition points or places of union, and no polymorphism. The following appear new: p-p-*hydroxybenzeneazocinnamic acid*, decomp. >240° (corr.), not cryst. liquid (*Et* ester, m.p. 156—158°); p-p-*methoxybenzeneazocinnamic acid*, decomp. >255° (corr.) after softening at 250° [*Me* ester, m.p. 218—220° (corr.); *Et* ester, m.p. 142° (corr.) after softening at 115°]; p-p-*ethoxybenzeneazocinnamic acid* (*Et* ester having three cryst. liquid phases); *Et* p-*cinnamateazo*-p'-*phenyl acetate*, m.p. 137—139°, flowing at 150—152° and transparent liquid at 161° (corr.); *Et* p-*cinnamateazo*-p'-*phenyl ethyl carbonate*, m.p. 158° after softening at 116°; pp'-*diethylcarbonatoazobenzene*, m.p. 123° and 98°; *Et* p-*cinnamateazo*-p'-*phenyl benzoate*, m.p. 220° (corr.) after softening at 140°, having three enantiotropic cryst. liquid phases and two cryst. solid forms; pp'-*dibenzoyloxyazobenzene*, m.p. 268° and 216°; *Et* p-*cinnamateazo*-p'-*phenol benzenesulphonate*, m.p. 110°, and -*dimethylaniline*, m.p. 164—166°; p-*azobenzylidenedimalonic acid*; p-*azocinnamic acid*, m.p. about 290° [corresponding *chloride*, Et_2 ester, softens at 157° and becomes transparent at 280° (corr.), Pr^{α}_2 ester, m.p. 120° and 209° (corr.), and Me_2 ester, m.p. 237° and 249° (corr.)]. H. W.

Two new colour indicators from β-naphthylamine. H. Eichler (Chem.-Ztg., 1937, **61**, 797—798).—Azo-dyes formed by coupling diazotised anthranilic and sulphanilic acids, respectively, with β-$C_{10}H_7$·NH_2 may be used as acidimetric indicators. J. S. A.

Action of hydrazine and methylhydrazine on 3-chloro-4 : 6-dinitrophenetole and 1-chloro-2 : 4-dinitronaphthalene and derivatives of the resulting compounds. J. L. Robert (Rec. trav. chim., 1937, **56**, 909—918; cf. A., 1937, II, 238).—1 : 3 : 4 : 6-$C_6H_2Cl_2(NO_2)_2$ and NaOEt–EtOH at 5° and finally at 100° give 3-chloro-4 : 6-dinitrophenetole (I), m.p. 112°, converted by N_2H_4,AcOH in EtOH at 100° into 4 : 6-*dinitro*-3-*ethoxyphenylhydrazine*, m.p. 202°, which on prolonged treatment with the reagent gives small amounts of 4 : 6-*dinitro*-1 : 3-*dihydrazinobenzene*, explodes at 196°. 3-Chloro-4 : 6-dinitrophenylhydrazine and NaOEt give 5-*chloro*-6-*nitrobeziminazole*, violent decomp. 158° (*Na* salt, m.p. 323°). N'-*Acetyl*-4 : 6-*dinitro*-3-*ethoxyphenylhydrazine* is described. (I) with NHMe·NH_2 in boiling EtOH affords α-4 : 6-*dinitro*-3-*ethoxyphenyl*-α-*methylhydrazine*, m.p. 151° (block) (*Ac* derivative, m.p. 206°). 1-Chloro-2 : 4-dinitronaphthalene and N_2H_4,H_2O in EtOH give various reduction and condensation products but replacement of Cl by NH·NH_2 does not occur; under similar conditions NHMe·NH_2,AcOH affords α-2 : 4-*dinitronaphthyl*-α-*methylhydrazine*, m.p. 152° (block). 4 : 6-*Dinitro*-3-*ethoxyphenylhydrazones*, 4 : 6-*dinitro*-3-*ethoxyphenyl*-α-*methylhydrazones*, and 2 : 4-*dinitronaphthyl*-α-*methylhydrazones* of the following substances have been prepared (m.p. are recorded in this sequence): CH_2O, m.p. 143—144°, 142—143°, 100° and 130°; MeCHO, m.p. 154°, 113—116°, 127°; $COMe_2$, m.p. 143—145°, 121—124°, 183°; $COEt_2$, m.p. 107—110°, 62—64°, 88°; Me hexyl ketone, m.p. 78°, 62—64°, and 54°; $CH_2Ac{\cdot}CO_2Et$, m.p. 153—156°, 104°. —; heptaldehyde, m.p. 108—109°, 86—87°, 85°; COPhMe, m.p. 220—223°, 141°, 182°; PhCHO, m.p. 248°, 171—172°, 203°; *o*-$C_6H_4Cl{\cdot}CHO$, m.p. 242—245°, 213°, 176°; *m*-$C_6H_4Cl{\cdot}CHO$, m.p. 244—249°, 174—176°, 157°; *p*-$C_6H_4Cl{\cdot}CHO$, m.p. 277°, 218—220°, 230°; *o*-$NO_2{\cdot}C_6H_4{\cdot}CHO$, m.p. 200°, 235—237°, 178°; *m*-$NO_2{\cdot}C_6H_4{\cdot}CHO$, m.p. 287°, 236—237°, 212°; *p*-$NO_2{\cdot}C_6H_4{\cdot}CHO$, m.p. 336°, 250—255°, 269°; *o*-$OH{\cdot}C_6H_4{\cdot}CHO$, m.p. 284°, 162°, 206°; *p*-$OH{\cdot}C_6H_4{\cdot}CHO$, m.p. 263°, 239°, 209°; *p*-$OMe{\cdot}C_6H_4{\cdot}CHO$, m.p. 242°, 204—205°, 188°; *p*-$C_6H_4Me{\cdot}CHO$, m.p. 255—259°, 186°, 183°; *p*-$C_6H_4Pr^{\beta}{\cdot}CHO$, m.p. 240—242°, 164°, 141°; 4-hydroxy-3-methoxybenzaldehyde, m.p. 252—255°, 156°, 175°; 3 : 4-CH_2O_2:$C_6H_3{\cdot}CHO$, m.p. 279°, 191—192°, 185°; furfuraldehyde, m.p. 225—228°, 139°, 202°; 5-methylfurfuraldehyde, m.p. 199° and 237—239°, 173°, 167° and 175°; 5-hydroxymethylfurfuraldehyde, m.p. 177—180°, 136—137°, 122°. The colours and solubilities of the compounds are tabulated. H. W.

Mechanism of the diazoaminobenzene conversion. H. V. Kidd (J. Org. Chem., 1937, **2**, 198—208; cf. A., 1933, 1044; 1936, 465).—Diazoaminobenzene (I) with conc. HCl at <0°, followed by β-$C_{10}H_7{\cdot}OH$–NaOH, gives 1-benzeneazo-β-naphthol (II) (91% yield) and NH_2Ph (96% yield as hydrochloride). A solution of NH_2Ph (1 mol.) in aq. HCl (2 mols.) at −2° treated with $NaNO_2$ (0·5 mol.) and kept in the dark at 0° for 7 days slowly deposits aminoazobenzene (III). The amount of PhN_2Cl, determined as (II), decreases by 75% on keeping for 12 days at 0°; only 14% is converted into (III). Theories of the conversion of diazoamino-compounds are reviewed; that of unstable intermediates is less satisfactory than that of primary fission and subsequent *p*-combination. The reaction mechanism is discussed from the electronic viewpoint, with special reference to *p*-$C_6H_4Me{\cdot}NH{\cdot}N{:}NHPh$. E. W. W.

Condensation of tertiary heptyl alcohols with phenol in presence of aluminium chloride. R. C. Huston and G. W. Hedrick (J. Amer. Chem. Soc., 1937, **59**, 2001—2003; cf. A., 1936, 602).—The following are prepared from PhOH (0·3 mol.), the *tert.* alcohol quoted (0·25 mol.), and $AlCl_3$ (0·125 mol.) in light petroleum at 0—30°: γ-*p*-hydroxyphenyl-γ-methylhexane (from $CMeEtPr^{\alpha}{\cdot}OH$), b.p. 124·6°/4 mm., 278·5°/748·5 mm. (*benzoate*, m.p. 38—39°; o-*chlorobenzoate*, m.p. 25—26°; α-*naphthylcarbamate*, m.p. 82·3°); β-p-*hydroxyphenyl*-β-*methylhexane* (from $CMe_2Bu^{\alpha}{\cdot}OH$), b.p. 123·5°/4 mm., 277°/749·5 mm., m.p. 16—17° (*benzoate*, m.p. 36—37°; o-*chlorobenzoate*, b.p. 177—179°/2 mm.; α-*naphthylcarbamate*, m.p. 110—111°); β-p-*hydroxyphenyl*-βδ-*dimethylpentane* (from $CMe_2Bu^{\beta}{\cdot}OH$), b.p. 115—117°/4 mm., 273°/748·5 mm., m.p. 31—32° (*benzoate*, m.p. 71—72°; o-*chlorobenzoate*, m.p. 51—52°; α-*naphthylcarbamate*, m.p. 114—115°); γ-p-*hydroxyphenyl*-γδ-*dimethylpentane* [from $CMeEtPr^{\beta}{\cdot}OH$ (prep. from $COMePr^{\beta}$ and MgEtBr)], b.p. 125—127°/4 mm., 272°/748·5 mm., m.p. 42—43° (*benzoate*, m.p. 40—41°; o-*chlorobenzoate*, m.p. 42—43°; α-*naphthylcarbamate*,

m.p. 112—113°); β-p-*hydroxyphenyl*-β*γ*-*dimethylpentane* (from *sec.*-$BuCMe_2$·OH), b.p. 117—119°/4 mm., 281°/748·5 mm., m.p. 49—50·5° (*benzoate*, m.p. 44—45°; o-*chlorobenzoate*, b.p. 175—178°/2 mm.; α-*naphthylcarbamate*, m.p. 122—123°); *γ*-p-*hydroxyphenyl*-*γ*-*ethylpentane* (from CEt_3·OH), b.p. 120—122°/4 mm., 275°/749·5 mm., m.p. 75·5—76·5° (*benzoate*, m.p. 74—75°; o-*chlorobenzoate*, m.p. 67—68°; α-*naphthylcarbamate*, m.p. 133—135°); β-p-*hydroxyphenyl*-β*γγ*-*trimethylbutane* [from CMe_2Bu^{γ}·OH (prep. from $COMeBu^{\gamma}$ and MgMeI)], b.p. 287°/748·5 mm., m.p. 133—134° (*benzoate*, m.p. 84—84·5°; o-*chlorobenzoate*, m.p. 83—85°). The above phenols are also prepared (diazo-method) from the corresponding p-*aminophenyl* derivatives, b.p. 117—118°/5 mm., 145—146°/10 mm., 124—125°/5 mm., 146—148°/11 mm., 120—121°/5 mm., 128—131°/5 mm., and m.p. 55—56°, respectively, which are obtained by reduction of the respective p-*nitrophenyl* derivatives, b.p. 292°/741 mm., 291°/741 mm., 284°/741 mm., 285°/741 mm., 277°/741 mm., 282°/741 mm., and m.p. 108°, which are prepared by nitration of the appropriate $CPhAlk_3$ and are oxidised to *p*-NO_2·C_6H_4·CO_2H. H. B.

Copper compounds of *o*-aminophenol and its *N*-alkyl derivatives. F. Horn (J. pr. Chem., 1937, [ii], **149**, 298—300).—Fehling's solution and *o*-NH_2-phenols give, but not quantitatively, the following ppts.: from *o*-NH_2·C_6H_4·OH $C_{12}H_{12}O_2N_2Cu$, amorphous, m.p. (+H_2O) 225—230° (decomp.), (anhyd.) 220—225° (decomp.); from *o*-NHMe·C_6H_4·OH $C_{14}H_{16}O_2N_2Cu$, amorphous, +$2H_2O$ and anhyd., m.p. 160—165° (decomp.); from *o*-NMe_2·C_6H_4·OH $C_{16}H_{20}O_2N_2Cu$, m.p. 218—219° (decomp.); from *o*-NEt_2·C_6H_4·OH $C_{20}H_{28}O_2N_2Cu$, m.p. 216° (decomp.). The products are probably complex *salts*, since none are formed from the *m*- or *p*-isomerides (*p*-NH_2·C_6H_4·OH ppts. Cu_2O). They are used to separate the *o*-compounds from mixtures. *o*-*Dimethylaminophenol H oxalate* has m.p. 167—169° (decomp. 172°). R. S. C.

New aromatic fluorine derivatives. (Mme.) H. Degiorgi and E. V. Zappi (Bull. Soc. chim., 1937, [v], **4**, 1636—1642; cf. A., 1936, 1374).—5-Nitro-*m*-anisidine (improved prep.) is converted into 5-*nitroanisole*-3-*diazonium borofluoride*, m.p. 150° (decomp.), and thence into 5-*fluoro*-3-*nitroanisole* (I), which (Sn–HCl) yields 5-*fluoro*-m-*anisidine sulphate* (+$2H_2O$) [reconverted by diazotisation etc. into (I)]. Hydrolysis of (I) gives 5-*fluoro*-3-*nitrophenol* (II), m.p. 112° [methylated to (I)]. 3 : 5-Dinitrophenetole (improved prep.) is reduced (Na_2S) to 5-nitro-*m*-phenetidine, from which 5-*nitrophenetole*-3-*diazonium borofluoride*, decomp. 110°, is obtained, and thence 5-*fluoro*-3-*nitrophenetole*, m.p. 63·5—64°, hydrolysed to (II). 3 : 5 : 1-$(NO_2)_2C_6H_3$·NH_2, from the azide (cf. A., 1934, 1343), is converted into 3 : 5-*dinitrobenzene*-1-*diazonium borofluoride*, decomp. 203°, and into 5-*fluoro*-m-*dinitrobenzene*, m.p. 43°, reduced (NH_4SH) to 5-*fluoro*-m-*nitroaniline*, m.p. 115—116° (converted into *m*-C_6H_4F·NO_2). E. W. W.

Compounds of phenyl *p*-nitrophenyl sulphide and ether with sulphuric acid. Example of thioquinonoid formation. H. H. Hodgson and R. Smith (J.C.S., 1937, 1634—1637).—F.p. measurements show the existence of 2 : 1 and 1 : 1 *compounds*, f.p. 51·7° and 50·3°, respectively, of *p*-NO_2·C_6H_4·SPh (I) and H_2SO_4 and of a 1 : 1 *compound*, m.p. 51·8°, of *p*-NO_2·C_6H_4·OPh (II) and H_2SO_4. Quinonoid structures, involving O^{IV} and S^{IV}, are postulated for these compounds; the formation by (I) of the acid salt shows it to be more strongly basic than (II). The compounds decompose when heated for some time. Some double mols. are formed in solution in the org. ingredient, but not in H_2SO_4. R. S. C.

Œstrogenic substance from the demethylation of anethole. A. Serini and K. Steinruck (Naturwiss., 1937, **25**, 682—683).—Demethylation of anethole by MgEtI yields, in addition to hydroxypropenylbenzene, a substance (I) (*Ac*$_2$ derivative, $C_{26}H_{34}O_4$, m.p. 186°); demethylation by $MgPr^{\alpha}I$ yields the homologue (*Ac*$_2$ derivative, $C_{28}H_{38}O_4$, m.p. 175°) of (I). Both Ac_2 derivatives are active (Allen–Doisy rat-unit 5—10 μg.); they are probably [*p*-OAc·C_6H_4·CH(CHMeR)·]$_2$ (R = Et or Pr^{α}) (cf. Dodds and Lawson, A., 1937, II, 229, 361). F. O. H.

New form of resorcinol.—See A., I, 502.

Phase diagrams of binary systems of guaiacol and amines and of benzylamine with phenols. N. A. Pushin and I. I. Rikovski (Annalen, 1937, **532**, 294—299).—Guaiacol exists in an α-modification stable between 30° and −3·5° and a β-*form* stable below −3·5°. In the cryst. condition it does not form definite compounds or solid solutions with C_6H_6 or $NPhMe_2$ although it gives an equimol. compound with NH_2Ph. It forms *compounds* with quinoline (1 : 1), m.p. 12°, NHPh·NH_2 (1 : 2), m.p. 16°, and piperidine (2 : 1), m.p. 76°. Thermal analysis shows that NH_2·CH_2Ph gives *compounds* with PhOH (1 : 1), m.p. 22·0°, and (1 : 3), m.p. 15·3°, *o*-cresol (1 : 1), m.p. 7·5°, *m*-cresol (1 : 1), m.p. 36·4°, *p*-cresol (1 : 1), m.p. −6°, and (1 : 3), m.p. 20°, *o*-C_6H_4Cl·OH (1 : 1), m.p. 47·5°, and (1 : 3), m.p. 55°, *p*-C_6H_4Cl·OH (1 : 1), m.p. 16°, and (1 : 3), m.p. 55°, and guaiacol (1 : 1), m.p. 15·5°, and (1 : 3), m.p. 32°. H. W.

Synthesis of 3-iodoveratrole. F. Mauthner (J. pr. Chem., 1937, [ii], **149**, 328—329).—Veratrole-3-carboxylic acid gives successively the *chloride* (by PCl_5) and *amide*, m.p. 93—94°, 3-*amino*- (by NaOCl), b.p. 136—138°/15 mm., and 3-*iodo*-*veratrole*, m.p. 45—46°, b.p. 144—145°/14 mm. R. S. C.

Trinitrophloroglucinol. F. Šorm and Z. Dra-palová (Chem. Obzor, 1937, **12**, 153—156).—By boiling 1 : 3 : 5-trichloro-2 : 4 : 6-trinitrobenzene (I) with a dil. (3%) aq. EtOH solution of excess of alkali hydroxide, a 55% yield of the normal alkali salt of trinitrophloroglucinol (II) was obtained. (I) was converted by a boiling aq. EtOH solution of NH_3 into 1 : 3 : 5-trinitro-2 : 4 : 6-triaminobenzene, converted by boiling with aq. NaOH into the normal Na salt of (II) in 70% yield. The preps. of the normal K, NH_4, Li, Ba, Sr, Ca, Cd, Pb, and Ag salts of (II) are described. F. R.

Esterification of alcohols. W. Hückel, F. Nerdel, and F. Reimer (J. pr. Chem., 1937, [ii], **149**, 311—316).—By partial reaction with $COCl_2$–

C_5H_5N–Et_2O *trans*-decahydro-β-naphthol, m.p. 53° (*carbonates*, m.p. 99° and 92°), is freed from its more reactive isomeride, m.p. 75° (*carbonates*, m.p. 119° and 78—79°). *trans*-2-Hydrindanol is shown to be a racemate by formation of *carbonates*, m.p. 73—74° and 52—56°. *p*-Nitrobenzoates are not readily obtained from *tert.* alcohols, except from alcohols, $CRMe_2$·OH. The following p-*nitrobenzoates* are described: Bu$^{\gamma}$, m.p. 115—117°, *cyclo*hexyldimethylcarbinyl, m.p. 101—103°, and 1-propyl-1-*cyclo*hexyl (poor yield), m.p. 46—48°. Camphene hydrate, 1-*iso*propyl*cyclo*hexan-1-ol, and trans-2-*methyldecahydro*-2-*naphthol*, m.p. 92—93° (p-*nitrobenzoate*, m.p. 112—114°, prepared by K in PhMe), do not react with *p*-NO_2·C_6H_4·COCl in C_5H_5N. R. S. C.

Preparation of *p*-phenyltriphenylcarbinol and existence of a metastable form. D. B. Clapp and A. A. Morton (J. Amer. Chem. Soc., 1937, **59**, 2074—2075).—*p*-C_6H_4PhCl (0·8 mol.), $COPh_2$ (0·8 mol.), and Na powder (0·2 mol.) in C_6H_6 give 67% of *p*-phenyltriphenylcarbinol, m.p. (stable) 135—136°; the first prep. gave a metastable form, m.p. 112—113°. H. B.

Preparation and pyrolysis of triphenylmethyl ethers of complex function. C. D. Hurd and E. M. Filachione (J. Amer. Chem. Soc., 1937, **59**, 1949—1952).—*Et* α-*triphenylmethoxypropionate*, m.p. 79—80°, decomposes in the anticipated manner at 300° (bath) in N_2, forming $AcCO_2Et$ (71%) and $CHPh_3$ (74%). CPh_3·O·CH_2·CH_2·OH, m.p. 102—103° (lit. 98—100°), undergoes disproportionation at 140—145°/6 mm. or atm. pressure to $(CH_2$·$OH)_2$ and $(CH_2$·O·$CPh_3)_2$ (I), and is formed when (I) is heated with an excess of $(CH_2$·$OH)_2$. Decomp. of (I) at 340—350° (bath) gives $CHPh_3$ (61%), $COPh_2$, CH_2O, and CO; $(CHO)_2$ or CPh_3·O·CH_2·CHO may have been formed and undergone further decomp. α-*Triphenylmethoxy*-β-*ethoxyethane*, m.p. 77—78°, at 325—330° (bath) affords $CHPh_3$, $COPh_2$, MeCHO, OEt·CH_2·CH_2·OH, and $(CH_2$·$OEt)_2$. αβ-*Ethylideneglycerol* CPh_3 *ether* has m.p. 105—106°. The above CPh_3 ethers are prepared from the OH-compounds and CPh_3Cl in C_5H_5N. H. B.

Action of magnesium phenyl bromide on chloroacetyl chloride and related compounds. J. S. W. Boyle, A. McKenzie, and W. Mitchell (Ber., 1937, **70**, [*B*], 2153—2160).—Addition of CHPhCl·COCl to MgPhBr in Et_2O gives αα*ββ-tetraphenylethanol*, m.p. 232·5—233° [identical with the product obtained from MgPhBr and phenyldeoxybenzoin (I)], and resin, whereas (I) results when the order of admixture of the reactants is reversed. CH_2Cl·COCl and MgPhBr give αββ-triphenylethanol, m.p. 87·5—88·5°, and *as*-diphenylchlorohydrin, m.p. 66°. αα*β*-Triphenylethylene glycol, m.p. 163°, is derived from $CHCl_2$·CO_2H and MgPhBr. *r-γγγ*-Trichloro-β-hydroxybutyric acid or its Et ester and MgPhBr afford r-α*γ-dihydroxy*-αα*-diphenyl*-*γ-trichloromethylpropane*, m.p. 178·5°, converted by boiling 2N-NaOH into α*γ-dihydroxy*-*γγ-diphenyl*-n-*butyrolactone*, m.p. 110°. *Me* (—)-*γγγ-trichloro*-β-*hydroxybutyrate*, m.p. 62·5—63°, $[\alpha]_D$ —33° in EtOH, or the corresponding acid do not give cryst. compounds with MgPhBr. Definite compounds could not be obtained from MgPhBr and dimethylmalic ester. H. W.

Derivatives of *cyclo*-pentane- and -hexane-1 : 2-diols. M. Mousseron and R. Granger (Compt. rend., 1937, **205**, 327—329).—Addition of Cl_2 and Br to *cyclo*hexene affords only trans-1 : 2-*dichloro*- (I), b.p. 75°/15 mm. and -1 : 2-dibromo-*cyclo*hexane, respectively, identical with the products obtained by interaction of 2-chloro- (II) and 2-bromo-*cyclo*hexanol (III) with PCl_5 and PBr_3. 1-Methyl-Δ^3-*cyclo*hexene having $[\alpha]_D$ +110° affords with Br two isomeric *forms*, b.p. 105°/15 mm. and 108°/15 mm., of 3 : 4-dibromo-1-methyl*cyclo*hexane. (II) with PBr_5 or (III) with PCl_5 affords 1-*chloro*-2-*bromo*-cyclo*hexane*, b.p. 94°/17 mm. *trans*-(II) when heated with HCl affords some of the *cis*-isomeride. Prolonged interaction of (II) with a hot solution of NaOAlk affords 2-alkyloxy*cyclo*hexanol. The following are similarly prepared (b.p. at 760 mm.): 2-*methoxy*-, b.p. 175°, and 2-*ethoxy*-cyclo*pentanol*, b.p. 182°; 2-*propoxy*-, b.p. 205°, 2-cyclo*hexoxy*-, m.p. 50°, 2-*methoxy*-1-*methyl*-, b.p. 181°, and -1-*ethyl*-cyclo*hexanol*, b.p. 186°. 1 : 2-Dibromocyclanes when heated with conc. EtOH–KOH or NaOAlk afford the corresponding 1 : 2-di-ethers. The following are prepared (b.p. at 760 mm.): 1 : 2-*dimethoxy*-, b.p. 108°, and 1 : 2-*diethoxy*-cyclo*pentane*, b.p. 126°; 1 : 2-*diethoxy*-, b.p. 151°, 1 : 2-*dipropoxy*-, b.p. 159°, 1 : 2-*diisopropoxy*-, b.p. 160°, 1 : 2-*dibutoxy*-, b.p. 192°, and 1 : 2-*di*cyclo*hexoxy*-cyclo*hexane*, b.p. 120°/15 mm. The above mono- and di-ethers of *cyclo*hexanediol with PBr_5 afford 1 : 2-dibromo*cyclo*hexane. Oxidation (CrO_3) of 2-alkyloxy-*cyclo*pentanol and -*cyclo*hexanol affords 2-alkoxy-*cyclo*pentanone and -*cyclo*hexanone, respectively. The following are prepared (b.p. at 750 mm.): 2-*methoxy*-, b.p. 179°, and 2-*ethoxy*-cyclo*pentanone*, b.p. 186°, and 2-*propoxy*cyclo*hexanone*, b.p. 209°.

J. L. D.

Derivatives of phenyl- and *s*-diphenyl-ethylene glycol. L. Palfray and R. Pannelier (Bull. Soc. chim., 1937, [v], **4**, 1913—1916).—Phenylethylene glycol (*bisphenylurethane*, m.p. 148°) with allophanyl chloride in C_6H_6 yields a *mono*-, m.p. 168°, and *di-allophanate*, m.p. 240—241°; hydrobenzoin similarly yields a *di-allophanate*, m.p. 280°, but does not react with PhNCO. J. D. R.

Manufacture of diamino-alcohols of the aromatic series.—See B., 1937, 1024.

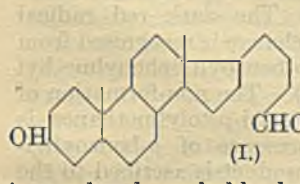
Sterols. XIX. *epi*Ergosterol and *epi*-α-ergostenol. R. E. Marker, O. Kamm, J. F. Laucius, and T. S. Oakwood (J. Amer. Chem. Soc., 1937, **59**, 1840—1841).—Ergostatrienone (Oppenauer, A., 1937, II, 250) is reduced [$Al(OPr^{\beta})_3$ in $Pr^{\beta}OH$ followed by MeOH–KOH] to ergosterol and epi*ergosterol* (I), m.p. 152°, $[\alpha]_D^{25}$ +50° in $CHCl_3$ (*acetate*, m.p. 126°). (I), which is not pptd. by digitonin, and is not identical with lumisterol. α-Ergostenone [from α-ergostenol (II) and Cu powder at 250°/4 mm.] is similarly reduced to (II) and epi-α-*ergostenol*, m.p. 188·5°, $[\alpha]_D^{25}$ +5·3° in $CHCl_3$ (*acetate*, m.p. 119·5°). H. B.

Fission of sterol digitonides and other molecular compounds by distillation in high vacuum.

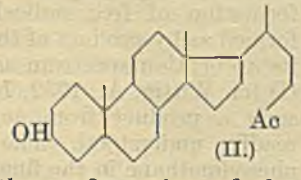
A. VON CHRISTIANI and M. PAILER (Mikrochim. Acta, 1937, **1**, 26—29).—Cholesterol, coprosterol, etc. from the digitonides, and $C_{10}H_8$, indene, etc. from the picrates, may be recovered in pure form in 70—90% yield by heating the mol. compounds at 100—250° in a high vac. J. S. A.

Polyterpenes and polyterpenoids. CXVII. Conditions and mechanism of the dehydrogenation of homologous sterols and of cholic acid. L. RUZICKA and M. W. GOLDBERG (Helv. Chim. Acta, 1937, **20**, 1245—1253).—If possible, the temp. of dehydrogenation of cholesterol (I) or cholic acid (II) should be $>350°$ if the formation of chrysene is to be avoided and the primary products are to be isolated (cf. Diels *et. al.*, A., 1927, 241, 1930, 470; Ruzicka *et al.*, A., 1933, 820). Further examination shows that the main product of the dehydrogenation of ergosterol (III) with Se according to the older or newer conditions of Diels (A., 1930, 470; 1937, II, 95) is the hydrocarbon $C_{26}H_{26(24)}$, fractionation of which appears impossible by methods dependent on solubility or volatility. Re-examination confirms the homogeneity of the hydrocarbon, m.p. 205—206°, obtained by dehydrogenation of phytosterol (IV); analyses thereof and of the ketone, m.p. 204—204·5°, derived therefrom favour the respective formulæ $C_{27}H_{26}$ and $C_{27}H_{24}O$. At a temp. $\geqslant 350°$, therefore, dehydrogenation of (II) C_{24}, (I) C_{27}, (III) C_{28}, and (IV) C_{29} occurs with loss of 2 C and formation of a fifth ring from the long side-chain. These hydrocarbons probably represent a homologous series and have almost identical absorption spectra. Since the product $C_{22}H_{16}$ from (II) is methylnaphthofluorene it is probable that this or a very similar ring system is present in the other hydrocarbons. The distribution of the side-chains is unknown but must be such that a place is available in the aromatic ring system for the Me and Et group of the more complex sterols. H. W.

Sex hormones. XXV. Oxidation of saturated sterol derivatives with chromium trioxide. L. RUZICKA, M. OBERLIN, H. WIRZ, and J. MEYER (Helv. Chim. Acta, 1937, **20**, 1283—1290).—The mother-liquors obtained after removal of androsterone acetate semicarbazone from the products of the oxidation of *epi*cholestanyl acetate by CrO_3 in AcOH at about 90° (A., 1934, 1221) yield the *semicarbazone*, m.p. 224·5—225·5°, of 3-*epi*acetoxy*allo*cholanaldehyde (I); the structure of the compound



(I.)



(II.)

is rendered probable by the co-formation of the corresponding acid in considerable amount. In addition, the *semicarbazone*, m.p. 221—223°, of *epi*norcholestan-3-ol-25-one (II) is obtained, produced in much larger proportion when the oxidation is effected at 25—30°. (II) has m.p. 181—182·5° (corr.), and yields an *acetate* (III), m.p. 111° (corr.). Oxidation of (II) with CrO_3 in AcOH affords the *diketone*, $C_{26}H_{42}O_2$, m.p. 139·5—140·5° (corr.). Condensation of (III) with a large excess of MgMeI followed by hydrolysis affords 25-*hydroxycholestanol*, m.p. 191—193° (corr.), transformed by Ac_2O in C_5H_5N into the *monoacetate*, m.p. 154° (corr.). (III) with PhCHO and HCl in AcOH gives the noncryst. :*CHPh* derivative, which is oxidised by CrO_3 in AcOH and then hydrolysed to 3-*epi*hydroxy*allo*cholanic acid, m.p. 218—220° (corr.) [Me ester, m.p. 166—168° (corr.)]. H. W.

Vitamin-D_4.—See A., III, 327.

Phytosterol, $C_{28}H_{47}\cdot OH$, and ketone, $C_{31}H_{52}O$, from *Citrus grandis*.—See A., III, 244.

Cumotocopherol, $C_{28}H_{48}O_2$, and its allophanate, m.p. 146°, $[\alpha]_D^{18}$ +6·7° in $CHCl_3$.—See A., III, 497.

Pregnane-3 : 17 : 20-triol, m.p. 243—244°, and its diacetate, m.p. 136·5°.—See A., III, 361.

Absorption spectra of compounds related to sterols.—See A., II, 494.

Tertiary alcohols of the *cyclo*pentanopolyhydrophenanthrene series.—See B., 1937, 1135.

Synthesis of 9 : 10-dihydroxy-5-phenyl-9 : 10-dialkyl-9 : 10-dihydro-1 : 2-benzanthracenes and related compounds. W. E. BACHMANN and J. T. BRADBURY (J. Org. Chem., 1937, **2**, 175—182).—1 : 2-Benzanthraquinone and MgMeI or MgEtBr give 9 : 10-*dihydroxy*-9 : 10-*dimethyl*-, m.p. 181·5—182·5°, and -9 : 10-*diethyl*-9 : 10-*dihydro*-1 : 2-*benzanthracene*, m.p. 145—145·5°. The Et_2, but not the Me_2, compound has œstrogenic activity. With MgPr^{a}Br, a *substance*, $C_{21}H_{18}O_2$, m.p. 91—94°, is obtained. 5-Keto-5 : 6 : 7 : 8-tetrahydro-1 : 2-benzanthracene [from β-(3-phenanthroyl)propionic acid, obtained by the Friedel–Crafts reaction from phenanthrene and succinic anhydride, together with β-(2-phenanthroyl)-propionic acid, new m.p. 207—208°; cf. A., 1933, 1043] and MgPhBr give 5-*hydroxy*-5-*phenyl*-5 : 6 : 7 : 8-*tetrahydro*-1 : 2-*benzanthracene*, m.p. 157—159°, dehydrated ($KHSO_4$) to 5-*phenyl*-7 : 8-*dihydro*-1 : 2-*benzanthracene*, m.p. 125—126°, dehydrogenated (S; Cu) to 5-*phenyl*-1 : 2-*benzanthracene*, m.p. 151—152° (*picrate*, m.p. 165—166°). This is oxidised ($Na_2Cr_2O_7$–AcOH) to 5-*phenyl*-1 : 2-*benzanthraquinone*, m.p. 189—189·5°, from which MgMeI, MgEtBr, and MgPr^{a}Br give respectively 9 : 10-*dihydroxy*-5-*phenyl*-9 : 10-*dimethyl*-, m.p. 160—164° (cis + trans?) recryst. to a product, m.p. 130°, resolidifying to remelt at 215—216°, -9 : 10-*diethyl*- (I), m.p. 147·5—148°, and -9 : 10-*di*-n-*propyl*-9 : 10-*dihydro*-1 : 2-*benzanthracene* (II), m.p. 191·5—192·5°. Both (I) and (II) are œstrogenic. MgPhBr gives a mixture containing small quantities of the 9 : 10-*diphenyl* compound (?), m.p. 240° (decomp.), with Ph_2. E. W. W.

Constitution of natural phenolic resins. IX. Structure of lariciresinol. Preliminary experiments on the synthesis of lignandiols. R. D. HAWORTH and W. KELLY (J.C.S., 1937, 1645—1649).—Structures assigned (A., 1937, II, 202) to lariciresinol (I) and *iso*lariciresinol (II) are confirmed. Lignan is adopted as a generic name for substances of bisconiferyl structure. Unsuccessful attempts to

synthesise lignandiols and successful syntheses of aryltetronic acids are described. Anhydro*iso*lariciresinol Me_2 ether is unaffected under conditions causing the change of (I) into (II); with $Pb(OAc)_4$ at 70—80° it gives *dehydroanhydroisolariciresinol Me_2 ether*, m.p. 201—202°. The Me_2 ether of (I) gives *lariciresinol CPh_3 ether Me_2 ether*, m.p. 134°, converted by 80% HCO_2H into the (*HCO*)$_2$ derivative, m.p. 102—103°, of *iso*lariciresinol Me_2 ether. $CH_2Bz{\cdot}CHBz{\cdot}CO_2Et$ and $(CHBz{\cdot}CO_2Et)_2$ do not condense with CH_2O, HCO_2Et, or $Et_2C_2O_4$; the former ester with alkali gives $CH{<}^{CPh{\cdot}O}_{CBz{-}CO}$; the latter ester with CH_2O and alkali gives BzOH, and with conc. H_2SO_4 gives Et_2 2 : 5-diphenylfuran-3 : 4-dicarboxylate, which resists reduction. *Et* αβ-*diveratroylpropionate* [from ω-bromoacetoveratrone and $(OMe)_2C_6H_3{\cdot}CO{\cdot}CHNa{\cdot}CO_2Et$], m.p. 110—111°, with 10% KOH–MeOH gives the *lactone*, m.p. 155—156°, of *γ-hydroxy-α-veratroyl-γ-3 : 4-dimethoxyphenyl-Δ$^{\beta}$-butenoic acid* (*K* salt), or, when 0·1N-NaOH is dropped into its boiling solution in aq. MeOH, affords αβ-*diveratroylethane*, m.p. 180—181°, converted by HCl–MeOH into 2 : 5-*di*-3′ : 4′-*dimethoxyphenylfuran*, m.p. 154—155° (no $FeCl_3$ colour), insol. in NaOH. $Et_2C_2O_4$ and acetoveratrone (III) give *Et veratroylpyruvate*, m.p. 104—105° [corresponding *acid*, m.p. 192—193° (decomp.)], which does not react with $CH_2(CO_2Et)_2$, $CH_2Ac{\cdot}CO_2Et$, or $CN{\cdot}CH_2{\cdot}CO_2Et$; (III), veratroylacetonitrile, and $CH_2Ac{\cdot}CO{\cdot}CO_2Et$ are similarly unreactive. α-Veratroyl-β-3 : 4-dimethoxybenzylbutyrolactone with CH_2O in cold 2% NaOH gives veratric acid and an oil, but with hot 2% NaOH yields *γ-veratroyl-γ-3 : 4-dimethoxyphenylisobutyl alcohol* (IV), m.p. 98—99°, which with HCl–AcOH (not –MeOH) affords 6 : 7-*dimethoxy*-4-3′ : 4′-*dimethoxyphenyl*-2-*chloromethyl*-1 : 2-*dihydronaphthalene*, m.p. 108—109°, converted by hot 5% KOH–MeOH into (?) 6 : 7-*dimethoxy*-1-3′ : 4′-*dimethoxyphenyl*-3-*methylnaphthalene*, m.p. 140°, sublimes at 200—220°(bath)/0·1 mm. CH_2O reacts with (IV) in presence of alkali, but gives indefinite products. The (CH_2O_2)-*analogue*, m.p. 103—104° (*oxime*, m.p. 139—140°), of (IV) is prepared. β-*Keto-α-cyano-γ*-p-*nitrophenoxypropylbenzene*, m.p. 156—157°, is obtained only in poor yield from $CH_2Ph{\cdot}CN$ and $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO_2Et$. β-*Keto-α-cyano-γ-benzyloxypropylbenzene* (obtained readily from $CH_2Ph{\cdot}CN$ and $CH_2Bz{\cdot}CO_2Me$), m.p. 72—73°, with HCl–MeOH gives phenyltetronic acid, converted by H_2O at 200° in poor yield into $CH_2Ph{\cdot}CO{\cdot}CH_2{\cdot}OH$. 4-β-*Keto-α-cyano-γ-benzyloxypropyl*-3 : 4-*dimethoxy*-, m.p. 78—79°, and -3 : 4-*methylenedioxy-benzene*, m.p. 72—73°, and 3 : 4-*dimethoxy*-, m.p. 211—213°, and *-methylenedioxy-phenyltetronic acid*, m.p. 268° (decomp.), are similarly prepared. R. S. C.

Direct synthesis of dihydro*iso*lauronolic and *iso*lauronolic acids. P. C. Guha and K. S. Subrahmaniyan (Current Sci., 1937, **6**, 94—95).—$CMe_2Ac{\cdot}CO_2Et$ with $CO_2Et{\cdot}CHBr{\cdot}CH_2{\cdot}CO_2Et$ and Zn gives *Et* β-*hydroxy*-β′-*carbethoxy*-αα*β-trimethyladipate* (*acid*, m.p. 165—166°) and *Et γ-carbethoxy*-αα*β-trimethyl*-Δ$^{\beta}$-*butene*-α*δ-dicarboxylate*, b.p. 155—162°/5 mm. (*acid*, m.p. 239—240°; *trianilide*, m.p. 235°; *anilide anil*, m.p. 212°), which with Na yields enolic *Et* 1 : 1 : 2-*trimethyl*-Δ^2-cyclo*penten*-5-*one*-3 : 4-*dicarboxylate*, b.p. 125—128°/3 mm., hydrolysed to the -3-*carboxylic acid*, m.p. 186—187° (*oxime*, m.p. 139—140°; *semicarbazone*, m.p. 225°), which on Clemmensen reduction gives dihydro*iso*lauronolic acid. F. R. G.

Reformatsky reaction with benzamide. A. Banchetti (Atti R. Accad. Lincei, 1937, [vi], **25**, 485—488).—NH_2Bz, Zn, and $CH_2Br{\cdot}CO_2Et$ give a product which after treatment with H_2SO_4 gives BzOH and resins, but no $CH_2Bz{\cdot}CO_2Et$, $NHBz{\cdot}CH_2{\cdot}CO_2Et$, or $(CH_2{\cdot}CO_2Et)_2$. If the product is not acidified, but extracted with (damp) Et_2O, a *substance* $(NH_2Bz)_2,ZnBr_2$ (I), m.p. 157—158°, is obtained. It is suggested that a compound $BrZn{\cdot}NH_2Bz{\cdot}CH_2{\cdot}CO_2Et$ is formed, and converted by H_2O into (I), ZnO, and EtOAc. E. W. W.

Preparation of 2 : 4-dinitro-benzonitrile and -benzoic acid. F. R. Storrie (J.C.S., 1937, 1746).—Prep. of these substances is improved [85% and 95% yield, respectively, from $(NO_2)_2C_6H_3{\cdot}NH_2$]. R. S. C.

Thermal decomposition of dibenzoyl peroxide in presence of deuterium. H. Erlenmeyer and W. Schoenauer (Helv. Chim. Acta, 1937, **20**, 1015—1016).—The reaction gives Ph_2 free from D, indicating the improbability of the intermediate production of free radicals. H. W.

[Attempted] synthesis of acyloins. K. Bernhauer and R. Hoffmann (J. pr. Chem., 1937, [ii], **149**, 317—320).—Unsaturated esters do not give acyloins with Na in xylene etc. $CHMe{:}CH{\cdot}CO_2Et$ is mainly resinified. Et α-*cyclo*geranate gives a poor yield of a *substance*, m.p. 112—113°. $CHPh{:}CH{\cdot}CO_2R$ (R = Me, Et, Bu, or CH_2Ph) gives a *ketone*, $C_{16}H_{16}O$, m.p. 176° (p-*nitrophenylhydrazone*, m.p. 222°; *semicarbazone*, m.p. 164—165°; oxidised to BzOH; reduced by Zn-HCl to a *substance*, $C_{16}H_{18}$, m.p. 64—65°), and a small amount of a *ketone*, m.p. 108—110°. R. S. C.

Occurrence of free radicals in chemical reactions. IX. A. Thermal decomposition of acylazotriphenylmethanes. B. Mode of reaction of diacyl peroxides. H. Wieland, T. Ploetz, and H. Indest (Annalen, 1937, **532**, 166—190; cf. A., 1934, 1215; 1935, 77).—A. Thermal decomp. of acylazotriphenylmethanes occurs mainly, $R{\cdot}CO{\cdot}N_2{\cdot}CPh_3 \rightarrow R{\cdot}CO{\cdot}CPh_3 + N_2$, and is independent of the formation of free radicals. The dark red radical formed as by-product of the change is recognised from its absorption spectrum as *p*-benzoyltriphenylmethyl (I) (cf. Wittig, A., 1932, 746). The non-formation of such a product from acylazotri-*p*-tolylmethanes is readily understood. The presence of *p*-benzoyltriphenylmethane in the final product is ascribed to the hydrogenation of (I) by some unknown agent. The radical is the primary product, but this does not arise immediately from the N_2 compound since, under favourable circumstances, evolution of N_2 ceases before the red colour commences to develop. The red radical is decolorised by the N_2 compound in the act of its decomp.—not by the substance itself—since it also disappears when the N_2 compound is

decomposed by heat in its solution. The exact agent has not been identified, but it cannot be CPh_3. The radical not only appears in the free state after complete decomp. of the N_2 compound, but is present in latent form in the reaction solution, but not as dimeric ethane. If the radical is removed by O_2 the solution remains pale; addition of CPh_3 causes rapid liberation of the free radical and CPh_3 is simultaneously utilised. The form of union of the acyltriphenylmethyl is not obvious. It is also liberated by NH_2Ph, NH_3, and other bases, and considerable possibility of a nitrogenous intermediate exists. This is supported by the observation that evolution of N is never quant. and part remains as a substituted hydrazine. The change can therefore be: $R{\cdot}CO{\cdot}N_2{\cdot}CPh_3 \rightarrow R{\cdot}CO{\cdot}N{:}N{\cdot} + CPh_3$. Explosive decomp. of acylazo-compounds (without solvent) is accompanied by production of small amounts of the aldehyde corresponding with the acyl residue; this is never formed during the regulated decomp. *Triphenylmethylpyridine*, m.p. 264—267° (*hydrochloride*), *benzoylazotri-p-tolylmethane*, *formylazotriphenylmethane*, m.p. 156—157°, *benzoylazo-p-benzoyltriphenylmethane*, *benzoyl-p-benzoyltriphenylmethane*, m.p. 142°, and the *compound*, $C_{30}H_{30}O_2$, m.p. 212°, are incidentally described.

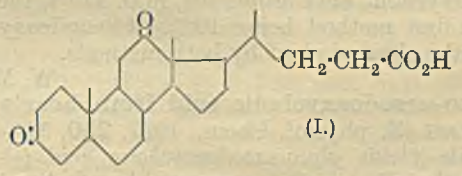
B. The decomp. of further diacyl peroxides is investigated. *Bz α-naphthoyl peroxide*, m.p. 67°, from α-$C_{10}H_7{\cdot}COCl$ and NaO_2Bz in aq. $COMe_2$ at 0°, when heated in admixture with sand, gives some CO_2 and BzOH. The neutral product is hydrolysed to BzOH, α-$C_{10}H_7{\cdot}COCl$, some PhOH and higher phenols, naphtholcarboxylic acids, and more complex acids which give sparingly sol. Na salts. *Bz phenylacetyl peroxide*, m.p. 35·5° (decomp.), decomposes very readily and almost quantitatively into CO_2 and $CH_2Ph{\cdot}OBz$, whereas with $BzO_2{\cdot}CO{\cdot}CH_2{\cdot}CH_2Ph$ change occurs only at 80° and is accompanied by side reactions. This influence of Ph renders understandable the failure to prepare $(CHPh_2{\cdot}CO)_2O_2$, $BzO_2{\cdot}CHPh_2$, or $(CPh_3{\cdot}CO)_2O_2$. Thermal decomp. of Bz_2O_2 in $CHPh_3$ at 100° gives $CPh_3{\cdot}OBz$, BzOH, C_6H_6, and sometimes p-$C_6H_4Ph{\cdot}CO_2H$, the changes being explained, $Bz_2O_2 + CHPh_3 \rightarrow BzOH + CPh_3{\cdot}OBz$ and $Bz_2O_2 + CHPh_3 \rightarrow CPh_3{\cdot}OBz + CO_2 + C_6H_6$. Bz_2O_2 and CPh_3, whether obtained in the usual manner or from specially purified CPh_3Cl and Hg, give much lower yields of CPh_4 than those claimed by Medvedev and Alexeeva (A., 1932, 379). The main products are $CPh_3{\cdot}OBz$ and BzOH; $COPh_2$ does not appear. CPh_4 is accompanied by an inseparable mixture of hydrocarbons. The possibility that the fourth Ph is yielded by Bz_2O_2 is rendered improbable by the small amount of CO_2 evolved and is excluded by the observation that CPh_4 also results when $(p\text{-}C_6H_4Ph)_2O_2$ is used. It therefore arises from C_6H_6 probably according to $Bz_2O_2 + CPh_3 \rightarrow CPh_3{\cdot}OBz + PhCO_2$; $PhCO_2 + C_6H_6 \rightarrow BzOH + Ph$; $Ph + CPh_3 \rightarrow CPh_4$. Et_2O does not appear to react with CPh_3. H. W.

Iodonitrotyrosine. R. Zeynek (Biochem. Z., 1937, **293**, 432—434).—3-Nitrotyrosine when treated with HIO_3 and HI gives an *iodonitrotyrosine*, m.p. 220° (decomp.), α_D +10—11° in 4% HCl, in which the I is *ortho* to the OH. P. W. C.

New synthesis of caronic acid. R. Ghosh (J. Indian Chem. Soc., 1937, **14**, 449—451).—$CHNa(CO_2Et)_2$ and $CMe_2Br{\cdot}CHBr{\cdot}CO_2Et$ give *Et*$_3$ 2 : 2-*dimethylcyclopropane*-1 : 1 : 3-*tricarboxylate*, b.p. 153°/9 mm., converted by KOH–EtOH into *cis*- with a small amount of *trans*-caronic acid, and by HCl into terebic acid. E. W. W.

Unexpected complication in the replacement of a diazo-group. V. M. Rodionov and A. M. Fedorova (Bull. Soc. chim., 1937, [v], **4**, 1703—1707).—The *diazonium sulphate* from 3-aminophthalic acid gives with MeOH at 40—50°, not 3-methoxyphthalic acid, but m-$OMe{\cdot}C_6H_4{\cdot}CO_2H$. *o-Carboxybenzenediazonium sulphate* [obtained using *n*-$C_5H_{11}{\cdot}O{\cdot}NO$] with MeOH gives o-$OMe{\cdot}C_6H_4{\cdot}CO_2Me$ (and some BzOH and salicylic acid). *6-Carboxy-2 : 3-methoxybenzenediazonium chloride* and *2-carboxy-3 : 4-dimethoxybenzenediazonium sulphate* both yield 1 : 2 : 3-$C_6H_3(OMe)_3$, accompanied respectively by *m*- and *o*-veratric acid. E. W. W.

Δ^4-3 : 12-Diketocholenic acid and its attempted transformation into 3 : 12-diketo*allo*-cholanic acid. J. Sawlewicz and T. Reichstein (Helv. Chim. Acta, 1937, **20**, 992—998).—*4-Bromo-3 : 12-diketocholanic acid* is converted by boiling C_5H_5N into Δ^4-3 : 12-*diketocholenic acid* (I), m.p. 199—201°, also obtained with acetoxy-3 : 12-diketocholanic acid by means of KOAc. (I) and CH_2N_2 afford *Me*



(I.)

Δ^4-3 : 12-*diketocholenate* (II), m.p. 154—155°. Hydrogenation (Raney Ni in MeOH) of (II) gives a product separated by digitonin into (after hydrolysis) α-3-hydroxy-12-ketocholanic acid (oxidised deoxybilianic acid) and Me β-3-hydroxy-12-ketocholanate, m.p. 126—128° (corr.); the corresponding acid, m.p. 224—225° (corr.), is oxidised to dehydrodeoxycholic acid. Hydrogenation of (II) with Pd and Pt successively is described. H. W.

Δ^5-3-Hydroxyætiocholenic acid and its transformation products. M. Steiger and T. Reichstein (Helv. Chim. Acta, 1937, **20**, 1040—1054).—Gradual addition of Me 3-hydroxybisnorcholenate in PhMe to MgPhBr in boiling Et_2O gives a *by-product*, m.p. about 165° (corr.; decomp.), and, mainly, *diphenyl-Δ^5-3-hydroxyternorcholenylcarbinol*, m.p. 113° (corr.). The corresponding *monoacetate*, m.p. about 177° (corr.), and, after re-solidification, m.p. 188—189° (corr.), is transformed by boiling AcOH into αα-diphenyl-β-Δ^5-acetoxycholenyl-β-methylethylene (I), m.p. 221—222° (corr.), hydrolysed to the corresponding OH-compound, m.p. about 106° (corr.) after becoming opaque at about 85°. Bromination of (I) in $CHCl_3$ affords the *dibromide*, m.p. 171—174° (corr.), oxidised and then debrominated to Δ^5-3-*acetoxyætiocholenic acid* (II), m.p. 241—242° (corr.), $[\alpha]_D^{19}$ −19·9° in $COMe_2$ [*Me* ester, m.p. 153—154° (corr.)], a keto-fraction consisting chiefly of the acetates of pregnenolone and

trans-dehydroandrosterone, and a non-ketonic *product*, m.p. 171—173°. Δ^5-3-*Hydroxyætiocholenic acid* (III) [*Me* ester, m.p. 179—181° (corr.)] has m.p. 280—281° (corr.; decomp.). Hydrogenation (Pt in AcOH) of (II) affords β-3-*acetoxyætio*allo*cholanic acid*, m.p. 247—249° (corr.), [*Me* ester, m.p. 142—144° (corr.)], hydrolysed to β-3-*hydroxyætio*allo*cholanic acid* (IV), m.p. 256—258° (corr.) after becoming opaque at 145—150° [*Me* ester (V), m.p. 166—170° (corr.) or (as hydrate), m.p. about 90—100° and, after re-solidification, m.p. 166—170° (corr.)]. Oxidation of (IV) with CrO_3 in AcOH gives 3-*ketoætio*allo*cholanic acid*, m.p. 253—256° (corr.) (*Me* ester, m.p. 176—179°), reduced by Zn wool in HCl–AcOH to ætio*allo*cholanic acid, m.p. 229—231° (corr.). Bromination followed by oxidation and debromination of (III) gives Δ^4-3-*ketoætiocholenic acid*, m.p. 236—242° (corr.), the *Me* ester, m.p, 130—131°, of which is hydrogenated (Pd followed by PtO_2) to (V) and Me ætiolithocholate, m.p. 143—144° (corr.). Ætiolithocholic acid is oxidised by CrO_3 in AcOH to 3-*ketoætiolithocholanic acid*, m.p. 246—249° (corr.) [*Me* ester, m.p. 147—149° (corr.)], reduced (Clemmensen) to ætiocholanic acid.

H. W.

Synthesis of ursodeoxycholic acid. S. Miyazi (Z. physiol. Chem., 1937, **250**, 31—33; cf. Imai, A., 1937, II, 377).—3-Hydroxy-7-ketocholanic acid in EtOH with NaOEt at 200° for 10 hr. or in AcOH containing 0·033% of conc. HCl with PtO_2–H_2 gives ursodeoxycholic acid (*diformate*, m.p. 170°), the yield by the first method being 10%. Chenodeoxycholic acid is the chief product by both methods.

W. McC.

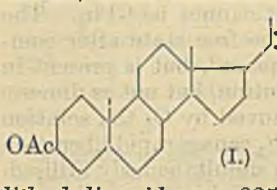
Glyco-ursodeoxycholic acid from bear's bile. S. Miyazi (Z. physiol. Chem., 1937, **250**, 34—36).—The bile yields *glyco-ursodeoxycholic acid* ($+H_2O$), m.p. 232°, $[\alpha]_D^{20}$ +51·28°, converted by alkaline hydrolysis into glycine and ursodeoxycholic acid (I). An improved method of isolating (I), cholic and chenodeoxycholic acid from the bile is described.

W. McC.

Oxidation of cholic and deoxycholic acid with CrO_3. Colour reaction of ketocholanic acid with *m*-dinitrobenzene. K. Kaziro and T. Shimada (Z. physiol. Chem., 1937, **249**, 220—224).—Cholic acid in AcOH with aq. CrO_3 at 0° gives in 6—7 hr. a 65% yield of 3-hydroxy-7 : 12-diketocholanic acid but no 3 : 12-dihydroxy-7-ketocholanic acid. In the same way deoxycholic acid yields (much more slowly) 3-hydroxy-12-ketocholanic acid and 7 : 12-dihydroxy-3-ketocholanic acid yields dehydrocholic acid. Hence OH at $C_{(12)}$ is more easily oxidised than OH at $C_{(3)}$ and OH at $C_{(7)}$ than OH at $C_{(12)}$. Ketocholanic acids having CO at $C_{(3)}$ (but not other ketocholanic acids) give a violet colour with alkaline *m*-$C_6H_4(NO_2)_2$. (Cf. Zimmermann, A., 1935, 1032.)

W. McC.

Degradation of lithocholic acid to ætiolithocholic acid. J. Sawlewicz and T. Reichstein (Helv. Chim. Acta, 1937, **20**, 949—953).—Addition of MgPhBr in Et_2O to Me bisnorlithocholate (Reindel and Niederländer, A., 1935, 1494) in boiling PhMe gives the non-cryst. diphenylcarbinol, which is treated with Ac_2O in C_5H_5N and then with boiling AcOH; after chromatographic purification the product yields



(I.)

αα-*diphenyl*-β-3-*acetoxyætiocholyl*-β-*methylethylene* (I), m.p. 161—163° after softening at about 157°. (I) by CrO_3 in AcOH at 100° yields *acetylætiolithocholic acid*, m.p. 225—226° (corr.) (*Me* ester, m.p. 113—118°), hydrolysed to ætiolithocholic acid, m.p. 273—275° after becoming opaque at about 120°, $[\alpha]_D^{18}$ +50°±2° in dioxan [Me ester, m.p. 141—142° (corr.)].

H. W.

Condensation of succinic anhydride with the methyl ethers of dihydric phenols. G. A. Dalal and K. S. Nargund (J. Indian Chem. Soc., 1937, **14**, 406—410).—The condensation ($AlCl_3$) of $(CH_2{\cdot}CO)_2O$ with the Me_1 and Me_2 ethers of dihydric phenols in $PhNO_2$, CS_2, and $C_2H_2Cl_4$ is described. The following substituted γ-keto-δ-phenylbutyric acids were prepared: 3 : 4- (*Me* ester, m.p. 90°, *Et* ester, m.p. 70°) and 2 : 4-dimethoxy- (*Et* ester, m.p. 70°; *semicarbazone*, m.p. 160°) [also synthesised from $(CH_2{\cdot}CO)_2O$, 1 : 2 : 4-$C_6H_3I(OMe)_2$, and Mg]; 5-*bromo*-, m.p. 178°, and 5-*nitro*-2 : 4-*dimethoxy*-, m.p. 173°, 2-hydroxy-4-methoxy- (*Et* ester, m.p. 68°; *semicarbazone*, m.p. 175°), and 2 : 5-dimethoxy- (*Me* ester, m.p. 54°; *Et* ester, m.p. 46°; *semicarbazone*, m.p. 195°). Guaiacol and *p*-OH·C_6H_4·OMe do not condense.

A. Li.

Anisylmalonic acid and its derivatives. J. B. Niederl, R. T. Roth, and A. A. Plentl (J. Amer. Chem. Soc., 1937, **59**, 1901—1903).—The following are prepared (usual methods) from *Et* α-*cyano*-α-*anisylacetate*, b.p. 152—153°/2 mm., which is obtained in 50—55% yield from *p*-OMe·C_6H_4·CH_2·CN, Et_2CO_3, and Na in Et_2O: *anisylmalonic acid*, m.p. 137—138° (*Et H*, m.p. 77—78°, and *Et*$_2$, b.p. 152—153°/2·5 mm., esters; *diamide*, m.p. 190—191°); *Et* α-*cyano*-α-*anisyl-propionate*, b.p. 136—138°/0·5 mm., and -*butyrate*, b.p. 142—143°/0·5 mm.; α-*cyano*-α-*anisyl-acetamide*, m.p. 144—145°, -*propionamide*, m.p. 143—144°, and -*butyramide*, m.p. 138°. *p*-C_6H_4Me·OMe with Na and CO_2 in amyl chloride (cf. Morton and Hechenbleikner, A., 1937, II, 101) gives 2 : 5-OMe·C_6H_3Me·CO_2H. *p*-OH·C_6H_4·$CH(CO_2H)_2$ (or derivatives) could not be obtained by direct condensation of $CH_2(CO_2Et)_2$ and PhOH or by rearrangement of OPh·$CH(CO_2H)_2$ (and its derivatives).

H. B.

Syntheses in the hydroaromatic series. II. Diene synthesis of derivatives of 1-acetylenyl- and 1-vinyl-3 : 4-dihydronaphthalene. (Frln.) E. Dane, O. Höss, A. W. Bindseil, and J. Schmitt (Annalen, 1937, **532**, 39—51).—Diene syntheses are recorded for 6-*methoxy*-1-*acetylenyl*- (I) and -1-*vinyl*-3 : 4-*dihydronaphthalene* (II). 1-Keto-6-methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene does not react with C_2H_2 in the presence of $NaNH_2$, but with a large excess of MgBr·C:CH gives a little 1-hydroxy-6-methoxy-1-acetylenyl-1 : 2 : 3 : 4-tetrahydronaphthalene (not obtained pure) with (I), b.p. 124—130°/0·5 mm. (formed by dehydration of the alcohol), and *di*-1-6-*methoxy*-3 : 4-*dihydronaphthylacetylene*, m.p. 177° (formed as main product if less MgBr·C:CH is

used). Maleic anhydride (III) and (I) in Et_2O give 7-*methoxy*-1 : 2 : 9 : 10-*tetrahydrophenanthrene*-1 : 2-*dicarboxylic anhydride* (IV), m.p. 200°, and 7-*methoxy*-3 : 11-endo-αβ-*dicarboxyethylene*-1 : 2 : 3 : 9 : 10 : 11-*hexahydrophenanthrene*-1 : 2-*dicarboxylic anhydride*, m.p. 263° (decomp.), obtained also from (IV) and (III), dissociating into (IV) and (III) at 228—230°/12 mm., resisting hydrogenation, and giving with CH_2N_2 the Me_4 ester, m.p. 195°, of the corresponding *tetracarboxylic acid*. Hydrolysis of (IV) by NaOH gives the corresponding *dicarboxylic acid*, m.p. 206° (decomp.) (Me_2 ester, m.p. 117°); hydrogenation (Pd–$CaCO_3$) of (IV) in PhOMe gives the H_8-*anhydride*, m.p. 181°, converted into the H_8-*dicarboxylic acid*, m.p. 185° (decomp.) [Me_2 ester (V), m.p. 123°], which with HBr–AcOH gives 7-*hydroxyoctahydrophenanthrene*-1 : 2-*dicarboxylic acid*, $+0{\cdot}5H_2O$, m.p. 199—200° (decomp.). Partial hydrogenation (Pd–$CaCO_3$) of (I) gives (II), which with (III) gives 7-*methoxyhexahydrophenanthrene*-1 : 2-*dicarboxylic anhydride*, m.p. 200°, converted by CH_2N_2 into the Me_2 ester, m.p. 117°, of the corresponding acid, which affords (V) when hydrogenated. *p*-Benzoquinone and (I) give oils, but (II) gives 3 : 6-*diketo*-10-*methoxytetrahydrochrysene*, m.p. 150—160° (decomp.). 1-Keto-1 : 2 : 3 : 4-tetrahydronaphthalene and MgBr·C:CH give impure 1-*hydroxy*-1-*acetylenyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* and *di*-1-3 : 4-*dihydronaphthylacetylene*, m.p. 124°, hydrogenated to αβ-*di*-1-1 : 2 : 3 : 4-*tetrahydronaphthylethane*, m.p. 77°; heating the alcohol with porcelain at 100° gives 1-*acetylenyl*-3 : 4-*dihydronaphthalene*, b.p. 112°/2 mm., which does not react with (III). Partial hydrogenation gives 1-*vinyl*-3 : 4-*dihydronaphthalene*, which with (III) gives *hexahydrophenanthrene*-1 : 2-*dicarboxylic anhydride*, m.p. 213° [hydrolysed to the *dicarboxylic acid*, m.p. 214—215° (decomp.) (Me_2 ester, m.p. 99°)], and with *p*-benzoquinone gives 3 : 6-*diketotetrahydrochrysene*, m.p. 145—146°. R. S. C.

Molecular resonance systems. V. New phthaleins. G. Schwarzenbach and M. Brandenberger (Helv. Chim. Acta, 1937, **20**, 1253—1260).—Reduction of nitrated diphenylphthalide gives a non-separable mixture of products from which phenolphthalein (I) is obtained in small quantity through the tetrazonium salt. $C_6H_4{<}\overset{CCl_2}{CO}{>}O$ condenses satisfactorily with $NPhMe_2$ (Friedel–Crafts) but the method is useless with NH_2Ph and unsatisfactory with NHPhAc. $CO(NHPh)_2$ with *o*-$C_6H_4{<}\overset{CCl_2}{CO}{>}O$ and $AlCl_3$ in $PhNO_2$ gives an amorphous product (II) converted by conc. HCl at 140° into CO_2 and 4 : 4′-*diaminodiphenylphthalide* (*anilinephthalein*) (III), m.p. 204°, the colourless solution of which in cold AcOH becomes violet when warmed whilst it is colourless in neutral or basic media or in strong acids. 4 : 4′-*Diaminodiphenylphthalimide* is obtained from (II) and conc. NH_3 at 130°. The constitution of (III) is established by its conversion into (I), only a small proportion of which can be caused to crystallise, so that the remainder is identified by conversion through the oxime, m.p. 212°, into *p*-hydroxybenzoyl-*o*-benzoic acid, m.p. 213°. Ditolylphthalide is oxidised by CrO_3 in AcOH to *diphenylphthalide*-4 : 4′-*dicarboxylic acid*, m.p. 304°, transformed by successive treatments with boiling $SOCl_2$ and NH_3 in CCl_4 into the corresponding *diamide*, m.p. 313°, which is degraded (Hofmann) to (III). (III) with boiling Ac_2O gives non-cryst. *acetanilidephthalein* of indefinite m.p. 4 : 4′-*Dibenzenesulphonamidophenylphthalide* is amorphous. *Dithiophenolphthalein* is described. H. W.

3′ : 5′ : 3″ : 5″-Tetrabromo-4′ : 4″-dihydroxy-1 : 4-diphenylnaphthalene-2 : 3-dicarboxylic anhydride. R. Weiss (Monatsh., 1937, **71**, 6—9).—2 : 5-Di-(*mm*′-dibromo-*p*-hydroxyphenyl)-3 : 4-benzofuran (I) with maleic anhydride in PhMe yields a cryst. additive product, which with HCl–EtOH affords 3′ : 5′ : 3″ : 5″-*tetrabromo*-4′ : 4″-*dihydroxy*-1 : 4-*diphenylnaphthalene*-2 : 3-*dicarboxylic anhydride*, m.p. 353°. The Et_2 ester, m.p. 195—196°, is similarly formed from (I) and $(CH{\cdot}CO_2Et)_2$. J. D. R.

Substance, $C_{15}H_{16}O_7$, m.p. 154—156°, from urine.—See A., III, 384.

Reaction of maleic anhydride with α- and β-benzaldoxime: benzoylaspartic acid. G. La Parola (Gazzetta, 1937, **67**, 481—486).—Either α- or β-benzaldoxime with maleic anhydride in C_6H_6 gives benzoylaspartic acid and PhCHO. E. W. W.

Synthesis of *o*-cyano-aldehydes. I. S. N. Chakravarti and K. Ganapati (J. Indian Chem. Soc., 1937, **14**, 463—467).—*o*-*Cyanobenzaldehyde* (I), m.p. 76°, is obtained (in poor yield) by $KMnO_4$–Na_2CO_3 oxidation of *o*-cyanocinnamic acid (A., 1928, 835); *o*-CN·C_6H_4·CO_2H and an acid, m.p. 197—202°, are also formed. Similarly 6-*cyano*-3-*methoxybenzaldehyde*, m.p. 107°, is obtained, with a substance, m.p. 218°, and an acid, m.p. 132°, by oxidation of 6-*cyano*-3-*methoxy*-, m.p. 220°, obtained from 6-*amino*-3-*methoxy-cinnamic acid*, m.p. 186° [*hydrochloride*, m.p. 204° (decomp.)] (from the NO_2-acid). 2-*Amino*-3-*methoxy*-, m.p. 189° (decomp.), is converted into 2-*cyano*-3-*methoxy-cinnamic acid*, m.p. 149°. Attempts to convert *o*-NH_2-derivatives of Schiff's bases, oximes, and acetals into cyano-aldehydes through the diazo-compounds were not successful. E. W. W.

(A) Preparation of some *p*-dialkylaminobenzaldehydes. (B) Condensations of *p*-dialkylaminobenzaldehydes with nitrotoluenes. J. F. J. Dippy, L. T. Hogarth, H. B. Watson, and F. R. Williams (J.S.C.I., 1937, **56**, 346—348T, 396—397T).—(A) Different methods of preparing the aldehydes are compared, with special reference to the yields of *p*-β-hydroxyethylalkylaminobenzaldehydes which can be obtained. The following new aldehydes are described; p-*ethyl*-β-*hydroxyethylamino*-, m.p. 45—47° [*semicarbazone*, m.p. 194° (decomp.)], p-β-*hydroxyethylbutylamino*- (*semicarbazone*, m.p. 158—160°), and 2-*methyl*-4-β-*hydroxyethylbutylamino-benzaldehyde*, b.p. 183°/5 mm. (*semicarbazone*, m.p. 151°). They are best prepared from the appropriate *tert.* bases by a modification of the method of Walter (G.P. 118,567).

(B) The following new stilbenes have been obtained by the interaction of 2 : 4-dinitrotoluene with the required aldehydes in presence of a little piperidine :

2 : 4-*dinitro*-4′-*diethylamino*-, m.p. 149°, 2 : 4-*dinitro*-4′-*ethyl*-β-*hydroxyethylamino*-, m.p. 174—176°, 2 : 4-*dinitro*-4′-β-*hydroxyethylbutylamino*-, m.p. 220°, and 2 : 4-*dinitro*-4′-β-*hydroxyethylbutylamino*-2′-*methyl-stilbene*, m.p. 120°. 2-*Nitro*-4-*amino*-4′-*dimethylamino-stilbene* is obtained by reduction of 2 : 4-dinitro-4′-dimethylaminostilbene by ammonium sulphide. It is difficult or impossible to condense aldehydes with *p*-nitrotoluene. 4-Nitro-4′-dimethylaminostilbene is obtained in 46% yield from *p*-dimethylaminobenzaldehyde and *p*-nitrophenylacetic acid in presence of piperidine.

β-*apo*-4-Carotenal, a further degradation product of β-carotene. P. KARRER, U. SOLMSSEN, and W. GUGELMANN (Helv. Chim. Acta, 1937, **20**, 1020—1024; cf. A., 1937, II, 378).—Further examination of the products of the oxidation of carotene by $KMnO_4$ leads to the isolation of β-apo-4-*carotenal*, $CH_2<^{CH_2\cdot CMe_2}_{CH_2-CMe}>C\cdot CH:[CH\cdot CMe:CH\cdot CH]_2:CH\cdot CH:CMe\cdot CHO$ [*oxime*, m.p. 165°; *semicarbazone*, m.p. 217° (decomp.) after softening at 214°], and ψ-α-carotene, m.p. 169—170°. It is proposed to base the names of the compounds obtained by the stepwise oxidation of carotenoids on that of the carotenoid and to indicate the shortening of the chain by the prefix "*apo*"; the number indicates the distance of the affected from the terminal double linking. Hence carotenal (*loc. cit.*) is β-*apo*-2-carotenal. H. W.

Preparation of *cyclo*butanone. N. J. DEMIANOV and S. M. TELNOV (Bull. Acad. Sci. U.R.S.S., Sér. Chim., 1937, 529—538).—1-*cyclo*Butane*spiro*hydantoin and 8% aq. NaOH (14 hr. at the b.p.) yield 1-*amino*cyclo*butane*-1-*carboxylic acid*, m.p. 245—248° (decomp.), converted by the action of HNO_2 into 1-hydroxy*cyclo*butane-1-carboxylic acid (I), and by aq. NaOCl into the chloroamine, which yields *cyclo*butanone (II) in 74% yield when steam-distilled. (I) does not give (II) when heated with H_2SO_4. R. T.

Catalytic hydrogenation of *cyclo*hexanone. B. FORESTI (Annali Chim. Appl., 1937, **27**, 359—365).—Hydrogenation (Pt) of *cyclo*hexanone produces *cyclo*hexanol (I) with a little *cyclo*hexane (II) when carried out in acid medium (H_2SO_4–N-K_2SO_4, p_H 1) but only (I) in alkaline medium (p_H 12). (II) is produced directly from (I) in acid medium. A nomogram has been constructed by means of which the proportions of the substituents in the ternary mixture may be calc. from the amount of H_2 consumed and the *n* of the org. phase. L. A. O'N.

Action of primary amines on αβ-dibromopropiophenone. B. REICHERT and F. MOLDENHAUER (Arch. Pharm., 1937, **275**, 537—540).—$COPh\cdot CHBr\cdot CH_2Br$ and NH_2Me in C_6H_6 give β-*bromo*-α-*methylaminopropiophenone*, m.p. <0° [*hydrobromide*, m.p. 177—178° (decomp.)], *Ph* α-*methylaminovinyl ketone*, m.p. 170—172° (decomp.) [*hydrobromide*, m.p. 261—263° (decomp.)], and *di*-[β-*bromo*-α-*benzoylethyl*]*methylamine*, m.p. 222—223° (decomp.). NH_2Et gives similarly β-*bromo*-α-*ethylaminopropiophenone hydrobromide*, m.p. 172—173° (decomp.). R. S. C.

Action of hydrogen bromide on benzaldehyde and methyl ethyl ketone. (SIGNA.) G. MASSARA (Gazzetta, 1937, **67**, 440—443; cf. A., 1933, 716).—PhCHO + COMeEt with dry HBr give benzylidenebutanone, the compound $C_{18}H_{17}OBr$ (A., 1916, i, 372), and 3 : 4-diphenyl-2-benzylidene-5-methyl-Δ^3-*cyclo*pentenone, new m.p. 160—161° (cf. A., 1929, 703). E. W. W.

Substances containing the β-ionone ring. Action of organomagnesium compounds on β-ionone. A. GIACALONE (Gazzetta, 1937, **67**, 464—468).—β-Ionone (I), $CH_2Br\cdot CO_2Et$, and Mg give a better yield of Et δ-(1 : 1 : 3-trimethyl-2-Δ^2-*cyclo*hexenyl)-β-methylbutadiene-α-carboxylate than when Zn is used (A., 1932, 852), but ionene (II) is also formed. From (I) and MgMeI, (II) and CH_4 are obtained; using $MgBu^\beta Br$, a small amount of (II) is formed. E. W. W.

Oxidation of desylamine and benzoin methyl ether.—See A., I, 623.

Phenyl benzyl ketimine and derivatives. K. N. CAMPBELL (J. Amer. Chem. Soc., 1937, **59**, 2058—2061).—*Ph benzyl ketimine* (I), m.p. 57°, obtained from its *hydrochloride* (II), m.p. 210—211° (decomp.) [prep. from PhCN and $CH_2Ph\cdot MgCl$ (excess) followed by HCl], hydrolyses rapidly in moist air to NH_3 and $COPh\cdot CH_2Ph$. The N-*Cl*-derivative (III), m.p. 78°, of (I) is obtained from (I) (in $CHCl_3$) and aq. NaOCl; (III) and HCl in light petroleum give (II). (III) does not lose HCl (to give a cyclic imine) when treated with Ag_2O (in C_6H_6) or dry KOH (in Et_2O); with aq. EtOH–KOH, benzilic acid and gummy products are produced. The N-*Br*-derivative, m.p. about 55°, of (I) is prepared from (II) and aq. KOBr. H. B.

Reduction of unsaturated ketones. J. F. J. DIPPY and R. N. LEWIS (Rec. trav. chim., 1937, **56**, 1000—1006).—Reduction of substituted Ph styryl ketones to the corresponding saturated ketones is best effected by Na and AcOH; secondary diketonic products are formed only at elevated temp. Cl or NO_2 inhibits reduction. The following new or revised data are recorded: Ph *o*-methoxystyryl ketone, m.p. 57°; *Ph o-chlorostyryl ketone*, m.p. 48°; Ph *p*-chlorostyryl ketone, m.p. 114·5°; Ph *o*-nitrostyryl ketone, m.p. 126°; *benzylacetophenone*-2 : 4-*dinitrophenylhydrazone*, m.p. 166° (the corresponding semicarbazone could not be obtained); *αγδζ-tetraphenylhexane*-α*ζ-dione*, m.p. 243°; *Me* δ-*phenyl*-n-*butyl ketone*, b.p. 160—162°/20—23 mm. (*semicarbazone*, m.p. 156—157°); *Ph* β-*o-methoxyphenylethyl ketone*, b.p. 227—230°/20 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 104·5°); α*ζ-diphenyl*-γδ-*dianisylhexane*-α*ζ-dione*, m.p. 232°. Styryl Me ketone is reduced (Clemmensen) to *n*-propylbenzene. H. W.

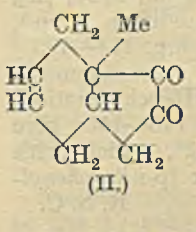
***o*-Nitrochalkones.** I. TANASESCU and A. BACIU (Bull. Soc. chim., 1937, [v], **4**, 1742—1759).—Interaction of *o*-$NO_2\cdot C_6H_4\cdot CHO$ with the appropriate substituted acetophenone in EtOH affords the following: 2-*nitro*-, m.p. 124°, 4′-*chloro*-2-*nitro*-, m.p. 148°, 4′-*bromo*-2-*nitro*-, m.p. 137°, 2-*nitro*-4′-*methyl*-, m.p. 111°, 2-*nitro*-3′ : 4′-*dimethyl*-, m.p. 128°, 2-*nitro*-2′ : 4′-*dimethyl*-, m.p. 93°, 2-*nitro*-2′ : 5′-*dimethyl*-, m.p. 102°, 2 : 2′-*dinitro*-, m.p. 152—153°, 2 : 4′-*di*-

nitro-, m.p. 179°, 2-*nitro*-4′-*cyano-*, m.p. 186—187°, 2-*nitro*-4′-*carboxy-*, m.p. 245—246° (*Me* ester, m.p. 173—174°), 6′-*chloro*-2-*nitro*-3′-*methyl-*, m.p. 117°, 2 : 3′-*dinitro*-4′-*methyl-*, m.p. 195°, 4′-*bromo*-2 : 3′-*dinitro-*, m.p. 202—203°, 2-*nitro*-4′-*amino-*, m.p. 178—181°, and *forms*, m.p. 82° and 184° (*hydrochloride*, m.p. 207—210°; *semicarbazone*, m.p. 203—204°; *Ac* derivative, m.p. 234° and 230—231°), 2-*nitro*-4′-*benzamido-*, m.p. 182—183°, 2-*nitro*-4′-*dimethylamino-*, m.p. 110—111°, 2-*nitro*-4′-*methylamino-*, m.p. 153—154°, 2-*nitro*-3′-*acetamido-*, m.p. 182° (*phenylhydrazone*, m.p. 98°), 2-*nitro*-3′-*amino-*, m.p. 142° (*hydrochloride*, m.p. 195—199° decomp.), 2 : 3′-*dinitro*-4′-*amino-*, m.p. 240—241°, and 3′ : 5′-*dibromo*-2-*nitro*-4′-*amino-chalkone*, m.p. 208—209°. 1 : 4-$C_{10}H_6Me$·COMe and *o*-NO_2·C_6H_4·CHO yield 4-*methyl*-α-*naphthyl* 2-*nitrostyryl ketone*, m.p. 111—112°. When boiled with EtOH–NaOH, these chalkones yield red solutions which with conc. HCl afford indigotin. They are decomposed by sunlight. Those chalkones having electropositive substituents are liable to exhibit polymorphism. J. D. R.

Retene. IX. Synthesis of 5 : 6-benzoretene and its derivatives. D. E. Adelson and M. T. Bogert (J. Amer. Chem. Soc., 1937, **59**, 1776—1782).—6-Acetylretene and Br in cold Et_2O give 6-*bromoacetyl-* (I), m.p. 98·5—99°, and a little 6-*dibromoacetyl-retene*, m.p. 157·5—158°; both are oxidised (I–KI in dioxan–10% NaOH) to retene-6-carboxylic acid (II). (I) and $CHNa(CO_2Et)_2$ in C_6H_6 lead to β-6-*retoylpropionic* [*γ-keto-γ*-1-*methyl*-7-*isopropyl*-6-*phenanthrylbutyric*] *acid* (III), m.p. 201—202° [*Me* ester, m.p. 108—109° (*oxime*, m.p. 126—127°)], also prepared from retene, $(\cdot CH_2\cdot CO)_2O$, and $AlCl_3$ in C_6H_6, which is reduced (Clemmensen) to *γ*-6-*retylbutyric acid* (IV), m.p. 179—179·5° [*Me* ester (V), m.p. 66·5—67·5°]. (III) is oxidised (NaOCl) to (II). (IV) and $SnCl_4$ at 105—110°, or its chloride and $AlCl_3$ in C_6H_6, give 1′-*keto*-1′ : 2′ : 3′ : 4′-*tetrahydro*-5 : 6-*benzoretene* (VI), m.p. 139·5—140° [*oxime*, m.p. 203—204° (decomp.); *semicarbazone*, m.p. 242—244° (decomp.)], reduced (Wolff) to 1′ : 2′ : 3′ : 4′-*tetrahydro*-5 : 6-*benzoretene*, m.p. 88—89° (*picrate*, m.p. 159—160°), which is dehydrogenated (S at 220—230°) to 5 : 6-*benzoretene*, m.p. 98—99° (*picrate*, m.p. 144—144·5°). (VI) is reduced (Na, EtOH) to the 1′-*OH*-derivative, m.p. 131—132° (*picrate*, m.p. 154·5—155°). The product from (V), $Et_2C_2O_4$, and NaOEt is converted by 80% H_2SO_4 at 100° into 3′ : 4′-*dihydro*-5 : 6-*benzoretene*-1′ : 2′-*dicarboxylic anhydride*, m.p. 219—220° (corresponding Me_2 ester, m.p. 145·5—146·5°), dehydrogenated (S at 230—250°) to the *anhydride* (VII), m.p. 244·5—245·5°, of 5 : 6-*benzoretene*-1′ : 2′-*dicarboxylic acid*, m.p. 240—241° (decomp.). (VII) appears to have no œstrogenic activity. β-6-*Retoyl*-α-*methylpropionic acid*, m.p. 210—211° [*Me* ester, m.p. 96—97° (*oxime*, m.p. 135—135·5°)], prepared (as above) from (I) and $CNaMe(CO_2Et)_2$ or from retene and methylsuccinic anhydride, is reduced (Clemmensen) to *γ*-6-*retyl*-α-*methylbutyric acid*, m.p. 131—132°, which is converted (85% H_2SO_4) into 1′-*keto*-2′-*methyl*-1′ : 2′ : 3′ : 4′-*tetrahydro*-5 : 6-*benzoretene*, m.p. 120·5—121·5°. All m.p. are corr. H. B.

Additive products of *o*-nitrobenzaldehyde with substituted acetophenones. I. Tanasescu and A. Baciu (Bull. Soc. chim., 1937, [v], **4**, 1673—1683; cf. A., 1932, 625).—*o*-NO_2·C_6H_4·CHO, COMeR (R = Ph etc.), and Na_3PO_4 in aq. EtOH yield the following OH-ketones (m.p. of respective Bz derivatives given within parentheses): phenyl (improved yield), p-*chloro-*, m.p. 97° (179°), and p-*bromo-phenyl*, m.p. 116° (174°), p-*tolyl*, m.p. 82° (170°), 4-o-*xylyl*, m.p. 98—99° (158—159°), p-*anisyl*, m.p. 139·5° (143°) (also obtained using KOH–EtOH), o-, m.p. 139°, and p-*nitrophenyl*, m.p. 127° (155°), p-*cyano-*, m.p. 138·5—139° (147—148°), and 4-*bromo*-3-*nitro-phenyl*, m.p. 152° (205—207°), 2-*nitro*-p-*tolyl*, m.p. 131°, and p-*carboxyphenyl* β-*hydroxy*-β-o′-*nitrophenylethyl ketone*, m.p. 219—220° (226—227°). All the above compounds, especially the last, readily yield indigotin when treated with alkali. *m-* and *p*-Amino-, 3-nitro-4-amino-, 3 : 5-dibromo-4-amino-, 2 : 5- and 2 : 4-dimethyl-, and 2-chloro-5-methyl-acetophenone yield only compounds of type CHR:CH·COR′. E. W. W.

Syntheses in the hydroaromatic series. I. Condensation of methyl*cyclo*pentenedione with butadiene. (Frln.) E. Dane, J. Schmitt, and C. Rautenstrauch (Annalen, 1937, **532**, 29—38).—·CO·CO· activates an αβ-ethylenic linking, at least in the *cyclo*pentane ring, to make it reactive towards $(CH_2{:}CH)_2$. *cyclo*Pentene and SeO_2 in Ac_2O give Δ^2-cyclo*pentenyl acetate*, b.p. 154—155°, and Δ^4-cyclo*pentene*-1 : 3-*diol diacetate*, b.p. 120—130°/15 mm.; the former is the main product at 100° in an open vessel and the latter in a closed tube at 100°. The monoacetate with cold 2N-NaOH gives Δ^2-cyclo*pentenol*, b.p. 137° (*phenylurethane*, m.p. 128—129°; *dinitrobenzoate*, m.p. 126°). The *diacetate* is hydrolysed by H_2O and with aq. $NaHCO_3$ rapidly gives Δ^4-cyclo*pentene*-1 : 3-*diol*, b.p. 107°/12 mm., which reduces warm Fehling's solution and ammoniacal $AgNO_3$ or Ag_2CO_3 (slowly in the cold), and gives no cryst. phenylurethane or dinitrobenzoate; use of dil. alkali hydroxide leads to an isomeric *diol*, which gives a *diphenylurethane*, m.p. 195°, and *diurethane*, m.p. 123°. Δ^1-Methylcyclopentene and SeO_2 give a 35% yield of 2-*methyl*-Δ^2-cyclo*pentenyl acetate* (I), b.p. 60—60·5°/12 mm., with some diacetate and methylcyclopentenone; cold KOH or NaOH hydrolyses (I) to 2-*methyl*-Δ^2-cyclo*pentenol*, m.p. 59·5—60°/12 mm. (*phenylurethane*, m.p. 103°), but use of crude (I) leads also to some 5-2′-*methyl*-$\Delta^{2'}$-cyclo*pentenyl*-2-*methyl*-Δ^2-cyclo*pentenone*, b.p. 115°/0·1 mm., m.p. 106°. Oxidation (CrO_3) leads to 2-*methyl*-Δ^2-cyclo*pentenone*, b.p. 53°/12 mm. [*semicarbazone*, m.p. 213° (slow heating), 220° (decomp.; rapid heating); *oxime*, m.p. 128°], which with SeO_2 in AcOH at 120° gives Δ^3-cyclo*pentene*-1 : 2-*dione*, m.p. 85° (oily enolic *form*; *quinoxaline*, m.p. 135°). This adds $(CH_2{:}CH)_2$ in dioxan at 110—130° to give the *diketone* (II), m.p. 110°.



(II.)

R. S. C.

Condensation of fluorene with acetone. II. H. France, P. Maitland, and S. H. Tucker (J.C.S., 1937, 1739—1745; cf. A., 1930, 85).—Fluorene (I) with

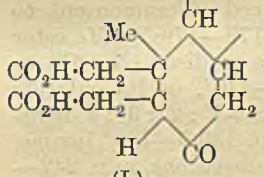
$COMe_2$ containing KOH gives a 50% yield of *Me* β-9-*fluorenylisobutyl ketone* (II), m.p. 77—78° (*piperonylidene*, m.p. 167—168°, and 6-*bromopiperonylidene* derivative), also obtained less well using mesityl oxide (III), (I), and KOH or from (III) and Na fluorenyl (IV) in Et_2O. Fluorenol, obtained from fluorenone (V) by Mg in MeOH at 45°, gives 9-bromo- and thence by $AgNO_3$ in hot MeOH 9-methoxyfluorene, which gives (IV) by Schlenk's method. With $CH_2Ph{\cdot}OBz$ (IV) gives 9-benzoylfluorene. Neither 9-fluorenyldimethylcarbinyl chloride nor bromide reacts with $CHAcNa{\cdot}CO_2Et$. Dry distillation of (II) gives (I), (III), and $COMe_2$; heating with KOH–EtOH, Na in xylene, or K in C_6H_6 gives (I); K gives also 9-*iso*propylidenefluorenone, which, when kept, yields (V). Oxidation of (II) with $KMnO_4$ gives (?) β-*hydroxy*-β-9-*fluorenylisobutyl Me ketone*, m.p. 120—122°; with $Na_2Cr_2O_7$ gives (V), with NaOBr, $CHBr_3$, and with NaOI, CHI_3. The *semicarbazone*, m.p. 218°, of (II) with NaOEt gives β-9-*fluorenyl*-β-*methylpentane* (VI), m.p. 84—85°, also obtained by Clemmensen reduction, with a *substance* (VII), $C_{19}H_{20}$, m.p. 103—104° (formed as sole product by HI). $CMe_2Pr^{\alpha}Cl$ (modified prep.) gives a Grignard reagent, which with (V) affords (VI), which is also obtained from the chloride and Et sodiofluorene-oxalate (VIII) or, in very poor yield, potassiofluorene-carboxylate. α-9-*Fluorenylisopropyl iodide*, m.p. 95—97°, is prepared from the alcohol. $Bu^{\gamma}I$ or $Bu^{\gamma}Cl$ with (VIII) gives 2% of *tert.*-butylfluorene, m.p. 101—102°. With HBr–AcOH (II) gives a substance, m.p. 95—105°, which rapidly decomposes to HBr and a *substance*, $C_{19}H_{18}$, m.p. 77—79°, oxidised to a *keto-acid*, $C_{19}H_{18}O_3$, m.p. 163—164°, and hydrogenated (Pd) in warm AcOH to (VII). With $ZnCl_2$ at 240—250° (II) gives (VII) and a *substance*, $C_{16}H_{14}$, m.p. 133—134°, also obtained by P_2O_5 at 250°. The *oxime*, m.p. 109—110° (*Ac* derivative, m.p. 90—94°), of (II) with PCl_5 gives an *amide*, $C_{19}H_{21}ON$, m.p. 167—169°, yielding uncrystallisable bases when hydrolysed. The *Br*-, m.p. 83—85°, Br_2-, anhyd. and +EtOH, m.p. 102—104°, and Br_3-, m.p. 173—175°, -derivatives of (II) are oxidised (CrO_3) to (V) and thus do not contain Br in the nucleus; no acid was obtained from the Br_3-compound by KOH. With HNO_3–H_2SO_4–AcOH (II) gives a NO_2-derivative, m.p. 110—114° (in one experiment a *substance*, $C_{16}H_{15}O_3N$, m.p. 98—100°), reduced by Na_2S to a *substance*, $C_{19}H_{21}ON$, m.p. 143—146°. R. S. C.

Hydroxybenzofluorenones.—See B., 1937, 1025.

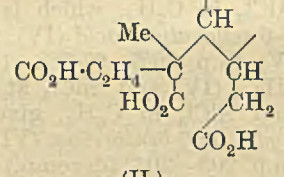
Preparation of 2-hydroxy-5-methoxyacetophenone. F. Mauthner (J. pr. Chem., 1937, [ii], **149**, 324—327).—*p*-$C_6H_4(OAc)_2$ (modified prep.), m.p. 121°, and *p*-$OMe{\cdot}C_6H_4{\cdot}OAc$ (I), b.p. 134—135°/18 mm., do not undergo the Fries rearrangement. MeCN and (I) do not undergo the Hoesch reaction. *p*-$C_6H_4(OH)_2$, AcOH, and $ZnCl_2$ at 145—150° give 2 : 5-*dihydroxyacetophenone*, m.p. 202°, which with NaOH–Me_2SO_4 gives the 5-Me ether (*p-nitrophenylhydrazone*, m.p. 215—216°). R. S. C.

Dioximes. CXXIII. G. Ponzio and G. Tappi (Gazzetta, 1937, **67**, 518—526).—Phenylmethyltriketone-" α "-trioxime (I) (A., 1936, 1383) and N_2O_4 give α-phenyl-γ-methyltriketonetrioxime αγ- and βγ-peroxides, and the αβ-*peroxide*, *i.e.*, the *oxime*, $OH{\cdot}N{:}CMe{\cdot}C(=N{\cdot}O{\cdot}O{\cdot}N)CPh$ (II), m.p. 135° (*Ac* derivative, m.p. 100°; *Bz* derivative, m.p. 130—131°), of *acetylphenylglyoxime* [α-*phenyl*-γ-*methyltriketone*-αβ-*dioxime*] *peroxide*, m.p. 79—80° [*phenylhydrazone*, m.p. 160°; *semicarbazone*, m.p. 218—219° (decomp.)], obtained by HCl hydrolysis of (II), into which it is reconverted by NH_2OH,HCl. With N_2O_4 in Et_2O, or with HNO_3 (*d* 1·40), (II) gives *phenyl*-(αα-*dinitroethyl*)*glyoxime peroxide*, m.p. 135—136°. Phenylmethyltriketone-" β "-trioxime (III) (A., 1922, i, 1039) is distinguished from (I) by the m.p. of its Bz_3 derivative, m.p. 181—182°; with N_2O_4 (III) gives the same products as (I). " β "-Benzoylmethylglyoxime (A., 1922, i, 1038) (*semicarbazone*, m.p. 247—248°) with Me_2SO_4 yields a Me_2 ether, m.p. 68—69°. E. W. W.

Sulphonic acids of sterol derivatives. A. Windaus and E. Kuhr (Annalen, 1937, **532**, 52—68).—Δ^4-Cholestenone and Ac_2O–H_2SO_4 give an 85% yield of the 6-*sulphonic acid* (I), m.p. 193—195° (decomp.) [various *salts* described; *Me* ester, m.p. 149—150°; *phenylhydrazone*, m.p. 212—214° (decomp.)]. The alkali salts foam in H_2O, are colloidal, and, as does also (I), cause cholesterol, benzpyrene, and methylcholanthrene to remain dissolved in H_2O. Hydrogenation in the presence of Pd–C in AcOH gives a H_2-*acid*, m.p. 223—225° (decomp.) (*Me* ester, m.p. 172—173°), but use of PtO_2 leads to a H_4-*acid*, sinters at 190°, decomp. 200° (*Me* ester, m.p. 155°), oxidised to the acid (II), $C_{27}H_{44}O_5$, m.p. 218—220°. The position of the SO_3H is determined by



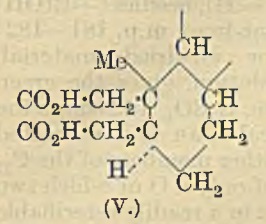
(I.)



(II.)

oxidation of (I) by $KMnO_4$ to the acid (III), $C_{26}H_{44}O_6$, m.p. (anhyd.) 136—141° and (+AcOH) 97—99°, and *cholestane*-3 : 6-*dione*-4 : 5-*diol*, m.p. 220—225° (decomp.) after sintering at 210°, which readily loses H_2O (*e.g.*, with 5% HCl–EtOH) to give the enolic Δ^4-*cholestene*-3 : 6-*dion*-4-*ol*, m.p. 148—149°, also obtained from Δ^4-*cholestene*-3 : 6-*dione* (IV). *Sulphonic acids* are also prepared from (IV), decomp. about 150° [*Cu* salt; *Me* ester, m.p. 164—165° (decomp.)], Δ^5-cholesten-7-one, m.p. 178—180° (decomp.) [*Me* ester, m.p. 180—181° (decomp.)], androstenedione, decomp. about 196° [*Me* ester, m.p. 159—160° (decomp.)], and progesterone, m.p. 190—192° (decomp.) (*Me* ester, m.p. 160—161°). Cholestan-3-one gives the 2-*sulphonic acid*, m.p. about 148° after sintering [*Me* ester, m.p. 206—208° after sintering; *phenylhydrazone*, m.p. about 180° (decomp.)], oxidised by CrO_3 or HNO_3 to the acid (V), m.p. 191—194° (Me ester, new m.p. 60°) (A., 1914, i, 1066), and 2-bromocholestanone gives the enol *acetate*, m.p. 106—107°. Coprostanone gives similarly the 2-*sulphonic acid* (*Me* ester, m.p. 171—172°, and an isomeric *ester*), oxidised

to the *acid* (VI), m.p. 201—202°. *Cholesterylene*-x-*sulphonic acid* (*Me* ester, m.p. 175—176°; *Li*, decomp.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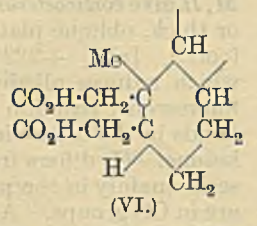
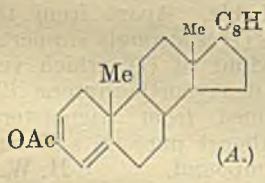

(VI.)

from 220°, *Na*, and *K* salts) has little or no antirachitic activity. R. S. C.

Enolic derivatives of progesterone and other αβ-unsaturated steroid ketones. U. Westphal (Ber., 1937, 70, [*B*], 2128—2136; cf. A., 1937, II, 25).—Treatment of testosterone (I) with boiling Ac_2O–AcCl gives the enol diacetate, m.p. 153—155°, $[\alpha]_D^{20}$ −151° in $CHCl_3$, hydrolysed by H_2SO_4 to (I); it shows protracted physiological activity. Progesterone (II) is transformed into the corresponding enol acetate, m.p. 138°, $[\alpha]_D^{20}$ −41·9° in $CHCl_3$, and enol *propionate*, m.p. 134—136°, $[\alpha]_D^{20}$ −40·6° in $CHCl_3$, by a mixture of the requisite acid anhydride and chloride, whereas for the prep. of the enol *butyrate*, m.p 116—118°, $[\alpha]_D^{20}$ −37·8° in $CHCl_3$, it is necessary to use $Pr^{\alpha}CO_2Na$ and $(Pr^{\alpha}CO)_2O$. Physiologically the action of these esters is practically indistinguishable from that of (II), to which they are somewhat inferior. The ultra-violet absorption spectra of the esters establishes the presence of a conjugated double linking similar to that of cholestenone enol acetate (III). This does not react readily with maleic anhydride (IV) and under more drastic conditions a *product*, m.p. about 260° (decomp.), mol. wt. about 1800 (very sparingly sol. *Na* salt), is produced. It differs from all known adducts of (IV) and sterols. (III) is therefore (*A*). The double linkings in the esters are therefore at Δ³ and Δ⁵.


(*A*.)

H. W.

Attempted partial reduction of androstenedione. U. Westphal and H. Hellmann (Ber., 1937, 70, [*B*], 2136—2140).—Androstene-3 : 17-dione is transformed into the 3-*monosemicarbazone*, decomp. 234°, the constitution of which is established by its absorption spectrum. This is reduced by Na and $Pr^{\beta}OH$ and then hydrolysed to testosterone, freed from androstenediol by Girard's "ketone reagent *T*." H. W.

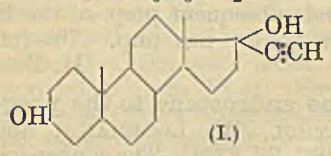
Sterols. XX. The pregnanolones. R. E. Marker, O. Kamm, and E. L. Wittle (J. Amer. Chem. Soc., 1937, 59, 1841—1843).—Partial reduction (H_2, PtO_2, EtOH) of pregnanedione (I) gives *epi*pregnan-3-ol-20-one, new m.p. 149° (cf. A., 1937, II, 424) (*acetate*, m.p. 112°; *semicarbazone*, m.p. 245°), also obtained by limited acetylation (AcOH–Ac_2O) of pregnanediol and subsequent oxidation (CrO_3). Reduction (H_2, PtO_2, AcOH–HBr) of (I) affords mainly pregnan-3-ol-20-one, m.p. 149° (*acetate*, m.p 121°; *semicarbazone*, m.p. 245°); androstanedione similarly gives androsterone. The OH-ketones are purified by treatment of the crude reaction products with Girard's reagent and subsequent prep. of the H succinates. *epiallo*Pregnanolone has m.p. 176° (cf. *ibid.*, 250). H. B.

Conversion from the androstane to the pregnane series. J. Kathol, W. Logemann, and A. Serini (Naturwiss., 1937, 25, 682).—The conversion is effected by C_2H_2 and its derivatives. Thus dehydroandrosterone and C_2H_2 afford Δ⁵·⁶-17-*ethinylandrostene*-3 : 17-*diol*, m.p. 240° (*Ac*, m.p. 175°, and Ac_2 derivative, m.p. 169°), which with O_3 yields 3 : 17-*diacetoxyætiocholenic acid*, m.p. 246°. *iso*Androsterone with C_2H_2 gives 17-*ethinyl*iso*androstane*-3 : 17-*diol*, m.p. 257°, partly hydrogenated to 17-*ethenyl*iso*androstane*-3 : 17-*diol*, m.p. 207°, oxidation of which by perphthalic acid affords the corresponding *oxide*, m.p. 182°, whilst OsO_4 and reductive degradation gives 3 : 17 : 20 : 21-tetrahydroxy*allo*pregnane. The ethinyl derivatives exhibit more of the characteristics of female than of male hormones. F. O. H.

New compounds of the follicle hormone series. K. Miescher and C. Scholz (Helv. Chim. Acta, 1937, 20, 1237—1244).—The enhanced activity of sex hormones induced by suitable esterification is attributed to delayed resorption and consequent better utilisation of the hormone. The delay is due in part to impeded diffusion and probably, in part to solubility and hydrolysis. Œstrone (I) and $(CHMe_2{\cdot}CO)_2O$ in C_5H_5N at 120—125° yield *æstrone* iso*butyrate*, m.p. 120—121°; the corresponding n-*hexoate*, m.p. 94·5—95°, and *stearate*, m.p. 81·5—82·5°, are obtained by use of the requisite acid chloride. Similar methods lead to the prep. of *æstradiol* 3 : 17-*diiso*butyrate, m.p. 100·5—101·5°, and 3 : 17-*dipalmitate*, m.p. 63—65°. *Œstradiol* 3-*mono*-n-*butyrate*, m.p. 98—99°, and 3-*monostearate*, m.p. 78—79°, are obtained by hydrogenation (Adams) of the corresponding œstrone esters. Partial hydrolysis of the requisite normal esters by K_2CO_3 in 95% MeOH affords *æstradiol* 17-*mono*iso*butyrate*, m.p. 183—183·5°, 17-*mono*-n-*valerate*, m.p. 144—145°, and 17-*mono*-n-*hexoate*, m.p. 112—112·5°. Œstradiol 3-benzoate (from the alcohol and BzCl), *n*-valeric anhydride, and C_5H_5N give *æstradiol* 3-*benzoate* 17-n-*valerate*, m.p. 133—133·5°. Similar methods lead to *æstradiol* 17-*benzoate* 3-*propionate*, m.p. 165—166°, and 17-*benzoate* 3-n-*butyrate*, m.p. 141·5—142° (hydrolysed to *æstradiol* 17-*monobenzoate*, m.p. 92·5—94°). Successive treatments of œstradiol in dioxan with $COCl_2$ and MeOH or EtOH afford 17-*methylcarbonato*-, m.p. 216·5—218°, or *ethylcarbonato*-, m.p. 171—172°, -*æstradiol*. 3 : 17-*Diethylcarbonato*-*æstradiol* has m.p. 138—139°. The Na derivative of (I) and allyl bromide give *æstrone allyl ether*, m.p. 108—109°, which is isomerised in boiling $NPhEt_2$ to the amorphous C-*allylæstrone* (*benzoate*, m.p. 155—160°). *Œstrone cinnamyl ether* has m.p. 149—149·5°. H. W.

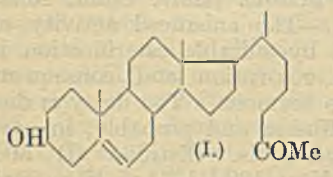
Sex hormones. XXIV. Addition of acetylene to the 17-keto-group of *trans*-androsterone and Δ⁵-*trans*-dehydroandrosterone. L. Ruzicka and K. Hofmann (Helv. Chim. Acta, 1937, 20, 1280—1282).—A solution of K in liquid NH_3 is treated with

C_2H_2 until it is decolorised and *trans*-dehydroandrosterone in C_6H_6–Et_2O is added; after treatment with Girard's reagent, the product gives Δ^5-17-*acetylenylandrostene*-3-trans-17-*diol* (I), m.p. 240—242° [3-*monoacetate*, m.p. 175—176° after softening at 170°; *diacetate*, m.p. 169—169·5°, hydrolysed to (I)]. Similarly *trans*-androsterone gives 17-*acetylenylandrostane*-3-trans-17-*diol*, m.p. 255—257° (3-*monoacetate*, m.p. 205—207°; *diacetate*, m.p. 199—250°). H. W.



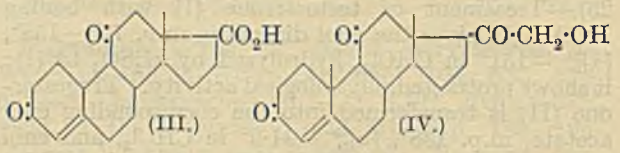
(I.)

Sex hormones. XXVI. Oxidation of cholesteryl acetate dibromide with chromium trioxide. L. Ruzicka and W. H. Fischer (Helv. Chim. Acta, 1937, **20**, 1291—1297).—The main portion of the acetate of *trans*-dehydroandrosterone is removed as semicarbazone from the debrominated neutral products of the oxidation of cholesteryl acetate dibromide by CrO_3 in AcOH at 28—30°. The mother-liquors give a mixture of semicarbazones which is treated successively with acid and alkali; the product when crystallised from MeOH yields Δ^5-*norcholestene*-3-trans-*ol*-25-*one* (I), m.p. 125—127° [*benzoate*, m.p. 144—145°; acetate, m.p. 141·5—142°, and its *semicarbazone*, m.p. 237—238° (decomp.)], oxidised through the dibromide to a *diketone*, $C_{26}H_{40}O_2$. Catalytic hydrogenation of (I) gives a mixture of the saturated OH-ketone and the corresponding diol, oxidised by CrO_3 to a saturated diketone identical with that derived from *epi*cholestanyl acetate. The constitution of (I) is thus established. (I) is physiologically inactive. The mother-liquors from (I) yield *trans*-dehydroandrosterone and Δ^5-pregnanolone. H. W.

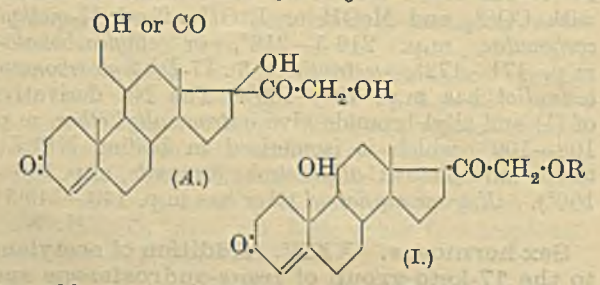


(I.)

Constituents of the adrenal gland. X. Corticosterone. T. Reichstein (Helv. Chim. Acta, 1937, **20**, 953—969; cf. A., 1936, 1382).—Further examination of substance *H* (*loc. cit.*) discloses the presence of *substance M*, an αβ-unsaturated ketone, $C_{21}H_{30}O_5 \pm H_2$, m.p. 207—210° (corr.; slight decomp.) when slowly heated; it reduces alkaline Ag solution, gives the green fluorescence reaction with conc. H_2SO_4, the absorption spectrum of an αβ-unsaturated ketone, and is oxidised by CrO_3 to adrenosterone. It resembles very closely substance *Fa* but is distinguished by cryst. form. It is isomeric with *Fa* or distinguished therefrom by 2H so that the partial structure *A* is probable for it. It is biologically inactive in the quantity available. After removal of *M*, *H* give *corticosterone* [(I), R = H], needles (+EtOH) or thick, oblique plates (solvent-free), m.p. 181—182° (corr.), $[\alpha]_D^{15}$ +223°±3° for air-dried material, which reduces alkaline Ag solution, gives the green fluorescence reaction with conc. H_2SO_4, and shows the bands in the ultra-violet typical of an αβ-unsaturated ketone. (I) differs from the other members of the C_{21} series mainly in the presence of only 4 O of which two are in CO groups. A third lies in a readily esterifiable OH since (I) gives an *acetate* (II) [(I), R = Ac], various forms all of m.p. about 145—146·5°, and, after resolidification, m.p. 152·5—153° (corr.), a *butyrate*, m.p. 170—171° (corr.), very suitable for diagnosis, a *benzoate*, m.p. 201—202° (corr.), a *H succinate*, m.p. 194—195°, a *palmitate*, m.p. 87—93°, and an *oleate*, m.p. 79—81°. (I) is oxidised by CrO_3 to the *acid* (III), m.p. about 266—272° (corr.) [*Me* ester, m.p. 174—178° (corr.)]. The occurrence of the fourth O of (I) in a *sec.* OH is established by the mild oxidation of (II) with CrO_3 to *dehydrocorticosterone acetate*, m.p. 178—180·5° (corr.), which retains the reducing group; it is hydrolysed to *dehydrocorticosterone*, m.p. about 177—180° after softening at 170°, identical with the substance *A* of Kendall. The exact position of the *sec.* OH is uncertain but in analogy with substances *A*, *C*, *D*, *E*, *Fa*, and *M* it is probably attached to $C_{(11)}$ or $C_{(12)}$; on purely chemical grounds attachment to $C_{(11)}$ is the more probable. Apart from this uncertainty, the structure of (I) is strongly supported by the physiological behaviour of (I), which very closely resembles that of deoxycorticosterone (21-hydroxyprogesterone) obtained from stigmasterol. Substance *K* (*loc. cit.*) is almost pure (I) and need not be regarded as a new compound. H. W.

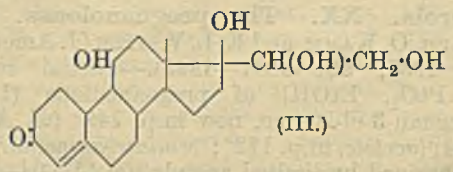


(III.) (IV.)



(I.)

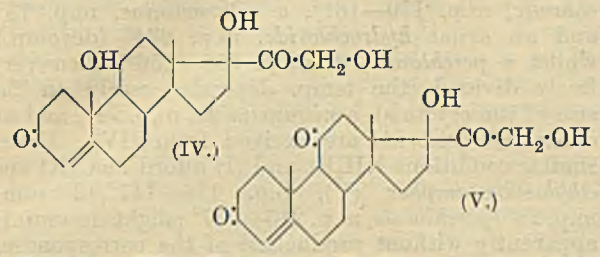
Constituents of the adrenal gland. XI. Constitution of the $C_{21}O_5$ group. T. Reichstein (Helv. Chim. Acta, 1937, **20**, 978—991; cf. A., 1937, II, 380).—The location of the last O of substance *A* (*loc. cit.*) permits further conclusions with regard to the other $C_{21}O_5$ substances since these can all be converted into the same triketone. Substance *E*, anhyd. or (+1H_2O), m.p. about 120° (decomp.), is oxidised by CrO_3 to adrenosterone (I) whereas with HIO_4 it affords Δ^4-*androsten*-11-*ol*-3:17-*dione* (II), m.p. 189—190° (corr.), readily converted by CrO_3 into



(III.)

(I). Hence *E* is (III), the position of the double linking being fixed since it has the spectrum of an αβ-unsaturated ketone and only one CO is now shown to be present. It can therefore be only in Δ^1 or

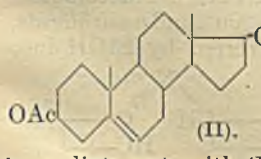
Δ^4 position, the latter being much the more probable by reasons of analogy. Substance *M* is oxidised by CrO_3 in AcOH to (I) and by $Pb(OAc)_4$ to (II); it



is therefore (IV). Substance *M* gives a *monoacetate*, m.p. 223—225° (corr.), which is not attacked by HIO_4 but is oxidised by CrO_3 in AcOH to the *monoacetate*, m.p. 239—241° after becoming opaque at 70—100°, of substance *Fa* which is therefore (V). Fuller data for substances *C* and *D* could not be obtained owing to lack of material. *C* does not give a pure product with $Pb(OAc)_4$. *D* gives a *diacetate*, m.p. 224—226° (corr.) after becoming opaque at about 90°, which is oxidised by CrO_3 in AcOH to androstane-3-ol-11 : 17-dione acetate. *C* yields a *diacetate*, m.p. 204—206°, which gives ill-defined compounds when oxidised. The following identities are established among the compounds isolated by Reichstein (R), Wintersteiner and Pfiffner (W) and Kendall *et al.* (K): substances *A* (R), *A* (W), and *D* (K); *C* (R), *D* (W), and *C* (K); *D* (R) and *G* (K); *Ea* (R), *Fa* (W), and *E* (K); andrenosterone (R) and ketone 4 (K); corticosterone (R) and compound *B* (K); dehydrocorticosterone (R) and compound *A* (K); substance *L* (R) and compound *G* (W); compound *M* (R) and *F* (K). The problem of the isolation of the active hormone is not completely solved since amorphous fractions are isolable from the gland which excel any of the cryst. materials in cortin activity. Either a more powerful substance is present or two components are required for the development of full activity, one of which may be only an activator. The possible mode of biosynthesis is discussed.

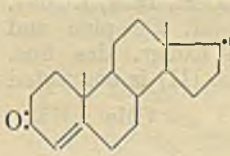
H. W.

Constituents of the adrenal gland. XII. Deoxycorticosterone (21-hydroxyprogesterone) from Δ^5-3-hydroxyætiocholenic acid. M. Steiger and T. Reichstein (Helv. Chim. Acta, 1937, **20**, 1164—1179).—Treatment of Δ^5-3-acetoxyætiocholenic acid with $SOCl_2$ in C_6H_6 yields the corresponding *chloride* (I), m.p. about 165° (decomp.) when rapidly heated, frequently accompanied by the *anhydride*, m.p. 331—332° (corr.; slight decomp.). CH_2N_2 and (I) in abs. Et_2O give Δ^5-21-*diazo*-3-*acetoxypregnen*-20-*one* [(II), R = CHN_2], m.p. about 148—150° (decomp.), which does not give a ppt. with digitonin (III) in 80% EtOH, hydrolysed by cold KOH–EtOH to Δ^5-21-*diazo*-3-*hydroxypregnen*-20-*one* (IV), m.p. 144° (corr.; decomp.), which gives an immediate ppt. with (III) in 80% EtOH. 2N-H_2SO_4 and (II) in dioxan yield Δ^5-21-*hydroxy*-3-*acetoxypregnen*-20-*one* [(II), R = CH_2·OH], m.p. 149—156° (corr.), hydrolysed by acid to Δ^5-21 : 3-*dihydroxypregnen*-20-*one*, m.p. (indef.) 139—159°. Treatment



(II).

of (II) in anhyd. Et_2O with HCl at 0° affords Δ^5-21-*chloro*-3-*acetoxypregnene*-20-*one* (V) [(II), R = CH_2Cl], m.p. 157—158° (corr.), whence the corresponding 3-OH-*derivative*, m.p. 162—164°. Both Cl-ketones reduced cold Ag_2O–NH_3 solution. Direct oxidation of (V) with CrO_3 in AcOH gives mainly Δ^4-21-*chloropregnene*-3 : 6 : 20-*trione*, m.p. 215—220° (corr.); if the double linking is protected by bromination previous to the oxidation, the reaction occurs in the desired sense but subsequent debromination with Zn or with KI also removes Cl from $C_{(21)}$ and progesterone results. AcOH converts (IV) into Δ^5-3-*hydroxy*-21-*acetoxypregnen*-20-*one*, m.p. 184—185° (corr.) [the corresponding *Bz* derivative has m.p. 171—173° (corr.)], brominated in $CHCl_3$ and then oxidised and debrominated to Δ^4-3-*keto*-21-*acetoxypregnen*-20-*one* (VI), m.p. 157—159° (corr.), $[\alpha]_D^{19}$ +177°±4° in abs. EtOH, hydrolysed to Δ^4-3-*keto*-21-*hydroxypregnen*-20-*one* (*deoxycorticosterone*), m.p. 141—142° (corr.), $[\alpha]_D^{22}$ +178°±3° in abs. EtOH, the simplest known compound with cortin activity.



H. W.

Oxidation–reduction potentials of hydroxynaphthaquinones in alkaline solutions.—See A. I, 620.

Kinetics of the production of anthraquinone compounds from benzoylbenzoic acid derivatives. R. Oda and K. Tamura (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1937, **32**, 263—273).—The rate of cyclisation of *o*-C_6H_4Bz·CO_2H, *o*-4′-toluyl-, *o*-4′-chlorobenzoyl-, *o*-α-naphthoyl-, and *o*-5 : 6 : 7 : 8-tetrahydro-2-naphthoyl-benzoic acid to anthraquinone and its derivatives, under the action of 95·6% H_2SO_4, is studied at varying temp.; velocity coeffs., and, for the first three reactions, energies of activation, are calc. It is assumed that addition of H_2SO_4 precedes condensation, and that the velocity of addition is significant. *o*-3′-Nitrobenzoylbenzoic acid does not condense. 1-*o*-Carboxyanilinoanthraquinone cyclises very rapidly [to the acridone]. E. W. W.

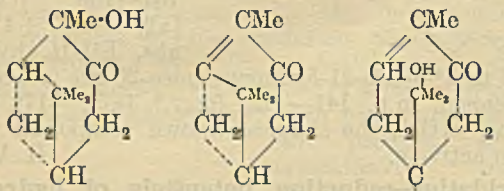
[Ring] conversion reaction in the reduction of menthones by Clemmensen's method. A. Auterinen (Suomen Kem., 1937, **10**, B, 22—23).—Menthone Et ether with Na dissolving in EtOH affords 3-hydroxy-5-ethoxy-1 : 1-dimethyl*cyclo*hexane, oxidised (CrO_3) to 3-*ethoxy*-5 : 5-*dimethyl*cyclo*hexanone*, b.p. 124—126°/32 mm. (*semicarbazone*, m.p. 188—188·5°). 1 : 1-Dimethyl*cyclo*hexane-3 : 5-diol (A., 1913, i, 607) with Ac_2O in a mixture of boiling EtOAc, $CHCl_3$, and C_6H_6 affords the Ac_1 (I), b.p. 148—150°/18 mm., and Ac_2 derivatives. The former with CrO_3 affords a substance which when distilled in air loses AcOH to give 5-keto-1 : 1-dimethyl-Δ^2-tetrahydrobenzene (II), and when distilled in vac. gives 3-*acetoxy*-5 : 5-*dimethyl*cyclo*hexanone*, b.p. 77—78°/0·044 mm. (I) affords the dinitrophenylhydrazone and semicarbazone of (II). Hydrolysis of (I) with HCl gives (II); with N-NaOH a *dimeride* (?), m.p. 97—99·5°, of (II) is formed. Prolonged action of conc. HCl at room temp. on (II) affords a small amount of an unidentified oil. (II) when reduced (Clemmensen)

affords a product from which the semicarbazones of 3 : 3-dimethyl*cyclo*hexanone and 2 : 4 : 4-trimethyl-*cyclo*pentanone (cf. A., 1935, 1239) are isolated.

J. L. D.

Electrochemical oxidation of pinene. F. Fichter and G. Schetty (Helv. Chim. Acta, 1937, **20**, 1304—1308).—Electro-oxidation at a PbO_2 anode of pinene emulsified by invadin *B* in aq. H_2SO_4 gives HCO_2H, terebic acid (I), and *p*-cymene. In EtOH–H_2SO_4 the products are dipentene, cineole, α-terpineol, $EtHSO_4$, (I), and *cis*-terpin. H. W.

New example of the transformation of a given active pinene into two compounds of inverse optical activity (carvones). M. Delépine (Bull. Soc. chim., 1937, [v], **4**, 1669—1673; cf. A., 1924, i, 1084, 1088).—The (—)-*keto-alcohol* (I) (cf. Delépine and Grandperrin, Compt. rend. 65e Congr. des Soc. savantes, 1932, 101) from *d*-pinene (II) is converted



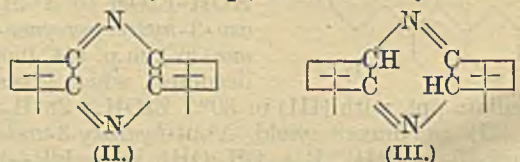
into its (+)-*semicarbazone*, which with $H_2C_2O_4$ in EtOH gives *d*-carvone (yielding *d*-carvoxime). The intermediates (III) and (IV) are suggested. *l*-Carvoxime is obtained from (II) in the usual way through *d*-limonene and its nitrosochloride.

E. W. W.

Thioborneol and *iso*thioborneol. Mercaptides of thioborneol. J. Haraszti (J. pr. Chem., 1937, [ii], **149**, 301—310).—Pure bornyl chloride and MgEtBr give Mg bornyl bromide, which with S gives thioborneol (I), m.p. 112·5—113°, with a little thiocamphor, m.p. 125—130° (oxime, m.p. 118—118·5°), and bornyl disulphide, m.p. 195° [reduced by Zn–HCl to (I)]. *iso*Bornyl chloride (modified prep.), however, gives camphane. Thus (I) is related to borneol; it gives *Pb*, m.p. 250—260° (decomp.), Hg^{II}, m.p. 175°, Cu^{I}, m.p. 120—125°, *Bi*, m.p. 172—175°, and *Au*, m.p. about 195—200° (decomp. 220—230°), salts and *salts*, $(C_{10}H_{17}S)_2BiI$, decomp. 140—150°, and $TlS{\cdot}C_{10}H_{17}{\cdot}C_{10}H_{17}{\cdot}SH$, m.p. 166°. R. S. C.

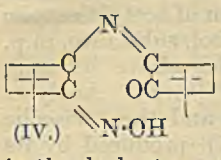
Action of primary aliphatic bases on camphorquinone. II. H. Rupe and A. T. di Vignano (Helv. Chim. Acta, 1937, **20**, 1078—1097; cf. A., 1934, 1224).—Camphorquinone (I) condenses very readily at the β-CO with primary aliphatic amines and under pressure and at >100° the main products are alkylaminocamphors (II) with small amounts of the corresponding *epi*camphor bases, the alkyl of the amine behaving as reducing agent; pyrazine compounds are also formed. At lower temp. and in open vessels alkylimino-bases of camphor are almost exclusively formed; these are readily hydrogenated to (II). Oxidation of camphor by SeO_2 in boiling Ac_2O gives (I) in 90% yield. (I) and NH_2Me in abs. EtOH at 112—115°/6—7 atm. give $CH_2(OEt)_2$, iso*dicamphenepyrazine*, *methylaminocamphor* (III), b.p. 109·5—110°/12 mm., which can be preserved only under N_2 in the dark, and *methylaminoepicamphor* (IV), b.p. 111·5—112°/11·5 mm., which resinifies less readily than (III) on exposure to air. (III) gives a *perchlorate*, m.p. 179—181°, a *nitrosoamine*, m.p. 73°, and an *oxime hydrochloride*, m.p. 234° (decomp.), whilst a *perchlorate*, decomp. 255—256° when very finely divided (the temp. depends greatly on the size of the crystals), a *nitrosoamine*, m.p. 71°, and an *oxime hydrochloride* are derived from (IV). Under similar conditions NH_2Et and (I) afford MeCHO and *ethylaminocamphor* (V), b.p. 116—117°/12 mm., m.p. 28° [*perchlorate*, m.p. 215—217° (slight decomp.)], apparently without production of the corresponding *epi*-compound. Me_2SO_4 and (V) readily give *methylethylaminocamphor*, b.p. 119—119·5°/12·5 mm. [*perchlorate*, m.p. 204—205° (decomp.)], identical with the product obtained by treating (III) with Et_2SO_4. *Methylethylaminoepicamphor* (*perchlorate*, m.p. 184—187°), has b.p. 122—124°/12·5 mm. Reduction (Ni in EtOH–H_2O) of (III) gives *methylaminoborneol*, b.p. 131—134°/12 mm. [*hydrochloride*, m.p. 315° (decomp.)], probably not sterically homogeneous. Reduction of (III) with Na and C_6H_6 affords a *methylaminoborneol*, m.p. 84—85° (*hydrochloride*, m.p. >300° after becoming discoloured at 250°) which contains 2 active H (Zerevitinov). Hydrogenation (Ni in H_2O–EtOH at room temp.) of (IV) gives *methylaminoepiborneol*, b.p. 134—135°/12 mm., m.p. 116° after softening at 106° (*hydrochloride*, slow decomp. <250°), in 95·5% yield. Treatment of (I) with NH_2Me in boiling abs. EtOH for 20 min. followed by preservation at room temp. for 24 hr. gives *methyliminocamphor*, b.p. 112—114°/11 mm., m.p. 84—85°, $[\alpha]^{20}$ +173·3° in C_6H_6; it is readily hydrogenated (Na in EtOH) to (III) with a very small proportion of (IV). Similar treatment of (I) with 33% NH_2Et in abs. EtOH yields *ethyliminocamphor*, m.p. 63—64°, $[\alpha]_D^{20}$ +176·3° in C_6H_6. Condensation of (I) with NH_3 occurs less readily than with NH_2Me and leads to α-aminocamphor, b.p. 120—122°/14 mm., which, according to the behaviour of its hydrochloride and oxime, is homogeneous. It gives dihydrodicamphenepyrazine, m.p. 114—115°. H. W.

Constitution and synthesis of *iso*dicamphenepyrazine. H. Rupe and A. T. di Vignano (Helv. Chim. Acta, 1937, **20**, 1097—1117).—The basic distillate of high b.p. from the condensation of camphorquinone (I) and NH_2Me at high temp. affords *iso*dicamphenepyrazine (II), m.p. 204·5—205°, $[\alpha]_D^{20}$ +13·23° in C_6H_6 [obtained by Einhorn and Jahn (A., 1903, i, 43) from aminocamphor and its hydrochloride], and iso*dihydrodicamphenepyrazine* (III), b.p. 197—198°/12·5 mm., m.p. 71—72°, $[\alpha]_D^{20}$ +387·63° in C_6H_6, +330·2° in $CHCl_3$. (II) gives a methiodide, decomp. 259°, *picrate*, m.p. 204—206°, and *aurichloride*, m.p. 254—255° (decomp.), converted by EtOH into



the "modified *salt*," decomp. 249—251°. (III) affords a *perchlorate*, decomp. 246·5°, *picrate*, decomp.

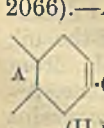
196·5° or 190° when finely divided, *hydriodide*, decomp. 231° after becoming discoloured at 208°, and *methiodide*, decomp. 245—246°, which gives (I) when heated and is transformed by Ag_2O into N-*methyl*-iso*dihydrodicamphenepyrazinium hydroxide*, m.p. 190—200° after softening at 100° (*picrate*, decomp. 179°).


(IV.)

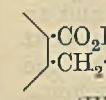
α- or β-2 : 3-Diaminocamphane with (I) with $ZnCl_2$ in AcOH gives (III) in better yield but throws no light on the constitution of the product. Aminocamphoroxime with (I) and cryst. NaOAc in EtOH in the dark at room temp. or, more rapidly, in boiling solution yields *oximinocamphyliminocamphor* (IV), m.p. 174—175° (decomp.) when finely divided, $[\alpha]_D^{20}$ −225·9° in C_6H_6, which is readily hydrolysed by acids and is hydrogenated (Ni) to (III), also obtained when the mixture of amino-camphor and -*epi*-camphor as obtained by its hydrolysis is preserved for several weeks. Oxidation of (III) readily yields (II) thus establishing the constitution of the latter. Hydrogenation (Ni or Pd at 80°/10 atm.) of (II) or (III) appears impossible but they are converted by Na and EtOH into iso*tetrahydrodicamphenepyrazine* (V), m.p. 113·5—114·5°, b.p. 202—204°/11 mm., $[\alpha]_D^{20}$ +80·60° in C_6H_6 [*perchlorate*, decomp. 231—233°; *hydriodide*, m.p. >310°; $(NO)_2$-*derivative*, m.p. 144—145° (decomp.)], which contains two active H (Zerevitinov). The following experiments were made in attempts to explain the production of dihydrodicamphenepyrazines by the action of (I) on alkylamines. Methylaminocamphor is unchanged when strongly heated. NH_3–EtOH and (I) at 100° give exclusively iminocamphor or, if action is greatly prolonged, a rosin-like mass from which a derivative of (III) could not be extracted. MeI in boiling MeOH transforms (V) into NN′-*dimethyl*iso*tetrahydrodicamphenepyrazine*, m.p. 86—87°, $[\alpha]_D^{20}$ +64·88° in C_6H_6 (*hydriodide*, decomp. 252—257°; *picrate*, decomp. 151—153°), which reduces acid or neutral $KMnO_4$ and immediately decolorises Br in $CHCl_3$; it passes at 270—290° into (II), unsaturated hydrocarbons, CO, H_2, CH_4, C_2H_6, and N_2. H. W.

Synthesis of thujane. P. C. Guha and S. Krishnamurthy (Current Sci., 1937, **6**, 56—57).—Et 1-methyl-3-*iso*propyl*cyclo*pentan-2-one-1-carboxylate is reduced (Na–Hg) to the corresponding *sec.* alcohol, b.p. 153—156°/11 mm. (*phenylurethane*, m.p. 144—145°), dehydrated (P_2O_5) to the *cyclo*-pentene compound, b.p. 114—115°/11 mm. This substance and CH_2N_2 give the *dicyclo*-0 : 1 : 3-hexane derivative, b.p. 130—132°/12 mm., hydrolysed (KOH) to the carboxylic acid, m.p. 93—94°, which is decarboxylated to thujane. F. R. S.

Cedrene. II. Methyl-oxidation of cedrene by selenious acid to primary cedrenol and to cedrenal. W. Treibs (Ber., 1937, **70**, [*B*], 2060—2066).—Artificial cedrene (I), obtained by short treatment of cedrol with 95% HCO_2H, is oxidised by SeO_2 in Ac_2O to iso*cedrenol* (II), b.p. 165°/20 mm., α_D −76·5°. (*H phthalate*, m.p. (indef.) 95°; *acetate*, b.p. 174°/20 mm.). Treatment of (II) with hot, 95% HCO_2H gives


(II.)

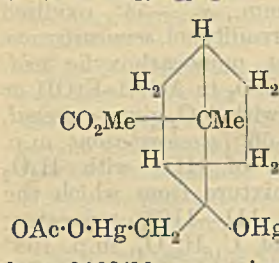
immediately an isomeric, saturated, probably tetracyclic *alcohol*, b.p. 160°/20 mm., α_D −58°, oxidised to an *aldehyde* which affords a readily sol. *semicarbazone* and thence to a poorly cryst. monocarboxylic *acid*. Farther oxidation of (II) by CrO_3 in AcOH–EtOH or more drastic oxidation of (I) with SeO_2 gives *cedrenal*, (III), b.p. 163°/20 mm., α_D −56° [*semicarbazone*, m.p. 248° (decomp.)]. Treatment of (III) with H_2O_2 and KOH–MeOH gives a mixture from which the *ester*, $C_{17}H_{30}O_4(OMe)_2$, m.p. 111—112°, separates; this is hydrolysed to the *acid*, $C_{16}H_{28}O_4$, m.p. 158° (decomp.), derived by addition of 1 H_2O and 1 MeOH to cedrenal oxide. Oxidation of (II) with CrO_3 (= 2O) in AcOH gives *cedrenecarboxylic acid*, m.p. 122° (*Me* ester, m.p. 167—169°/20 mm., α_D −71°), isomerised by Br in $CHCl_3$ to the *acid*, m.p. 149—150°. Oxidation of (II) with $KMnO_4$ in aq. $COMe_2$ yields *norcedrenedicarboxylic acid* (IV), b.p. 330°/atm. pressure, m.p. 209°, which is unusually stable towards chemical reagents. The *Me H* ester, m.p. 97—98° and *Me*$_2$ ester, b.p. 173°/20 mm., hydrolysed to an isomeric *Me H* ester, m.p. 124°, are described. H. W.


(IV.)

Terpene compounds. I. Synthetic study on the structure of azulene. N. N. Chatterjee (J. Indian Chem. Soc., 1937, **14**, 417—420; cf. Bardhan, A., 1935, 748).—Preliminary to attempting the synthesis of azulene, 3-*methyl*-1-iso*propylideneindene* (I), m.p. 49°, was synthesised as follows: Et Δ^1-tetrahydrobenzoate treated successively with Et sodiocyanoacetate and $CH_2Br{\cdot}CO_2Et$ gives *Et* 1-*carbethoxycyclohexane*-2-α-*cyanosuccinate*, b.p. 204—206°/4 mm., hydrolysed and esterified to the *Et* 1-*carbethoxy*-2-*succinate*, b.p. 177—185°/7 mm. This with Na yields *Et* (0 : 3 : 4-dicyclo)*nonan*-2-*one*-3 : 4-*dicarboxylate*, b.p. 188°/8 mm. (the Na derivative of which, with MeI, gives the *Et* 3-*methyl*-3 : 4-*dicarboxylate*, b.p. 174°/7 mm.), hydrolysed to the 4-*carboxylic acid*, m.p. 136° (*semicarbazone*, m.p. 220°). The *Et* ester, b.p. 143—144°/8 mm. (*semicarbazone*, m.p. 159°), of this with MgMeI gives 2-α-*hydroxymethyl*-4-α-*hydroxy*isopropyl-(0 : 3 : 4-dicyclo)*nonane*, b.p. 154°/4 mm., which yields (I) when heated with Se. A. Li.

Teresantalic and *iso*teresantalic acid. H. Steiger and H. Rupe (Helv. Chim. Acta, 1937, **20**, 1117—1146).—Conversion of Me teresantalate into its hydrobromide and removal of HBr by NH_2Ph followed by fractional distillation of the product gives Me *iso*teresantalate (I), b.p. 91·2°/10 mm., $[\alpha]_D^{20}$ −133·46°, hydrolysed to homogeneous *iso*teresantalic acid (II), m.p. 137°, b.p. 141—143°/16 mm., $[\alpha]_D^{20}$ −150·82° in C_6H_6. Examination of the more volatile ester fractions discloses the presence of esters other than those derived from teresantalic acid or (II). The residue from the distillation of crude (I) contains unstable esters which are hydrolysed to (II) and an acid of higher m.p., the Semmler–Bartlett lactone (III) identified by hydrolysis to *apo*borneolcarboxylic acid, and a viscous yellow liquid, b.p. 196—204°/10 mm., which is not homogeneous but is converted by HCl or HBr in Et_2O into *compounds*, $C_{17}H_{24}O_2NCl$

(IV) and $C_{17}H_{24}O_2NBr$, m.p. 194° and 203°, respectively. The corresponding *base* (V), m.p. 45°, gives an *Ac* derivative, m.p. 120°. Treatment of (IV) with boiling KOH–MeOH gives (V) and a *compound*, m.p. 134°. Similar treatment of the fraction b.p. 203°/10 mm. gives the compound $C_{16}H_{19}ON$, m.p. 85°, of Rupe and Tomi (A., 1917, i, 138) and an *acid*, $C_{16}H_{21}O_2N$, m.p. 168°. Treatment of somewhat impure (I) with $Hg(OAc)_2$ in AcOH–H_2O gives the *acetomercuri*-compound (VI), m.p. 214° (corresponding *chloromercuri*-derivative, $C_{11}H_{14}O_3Cl_2Hg_2$, incipient softening, 160°), converted by NaOH and Zn powder in boiling EtOH into homogeneous (II); the OH-*acid*, $C_{10}H_{16}O_3$, m.p. about 205°, and the Müller lactone, $C_{10}H_{14}O_2$, m.p. 103°, are also produced. With Zn and HCl (VI) yields (III) and the corresponding OH-acid, m.p. 192°. Similar treatment of Me teresantalate with $Hg(OAc)_2$ affords HgOAc, a compound, $C_{12}H_{18}O_5Hg$, m.p. 208—210°, probably an acetomercuri-compound of an *apo*borneolcarboxylic acid, and an oil, converted by Zn and KOH in boiling EtOH into a ketodihydroteresantalic acid, m.p. 270°, possibly 1-*cis*-*apo*camphorcarboxylic acid. Oxidation of (II) in alkaline solution by $KMnO_4$ gives a neutral *substance*, $C_{10}H_{14}O_3$, m.p. 220°, probably a lactone of *apo*camphene hydratecarboxylic acid, a *substance*, $C_8H_{14}O$, b.p. 67·5°/11 mm., and a *compound*, $C_{10}H_{12}O_4$, m.p. 203°; this gives a *salt*, $C_{10}H_{12}O_5Ag_2$, decomp. 175°, but is converted by CH_2N_2 in Et_2O into the ester, $C_{12}H_{18}O_5$, b.p. 153°/10 mm., m.p. 42°, so that its constitution is not established. Similar oxidation of teresantalic and gives a dicarboxylic *acid*, $C_{10}H_{12}O_2$, m.p. 248° [Me_2 ester, b.p. 135°/10 mm.; $(NH_4)_2$ salt, decomp. 208°], and an unidentified *substance*, $C_{10}H_{12}O_3$, m.p. 189°. Ozonisation followed by methylation of (II) gives an *ester*, b.p. 128·2°/12 mm., hydrolysed to an *acid*, $C_9H_{14}O_4$, m.p. 123—124°, and an *acid*, m.p. 157°. Oxidation of (II) with HNO_3 (*d* 1·48) gives (III) and an *acid*, $C_{10}H_{12}O_5$ or $C_8H_{10}O_4$, m.p. 150°. Hydration of (II) with H_2SO_4 yields (III), converted into *apo*borneolcarboxylic acid (Me ester, b.p. 124°/10 mm., m.p. 40—41°). Boiling H_2O converts (II) into santene and Asahina's acid. Hydrogenation (Ni in EtOH–H_2O at room temp.) of (I) gives *Me dihydro*-iso*teresantalate*, b.p. 90·5°/10 mm., $[\alpha]_D^{20}$ +8·02°, hydrolysed by KOH–MeOH to *dihydro*iso*teresantalic acid*, m.p. 120—121°, $[\alpha]_D^{20}$ +7·03°. Similar hydrogenation of Na *iso*teresantalate yields a *dihydro*iso-*teresantalic acid*, m.p. 106—107°, $[\alpha]_D^{20}$ −25·01°. whereas in presence of Pd a third *isomeride*, m.p, 118°, $[\alpha]_D^{20}$ +23·47° in C_6H_6, is produced. H. W.



(VI.)

Polyterpenes and polyterpenoids. CXVI. Oxidation of acetyloleanolic acid by chromium trioxide with opening of the double linking. L. Ruzicka and S. L. Cohen (Helv. Chim. Acta, 1937, **20**, 1192—1200).—Repetition of the work of Schicke and Wedekind (A., 1933, 612) and consideration of the results in the light of that of Ruzicka and Hofmann (A., 1936, 477) lead to the conclusion that oleanolic acid does not give an oxidation product, $C_{25}H_{38}O_6$, containing 2 OH and 2 CO_2H. The assumption of such a product was conducive to the previous constitution with the double linking and CO_2H in ring E and its non-existence allows the formula of Ruzicka *et al.* (A., 1937, II, 202). Oxidation of acetyloleanolic acid by CrO_3 at 80° gives an alkali-sol. substance, m.p. about 235° (corr.), which solidifies above its m.p. and then melts again at 303—304° (corr.). Analyses of this "acetylviscolic acid" (I) and the "viscolic acid" (II), m.p. about 290° (corr.), produced by its hydrolysis agree with the formula of Wedekind but the figures differ little from those required for (II) or the lactonedicarboxylic acid (III), $C_{30}H_{46}O_2$, of Ruzicka and the identity of (II) with (III) is shown by its transformation into derivatives of (III) or of the corresponding *iso*-series. (I) is transformed by boiling Ac_2O into the anhydride, $C_{32}H_{46}O_7$, m.p. 306° (corr.), identical with Ruzicka's compound and obtained also from (II). Ac_2O and (II) in C_5H_5N yield (I). Treatment of (II) with CH_2N_2 and then with boiling Ac_2O gives an acetyl-lactone Me_2 ester, m.p. 186—187° (corr.), closely related to the product, m.p. 203—204° (corr.), of Ruzicka and, like it, hydrolysed to the Me H *iso*lactonedicarboxylate, m.p. 300—304°. H. W.

Polyterpenes and polyterpenoids. CXVIII. Catalytic hydrogenation of the αβ-unsaturated keto-group in glycyrrhetic acid and in keto-α-amyrin. L. Ruzicka, H. Leuenberger, and H. Schellenberg (Helv. Chim. Acta, 1937, **20**, 1271—1279).—Of the 4 O of glycyrrhetic acid (I) two are present in CO_2H and one in OH. The absorption spectrum suggests that the fourth O is present in an αβ-unsaturated keto-group as in ketoacetyloleanolic acid. This view is confirmed by hydrogenation (PtO_2 in cold AcOH) of Me glycyrrhetate, which gives *Me deoxyglycyrrhetate* (II), m.p. 248° (corr.) after softening, $[\alpha]_D$ +108° in $CHCl_3$. This is transformed by boiling Ac_2O into *Me acetyldeoxyglycyrrhetate*, m.p. 266—267° (corr.), $[\alpha]_D$ +120° in $CHCl_3$, also obtained by hydrogenation of Me acetylglycyrrhetate. (I) is hydrogenated similarly to *deoxyglycyrrhetic acid*, m.p. 330° (corr.), $[\alpha]_D$ +148° in $CHCl_3$, transformed by CH_2N_2 into (II). In all cases 2 H_2 is required and CO is transformed into CH_2. All the compounds give a pronounced yellow colour with $C(NO_2)_4$ in $CHCl_3$. Hydrogenation of keto-α-amyrin gives α-amyrin as main product apparently without admixture with the β-isomeride. α-Amyrin acetate is similarly obtained from keto-α-amyrin acetate. H. W.

Resins of native [German] conifers, their constituents and changes during the working of wood. H. Wienhaus [with, in parts, H. Ritter, W. Sandermann, H. Lambrecht, H. Engelhardt, H. H. Müller, R. Eck, K. Mucke, and E. Engelmann] (Papier-Fabr., 1937, **35**, 385—392).—A review. The following appears new. No experimental details are given. The most volatile part (20%) of the oil, *d* 1·332, $[\alpha]_D$ −53·8° in Et_2O, −37° in C_6H_6, from *Pinus sylvestris*, L., contains *d*-α- and β-pinene, Δ^3-carene, camphene, and limonene; the oil also contains cadinene, cadalene, alcohols, $C_{15}H_{24}O$ and $C_{15}H_{26}O$, and a *hydrocarbon*, $C_{12}H_{12}$, m.p. 83° (*quinone*, m.p.

142°). The resin acid (I), m.p. about 142°, $[\alpha]_D$ −112° (A., 1936, 1385), isomerises to abietic acid (II) when repeatedly crystallised from MeOH; its α rapidly becomes positive in 0·01N-HCl–Et_2O and then slowly slightly negative. Irradiation (ultra-violet) also gives an isomeride, $[\alpha]_D$ +30°; it contains some *d*-pimaric acid, since hydrogenation gives tetrahydropimaric acid as well as a *H_2-acid*, m.p. about 185°. Dehydrogenation by Pd–C gives about 80% of retene. The Me ester gives a mono-ozonide, $C_{21}H_{32}O_5$; mild treatment with $KMnO_4$ gives an amorphous *acid* (*K* salt), the *Me* ester, $(OH)_2C_{20}H_{29}\cdot CO_2Me$, m.p. 178°, of which gives unsatisfactory products when isomerised or oxidised. Fairly fresh resin from *Picea excelsa*, Lk., contains ≯18·5% of steam-volatile material, including *l*-α- and -β-pinene, a little Δ^3-carene, limonene, verbenone, verbenol, and a tetra-unsaturated diterpene, $C_{20}H_{32}$, and yields *p*-OH·C_6H_4·CH:CH·CO_2H and an acid, m.p. about 150°, $[\alpha]_D$ −102·4°. With 0·01N-HCl the latter acid gives (II) by way of an *isomeride*, m.p. 152°, $[\alpha]_D$ +41·7°; it is not homogeneous, since its cryst. *Na* salt regenerates an *acid*, $[\alpha]_D$ −146·7°; it gives a *H_2-acid*, m.p. 244° (*Me* ester, m.p. 184°) and, when oxidised, $Pr^{\beta}CO_2H$; when distilled, it yields an *acid*, m.p. 190°, $[\alpha]_D$ −42°, oxidised to an *acid*, $C_{20}H_{30}O_2(OH)_4$, m.p. 246°, also obtained from (II). The neutral part of a resin from *Picea excelsa* from North Sweden contained a dextrorotatory, autoxidisable, monocyclic *diterpene*, $C_{20}H_{32}$ (*H_8*-compound), and a doubly unsaturated, tert. *alcohol*, $C_{15}H_{24}O$. The turpentine from *Abies pectinata*, D.C., contains α- and β-pinene, camphene, sobrerol, $\Delta^{8'}$-n-*pentadecadienal* (hydrogenated to *n*-$C_{14}H_{29}\cdot OH$). 17% of a *substance*, $C_{17}H_{30}O_2$, m.p. 62° (contains one ethylenic linking and readily loses $1H_2O$), and 37—46% of acids, which crystallise with difficulty and contain *l*-pimaric acid. The turpentine from *Larix europœa*, D.C., contains 14% of volatile material (mostly α-pinene), oxygenated, unsaturated diterpenes, and acids which yield (II). With $NaHSO_3$, pinene suffers dehydrogenation and ring-fission, yielding cymene, $C_{10}H_8$ derivatives, borneol, azulenes, etc. Tsugalactone and pinoresinol arise by polymerisation of coniferyl alcohol. R. S. C.

Lignin. I. T. Lieser and V. Schwind (Annalen, 1937, **532**, 104—115).—Mixtures of AcOH and Ac_2O with relatively much H_2SO_4 dissolve pine wood almost completely. With less mineral acid acetolysis is much slower and is accompanied by maxima and minima indicating the production of substances which are first sol. and then insol. in alkali. Attempts to use partial acetolysis for the isolation of the components of the cell membrane by continuously withdrawing the acetolysate, diluting it with H_2O, and subjecting it to dialysis proceed non-uniformly chiefly owing to the formation of simple substances such as CH_2O, MeOH, and AcOH. The presence of OMe in all fractions is characteristic. Evidence of the existence of a compound of cellulose (I) and lignin (II) is obtained; this can be dissolved in fuming HCl at low temp. but decomposes into its components at higher temp. The introduction of Cu and treatment with CS_2 are used for the characterisation of OH in (II). Model experiments show that only primary and *sec.* OH participate in the xanthate reaction; these behave similarly towards $Cu(OH)_2$–NH_3, which also reacts with vicinal phenolic hydroxyls. With CS_2 and NaOH esterification is incomplete but becomes maximal when strong org. bases, *e.g.*, $NEt_4\cdot OH$, are used. Under these conditions the results given by the two methods are identical. Comparison of the results afforded by these methods with those based on acetylation and methylation leads to the conclusion that "$Cu(OH)_2$-NH_3-lignin" contains 6·1% of *sec.* and 4·2% of *tert.* OH. Use of the "$Cu(OH)_2$ method" for the determination of OH in (II) of the cell membrane and in its components [mannan, (I), (II), and xylan] indicates that an appreciable alteration of the OH content of (I) does not occur during the isolation process. H. W.

Constituents of pyrethrum flowers. VII. Behaviour of the pyrethrins on hydrogenation. H. L. Haller and F. B. LaForge. VIII. Presence of a new ester of pyrethrolone. F. B. LaForge and H. L. Haller (J. Org. Chem., 1937, **2**, 49—55, 56—61; cf. A., 1936, 1381).—VII. PtO_2-hydrogenation of an 80% pyrethrin-II concentrate in EtOH is rapid until 4 H are absorbed and then slow, finally stopping by inactivation of the catalyst; removal of the acids formed and addition of fresh catalyst leads to further hydrogenation of the neutral fraction. The products are chrysanthemumdicarboxylic acid Me_1 ester, tetra- and less hexa-hydropyrethrone (separated as semicarbazones, partly by crystallising and partly by dissolving the H_4-semicarbazone in dil. HCl); the amount of H ester is about 20% > that of the pyrethrones. A 55% pyrethrin-I concentrate hydrogenates similarly to chrysanthemumcarboxylic acid, tetra- and hexa-hydropyrethrone (more of the latter than in the former case); the amount of acid exceeds that of the pyrethrones by 50%. The amount of acid recovered approx. corresponds with that indicated by the Seil method. Hydrogenation may be a method of analysis.

VIII. Pyrethrin-I semicarbazone cannot be obtained pure and is unstable; hydrolysis gives pyrethrolone, chrysanthemum-carboxylic (I) and -dicarboxylic acid, and 7—8% of an *acid* (II), m.p. 41°, b.p. 175—185°/0·7 mm., [α] 0 (p-*phenylphenacyl*, m.p. 107°, and *Me* ester, b.p. 155°/1 mm.); analysis of the esters indicates $C_{16}H_{30}O_2$ as formula of (II), but titration indicates a mol. wt. of 290. Hydrogenation of (II) gives a *H_2-acid*, m.p. 53°. Denigès' reagent gives with (II) a colour similar to that with (I); the Ba salt is insol. (II) may be a mixture. R. S. C.

Plants used by the Indians against snake venom and malaria. E. C. Deger (Arch. Pharm., 1937, **275**, 496—503).—"Chalcupa," *Rauwolfia heterophylla*, contains dodecanedicarboxylic acid, glucosides, saponins, small amounts of tannins, a *Ca* salt, *chalcuparesene*, $C_{12}H_{22}O_4$, m.p. 165° (*NO_2*-derivative), *chalcupine*-A, $C_{14}H_{21}O_{12}N_3$, m.p. 170°, and *chalcupasulphine*, $C_{72}H_{129}O_{71}N_{12}S$ (an additive compound of *chalcupine*-B, $C_{15}H_{24}O_{11}N_6$, with, probably, a purine). Inorg. constituents of the plant are detailed; they include much Cl and SO_4, but little Na. Injections and infusions of Chalcupa are curative against snake-bite. R. S. C.

Saponins. XII. Sapogenin of *Gleditschia horrida*, Makino. S. KUWADA (J. Pharm. Soc. Japan, 1935, **55**, 1258—1264).—The *sapogenin*, $C_{31(30)}H_{50(48)}O_4$, m.p. 299—300° (decomp.), $[\alpha]_D^{20}$ +32·51° in $CHCl_3$, forms a *Me*$_1$ *ether*, m.p. 230·5°, and a *diacetate*, m.p. 219°. CH. ABS. (*r*)

Anthrone derived from barbaloin and *iso*barbaloin. J. H. GARDNER and L. JOSEPH (J. Amer. Pharm. Assoc., 1937, **26**, 794—796).—Aloin was fractionally crystallised from MeOH and the fractions were hydrolysed with aq. borax. The products were purified, reduced with $SnCl_2$–Sn–HCl, and acetylated. In all cases, the final product was chrysophanic acid-9-anthranol triacetate. Hence both barbaloin and *iso*barbaloin yield aloe-emodin-9-anthrone on hydrolysis (cf. McDonnell and Gardner, A., 1934, 774). F. O. H.

Pechmann's dye. Mechanism of the formation of products obtained by the action of alkali. P. CHOVIN (Compt. rend., 1937, **205**, 565—567).—The pure isomeride (I) of Pechmann's dye (II) is yellow. The action of EtOH–KOH on (I), (II), the yellow acid + $2H_2O$ (III) of Kugel (A., 1898, i, 198) and Bogert and Ritter (A., 1925, i, 255), and the yellow acid + $1H_2O$ (IV) of Dufraisse and Chovin (A., 1934, 1108) affords a red-violet salt + $2H_2O$ (V), which when acidified gives the corresponding acid which loses $1H_2O$ to form (IV). Brief interaction of acid with (V) affords (III) but prolonged interaction affords a colourless dihydrated acid probably identical with that obtained by Bogert and Ritter (A., 1925, i, 255). (V) results from the alkaline hydrolysis of both lactone rings. The restitution of one lactone ring gives (IV); when both lactone rings are reformed simultaneously (I) is formed; when they close successively, (II) is formed. J. L. D.

Chasmanthin. F. WESSELY and K. SCHÖNOL [with, in part, A. MÜNSTER and W. ISEMANN] (Monatsh., 1937, **71**, 10—26; cf. Feist, A., 1935, 864).—Chasmanthin (I) (improved prep. from *Colombo* root), $C_{20}H_{22}O_7$, m.p. 246°, contains one lactone grouping, and with NaOH gives *chasmanthin* A (II), m.p. 260°, $[\alpha]_D$ +18·47° in C_5H_5N, and *chasmanthin* B (III), m.p. 170—175° (decomp.), $[\alpha]_D$ +24·86° in C_5H_5N, both isomeric with (I). Acetylation of (I) with Ac_2O affords *acetylchasmanthin* I (IV), m.p. 290° (decomp.), hydrolysed (NaOH) to (III) and a little (II), whilst acetylation with Ac_2O–NaOAc yields *acetylchasmanthin* II (V), m.p. 272°, $[\alpha]_D$ +30·06° to +29·39° in C_5H_5N. Acetylation (NaOAc–Ac_2O or Ac_2O alone) of (II) or (III) affords (V), which does not depress the m.p. of *acetylpalmarin* (VI), m.p. 272°, $[\alpha]_D$ +12·65° in C_5H_5N (from palmarin and Ac_2O or NaOAc-Ac_2O). Methylation (Me_2SO_4–NaOH–EtOH) of (II) and (III) gives *methylchasmanthin* A, m.p. 260°, $[\alpha]_D$ +44·46° in C_5H_5N, and *methylchasmanthin* B (VII), m.p. 290°, $[\alpha]_D$ +44·32° in C_5H_5N, respectively, whilst (I), similarly treated, yields non-homogeneous products. Hydrogenation (Pd–H_2) of (I) gives hydrochasmanthic acid (VIII), m.p. 259°, methylated (Me_2SO_4–NaOH) to a Me ether, m.p. 195°, and esterified (CH_2N_2) to a Me ester, m.p. 180°, $[\alpha]_D$ −11·23° in C_5H_5N (cf. Feist, *loc. cit.*). Similar hydrogenation of (IV) affords an *acid*, which on hydrolysis gives (VIII), whilst (V) yields *acetylhydropalmaric acid*, m.p. 271°, $[\alpha]_D$ +39° to +37° in C_5H_5N, also obtained by hydrogenation of (VI). On hydrogenation (II) and (III) give hydropalmaric acid, whilst (VII) yields *hydromethylchasmanthic acid*, m.p. 252°, $[\alpha]_D$ +56° in C_5H_5N. J. D. R.

Clerodin, m.p. 161—162°.—See A., III, 287.

Arjunetin, $C_{11}H_{18}O_4$,H_2O, m.p. 215°, and an isomeride, m.p. 165°.—See A., III, 331.

Shonanic acid derivatives.—See A., III, 331.

Pseudoauxin and lumiauxin.—See A., III, 286.

Synthesis of benzfuran-2-carboxylic acid and -2-acetic acid. V. TITOFF, H. MÜLLER, and T. REICHSTEIN (Helv. Chim. Acta, 1937, **20**, 883—892).—Isatin is converted into coumarandione, which is condensed with $CH_2Br{\cdot}CO_2Et$ and NaOEt and then hydrolysed to *o-oxalophenoxyacetic acid* (I), $CO_2H{\cdot}CO{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}CO_2H$, m.p. 198—200° (corr.) (*Me*$_2$ ester, m.p. 76—78°). Attempted cyclisation of the acid with Ac_2O–H_2SO_4 yields *o*-$CO_2H{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}CO_2H$ and CO whilst the action of NaOH at 100° or 200° does not give the desired result. The ester is cyclised by Na in EtOH and then hydrolysed to *benzfuran*-1 : 2-*dicarboxylic acid* (II), m.p. 259—260° (decomp.), partly decarboxylated at 270° to *benzfuran*-2-*carboxylic acid* (III), m.p. 162° (decomp.), also obtained with (I) by the action of Ac_2O and NaOAc on (I) at 170—180°. Treatment of (III) with Cu powder in quinoline at 220—270° gives coumarone. $SOCl_2$ transforms (III) into *benzfuran*-2-*carboxyl chloride* (IV), b.p. about 122°/12 mm., m.p. 65°, converted by anhyd. HCN and C_5H_5N in Et_2O into the corresponding *cyanide*, m.p. 142° (corr.), which is hydrolysed by HCl–AcOH to *benzfuran*-2-*glyoxylamide*, m.p. 202—204° (corr.); this is transformed by 2N-NaOH into *benzfuran*-2-*glyoxylic acid* (V), m.p. 125—126° [*phenylhydrazone*, m.p. 194—196° (corr.)]. With boiling NH_2Ph followed by HCl (V) yields a nitrogenous *compound*, m.p. 116°, in place of the desired aldehyde. (IV) is transformed by CH_2N_2 in Et_2O into 2-*diazoacetylbenzfuran* (V), m.p. about 118° (decomp.), converted by Ag_2O–NH_3 into *benzfuran*-2-*acetamide*, m.p. 190—191°, whence *benzfuran*-2-*acetic acid* (VI), m.p. 89—90°. Alternatively (V) is transformed by Ag_2O–EtOH into *Et benzfuran*-2-*acetate*, b.p. 140—150°/12 mm., which is hydrolysed to (VI). The influence of (VI) on the growth of plants does not exceed that of benzfuran-1-acetic acid. H. W.

Fission of the coumarone nucleus. T. REICHSTEIN and J. BAUD (Helv. Chim. Acta, 1937, **20**, 892—894).—2-Bromobenzfuran reacts with difficulty with Mg, better with Mg–Cu alloy. The product is converted by CO_2 into benzfuran-2-carboxylic acid and mainly into *o-acetylenylphenol*, b.p. about 98°/12 mm. [*p-nitrobenzoate*, m.p. 107—108° (decomp.)]. H. W.

Heterocyclic compounds. IV. Coumarins from resacetophenone and ethyl acetoacetate and synthesis of coumarino-γ-pyrones. R. D. DESAI and S. A. HAMID (Proc. Indian Acad. Sci., 1937, **6**, A, 185—190, and Current Sci., 1937, **6**, 56).—Resacetophenone, $CH_2Ac{\cdot}CO_2Et$, and $POCl_3$ give

7-hydroxy-6-acetyl-4-methylcoumarin (I) (50% yield) [Ac derivative, m.p. 180° (lit. 172°); *semicarbazone*, m.p. 320°], which is brominated to the 3-*Br*-compound, m.p. 216° (*Ac* derivative, m.p. 195°), hydrolysed (Na_2CO_3) to 6-*hydroxy*-5-*acetyl*-3-*methylcoumarilic acid*, m.p. 260° (decomp.), and 6-*hydroxy*-5-*acetyl*-3-*methylcoumarone*, m.p. 138° [*Ac* derivative, m.p. 118°; *Me ether*, m.p. 94°; *semicarbazone*, m.p. 315° (decomp.)]. 7-Methoxy-6-acetyl-4-methylcoumarin is brominated to the *Br*-, m.p. 165°, and Br_2-derivatives, m.p. 207°. (I) and Ac_2O–NaOAc give 3′-*acetyldimethyl*-4 : 2′-*coumarino*-(7 : 6)-*γ*-*pyrone*, m.p. 245°, and 7-hydroxy-8-acetyl-4-methylcoumarin similarly yields 3′-*acetyl*-4 : 2′-*dimethylcoumarino*-(7 : 8)-*γ*-*pyrone*, m.p. 260°, along with substances of m.p. 320° and 300°. F. R. S.

Condensation of aldehydes with malonic acid in the presence of organic bases. IX. Condensation of β-hydroxynaphthaldehyde (2-hydroxy-1-naphthaldehyde). K. C. Pandya and T. A. Vahidy (Proc. Indian Acad. Sci., 1937, **6**, A, 181—184).—β-Hydroxynaphthaldehyde and $CH_2(CO_2H)_2$ condense (preferably in presence of a base) to give 5 : 6-benzocoumarin-3-carboxylic acid in good yield. F. R. S.

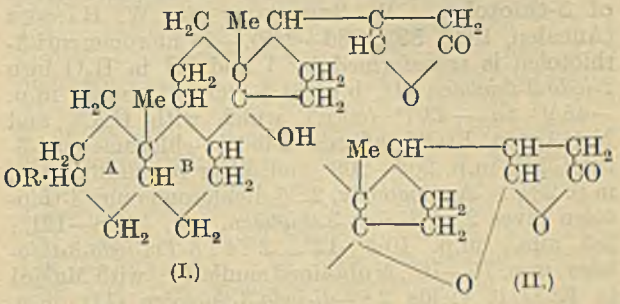
Aluminium chloride, a new reagent for the condensation of β-ketonic esters with phenols. S. M. Sethna, N. M. Shah, and R. C. Shah (Current Sci., 1937, **6**, 93—94).—PhOH and $CH_2Ac{\cdot}CO_2Et$ with $AlCl_3$ in Et_2O or $PhNO_2$ give 4-methylcoumarin in 30—40% yield. Similarly *o*-$OH{\cdot}C_6H_4{\cdot}COMe$ and *o*-$OH{\cdot}C_6H_4{\cdot}CO_2Me$ give Me 5-hydroxy-6-acetyl-, m.p. 165° (also prepared by Fries transformation of 5-acetoxy-), and 5-hydroxy-6-carbomethoxy-, m.p. 185—186°, decarboxylated to 5-hydroxy-4-methylcoumarin (cf. Limaye and Kelkar, A., 1937, II, 254). Condensation with H_2SO_4 yields the 7-OH-compounds (cf. Agarwal and Dutt, *ibid.*, 299). F. R. G.

Synthesis of flavonols. Oxidation of flavindogenides. J. Algar and (Miss) I. P. Carey (Proc. Roy. Irish Acad., **44**, B, 37—43).—3-Benzylideneflavanone is oxidised ($KMnO_4$–H_2SO_4) to 3-*hydroxy*-3-*benzoylflavanone* (I), m.p. 164—165° (*monoxime*, m.p. 225°), hydrolysed to flavanol and BzOH. With cold Ac_2O (I) gives the *monoacetate*, m.p. 179—180°, but with hot Ac_2O–NaOAc affords a *substance*, $C_{22}H_{16}O_4$, m.p. 135°, hydrolysed to BzOH, flavanol, and other substances. A similar series of reactions yields 3-*hydroxy*-2-*anisoylflavanone*, m.p. 153—154° (*monoacetate*, m.p. 157—158°), forming with Ac_2O–NaOAc a *substance*, m.p. 115°; 3-*hydroxy*-3-(3′ : 4′-*methylenedioxybenzoyl*)*flavanone*, m.p. 194—195° (*monoacetate*, m.p. 200—201°), with Ac_2O–NaOAc giving a *substance*, m.p. 148—149°; and 3-*hydroxy*-3-*benzoyl*-3′ : 4′-*methylenedioxyflavanone*, m.p. 196°. F. R. S.

Hydroxydiphenylene oxides.—See B., 1937, 1177.

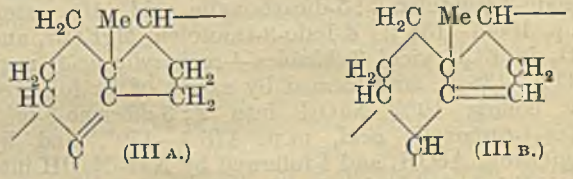
Photolytic production of formaldehyde in the eosin group. E. Baur and K. Gloor (Helv. Chim. Acta, 1937, **20**, 970—974; cf. A., 1937, II, 28, 318).—Me and Et esters of eosin and Et esters of rhodamines give CH_2O in the Baur–Fricker experiment. Non-esterified members of the eosin group do not give this effect. H. W.

Constitution of cerberin. T. Matsubara (Bull. Chem. Soc. Japan, 1937, **12**, 436—441).—Cerberin, new formula, $C_{29}H_{44}O_8$, anhyd. and $+0{\cdot}5H_2O$, m.p. 191—193°, $[\alpha]_D^{10{\cdot}5}$ −77·9° in $CHCl_3$, from the seed-kernels of *Cerbera Odollam*, Gaertner, is shown to be (I) (R = $C_6H_{11}O_4$; R *cis* to the Me on $C_{(10)}$; rings A and B *cis*) by the following reactions. It is a heart poison. It neutralises hot, but not cold, alkali, gives Legal's and Baljet's reactions, yields *dihydrocerberin*, $+0{\cdot}5H_2O$, m.p. 185—186°, and is thus a



(I.) (II.)

βγ-unsaturated lactone. It yields iso*cerberin* (II), m.p. 252—253°, $[\alpha]_D^{20}$ −73·8° in $CHCl_3$, which proves the presence of OH on $C_{(14)}$. When heated for a long time in 5% H_2SO_4–EtOH, it gives a methylpentose, *cerberose* (*osazone*, m.p. 121—122° or, dried at 100°/30 mm., 141—142°, $[\alpha]_D^{21}$ +62·5° in $CHCl_3$), and a mixture of *cerberigenin* [(I), R = H] (not isolated) and *anhydrocerberigenin* (III A or B), m.p. 220—222°, $[\alpha]_D^{21}$ +46·8°



(III A.) (III B.)

in $CHCl_3$ (formation of a *digitonide* fixes the position of the OH on $C_{(3)}$; *acetate*, m.p. 175—176°, $[\alpha]_D^{20}$ +58° in $CHCl_3$). With acid cerberigenin loses H_2O to give (III). Hydrogenation of (III) gives *tetrahydroanhydrocerberigenin*, m.p. 155—156°, oxidised by CrO_3 to *tetrahydroanhydrocerberigenone*, m.p. 181—182° (*oxime*, m.p. 210—212°). CrO_3 oxidises (III) to *anhydrocerberigenone*, m.p. 195—196°, $[\alpha]_D^{20}$ +74·4° in $CHCl_3$ (*oxime*, m.p. 221—223°). R. S. C.

Action of formaldehyde on ethyl pyromucate. D. Dinelli and G. B. Marini (Gazzetta, 1937, **67**, 417—424; cf. A., 1937, II, 429).—Et pyromucate (I) and paraformaldehyde (II) in H_2SO_4 (*d* 1·84) give a resinous product containing the 5 : 5′-*dicarbethoxy*-derivative, m.p. 192° [also obtained from dicarbethoxydifurylmethane and (II)], hydrolysed to the 5 : 5′-*dicarboxy*-derivative (III), no m.p. <280°, of 3 : 3′(or 4 : 4′)-*dihydroxymethyl*-2 : 2′-*difurylmethane internal ether*, m.p. 128° [from (III)], hydrogenated (PtO_2–AcOH) to an H_8-derivative, b.p. 150°/4 mm. The 5 : 5′-*dicarbethoxy*-derivative, m.p. 98°, hydrolysed to the 5 : 5′-*dicarboxy*-derivative, m.p. 252°, of αα-3 : 3′(or 4 : 4′)-*dihydroxymethyl*-2 : 2′-*difurylethane*, b.p. 133°/11 mm., is obtained from dicarbethoxy-

difurylethane (*loc. cit.*) and (II), or from (I) and $(MeCHO)_3$, followed by (II). E. W. W.

Thiophen series. XXXVI. 2-Phenylthiophen-5-carboxylic acid piperidide, a pepper-like substance of the thiophen series. W. Steinkopf and R. Gording (Biochem. Z., 1937, **292**, 368—370; cf. A., 1937, II, 163).—5-Iodo-2-phenylthiophen reacts with Mg in presence of EtBr and Et_2O. The solution with CO_2 etc. affords *2-phenylthiophen-5-carboxylic acid*, m.p. 184—185° (*acid chloride*, m.p. 80°; *piperidide*, m.p. 103—104°). F. O. H.

Thiophen series. XXXVII. Iodo-derivatives of 3-thiotolen. W. Steinkopf and W. Hanske (Annalen, 1937, **532**, 236—249).—2-Chloromercuri-3-thiotolen is transformed by I and KI in H_2O into *2-iodo-3-thiotolen* (I), b.p. 84·5—85·8°/11 mm., m.p. −45·9° to −43·7° (corr.), which with $HgCl_2$ and NaOAc in EtOH affords 2-iodo-5-chloromercuri-3-thiotolen, m.p. 208—209° and, after re-solidification, m.p. 284°. Analogously, 2 : 5-dichloromercuri-3-thiotolen gives 2 : 5-*di-iodo-3-thiotolen*, b.p. 120·8—121°/2·5 mm., m.p. 10·5—12°. 2 : 4 : 5-*Tri-iodo-3-thiotolen*, m.p. 75—76°, is obtained similarly; with MgMeI in Et_2O it yields 2 : 4-*di-iodo-3-thiotolen* (II), m.p. 56·5—57·5°, and 4-*iodo-3-thiotolen*, b.p. 88°/12 mm., m.p. −25° to −24·5° (corr.) [4-iodo-2 : 5-dichloromercuri-, m.p. 297° (decomp.), and -2 : 5-*diacetoxymercuri-*, m.p. 235·5° (decomp.), -3-thiotolen]. Treatment of the solution of it and MgEtBr in Et_2O with CO_2 at 0° leads to *4-iodo-3-thiotolen-2-carboxylic acid*, m.p. 208—209° (*K* salt) (whence 4 : 5-dibromo-3-thiotolen-2-carboxylic acid, m.p. 225·5—226·5°), and 4-iodo-3-thiotolen-2 : 5-dicarboxylic acid (Me_2 ester, m.p. 156·5—158°). 4-Iodo-3-thiotolen, MgEtBr, and CO_2 in Et_2O yield *3-thiotolen-4-carboxylic acid*, m.p. 136·5—138·5°, transformed by excess of Br followed by boiling 10% NaOH into 2 : 5-*dibromo-3-thiotolen-4-carboxylic acid*, m.p. 178·5—179°, and by $Hg(OAc)_2$, AcOH, and I followed by NaI–NaOH into 2 : 5-*di-iodo-3-thiotolen-4-carboxylic acid*, m.p. 181—183° (*K* salt). The successive action of Mg and CO_2 on (I) affords 3-thiotolen-2-carboxylic acid, m.p. 143—145°, the *Me* ester, b.p. 116—117·5°, of which is converted into 4 : 5-*di-iodo-3-thiotolen-2-carboxylic acid* (III), m.p. 264·5° (corr.) (*Me* ester, m.p. 157—158°), and 5-*iodo-3-thiotolen-2-carboxylic acid*, m.p. 178—179·5° (*Me* ester, m.p. 84—86°). 4 : 5-*Dibromo-3-thiotolen-2-carboxylic acid*, m.p. 228—229·5°, and its *Me* ester, m.p. 102—103°, are described. Treatment of (III) with $Hg(OAc)_2$ in boiling AcOH and of the product with 10% NaCl followed by 10% HCl gives 4 : 5-*di-iodo-3-thiotolen*, b.p. 98·5°/0·5 mm., m.p. 15·7—17·2°, whence 2 : 3 : 2′ : 3′-*tetraiodo*-4 : 4′-*dimethyl*-5 : 5′-*mercuridithienyl*, $C_{10}H_6I_4S_2Hg$, m.p. 290° (decomp.), *4-iodo-3-thiotolen-5-carboxylic acid*, m.p. 215—218° [*Me* ester (IV), m.p. 75·5—76·5°], and *Me* 2-*bromo*-4-*iodo-3-thiotolen-5-carboxylate*, m.p. 75·5—76·5°. $Hg(OAc)_2$ and I in AcOH transform (IV) into *Me* 2 : 4-*di-iodo-3-thiotolen-5-carboxylate*, m.p. 112—112·5° [corresponding *acid*, m.p. 240·5—242° (decomp.)]. 2 : 4-Di-iodo-3-thiotolen-5-carboxylic acid and $Hg(OAc)_2$ in boiling AcOH yield 2 : 4-*di-iodo*-5-*acetoxymercuri*-3-*thiotolen*, m.p. 218—220° (decomp.), transformed by NaCl followed by HCl into (II), which gives 2 : 4-*di-iodo*-5-*chloromercuri*-3-*thiotolen*, m.p. 228—229°. 5-*Iodo*-3-*thiotolen*, b.p. 86·5—87·5°/12 mm., m.p. −61° (corr.), gives 5-*iodo*-2-*chloromercuri*-3-*thiotolen*, m.p. 217° when rapidly heated and, after re-solidification, m.p. 282°. The decarboxylation of 5-bromothiophen-2-carboxylic acid and of 3 : 4 : 5-tribromothiophen-2-carboxylic acid is described. In all cases the m.p. of the I-derivatives become lower as the lability of the I atoms increases. The reactivity of I in the 2-thiotolens increases in the sequence 4 → 3 → 5 and in the 3-thiotolens in the order 4 → 2 → 5. 2 : 5-Di-iodothiophen is exceptional. H. W.

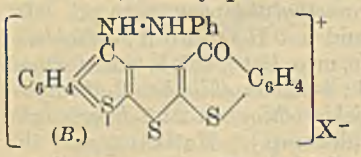
Thiophen series. XXXVIII. Chloro-derivatives of thiophen and the limited applicability of the method of mixed m.p. among isomeric thiophen derivatives. W. Steinkopf and W. Köhler (Annalen, 1937, **532**, 250—282).—Chlorination of thiophen invariably results in the production of mixtures of Cl-derivatives, the separation of which is very difficult on account of the close proximity of their b.p. The homogeneity of the materials is doubtful and they have therefore now been prepared by individual chemical methods. Frequently different compounds of similar m.p. in the thiophen series do not exhibit a depression of the m.p. when mixed. This occurs only with tri- and tetra-substituted thiophens and is favoured by the presence of three Cl, sometimes by two or three Br, but never by several I. Frequently the pairs of substances are shown to be completely isomorphous and to give identical absorption spectra in the ultra-violet. Distinction can be made by irradiation with ultra-violet light, when isomerides with the differentiating atom or group in the α-position give intense, bright colours whereas dull or different shades are obtained when it is in the β-position. Depression of the m.p. is not observed when 2- or 3-nitrothiophen or thiophen-2-sulphonyl chloride is mixed with the corresponding Se derivatives. Similar relationships are not observed in the C_6H_6 series. Crude 2-chlorothiophen (I) is transformed into 2-chloro-5-chloromercurithiophen (II), m.p. 223—224°, which when distilled with 10% HCl gives the homogeneous halide, b.p. 127—128·3° (corr.), m.p. −70° to −69°. I and KI convert (II) into *2-chloro-5-iodothiophen*, b.p. 95—96°/14 mm., m.p. −25° to −24° (corr.). Treatment of (I) with $Hg(OAc)_2$ in boiling AcOH gives *2-chloro-3 : 4 : 5-triacetoxymercurithiophen*, whence *2-chloro-3 : 4 : 5-trichloromercurithiophen*, which gives *2-chloro-3 : 4 : 5-tri-iodothiophen*, m.p. 126°. Br converts (I) into *2-chloro-3 : 4 : 5-tribromothiophen*, m.p. 91°; *2-chlorothiophen-5-sulphonyl chloride* is obtained by the successive action of $ClSO_3H$ at −10° and PCl_5 on (I). The dichlorothiophen fraction when treated with $Hg(OAc)_2$ and NaCl affords 2 : 5-*dichloro-3 : 4-dichloromercurithiophen*, m.p. 314—315°, whence 2 : 5-*dichlorothiophen*, b.p. 161—162° (corr.), m.p. −43·4° (corr.). 2 : 5-*Dichloro-3 : 4-di-iodothiophen*, m.p. 83°, 2 : 5 : 2′ : 5′-*tetrachloro*-3 : 3′-*di-iodo*-4 : 4′-*mercuridithienyl*, m.p. 238°, 2 : 5-*dichloro-3 : 4-dibromothiophen*, m.p. 65°, and 2 : 5-*dichloro*-3-*acetothienone*, m.p. 39°, are described. 2 : 5-Dichloro-3 : 4-di-iodothiophen is transformed by MgEtBr

followed by CO_2 in Et_2O into 2 : 5-*dichlorothiophen*-3 : 4-*dicarboxylic acid*. The trichlorothiophen fraction, b.p. 203—207°, gives with $Hg(OAc)_2$ in AcOH 2 : 3 : 5 : 2′ : 3′ : 5′-*hexachloro*-4 : 4′-*mercuridithienyl*, m.p. 242—243°, converted by $HgCl_2$ in $COMe_2$ into 2 : 3 : 5-*trichloro*-4-*chloromercurithiophen*, m.p. 211—212° (corresponding 4-*bromomercuri*-compound, m.p. 207°), whence 2 : 3 : 5-*trichlorothiophen*, b.p. 207·7—209·2° (corr.), which gives 2 : 3 : 5-*trichloro*-4-*bromothiophen*, m.p. 50·5—51°. 2 : 3 : 5-*Trichloro*-4-*iodothiophen* has m.p. 51°. The chlorothiophen fraction, b.p. 205—207°, and AcCl with $AlCl_3$ in light petroleum give 2 : 3 : 5-*trichloro*-4-*acetothienone*, m.p. 80°, in very small yield. Treatment of crude trichlorothiophen with conc. H_2SO_4 and conc. HNO_3 at 0° leads to 2 : 3 : 5-*trichloro*-4-*nitrothiophen*, m.p. 70°. 2 : 5-Dibromo-3-iodo-4-thiophenic acid is transformed by Cl_2 in distilling AcOH into 2 : 3 : 5-*trichloro*-4-*thiophenic acid*, m.p. 176—177°. 2 : 3 : 5-*Trichlorothiophen*-4-*sulphonyl chloride* has m.p. 57—58°. Tetrachlorothiophen is treated with MgEtBr in Et_2O and the crude Cl_3-derivative is converted by $HgCl_2$ and NaOAc in EtOH into 2 : 3 : 4-*trichloro*-5-*chloromercurithiophen*, m.p. 211° [whence 2 : 3 : 4-*trichlorothiophen*, b.p. 209·2—210·2° (corr.), m.p. −0·5°], and by $Hg(OAc)_2$ in boiling AcOH into 2 : 3 : 4 : 2′ : 3′ : 4′-*hexachloro*-5 : 5′-*mercuridithienyl*, m.p. 242—243°, whence 2 : 3 : 4-*trichloro*-5-*bromomercurithiophen*, m.p. 207°. 2 : 3 : 4-*Trichloro*-5-*iodothiophen*, m.p. 50—51°, 2 : 3 : 4-*trichloro*-3-*bromothiophen*, m.p. 50·5°, 2 : 3 : 4-*trichloro*-5-*acetothienone*, m.p. 80°, -5-*nitrothiophen*, m.p. 70°, and -*thiophen*-5-*sulphonyl chloride*, m.p. 55—56°, are obtained in the usual manner. Cl_2 and 2 : 3-dibromo-3-thiophenic acid in boiling AcOH give 2 : 3-*dichloro*-5-*thiophenic acid*, m.p. 196—197°, which is converted by $Hg(OAc)_2$ in boiling AcOH into 2 : 3-*dichloro*-4 : 5-*diacetoxymercurithiophen*, whence 2 : 3-*dichloro*-4 : 5-*dichloromercurithiophen*, which when distilled with dil. HCl gives 2 : 3-*dichlorothiophen* (II), b.p. 173—174° (corr.), m.p. −26·2° (corr.). This gives 2 : 3-*dichloro*-5-*chloromercurithiophen*, m.p. 269—270°, whence 2 : 3-*dichloro*-5-*iodothiophen*, m.p. 27°. 2 : 3-*Dichloro*-5-*bromothiophen*, b.p. 212—214°, m.p. 6°, 2 : 3-*dichloro*-5-*acetothienone*, m.p. 68°, 2 : 3 : 2′ : 3′-*tetrachloro*-5 : 5′-*dibromo*-4 : 4′-*mercuridithienyl*, m.p. 238—239°, 2 : 3-*dichloro*-5-*nitrothiophen*, m.p. 55—56°, and 2 : 3-*dichlorothiophen*-5-*sulphonyl chloride* (III), m.p. 55—56°, are obtained in the usual manner. 2 : 3-*Dichloro*-4 : 5-*di-iodo*-, m.p. 72°, and -4 : 5-*dibromo*-, m.p. 67·5°, -*thiophen* are described. Hydrolysis of (III) with boiling NaOH and treatment of the hydrolysate with Na–Hg in a current of steam gives 3-*chlorothiophen* (IV), b.p. 136—137° (corr.), m.p. −62°, whence 3-chloro-2-chloromercurithiophen, m.p. 137—138°, 3-*chloro*-2 : 5-*dichloromercurithiophen*, decomp. 275°, and 3 : 3′-*dichloro*-2 : 2′-*mercuridithienyl*, m.p. 174—175°. The successive action of MgEtBr and CO_2 on (II) affords 3-*chloro*-2-*thiophenic acid*, m.p. 175—176°. (IV) is converted by $Hg(OAc)_2$ in boiling AcOH followed by I into 3-*chloro*-2 : 4 : 5-*tri-iodothiophen*, m.p. 121°; 3-*chloro*-2 : 4 : 5-*tribromothiophen* has m.p. 91°. The residues obtained in the prep. of (IV) are dried, treated with PCl_5 and then with EtOH–KOH, thereby giving 2 : 4-*dichlorothiophen*, b.p. 174—175° (corr.), m.p. −34°; 2 : 4-*dichloro*-3 : 5-*dibromothiophen* has m.p. 72°. Passage of Cl_2 through 2 : 5-dimethylthiophen (V) in CCl_4 and treatment of the product with much Br gives 3 : 4-*dichloro*-2 : 5-*di*(*dibromomethyl*)*thiophen*, m.p. 112°, converted by Cl_2 in boiling CCl_4 into 3 : 4-*dichloro*-2 : 5-*di*(*dichloromethyl*)*thiophen*, m.p. 80°, and by pptd. $CuCO_3$ and hot H_2O into 3 : 4-*dichlorothiophen*-2 : 5-*dialdehyde*, m.p. 194°; this is transformed by H_2O_2–KOH into 3 : 4-*dichlorothiophen*-2-*aldehyde*, m.p. 72°, and 3 : 4-*dichlorothiophen*-2 : 5-*dicarboxylic acid*, m.p. 314—315° (decomp.). $Hg(OAc)_2$ and the acid in boiling AcOH yield 3 : 4-*dichloro*-2 : 5-*diacetoxymercurithiophen*, whence 3 : 4-*dichlorothiophen*, b.p. 184·5—185·5° (corr.), m.p. 1°, mercurated to 3 : 4-*dichloro*-2-*chloromercuri*-, m.p. 206—207°, and -2 : 5-dichloromercuri-, m.p. 347—349° after darkening, -thiophen. The latter substance with I and KI gives 3 : 4-*dichloro*-2 : 5-*di-iodothiophen*. 3 : 4-*Dichloro*-2 : 5-*dibromothiophen*, m.p. 75°, and 3 : 4-*dichloro*-2-*acetothienone*, m.p. 56°, are described. 3 : 4-*Dichloro*-2-*hydroxymethylthiophen*-5-*carboxylic acid* has m.p. 220—221°. 2 : 4 : 5-*Trichloro*-3-*thiotolen*, b.p. 115—116°/23 mm., m.p. −18° (corr.), is obtained from Cl_2 and the corresponding Br_3-compound in CCl_4. 2 : 4 : 5-Tri-iodo-3-thiotolen is converted by Cl_2 in $CHCl_3$ at 0° into 2 : 2 : 3 : 4 : 4 : 5 : 5-*heptachloro*-3-*methyltetrahydrothiophen*, m.p. 217—218·5° (decomp.). Drastic chlorination of thiophen or chlorination of 2-thiophenic acid in cold AcOH affords 2 : 3 : 3 : 4 : 5(or 2 : 2 : 3 : 4 : 5)-*pentachloro*-2 : 3-*dihydrothiophen*, b.p. 122—126°/13 mm. Br transforms (V) in CS_2 into 3 : 4-*dibromo*-2 : 5-*di*(*bromomethyl*)-*thiophen*, m.p. 132°, converted by Cl_2 into 3 : 4-*dibromo*-2 : 5-*di*(*dichloromethyl*)*thiophen*, m.p. 103°. 3 : 4-*Dibromothiophen*-2 : 5-*dialdehyde*, m.p. 227°, is oxidised by $KMnO_4$ to 3 : 4-*dibromothiophen*-2 : 5-*dicarboxylic acid*, m.p. 317—318°. 2 : 3-Dibromo-5-thiophenic acid is transformed into 2 : 3-*dibromothiophen*, b.p. 218·6—219·6° (corr.), m.p. −17·5° (corr.). Exhaustive treatment of 2-thiotolen with Br–H_2O leads to tetrabromothiophen, m.p. 115—117°.

H. W.

Thiophen series. XXXIX. Constitution of the salts of the phenylhydrazone of αβα′β′-thiophenobisthiochromone [bis(benzthio-1 : 4-pyrono-2 : 3)-2′ : 3′ : 5′ : 4′-thiophen]. W. Steinkopf (Annalen, 1937, **532**, 282—288; cf. A., 1937, II, 164).—Treatment of αβα′β′-thiophenobisthiochromone (*A*) with HCl, AcCl, or $SOCl_2$ in ordinary $CHCl_3$ (containing EtOH) gives the dihydrochloride, *A*,2HCl, m.p. 273° (AcCl or $SOCl_2$ being hydrolysed by EtOH). The more difficultly hydrolysed BzCl gives the *adduct*, 2*A*,3HCl, or if EtOH is removed as far as possible from the $CHCl_3$, a mixture of the *salts*, *A*,HCl and 3*A*,HCl. All these salts lose HCl when heated and ultimately show the m.p. of *A*; they are all of the same intensely yellow colour. H_2O hydrolyses them slowly. *A* and $NH_2{\cdot}NH{\cdot}CH_2Ph$ give a benzylhydrazone the *perchlorate*, decomp. 242—248°, of which closely resembles the phenylhydrazone salt. This observation excludes the quinonoid or quinolide structure of the latter (*loc. cit.*). The possibility of a radical structure is considered. Since direct action of I on the phenylhydrazone gives the *tri-iodide*,

$C_{24}H_{14}ON_2S_3I_3$, m.p. 120—122° (decomp.), I is added to $AgClO_4$ in C_6H_6 as long as decolorisation persists and the solution of the phenylhydrazone is added; no reaction occurs at room temp. and only a pale blue colour develops at 100°. The *perchlorate*, decomp. 290—310°, readily produced from the acetate, is not here formed. Also HI analogously gives the *hydriodide*, $C_{24}H_{14}ON_2S_3,HI$, decomp. 310—315°. The possibility that the salts arise by addition of acid to CO is negatived by the dissimilar behaviour towards H_2O of salts of *A* and of its phenylhydrazone. The salts must therefore arise by addition of acid to S of the thiochromone ring to which ·NH·NHPh is attached (cf. *B*).



H. W.

Thiophen series. XL. Mercury derivatives of thiophen. W. Steinkopf and A. Killingstad (Annalen, 1937, **532**, 288—293).—Dropwise addition of thiophen (I) to a boiling mixture of $HgCl_2$–NaOAc–H_2O–EtOH gives 2 : 5-*dichloromercurithiophen*, converted by short treatment with BzCl in $PhNO_2$ into *Ph* 2 : 5-*chloromercurithienyl ketone*, m.p. 244—246°, hydrolysed by superheated steam to *Ph* 2-*thienyl ketone*, m.p. 55—57°, and converted by I–aq. KI into *Ph* 5-*iodo*-2-*thienyl ketone*, m.p. 129—130°. If the reaction is protracted, 2 : 5-*dibenzoylthiophen*, m.p. 114—115°, is produced. 2 : 5-*Diacetoxymercurithiophen* is produced by addition of (I) to $Hg(OAc)_2$ in 50% AcOH at 45° and 2 : 5-dichloromercuri-3-thiotolen in the same manner as the thiophen derivative. The replacement of all the α-H atoms (and only these) by the action of $Hg(OAc)_2$ and 50% AcOH on thiophen derivatives appears general. Thus are produced 2-*bromo*-5-*acetoxymercurithiophen*, m.p. 135°, 5-*acetoxymercuri*-2-*thiotolen*, m.p. 133° (identified by conversion into 5-chloromercuri-2-thiotolen), 2 : 5-*diacetoxymercuri*-3-*thiotolen*, decomp. >240°, and 4-*bromo*-2 : 5-*diacetoxymercuri*-3-*thiotolen*, decomp. >270°. In the case of 2 : 5-dimethylthiophen the β atoms are replaced with production of 3 : 4-*diacetoxymercuri*-2 : 5-*thioxen*, decomp. >290°. H. W.

Thionaphthen-2-acetic acid. E. M. Crook and W. Davies (J.C.S., 1937, 1697—1698).—Thionaphthen (I), $CH_2Br·CO_2Et$ (II), and Cu give thionaphthen-acetic, m.p. 141°, or -diacetic acid according to the conditions. MgMeI does not react with (I) in Et_2O, but the MgBr-derivative is obtained by adding 2-bromothionaphthen and MeI to an excess of Mg and with CO_2 gives thionaphthen-2-carboxylic acid [S-*dioxide*, m.p. 218° (decomp.)], the chloride, m.p. 53—54°, of which affords a diazo-ketone, m.p. about 40° (decomp.), converted by Ag_2O–EtOH and subsequent hydrolysis into thionaphthen-2-acetic acid. $C_{10}H_8$ and (II) give a mixture of acids and a ketone. R. S. C.

[Enol-betaines. Derivatives of 3 : 5-diketopiperidine.] C. Gustafsson (Ber., 1937, **70**, [*B*], 2165—2166; cf. A., 1937, II, 386).—A reply to Kröhnke and Heffe (*ibid.*, 422). H. W.

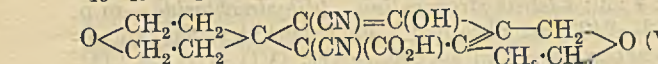
[Enol-betaines. Derivatives of 3 : 5-diketopiperidine.] F. Kröhnke (Ber., 1937, **70**, [*B*], 2166).—In reply to Gustafsson (preceding abstract) it is pointed out that enol-betaines are of three types, (1) the colourless compounds of high m.p. described by Benary (A., 1908, i, 600) and allied to those of Gustafsson, (2) the coloured, low-melting, basic methine enol-betaines of the pyridinium series, and (3) the benzoylenol-betaines of the pyridinium series which occupy an intermediate position. H. W.

3-Vinyl-pyridine and -piperidine. H. A. Iddles, E. H. Lang, and D. C. Gregg (J. Amer. Chem. Soc., 1937, **59**, 1945—1946).—3-α-Hydroxyethylpyridine (Strong and McElvain, A., 1933, 399) is converted by P_2O_5 (in xylene) or $SOCl_2$ (followed by EtOH–KOH) into 3-vinylpyridine (*hydrochloride*, m.p. 114—115°; *picrate*, m.p. 143—144°; *platinichloride*, m.p. 158—160°; *aurichloride*, m.p. 138—140°; *mercurichloride*, $C_7H_7N,HgCl_2$, m.p. 145—150°), which polymerises when kept. 3-α-Hydroxyethylpiperidine (*loc. cit.*) is dehydrated [conc. H_2SO_4, little AcOH, 180° (bath)] to 3-vinylpiperidine (*picrate*, m.p. 162—164°). H. B.

Condensation reactions of aldehydes and ketones with ammonia to pyridine bases. Condensations with acetaldehyde and crotonaldehyde. A. E. Tschitschibabin (Bull. Soc. chim., 1937, [v], 4, 1826—1831, 1831—1838).—The literature on the formation of C_5H_5N bases from MeCHO or crotonaldehyde (I) with NH_3 is critically reviewed. MeCHO and NH_3 passed over kaolin at 340—360° yield α- (II) and γ- (III) -picoline, 2- and 4-propylpyridine, 2-propenylpyridine, collidinealdehyde (IV), β-collidine (V), and an unidentified *collidine* (VI) (*picrate*, m.p. 142°). The bases are separated by fractional distillation and fractional crystallisation of the picrates. (I) and NH_3 similarly yield all the above bases except (VI), and tricrotonylidenetetramine (VII). $(MeCHO)_3$ and aq. NH_3 with NH_4OAc at 160—180° under pressure yield chiefly (IV) with a little (II), (III), and (V), whilst (I), NH_4OAc, and aq. NH_3 at 180° under pressure yield mainly (VII) and a little (IV). J. D. R.

Quinuclidine. ***Dicyclo*[2 : 2 : 2]aza-1-octane.** V. Prelog, D. Kohlbach, E. Cerkovnikov, A. Režek, and M. Piantanida (Annalen, 1937, **532**, 69—82).—Quinuclidine (I) is synthesised in good yield, the key intermediate being prepared by four methods. 4-Hydroxymethyltetrahydropyran (improved prep.) and PBr_3–C_5H_5N give 4-*bromomethyltetrahydropyran*, b.p. 85—86°/17 mm., and thence *tetrahydropyran*-4-*acetonitrile*, b.p. 125—126°/21 mm., and -4-*acetic acid* (II), b.p. 178°/20 mm., m.p. 54—55°. *Tetrahydropyran*-4-*yl benzenesulphonate*, an oil, or, less well, 4-*bromotetrahydropyran*, b.p. 60—61°/15 mm. (prep. from tetrahydropyran-4-ol by PBr_3–C_5H_5N), with $CH_2(CO_2Et)_2$ gives *Et*$_2$ *tetrahydropyran*-4-*malonate*, b.p. 156—160°/13 mm., converted into the corresponding *acid*, m.p. 151°, and thence into (II). Tetrahydro-γ-pyrone (III) with Zn–$CH_2Br·CO_2Et$ gives *Et* 4-*hydroxytetrahydropyran*-4-*acetate*, b.p. 132—140°/15 mm., the *Ac* derivative, b.p. 140—145°/21 mm., of which, when distilled at 1 atm., gives *Et tetrahydropyranylideneacetate*, b.p. 113°/15 mm. (large exaltation of [*R*]), hydrogenated (PtO_2; dry EtOH)

to the *Et* ester (IV), b.p. 108—110°/14 mm., of (II). $CN{\cdot}CH_2{\cdot}CO_2Et$, (III), and a trace of piperidine in C_6H_6 give *Et 4-tetrahydropyranylidenecyanoacetate*, m.p. 66—67° [and, in one experiment, a *substance* (V), $C_{18}H_{20}O_5N_2$, m.p. about 260° (decomp.)], hydrolysed



(V.)

by dil. acid to the corresponding *acid*, m.p. 137—138°, partly converted by heat into 2 : 3-*dihydropyran*-4-*cyanoacetic acid*, b.p. 135°/23 mm., hydrolysed by 20% H_2SO_4–EtOH to *Et* 2 : 3-*dihydropyran*-4-*acetate* [by hydrogenation gives (IV)], and converted by NaOEt–$C_6H_4Br{\cdot}CO{\cdot}CH_2Br$ into *Et* α-*cyano*-α-[2 : 3-*dihydropyran*-4-]β-p-*bromobenzoylpropionate*, m.p. 153—154°. Na–EtOH–C_6H_6 reduction of (IV) gives 4-β-*hydroxyethyltetrahydropyran*, b.p. 119—120°/14 mm. (*phenylurethane*, m.p. 70—71°), which with HBr gives αε-*dibromo*-γ-β′-*bromoethylpentane*, b.p. 185—186°/17 mm., converted by 20% NH_3–MeOH at 130—140° into (I), m.p. 158—159° (*picrate*, m.p. 275—276°). HBr at 100—110° converts (II) into δ-*bromo*-β-β′-*bromoethylvaleric acid*, m.p. 71—71·5° the *Me* ester (prep. by CH_2N_2) of which with NH_3–MeOH gives *Et piperidine*-4-*acetate*, b.p. 123—127°/15 mm. [*hydrochloride*; *platinichloride*, m.p. 192° (decomp.)], and thence the corresponding *acid*, m.p. 237—238° (decomp.) [*platinichloride*, m.p. 210—213° (decomp.); *PhSO*$_2$ derivative, cryst.].

R. S. C.

Synthesis of *dicyclo*[2 : 2 : 3]aza-1-nonane, quinuclidine-2-carboxylic acid, and β-4-piperidylpropionic acid. V. Prelog and E. Cerkovnikov (Annalen, 1937, **532**, 83—88).—4-Bromomethyltetrahydropyran and $CHNa(CO_2Et)_2$ give *Et*$_2$ 4-*tetrahydropyranylmethylmalonate*, b.p. 166—169°/13 mm., the corresponding *acid*, m.p. 114—115° (decomp.), from which, when heated, yields β-4-*tetrahydropyranylpropionic acid* (I), m.p. 92—93°. The *Et* ester, b.p. 134—139°/17 mm., of this acid with Na–EtOH–C_6H_6 gives 4-γ-*hydroxypropyltetrahydropyran*, b.p. 143—145°/20 mm., converted by HBr at 100° into αζ-*dibromo*-γ-β′-*bromomethylhexane*, b.p. 204°/21 mm. Yields in these reactions are good. The Br_3-compound with NH_3–MeOH at 130—140° gives 11·8% of dicyclo[2 : 2 : 3]-*aza*-1-*nonane*, m.p. 129° (*platini*-, m.p. 238—240°, and *auri*-*chloride*, decomp. about 250°; *picrate*, m.p. 288—289°). HBr and (I) give ε-*bromo*-γ-β′-*bromoethylhexoic acid* (II) (not obtained pure), the Et ester of which with NH_3–MeOH affords β-4-*piperidylpropionic acid*, m.p. 275—276° (decomp.) [*hydrobromide*, m.p. 220—222°; Et ester, b.p. 142—143°/15 mm. (platinichloride, m.p. 190—191°)]. Br–red P at 100° converts (II) into αε-*dibromo*-γ-β′-*bromoethylhexoic acid*, which with NH_3–MeOH gives *quinuclidine*-2-*carboxylic acid*, m.p. about 280° (decomp.) [*hydrobromide*; *methochloride*, m.p. 298° (decomp.)].

R. S. C.

Nitrogenous heterocyclic rings. XXXIII. Hydrogenation of o-phenylenediacetonitrile under high pressure. P. Ruggli and A. Staub (Helv. Chim. Acta, 1937, **20**, 925—927; cf. A., 1936, 64).—Hydrogenation (Ni in NH_3–EtOH) of *o*-$C_6H_4(CH_2{\cdot}CN)_2$ in a relatively large autoclave so that there is no considerable fall in pressure of H_2 during the reduction gives *o*-ββ-phenylenediethylamine [*o*-ββ′-diaminodiethylbenzene] (I), b.p. 156—175°/13 mm., in addition to benzohexamethyleneimine. (I) yields a methiodide, m.p. 227°, dihydrochloride, m.p. 253°, dipicrate, m.p. 235° (decomp.), and a Bz_2 derivative, m.p. 153°. It resembles the compound of Fries and Bestian (A., 1936, 714) rather than that of von Braun *et al.* (A., 1916, i, 130).

H. W.

Synthesis of 5- and 6-benzyloxyindoles and attempts to prepare 5- and 6-hydroxyindoles therefrom. H. Burton and J. L. Stoves (J.C.S., 1937, 1726—1728).—2-*Nitro*-4-*benzyloxytoluene*, m.p. 52°, prepared from 2-nitro-*p*-cresol and CH_2PhCl, with $Et_2C_2O_4$ and KOEt gives 2-*nitro*-4-*benzyloxyphenylpyruvic acid* (+H_2O), m.p. 89—90°, and 2 : 2′-*dinitro*-4 : 4′-*dibenzyloxydibenzyl*, m.p. 164—165°. The pyruvic acid is reduced [$Fe(OH)_2$] to 6-*benzyloxyindole*-2-*carboxylic acid*, m.p. 185—186° (decomp.), decarboxylated by heating in glycerol to 6-*benzyloxyindole*, m.p. 111—112°. 5-*Benzyloxyindole*-2-*carboxylic acid* (+H_2O), m.p. 190°, prepared from 2-nitro-5-benzyloxypyruvic acid, is decarboxylated to 5-*benzyloxyindole*, m.p. 96—97° (1-*Ac* derivative, m.p. 129—130°). Neither 5- nor 6-benzyloxyindole has been debenzylated, the products being dark-coloured complex phenolic substances.

F. R. S.

Diethylamides of indole-3-carboxylic, 3-indolylacetic, thionaphthen-2-carboxylic, and reduced 3-indolylacetic acids. R. Wegler and H. Binder (Arch. Pharm., 1937, **275**, 506—516).—Mg 3-indolyl iodide and $NEt_2{\cdot}COCl$ in Et_2O give *indolyl*-3-*carboxyldiethylamide*, m.p. 151—151·5° (*picrate*, m.p. 129·5—120°; *NO*-derivative, m.p. 241—242°, reduced to the N-*NH*$_2$-derivative, m.p. 177·5—178°; hydrolysed to the known acid), hydrogenated with difficulty to a mixture of H_2- and H_8-compounds (*picrates*, m.p. 182—183·5° and 195—198°). $NEt_2{\cdot}CH_2{\cdot}COCl$ similarly leads to 3-*indolylacetdiethylamide*, m.p. 101° (*picrate*, m.p. 139—140°; hydrolysed to the known acid), hydrogenated to the 2 : 3-H_2- [*picrate*, m.p. 170—172°; additive *compound* with 2-nitrohydrindene-1 : 3-dione, m.p. 184° (decomp.)] and H_8-*amide*, b.p. 146—147°/0·75 mm. (*picrate*, m.p. 177—178·5°). Mg 2-thionaphthenyl iodide and $NEt_2{\cdot}COCl$ give *thionaphthen*-2-*carboxyldiethylamide*, b.p. 220°/11 mm., also obtained from the acid chloride and $NHEt_2$, and hydrolysed to the known acid. 3-Nitriloindole and KOH–EtOH–H_2O give *indole*-3-*carboxylamide*, m.p. 200°. The indolediethylamides could not be obtained by other methods.

R. S. C.

Derivatives of di- and tetra-hydroquinoline.—See B., 1937, 1179.

α-6-Methoxy-8-quinolyl-β-alkylcarbamides. J. W. Boehmer (Rec. trav. chim., 1937, **56**, 901—906).—8-Amino-6-methoxyquinoline is transformed by the necessary alkylcarbimide in PhMe into α-6-*methoxy*-8-*quinolyl*-β-*alkylcarbamides* in which the *alkyl* is *Me* (I), m.p. 201°, *Et*, m.p. 188°, *Pr*$^{\alpha}$, m.p. 197°, *Pr*$^{\beta}$, m.p. 217°, *Bu*$^{\alpha}$, m.p. 194°, and Bu$^{\beta}$, m.p. 190°. All these compounds afford *hydrochlorides*. Only (I) appears to have any action on plasmodium relictum.

H. W.

Mechanism of decarboxylation. I. Decomposition of quinaldinic and *iso*quinaldinic acids in the presence of compounds containing carbonyl groups. P. DYSON and D. L. HAMMICK (J.C.S., 1937, 1724—1726).—When quinaldinic (I) and *iso*quinaldinic (II) acid are heated with excess of PhCHO, anisaldehyde, and COPhMe, CO_2 is evolved and products are obtained which indicate that the decarboxylation takes place thus: OH·CO·X + COYZ → OH·CXYX + CO_2 where X = quinolyl or *iso*quinolyl, and Y and Z = aryl, alkyl, or H. (I) with PhCHO gives *phenyl-2-quinolylcarbinol*, m.p. 50—60°, readily oxidised to the ketone, with anisaldehyde forms *anisyl 2-quinolyl ketone*, m.p. 78° (2 : 4-*dinitrophenylhydrazone*, m.p. 242°), and with COPhMe yields *phenyl-2-quinolylmethylcarbinol*, m.p. 100°. (II) and PhCHO afford *phenyl*-1-*isoquinolylcarbinol*, m.p. 106° (*Bz* derivative, m.p. 158—159°), oxidised ($K_2Cr_2O_7$) to the ketone. F. R. S.

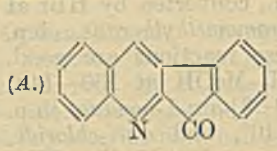
Iodo-derivatives of substituted phenylquinolinecarboxylic acids.—See B., 1937, 1270.

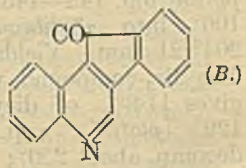
Derivatives of methylcholanthrene and heterocyclic derivatives of cholesterol. W. ROSSNER (Z. physiol. Chem., 1937, **249**, 267—274; cf. Dorée and Petrov, A., 1936, 69).—Methylcholanthrene (I) in C_6H_6 gives with conc. HNO_3 in AcOH for 3 hr. at 0° two $(NO_2)_2$-derivatives, m.p. 224° and 257°, respectively, and with Ac_2O and conc. H_2SO_4 a *monosulphonic acid* (II), m.p. 240° (*Me* ester, m.p. 274°). In the same way the condensation product (III) of cholestan-3-one and NHPh·NH_2 gives a *monosulphonic acid*, m.p. 235° (*Me* ester, m.p. 190°; *K* and *Na* salts). (III) with Se at 320° for 40 hr. gives a *compound* (IV), $C_{29}H_{39}N$, m.p. 203°; at 340° for 30 hr. (after 16 hr. at 320°) a *compound* (V), $C_{21}H_{17}N$, probably aminomethylcholanthrene, m.p. 225°; and at 360° (I). Cholestenone with NHPh·NH_2 yields a *compound* (VI), $C_{33}H_{47}N$, m.p. 195°, which with Se gives at 320° a *compound* (VII), $C_{29}H_{37}N$, m.p. 170°; at 340° for 30 hr. (after 16 hr. at 320) a *compound* (VIII), $C_{28}H_{27}N$; and at 360° (I). (II) is not carcinogenic. Formulæ are suggested for the compounds (III)—(VIII). W. McC.

Acridine derivatives as antimalarials. U. P. BASU and S. J. DAS-GUPTA (J. Indian Chem. Soc., 1937, **14**, 468—473).—5-Chloro-, m.p. 68—69° (cf. A., 1925, i, 65; 1931, 495), with PhOH–KOH at 140° gives 5-*phenoxy*-, m.p. 102° (*hydrochloride*, m.p. 223—225°), and with NEt_2·$[CH_2]_4$·NH_2 (I) and Cu at 150° gives 5-δ-*diethylaminobutyl*-1 : 2 : 3 : 4-*tetrahydroacridine* (*methylenedioxynaphthoate*, m.p. 216—220°). Et *cyclo*hexanone-2-carboxylate (II) and *p*-anisidine (III) give 7-*methoxy*-1 : 2 : 3 : 4-*tetrahydroacridone*, m.p. 295°, which with PCl_5, followed by PhOH at 150°, yields 5-*chloro*-7-*methoxy*- (IV), m.p. 122°, and 5-*phenoxy*-7-*methoxy*-1 : 2 : 3 : 4-*tetrahydroacridine* (V), m.p. 120° [*hydrochloride*, m.p. 220° (decomp.); *picrate*, m.p. 190—192°]. From (I), (IV), and Cu, or from (I) and (V) (both at 150°), the 7-*methoxy*-5-δ-*diethylaminobutyl* compound (*dihydrochloride*, m.p. 193—194°) is obtained. Similarly (IV) gives the 7-*methoxy*-5-γ-*diethylaminopropyl* compound (*dihydrochloride*, m.p. 228—229°). Et 5-methyl*cyclo*hexanone-2-carboxylate and (III) yield 7-*methoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydroacridone*, m.p. 335°, from which 5-*chloro*-7-*methoxy*-2-*methyl*-, m.p. 90°, 5-*phenoxy*-7-*methoxy*-2-*methyl*-, m.p. 103°, 7-*methoxy*-2-*methyl*-5-δ-*diethylaminobutyl*- (*dihydrochloride*, m.p. 203—204°), and 7-*methoxy*-2-*methyl*-5-γ-*diethylaminopropyl*-1 : 2 : 3 : 4-*tetrahydroacridine* (*dihydrochloride*, m.p. 242—243°) are obtained. Et 3-methyl*cyclo*hexanone-6-carboxylate and *p*-C_6H_4Cl·NH_2 (VI) give *Et* 2-(4′-*chloroanilino*)-4-*methyl*-Δ¹-cyclo*hexene*-1-*carboxylate*, m.p. 90°, which at 270° forms 7-*chloro*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydroacridone*, m.p. 375° (decomp.) (sealed tube), from which ($POCl_3$–PCl_5) 5 : 7-*dichloro*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydroacridine*, m.p. 89°, is obtained. Using (II) and (VI), 7-*chloro*-1 : 2 : 3 : 4-*tetrahydroacridone*, m.p. 380°, is formed. E. W. W.

3 : 10-Dihydroxy-1 : 2 : 3 : 4-tetrahydro-7′ : 8′-benzquinoline.—See B., 1937, 1179.

Polynuclear condensed systems with heterocyclic rings. W. BORSCHE and W. NOLL (Annalen, 1937, **532**, 127—145).—Phenylpyruvic acid (I) is transformed by *o*-NH_2·C_6H_4·CHO and NaOH in H_2O–EtOH at 100° into 3-*phenylquinoline*-2-*carboxylic acid* (II), m.p. 165° (decomp. into CO_2 and 3-phenylquinoline) (*Me* ester, m.p. 82°; *anilide*, m.p. 182—183°). Similarly, (I) condenses with isatin to 3-*phenylquinoline*-2 : 4-*dicarboxylic acid* (III), m.p. 271—272° (decomp.) (*Me*$_2$ ester, m.p. 124—125°; *dianilide*, m.p. 253—255°). Complete decarboxylation of (III) occurs at its m.p. whereas at 210—215° it affords 3-phenylquinoline-4-carboxylic acid (IV), decomp. 277° (Me ester, m.p. 76—77°; *anilide*, m.p. 222°). 5-Methylisatin and (I) yield 3-*phenyl*-6-*methylquinoline*-2 : 4-*dicarboxylic acid*, m.p. 281—282° (decomp.) [*Me*$_2$ ester, m.p. 131—132°; dianilide (+1H_2O), m.p. 155°], which passes at 220° into 3-*phenyl*-6-*methylquinoline*-4-*carboxylic acid* (V), m.p. 282° (decomp.) (*Me* ester, m.p. 111—112°; *anilide*, m.p. 286°), and at 290—295° into 3-*phenyl*-6-*methylquinoline*, b.p. 226°/17 mm., m.p. 63—64° (*picrate*, m.p. 256—257°). Treatment of (II) and (IV) with $AlCl_3$ in $PhNO_2$ affords 9-*keto*-1-*aza*-2 : 3-*benzofluorene* (*A*), m.p. 190·5°,

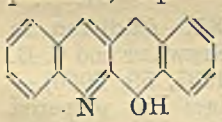




and 9-keto-3-aza-1 : 2-benzofluorene (*B*), m.p. 238° (*picrate*, m.p. 227—228°). The dichloride of (III) with $AlCl_3$ in $PhNO_2$ gives a mixture of 9-*keto*-1-*aza*-2 : 3-, m.p. 313° (decomp.) (*Na* salt), and 9-*keto*-3-*aza*-1 : 2- (VI), m.p. 185° (decomp.) and, after resolidification, m.p. about 235° (*Na* salt; *Me* ester, m.p. 206—207°), -*benzofluorene*-4-*carboxylic acid*. Ring-closure by conc. H_2SO_4 at 100° gives (*B*) from (IV), 9-*keto*-3-*aza*-p-*methyl*-1 : 2-*benzofluorene*, m.p. 237° [*picrate*, m.p. 252° (decomp.)], from (V), and (VI) from (III). (*A*) gives an *oxime*, m.p. 242—243° (decomp.), and a 2 : 4-*dinitrophenylhydrazone*, decomp. 333° (*hydrochloride*); it is reduced by N_2H_4,H_2O at 100° to 3-*aza*-1 : 2-*benzofluorene*, b.p. 240°/25 mm., m.p. 140°. Reduction with Sn and HCl leads to 1-*aza*-1 : 2 : 3 : 4-*tetrahydro*-2 : 3-*benzofluorene*, m.p.

119—122°, and 1-*azadihydro*-2 : 3-*benzofluorene hydrochloride*, m.p. 239—242° after softening at 217°. (*B*) similarly affords an *oxime*, m.p. 288°, and a 2 : 4-*dinitrophenylhydrazone*, m.p. 315° (decomp.); it is reduced to 3-*aza*-1 : 2-*benzofluorene*, b.p. 242°/14 mm., m.p. 165° [*picrate*, decomp. 192°; *hydrochloride*, m.p. 337—338° (decomp.)], or by Sn and HCl followed by acetylation to 3-*aza-acetyldihydro*-1 : 2-*benzofluorene*, m.p. 133—134°, hydrolysed to 3-*azadihydro*-1 : 2-*benzofluorene hydrochloride*, m.p. 293—295°. 3-*Aza*-p-*methyl*-1 : 2-*benzofluorene*, b.p. 246°/12 mm., m.p. 136—137°, gives a *hydrochloride*, decomp. 343—345°.

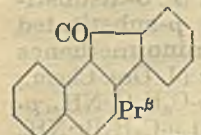
Benzylpyruvic acid (VII), *o*-NH_2·C_6H_4·CHO, and 18% NaOH at 100° yield 3-*benzylquinoline*-2-*carboxylic acid* (VIII) (+H_2O), m.p. about 105° and, after re-solidification, decomp. about 133° [*hydrochloride* (hydrated), m.p. 80—85°, (anhyd.), m.p. 166·5—168·5° (decomp.); *Me* ester, m.p. 62°; *anilide*, m.p. 144°]. 3-*Benzylquinoline*-4-*carboxylic acid* (IX), m.p. 230·5° (decomp.) (*Me* ester, m.p. 84—85°; *anilide*, m.p. 244°), is obtained by partial decarboxylation at 200° of 3-*benzylquinoline*-2 : 4-*dicarboxylic acid*, m.p. 188° (decomp.) (or, from AcOH, decomp. 186—188° after softening at 132°; from $COMe_2$, decomp. 186—188° after softening at 120°; Me_2 ester, m.p. 61—63°; *dianilide*, m.p. 204°), derived from (VII) and isatin; complete decarboxylation at 250° yields 3-*benzylquinoline*, b.p. 226°/19 mm., m.p. 65—67°. The



(*C.*)

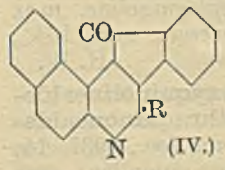
chloride of (VIII) is transformed by $AlCl_3$ in $PhNO_2$ into 1-*aza*-2 : 3-*benzoanthran*-9-*ol* (*C*), isolated as the *Al* derivative, $(C_{17}H_{16}ON)_3Al$, m.p. >360°. Similarly, (IX) gives 3-*aza*-1 : 2-*benzoanthran*-9-*ol* (X) (*hydrochloride*, decomp. >360°). Ring-closure with conc. H_2SO_4 appears less satisfactory. (X) gives an *Ac* derivative, m.p. 177—178° [*picrate*, m.p. 248—249° (decomp.)], and an *oxime*, m.p. 277—278° (decomp.). Reduction of it with N_2H_4,H_2O does not give a homogeneous material. With glycerol and 82% H_2SO_4 at 150° it gives 7-*aza*-5 : 6-*benzobenzanthrone*, m.p. 255°; it is oxidised by $Na_2Cr_2O_7$ and 30% H_2SO_4 to 3-*aza*-1 : 2-*benzoanthraquinone*, m.p. 186°, reductively acetylated to 3-*aza*-1 : 2-*benzoanthraquinol diacetate*, m.p. 267° (decomp.). H. W.

Polynuclear, condensed ring systems with heterocyclic rings. II. W. Borsche and F. Sinn (Annalen, 1937, **532**, 146—165).—$COPr^{\beta}$·CH_2Ph, isatin, and KOH in H_2O–EtOH at 100° give 3-*phenyl*-2-iso*propylquinoline*-4-*carboxylic acid*, m.p. 284° (decomp.), the chloride of which is converted by $AlCl_3$ in



(I.)

$PhNO_2$ into 4-iso*propyl*-3-*aza*-1 : 2-*benzofluorenone* (I), m.p. 184° [*picrate*, m.p. 233° (decomp.); 2 : 4-*dinitrophenylhydrazone*, m.p. 275° (decomp.)], reduced by N_2H_4,H_2O at about 200° to 4-iso*propyl*-3-*aza*-1 : 2-*benzofluorene*, m.p. 135°. 2-Chloro-3-phenylquinoline-4-carboxyl chloride similarly affords 4-*chloro*-3-*aza*-1 : 2-*benzofluorenone* (II), m.p. 214·5° [2 : 4-*dinitrophenylhydrazone*, m.p. 322—324° (decomp.)], which does not form a hydrochloride or picrate; it is transformed by N_2H_4,H_2O at 190—200° into 4-*hydroxy*-3-*aza*-1 : 2-*benzofluorene* (III), gradual decomp. 330° after becoming discoloured at 300°. 9-*Keto*-4-*methoxy*-3-*aza*-1 : 2-*benzofluorene*, m.p. 173° (2 : 4-*dinitrophenylhydrazone*, decomp. 328°; *oxime*, decomp. 240—245°, according to the rato of heating), does not give a hydrochloride or a picrate; it is converted by N_2H_4,H_2O into (III). NaOEt in EtOH and (II) afford 9-*keto*-3-*aza*-1 : 2-*benzofluorene*, m.p. 238° [*picrate*, m.p. 226—228°; 2 : 4-dinitrophenylhydrazone, m.p. 310—311° (decomp.)]. 2-Phenyl-5 : 6-benzoquinoline-4-carboxyl chloride (corresponding *anilide*, m.p. 269°) could not be cyclised by $AlCl_3$ or by conc. H_2SO_4 to the corresponding ketone; the cause does not lie in the inability of the COCl to react since 4-*benzoyl*-2-*phenyl*-5 : 6-*benzoquinoline*, m.p. 201°, which could not be oximated, is readily produced in presence of $AlCl_3$ and C_6H_6. 3-Phenyl-5 : 6-benzoquinoline-4-carboxyl chloride and $AlCl_3$ in $PhNO_2$ afford 9-*keto*-3-*aza*-1 : 2-1′ : 2′-*naphthafluorene* [(IV), R = H], m.p. 216° [*picrate*, m.p. 244°; *oxime*, m.p. 281° (decomp.); 2 : 4-*dinitrophenylhydrazone*, m.p. 313° (decomp.)],



(IV.)

reduced by N_2H_4,H_2O to 3-*aza*-1 : 2-1′ : 2′-*naphthafluorene*, m.p. 200° (*hydrochloride*; *picrate*, decomp. 241° after incipient blackening at about 225°). Phenylpyruvic acid, β-$C_{10}H_7$·NH_2, and $Pr^{\beta}CHO$ in boiling EtOH give 3-*phenyl*-2-iso*propyl*-5 : 6-*benzoquinoline*-4-*carboxylic acid*, m.p. 277° [decomp. into CO_2 and 3-*phenyl*-2-iso*propyl*-5 : 6-*benzoquinoline*, m.p. 124°); *picrate* of the *Me* ester, m.p. 202° (decomp.) after becoming discoloured], transformed into 9-*keto*-4-iso*propyl*-3-*aza*-1 : 2-1′ : 2′-*naphthafluorene* [(IV), R = Pr^{β}], m.p. 161° [*picrate*, m.p. 192—193°; *oxime*, m.p. 226° (decomp.); 2 : 4-*dinitrophenylhydrazone*, m.p. 297° (decomp.)], reduced to 4-iso*propyl*-3-*aza*-1 : 2-1′ : 2′-*naphthafluorene*, m.p. 202° [*picrate*, m.p. 216° (decomp.)]. 2 : 3-Diphenyl-5 : 6-benzoquinoline-4-carboxylic acid (*Me ester picrate*, m.p. 232°) is transformed by successive treatments with $SOCl_2$ and $AlCl_3$ in $PhNO_2$ into 9-*keto*-4-*phenyl*-3-*aza*-1 : 2-1′ : 2′-*naphthafluorene* [(IV), R = Ph], m.p. 211° [*picrate*, m.p. 249°; *oxime*, m.p. 242° (decomp.); 2 : 4-*dinitrophenylhydrazone*, m.p. 293° (decomp.)], whence 4-*phenyl*-3-*aza*-1 : 2-1′ : 2′-*naphthafluorene*, m.p. 234° (*picrate*, decomp. 228°).

CH_2Bz·CO_2Et, *o*-$NH_2C_6H_4$·CHO, and NaOH slowly and at room temp. afford 2-phenylquinoline-3-carboxylic acid, m.p. 229° (*anilide*, m.p. 180·5°), the chloride of which is cyclised by $AlCl_3$ in $PhNO_2$ to 4-aza-9-keto-2 : 3-benzofluorene, m.p. 175·5° [*picrate*, m.p. 198·5°; 2 : 4-*dinitrophenylhydrazone*, m.p. 301° (decomp.)], whence 4-*aza*-2 : 3-*benzofluorene*, decomp. 230—235° after becoming discoloured. This yields 9-*benzylidene*-4-*aza*-2 : 3-*benzofluorene*, m.p. 245—246° (decomp.), and 9-*ethoxalyl*-4-*aza*-2 : 3-*benzofluorene*, m.p. 233—234° (decomp.) (*oxime*, decomp. 199°; *Bz* derivative, m.p. 167—168°). $CH_2(CO_2Et)_2$ and *o*-C_6H_4Bz·NH_2 at 195—180° give *Et* 2-*hydroxy*-4-*phenylquinoline*-3-*carboxylate*, m.p. 274°, hydrolysed by conc. HCl to the corresponding *acid*, m.p. 283° (decomp.); this with $SOCl_2$ yields 2-*chloro*-4-*phenylquinoline*-3-*carboxyl chloride* (*Me* 2-*chloro*-4-*phenylquinoline*-3-*carboxylate*, m.p. 127—128°, cyclised to

1-*chloro*-9-*keto*-2-*aza*-3 : 4-*benzofluorene*, m.p. 215—217° (2 : 4-*dinitrophenylhydrazone*, decomp. 317°). $CH_2Bz{\cdot}CH_2{\cdot}CO_2H$, *o*-$NH_2{\cdot}C_6H_4{\cdot}CHO$, and 10% NaOH–MeOH at 100° yield 2-*phenylquinoline*-3-*acetic acid*, m.p. 191° (evolution of CO_2 and production of 2-phenyl-3-methylquinoline) [*picrate*, m.p. 215° (decomp.); *Me* ester, m.p. 88—89°], the ring *compound*, m.p. 367—370° (decomp.), from which contains S. Atophan is transformed into the chloride, which with $AlCl_3$ and C_6H_6 gives 4-*benzoyl*-2-*phenylquinoline*, m.p. 114° (*picrate*, m.p. 213—214°; *oxime*, m.p. 192—193°; 2 : 4-*dinitrophenylhydrazone*, m.p. 245—246°), reduced by N_2H_4,H_2O at 180° to 4-*benzyl*-2-*phenylquinoline* (*picrate*, decomp. 192°). 2-Chloroquinoline-4-carboxyl chloride, C_6H_6, and $AlCl_3$ yield 2-*chloro*-4-*benzoylquinoline*, m.p. 105—107° (2 : 4-*dinitrophenylhydrazone*, m.p. 247°). 2-Phenylquinoline, $AlCl_3$, and BzCl in CS_2 yield 2-p-*benzoylphenylquinoline*, m.p. 126° (*hydrochloride*, m.p. 196°; *picrate*, m.p. 164°; *oxime*, m.p. 185°). H. W.

Dyes derived from 8-hydroxyquinolinealdehydes and from 2-hydroxyanthraquinonealdehyde. S. K. Ray (J. Indian Chem. Soc., 1937, **14**, 414—416).—7-Aldehydo-8-hydroxyquinoline condenses (HCl) with $NPhMe_2$ or resorcinol, or (H_2SO_4) with *o*-hydroxytoluic acid (I), giving *leuco-bases*, m.p. respectively 177°, 148°, and 250°, oxidised by PbO_2 or $NO{\cdot}HSO_4$ to the *carbinols*. Condensation (H_2SO_4) with resorcinol or *m*-$OH{\cdot}C_6H_4{\cdot}NEt_2$ yields *pyronine dyes*, m.p. 80° and 86—87°. The 5-aldehyde gives similar results. 1-Aldehydo-2-hydroxyanthraquinone, when condensed (HCl) with $NPhMe_2$, or (H_2SO_4) with *m*-$OH{\cdot}C_6H_4{\cdot}NEt_2$ or (I), and the products oxidised, yields *dyes*, the first two having m.p. 78° and 135°. A. Li.

Syntheses of pyrazolone derivatives. I. Butyl- and *iso*butyl-antipyrine. A. Giacalone (Gazzetta, 1937, **67**, 460—463).—$CHBu^{\beta}Ac{\cdot}CO_2Et$ (new prep. using NaOEt and $CH_2Ac{\cdot}CO_2Et$ in EtOH, followed by $Bu^{\beta}I$) and $NHPh{\cdot}NH_2$ in AcOH give 1-*phenyl*-3-*methyl*-, m.p. 118°, which with MeI–MeOH yields 1-*phenyl*-2 : 3-*dimethyl*-4-iso*butylpyrazolone*, m.p. 56°. 1-*Phenyl*-3-*methyl*-, m.p. 95—96°, and 1-*phenyl*-2 : 3-*dimethyl*-4-n-*butylpyrazolone*, m.p. 44—45°, are prepared similarly. E. W. W.

Preparation of glyoxaline derivatives from acyloins. K. Bernhauer and R. Hoffmann (J. pr. Chem., 1937, [ii], **149**, 321—323).—Butyroin with PhCHO or CH_2O and NH_3–$Cu(OAc)_2$ gives 2-*phenyl*-4 : 5-*di*-n-*propyl*-, m.p. 175—176° (*hydrochloride*, m.p. 146—147°), and 4 : 5-*di*-n-*propyl*-*glyoxaline*, m.p. 65—68° (*hydrochloride*, decomp. 154—156°), respectively. Acetoin gives similarly 2-phenyl-4 : 5-dimethyl-, m.p. 242° (*hydrochloride*, m.p. 116—118°), and 4 : 5-dimethyl-glyoxaline, m.p. 115—117°, b.p. 125—135°/0·3 mm., respectively. Only the Ph bases crystallise well. R. S. C.

Glyoxaline group. VI. Opening of the benziminazole ring. B. Oddo and (Signa.) L. Raffa (Gazzetta, 1937, **67**, 537—543; cf. A., 1933, 285).—The MgBr derivative of benziminazole (I) with AcCl or EtCOCl in Et_2O yields 1-acetyl- (II) and 1-propionyl-benziminazole, which when boiled with the acid chloride give no other product. 1-Benzoyl-benziminazole with BzCl at the b.p., followed by hot H_2O, yields *o*-$C_6H_4(NHBz)_2$. With Ac_2O followed by hot H_2O, (I) gives *o*-$C_6H_4(NHAc)_2$ (III) and (II); (II) also gives (III). With aq. AcOH at 100°, however, (II) yields (I). E. W. W.

Aliphatic polyamines. VI. J. van Alphen (Rec. trav. chim., 1937, **56**, 1007—1012; cf. A., 1937, II, 302).—Even when an excess of primary amine is present, one mol. of $N(CH_2{\cdot}CH_2Cl)_3$ reacts with only two mols. of the former to give a derivative of 1-β-aminoethylpiperazine. $N(CH_2{\cdot}CH_2Cl)_3$,HCl (I) is converted by boiling NH_2Ph into 4-*phenyl*-1-β-*anilinoethylpiperazine*, m.p. 60°, converted by PhNCS into the *compound* $NPh<\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}>N{\cdot}CH_2{\cdot}CH_2{\cdot}NPh{\cdot}CS{\cdot}NHPh$, m.p. 105°, and by BzCl into 4-*phenyl*-1-β-*benzanilidoethylpiperazine*, m.p. 91°. (I) and NH_3 in EtOH–H_2O at 100° afford 1-β-*aminoethylpiperazine* ($+H_2O$), b.p. 260—280° (*picrate*, m.p. about 208°). 4-*Methyl*-1-β-*methylaminoethylpiperazine*, b.p. 240—260° (*oxalate*; *picrate*, decomp. about 210°), is described. 4-β-*Aminoethyl*-1-β-*aminoethylaminoethylpiperazine*, $NH_2{\cdot}[CH_2]_2{\cdot}NH{\cdot}[CH_2]_2{\cdot}N<\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}>N{\cdot}[CH_2]_2{\cdot}NH_2$, b.p. 235°/38 mm., gives a *H oxalate*, decomp. 208°, and *picrate*, decomp. 208°. Boiling piperidine and (I) afford *tri*-β-1-*piperidylethylamine* (*picrate*, m.p. 194°). H. W.

Derivatives of piperazine. XI. Addition to conjugate systems. II. V. E. Stewart and C. B. Pollard (J. Amer. Chem. Soc., 1937, **59**, 2006).—1 : 4-*Di*-(β-*aroyl*-α-*arylethyl*)*piperazines* are prepared (method: A., 1936, 1522) from piperazine and the following derivatives of Ph styryl ketone: 3-Me, m.p. 116—116·5°; 4′-chloro-4-methyl, m.p. 149·2—149·6°; 4′-bromo-3-methyl, m.p. 128·8—129·2°; 4′-chloro-3-methyl, m.p. 125·6—126°; 4′-chloro-4-methoxy, m.p. 152—152·5°; 4′-bromo-4-methyl, m.p. 153—153·5°; 4′-bromo-4-methoxy, m.p. 154·8—155·2°; 3 : 4′-Me_2, m.p. 165·5—166°; 4′-bromo-3 : 4-methylenedioxy, m.p. 154·5—155·2°. M.p. are corr. H. B.

Infra-red spectrum and molecular structure of diketopiperazine and tetramethyldiketopiperazine.—See A., I, 495.

Derivatives of pyrazolones and of tetrahydrodiazanaphthalene.—See B., 1937, 1179.

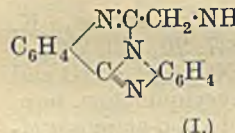
Substituted pyrimidines.—See B., 1937, 1270.

Condensations of aromatic amines with formaldehyde in media containing acid. VI. Use of formic acid in the preparation of 3 : 6-disubstituted dihydroquinazolines from *p*-substituted amines, and from their bis(arylamino)methanes and Schiff's bases. E. C. Wagner (J. Org. Chem., 1937, **2**, 157—166).—*p*-$C_6H_4Me{\cdot}NH_2$, *p*-$C_6H_4Cl{\cdot}NH_2$, *p*-$OMe{\cdot}C_6H_4{\cdot}NH_2$, *p*-$OEt{\cdot}C_6H_4{\cdot}NH_2$, and *p*-$C_6H_4Br{\cdot}NH_2$ with CH_2O and HCO_2H give 3-*p*-tolyl-6-methyldihydroquinazoline and its analogues. These are formed by way of (p-$C_6H_4Me{\cdot}NH)_2CH_2$ etc., and may also be obtained from the latter, the amine hydrochlorides, and CH_2O–HCO_2H, or from the trimeric Schiff's bases, (p-$C_6H_4Me{\cdot}N{\cdot}CH_2)_3$, amine, amine hydrochloride, and CH_2O–HCO_2H. The two

latter methods give better yields. The following are described. *NN'*-Methylenebis-*p*-chloroaniline, new m.p. 59—60°; NN'-*methylenebis*-p-*phenetidine*, m.p. 75° (the substance previously regarded as this compound is the trimeric *Schiff's base*, m.p. 90°); NN'-*methylenebis*-p-*bromoaniline*, m.p. 92° [another substance, m.p. 181° (decomp.), was previously so named (cf. A., 1908, i, 534)], which is reduced (Zn–HCl) to *p*-$C_6H_4Br{\cdot}NH_2$, *p*-$C_6H_4Br{\cdot}NHMe$, and *p*-$C_6H_4Br{\cdot}NMe_2$, and is converted by CH_2O into *trimeric methylene*-p-*bromoaniline*, m.p. 166°; *trimeric methylene*-p-*phenetidine*, m.p. 90°, similarly reduced to a mixture of amines; 6-*methoxy*-3-p-*anisyl*-3 : 4-*dihydroquinazoline*, m.p. 138° (corr.) [*picrate*, m.p. 214° (corr.)], hydrogenated to the 1 : 2 : 3 : 4-*tetrahydroquinazoline*, m.p. 135° (corr.); and 6-*ethoxy*-3-p-*phenetyl*-3 : 4-*dihydroquinazoline picrate*, m.p. 185·5° (corr.). 3-*p*-Tolyl-6-methyl-1 : 2 : 3 : 4-tetrahydroquinazoline and HCO_2H at 150° give the 3 : 4-dihydroquinazoline.

E. W. W.

Quinazolines. I. T. N. Ghosh (J. Indian Chem. Soc., 1937, **14**, 411—413).—1-Keto-3-benzamidomethyl-5 : 6-benz-2 : 4-oxazine (Ghosh, A., 1937, II, 393) condenses (Cu powder at 170°) with NH_2Ar to give 1-keto-2-aryl-3-benzamidomethyl-1 : 2-dihydroquinazolines: *phenyl*, m.p. 205° (hydrolysed by conc. HCl to hippuric acid and *o*-aminobenzanilide), p-*tolyl*, m.p. 195—196°, m-*tolyl*, m.p. 177—178°, and with *o*-$C_6H_4(NH_2)_2$ to give the *benziminazole* derivative, (I), m.p. 211—212° (*hydrochloride*, m.p. 225—231°).


(I.)

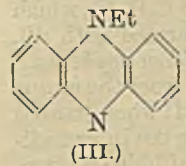
A. Li.

Fission of 2-hydroxy-3-tetrahydroxybutylquinoxalines. II. H. Ohle, W. Gross, and A. Wolter (Ber., 1937, **70**, [*B*], 2148—2152; cf. A., 1934, 392).—Fission of these compounds by $NHPh{\cdot}NH_2$ is not a true hydrolysis but a dehydrogenation. Its incidence is independent of the configuration of the side-chain and of the presence of an electrolytically dissociable OH at $C_{(2)}$. Me gulusonate and *o*-$C_6H_4(NH_2)_2$ an H_2O at 20° afford 2-*hydroxy*-3-l-*xylotetrahydroxybutylquinoxaline*, m.p. 170° (decomp.), $[\alpha]_D^{20}$ −62·0° in H_2O, converted by $NHPh{\cdot}NH_2$ in boiling H_2O into 2-hydroxyquinoxaline-3-aldehydephenylhydrazone, m.p. 283° (decomp.). 2-Hydroxy-3-*d*-arabotetra-acetoxybutylquinoxaline with CH_2N_2 in $CHCl_3$ slowly gives 2-*methoxy*-3-d-*arabotetra-acetoxybutylquinoxaline*, m.p. 154·5—156·5°, $[\alpha]_D^{20}$ −27·6° in $CHCl_3$, hydrolysed by NH_3–MeOH at 20° to 2-*methoxy*-3-d-*arabotetrahydroxybutylquinoxaline*, m.p. 183°, $[\alpha]_D^{20}$ −13·7° in C_5H_5N, which suffers fission into 2-*methoxyqyinoxaline*-3-*aldehydephenylhydrazone*, m.p. 145°. The isomeric 2-*keto*-1-*methyl*-3-*arabotetrahydroxybutyl*-1 : 2-*dihydroquinoxaline*, m.p. 187°, $[\alpha]_D^{17}$ −61·1° in C_5H_5N, is derived from Me glycosonate and *o*-$NH_2{\cdot}C_6H_4{\cdot}NHMe$, HCl, NaOAc, and H_3BO_3 in boiling EtOH. 2-Hydroxy-3-methylquinoxaline is transformed by CH_2N_2 in EtOH into 2-keto-1 : 3-dimethyl-1 : 2-dihydroquinoxaline, m.p. 87°. $AcCO_2H$ and *o*-$NH_2{\cdot}C_6H_4{\cdot}NHMe$ in presence of AcOH give *pyruv*-o-*methylaminoanil*, m.p. 139°. 2-*Keto*-1-*methyl*-3-*dibromomethyl*-1 : 2-*dihydroquinoxaline*, m.p. 178° (*phenylhydrazone*, m.p. 198°), is derived from 2-hydroxy-3-dibromomethylquinoxaline and CH_2N_2 in $CHCl_3$ or from $CHBr_2{\cdot}CO{\cdot}CO_2H$, *o*-$NH_2{\cdot}C_6H_4{\cdot}NHMe$,HCl, and borax in EtOH.

H. W.

Phenazine series. V. Reactions of 1 : 2 : 3 : 4-tetrahydrophenazine and related compounds. VI. Reactions of alkyl phenazonium salts; the phenazyls. H. McIlwain (J.C.S., 1937, 1701—1704, 1704—1711).—V. 1 : 2 : 3 : 4-Tetrahydrophenazine (I) and PhCHO give 1 : 4-*dibenzylphenazine*, m.p. 158° [*ferrichloride* (+AcOH), m.p. 200°], whilst (I) and *p*-$NO_2{\cdot}C_6H_4{\cdot}CHO$ yield 1-p-*nitrobenzyl*-3 : 4-*dihydrophenazine*, m.p. 172°, and 1 : 4-*bis*-p-*nitrobenzylphenazine*, m.p. 250°, reduced to 1 : 4-*bis*-p-*aminobenzyl*-1 : 2 : 3 : 4-*tetrahydrophenazine*, m.p. 176°. According to the time and amounts, (I) and *p*-$NMe_2{\cdot}C_6H_4{\cdot}CHO$ give 1-p-*dimethylamino*-3 : 4-*dihydrophenazine*, m.p. 158°, or 1 : 4-*bis*-p-*dimethylaminobenzylphenazine*, m.p. 207°. 1 : 2 : 3 : 4-*Tetrahydrophenazine monomethiodide*, m.p. 207°, with NaOH affords 9-*methyl*-2 : 3 : 4 : 9-*tetrahydrophenazine*, b.p. 170°/1 mm., and 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydrophenazine methiodide*, m.p. 175°, similarly gives 9-*methyl*-2 : 3 : 4 : 5 : 6 : 7 : 8 : 9-*octahydrophenazine*, b.p. 160°/1 mm.

VI. Phenazine methosulphate (II) is oxidised in air to a small amount of 2-keto-*N*-methylphenazine, m.p. 200°, also obtained by oxidation of *N*-methyldihydrophenazine. *N*-Methylphenazonium hydroxide, presumably the immediate product of the reaction between *N*-methylphenazonium salts and alkalis, is unstable even in absence of air. Under the influence of visible light, these salts oxidise more rapidly, producing mainly the 4-keto-compound, pyocyanine (45 mol. %), phenazine (47 mol. %), and small amounts of 1-hydroxyphenazine and 2-keto-*N*-methylphenazine. NaCN and (II) give N-*methylphenazyl*-2-*nitrile*, m.p. 145°, and N-*methyldihydrophenazine*-2-*nitrile*, m.p. 155°, which are interconvertible under certain conditions, and both yield phenazine-2-carboxylic acid. Na_2SO_3 and (II) afford *Na* N-*methyldihydrophenazinesulphonate* (+H_2O), which with K persulphate forms N-*methylphenazyl*- and then N-*methylphenazonium-sulphonic acid betaine*, with Na_2SO_3 giving *Na H* N-*methylphenazyldisulphonate betaine*. *Phenazine ethosulphate*, m.p. 190°, and $K_3Fe(CN)_6$–NaOH yield 2-*keto*-N-*ethylphenazine*, m.p. 174°, and with Na_2CO_3 in daylight, 4-*keto*-N-*ethylphenazine*, m.p. 187°, is obtained. The ethosulphate is reduced (Zn) to N-*ethyldihydrophenazine*, m.p. 99°, which with PbO_2 gives N-*ethylphenazyl* (III), m.p. 102°. MeMgI converts (II) into *NN*-dimethyl-*NN*-dihydrophenazine and other products.

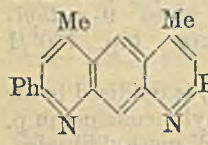

(III.)

F. R. S.

Reversible polymerisation as a cause of new types of absorption bands.—See A., I, 494.

Nitrogenous heterocyclic rings. XXX. 4 : 6-Diamino-1 : 3-diacetylbenzene and its transformation into derivatives of *lin.*-benzodipyridine. P. Ruggli and H. Reichwein (Helv. Chim. Acta, 1937, **20**, 905—913; cf. A., 1937, II, 214).—4 : 6-Dinitro-*m*-xylene in conc. H_2SO_4 is

oxidised by CrO_3–H_2SO_4 at −5° to 4 : 6-dinitro-*iso*phthalic acid, converted by $SOCl_2$ into the corresponding *chloride*, m.p. 106—108°, which gives a resin with $CHAcNa{\cdot}CO_2Et$ and could not be transformed into the corresponding cyanide. With CH_2N_2 in Et_2O it affords 4 : 6-*dinitro*-1 : 3-*bisdiazoacetylbenzene*, decomp. 146—149°, in which CO could not be detected and which gives resins when treated with Al–Hg, H_2S, or I. It is transformed by EtOH and conc. HCl into 4 : 6-*dinitro*-1 : 3-*dichloroacetylbenzene*, decomp. 155—159° after softening at 150°, which cannot be reduced in the usual manner but is converted by Cu in conc. H_2SO_4 at 60° into 4 : 6-*diamino*-1 : 3-*dichloroacetylbenzene* (I), decomp. about 200° when rapidly heated, which appears to pass in boiling $PhNO_2$ into an indigoid compound; its Ac_2 derivative, m.p. 175—176° (slight decomp.), and NaOH give a black vat *dye*. NaI and (I) in cold $COMe_2$ afford 4 : 6-*diamino*-1 : 3-*di-iodoacetylbenzene*, decomp. 165—170° (indef.). Zn dust and HCl or AcOH transform (I) into 4 : 6-*diamino*-1 : 3-*diacetylbenzene* (II), m.p. 234—233° (slight decomp.) (Ac_2 derivative, decomp. 240—245°).

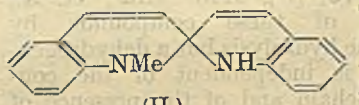

(III.)

This with COPhMe and KOH–MeOH at 110° gives 2 : 7-*diphenyl*-4 : 5-*dimethylbenzodipyridine* (III), decomp. 284—285° [*dipicrate*, decomp. (indef.) 210—260°]. With CH_2Ac_2 and piperidine at 225—230° (II) yields 3 : 6-*diacetyl*-2 : 4 : 5 : 7-*tetramethylbenzodipyridine*, decomp. 246—248° after darkening at 240° (*dipicrate*, decomp. 180°). With $CH_2Ac{\cdot}CO_2Et$ in boiling xylene (II) gives 2 : 7-*dihydroxy*-3 : 6-*diacetyl*-4 : 5-*dimethyl*- or 2 : 7-*diketo*-3 : 6-*diacetyl*-4 : 5-*dimethyl*-1 : 2 : 7 : 8-*tetrahydro-benzodipyridine*, decomp. about 415° after slow darkening above 310°. H. W.

Nitrogenous heterocyclic rings. XXXI. Synthesis of indigotin from *o*-substituted acetophenones. P. Ruggli and H. Reichwein (Helv. Chim. Acta, 1937, **20**, 913—918).—Gradual addition of Br in $CHCl_3$ to an irradiated solution of *o*-$C_6H_4Ac{\cdot}NO_2$ at 50° gives ω-bromo-*o*-nitroacetophenone (*compound*, $C_{13}H_{11}O_3N_2Br$, decomp. 230—240°, with C_5H_5N), reduced by Cu powder in conc. H_2SO_4 at 50° to ω-*bromo*-o-*aminoacetophenone*, m.p. 83—85° (decomp.) after softening at 80° (*compound*, $C_{12}H_{13}ON_2Br$, decomp. 210—223°, with C_5H_5N), which gives very little indigotin (I) when warmed with dil. NaOH in air. ω-*Bromo*-o-*acetamidoacetophenone*, m.p. 126—127° after softening at 120°, from the amine and Ac_2O in Et_2O, gives 73% yields of (I) when treated with dil. NaOH and air, thus suggesting the intermediate formation of acetylindoxyl. ω-Chloro-*o*-nitroacetophenone, from *o*-$NO_2{\cdot}C_6H_4{\cdot}COCl$ and CH_2N_2 followed by treatment of the N_2 compound with EtOH–H_2O–HCl, is similarly reduced to ω-*chloro*-o-*aminoacetophenone*, m.p. 112—113°, which gives only a green colour with aq. NaOH. From ω-*chloro*-o-*acetamidoacetophenone*, m.p. 123—125°, (I) is obtained in 63% yield. H. W.

Nitrogenous heterocyclic rings. XXXII. Benzodipyridine derivatives. IV. P. Ruggli and A. Staub (Helv. Chim. Acta, 1937, **20**, 918—925).—Et_2 *m*-xylylenedichloromalonate is converted by conc. H_2SO_4–HNO_3 (*d* 1·5) at 0° into Et_2 4 : 6-*dinitro*-m-*xylylenedichloromalonate*, m.p. 146°, which when hydrogenated (Ni in EtOH–EtOAc–H_2O) gives Et_2 2 : 7-*diketo*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydrobenzodipiperidine*-3 : 6-*dicarboxylate* (I), m.p. 252°. Et_2 *m*-xylylenedimalonate (II) is obtained from *m*-$C_6H_4(CH_2Br)_2$ and $CHNa(CO_2Et)_2$ or by condensing *m*-$C_6H_4(CHO)_2$ with $CH_2(CO_2Et)_2$ and piperidine to Et_2 m-*phenylenedimethylenemalonate* (III), b.p. 265°/11 mm., m.p. 102°, which is subsequently hydrogenated (Ni in EtOAc–EtOH–H_2O). The product gives a mixture of NO_2-derivatives from which (I) is obtained by reduction. 2 : 7-*Diketo-octahydrobenzodipyridine*-3 : 6-*dicarboxylic acid* has m.p. 412° (decomp.). Treatment of (III) with HNO_3 (*d* 1·5) at 0° yields Et_2 4-*nitro*-m-*phenylenedimethylenemalonate*, m.p. 79—80°, reduced to Et_2 4-*amino*-m-*phenylenedimethylenemalonate*, m.p. 172—175° after softening (*Ac* derivative, m.p. 150—160° after softening at 145°), which is cyclised by EtOH–conc. HCl at 100° to Et_2 3-*carboxycarbostyril*-6-*methylenemalonate*, m.p. 247—250°. *m*-$C_6H_4(CHO)_2$ and barbituric acid in boiling C_5H_5N afford m-*phenylenedimethylenebarbituric acid*, m.p. 335—340° (decomp.). $CO(NH_2)_2$ and (II) with NaOEt in EtOH yield m-*xylylenedibarbituric acid*, m.p. 271—272°. H. W.

Spiran derivative of the quinoline series. K. Maurer and H. Starck (Ber., 1937, **70**, [*B*], 2054—2058).—2-Methylquinoline with *o*-$NO_2{\cdot}C_6H_4{\cdot}CHO$ and $ZnCl_2$ at 140° yields to 2-*o*-nitrostyrylquinoline, m.p. 103°, reduced by $SnCl_2$ and HCl to 2-o-*aminostyrylquinoline*, m.p. 158° [*Ac* derivative, m.p. 181—182°; *methiodide* (I), m.p. 233°; *picrate*, m.p. 218°; *diperchlorate*, decomp. 261° or (+$12H_2O$), m.p. 120°; r-, m.p. 201°, and d-, m.p. 205°, -*camphorsulphonate*; d-*tartrate*, m.p. 212—213°; Fe^{II} and Fe^{III} salts].


(II.)

Cautious treatment of (I) with KOH–EtOH affords 1-*methyl*spiro*dihydroquinoline* (II), m.p. 115° (*picrate*, m.p. 233°; *diperchlorate*, decomp. 180—190° after becoming black at 150°; r-, m.p. 218°, and d-, m.p. 230°, -*camphorsulphonate*; d-*tartrate*, m.p. 192°), which gives no evidence of mol. asymmetry. It is particularly sensitive to Fe salts, with which it gives a red colour. H. W.

Compound $C_8H_{16}H_4N_2$, m.p. 256—257°, from scollop muscle.—See A., III, 339.

Pyrazoloanthraquinones.—See B., 1937, 1180.

Anthrapyrimidines.—See B., 1937, 1180.

Pyrrole series. III. Relation of tripyrrylmethane cleavage to methene synthesis. A. H. Corwin and J. S. Andrews (J. Amer. Chem. Soc., 1937, **59**, 1973—1980; cf. A., 1936, 1122).—Et 2-formyl-4-methylpyrrole-3 : 5-dicarboxylate (I) (1 mol.), Et 2 : 4-dimethylpyrrole-3-carboxylate (II) (1 mol.), and dry HCl in C_6H_{14} give 78% of the hydrochloride of 3 : 5 : 4′-*tricarbethoxy*-4 : 3′ : 5′-*trimethylpyrromethene* (III), m.p. 137° (decomp.) (*Cu* complex), together with some 3 : 5 : 4′ : 4″-tetracarbethoxy-4 : 3′ : 5′ : 3″ : 5″-pentamethyltri-2-pyrrylmethane (IV); with 2 mols. of (II), the sole product is (IV)

[also formed by fusion of (I) and (II) (2 mols.) at 190—200°]. Contrary to Fischer and Ernst (A., 1926, 621), (IV) undergoes cleavage. Thus, (IV) and HCl in Et_2O–HCO_2H (essential) give 4 : 4′-dicarbethoxy-3 : 5 : 3′ : 5′-tetramethylpyrromethene (V) [together with (III)], whilst (IV), (I), and HCl in Et_2O afford (III). The various reactions which occur with (I)—(IV) can be accounted for on the basis of varying reaction velocities. (III) and cold MeOH–KOH give 3 : 5 : 4′-*tricarbethoxy*-4 : 3′ : 5′-*trimethyldi*-2-*pyrrylcarbinol Me ether* (VI) (the *Et ether* is similarly obtained using EtOH–KOH), which undergoes the reactions postulated for the free carbinol. Thus, (VI) and HCl in C_6H_{14} afford (III); (VI), (II), and HCl in C_6H_{14} yield (IV); (VI), Et 1 : 2 : 4-trimethylpyrrole-3-carboxylate (VII), and HCl give (III) and no tripyrrylmethane (cf. below). Fusion of (VI) and (VII) at 145—150° furnishes 3 : 5 : 4′ : 4″-*tetracarbethoxy*-4 : 3′ : 5′ : 1″ : 3″ : 5″-*hexamethyltri*-2-*pyrrylmethane*, which according to expectations (cf. above) is cleaved by Et_2O–HCl to (III). Et 2-formyl-1 : 4-dimethylpyrrole-3 : 5-dicarboxylate (VIII) and (II) at 190—200° give 3 : 5 : 4′ : 4″-*tetracarbethoxy*-1 : 4 : 3′ : 5′ : 3″ : 5″-*hexamethyltri*-2-*pyrrylmethane*, m.p. 169—170° [also formed from (II), (VIII), and HCl in C_6H_{14}], which is cleaved by HCl to (V) (most rapidly in presence of HCO_2H) and (probably) a 1-methylpyrromethene (not isolated). 3 : 5 : 4′ : 4″-*Tetracarbethoxy*-1 : 4 : 1′ : 3′ : 5′ : 1″ : 3″ : 5″-*octamethyltri*-2-*pyrrylmethane*, m.p. 178°, is prepared from (VII) and (VIII). Various unidentified products are obtained from (I) and (VII) by fusion or condensation with HCl. H. B.

Residual affinity and co-ordination. XXXVII. Complex metallic salts containing 2 : 6-di-2′-pyridylpyridine (2 : 2′ : 2″-tripyridyl). (Sir) G. T. Morgan and F. H. Burstall (J.C.S., 1937, 1649—1655).—The two forms of 2 : 6-di-2′-pyridylpyridine (I) (2 : 2′ : 2″-*tripyridyl trihydrochloride tetrahydrate*, decomp. 280—285°) are dimorphous (cf. A., 1932, 284) and on oxidation ($KMnO_4$) give only pyridine-2-carboxylic acid, indicating that it is the central one of the C_5H_5N rings which is preferentially attacked. (I) acts as a tridentate group and furnishes many stable and characteristic co-ordination compounds, divided into two series, which contain severally 1 and 2 mols. of base to each atom of metal. The first series is of type [M tripy X] and [M tripy X]X, where M = Cu, Ag^+, Ag^{++}, Zn, Cd, Hg, Pd, Pt, and [$IrCl_3$ tripy]. The second is of type [M 2tripy]X_2 and [M 2tripy]X_3,nH_2O, where M = Fe^{++}, Co^{++}, Co^{+++}, Ni, Ru^{++}, Os^{++}, and Cr^{+++}. The following are described: 2 : 2′ : 2″-*tripyridyl-cupric chloride dihydrate*, *-argentous nitrate* and *perchlorate*, *-argentic nitrate*, *chlorate*, *perchlorate*, *dithionate*, and *persulphate*, *-zinc chloride*, *-cadmous chloride*, *-mercuric nitrate*, *-palladous chloride trihydrate*, and *-iridium trichloride*; *bis*-2 : 2′ : 2″-*tripyridyl-ferrous bromide tetrahydrate* (*monohydrate*) and *iodide monohydrate*, *-ruthenous chloride tetrahydrate*, *-osmous chloride tetrahydrate* and *iodide hydrate*, *-cobaltous bromide hydrate* (+3·5H_2O; *monohydrate*) and *iodide hydrate*, *-cobaltic chloride heptahydrate*, *-nickel bromide hydrate* (+3·5H_2O; *monohydrate*, *iodide hydrate*, and *tartrate tetrahydrate*, and *-chromic chloride dihydrate*. F. R. S.

Relation between taste and chemical constitution. Naphtho*iso*triazine group. IV. A. Neri. **V, VI.** A. Neri and (Signa.) G. Grimaldi. **VII—IX.** A. Neri (Gazzetta, 1937, 67, 448—453, 453—460, 468—472, 473—476, 477—481, 513—517; cf. A., 1937, II, 433).—IV. 2-Benzene- (I) and 2-*p*-sulphobenzene-azo-α-naphthylamine-4-sulphonic acid (II) with OMe·C_6H_4CHO in AcOH give *Na* 3-*phenyl*-2-p-*anisyl*-2 : 3-*dihydro*-1 : 3 : 4-*naphthoisotriazine*-6-*sulphonate* (+7H_2O), tasteless, and the Na_2 salt of the corresponding 3-p-*sulphophenyl*-acid, very sweet. Similarly *p*-sulphobenzeneazo-β-naphthylamine (III), and benzene- (IV) and *p*-sulphobenzene-azo-β-naphthylamine-6-sulphonic acid (V) give 2-p′-*sulphophenyl*-3-p-*anisyl*-2 : 3-*dihydro*-1 : 2 : 4-*naphthoisotriazine*, tasteless, and 2-*phenyl*-, slightly bitter, and 2-p′-*sulphophenyl*-3-p-*anisyl*-2 : 3-*dihydro*-1 : 2 : 4-*naphthoisotriazine*-8-*sulphonic acid*, tasteless.

V. Vanillin gives, from (I) and (II), 3-*phenyl*-, tasteless, and 3-p-*sulphophenyl*-2-(4′-*hydroxy*-3′-*methoxyphenyl*)-2 : 3-*dihydro*-1 : 3 : 4-*naphthoisotriazine*-4-*sulphonic acid*, slightly salty; from (III), 2-p-*sulphophenyl*-3-(4′-*hydroxy*-3′-*methoxyphenyl*)-2 : 3-*dihydro*-1 : 2 : 4-*naphthoisotriazine*, tasteless; and from (IV) and (V), 2-*phenyl*-, bitter, and 2-p-*sulphophenyl*-3-(4′-*hydroxy*-3′-*methoxyphenyl*)-2 : 3-*dihydro*-1 : 2 : 4-*naphthoisotriazine*-8-*sulphonic* acid, salty with sweet after-taste.

VI. MeCHO gives, from (I) and (II), 3-*phenyl*-, slightly bitter, and 3-p-*sulphophenyl*-2-*methyl*-2 : 3-*dihydro*-1 : 3 : 4-*naphthoisotriazine*-6-*sulphonic acid*, slightly sweet; from (III), 2-p-*sulphophenyl*-3-*methyl*-2 : 3-*dihydro*-1 : 2 : 4-*naphthoisotriazine*, tasteless; and from (IV) and (V), 2-*phenyl*-, bitter, and 2-p-*sulphophenyl*-3-*methyl*-2 : 3-*dihydro*-1 : 2 : 4-*naphthoisotriazine*-8-*sulphonic acid*.

VII. CHPh:CH·CHO gives, from (I) and (II), 3-*phenyl*-, sweet, and 3-p-*sulphophenyl*-2-*styryl*-2 : 3-*dihydro*-1 : 3 : 4-*naphthoisotriazine*-6-*sulphonic acid*, very sweet; from (III), 2-p-*sulphophenyl*-3-*styryl*-2 : 3-*dihydro*-1 : 2 : 4-*naphthoisotriazine*, tasteless; and from (IV) and (V), 2-*phenyl*-, tasteless, and 2-p-*sulphophenyl*-3-*styryl*-2 : 3-*dihydro*-1 : 2 : 4-*naphthoisotriazine*-8-*sulphonic acid*, tasteless.

VIII. By diazotisation, 1 : 4-NH_2·$C_{10}H_6$·SO_3H gives 2-α′-*naphthaleneazo*-α-*naphthylamine*-4 : 4′-*disulphonic acid* (G.P. 42,382), which with PhCHO and other aldehydes gives 2-*phenyl*-, tasteless, 2-p-*anisyl*-, sweet, 2-o-*hydroxyphenyl*-, tasteless, 2-(4′-*hydroxy*-3′-*methoxyphenyl*)-, tasteless, and 2-*styryl*-3-(4′-*sulpho*-α-*naphthyl*)-2 : 3-*dihydro*-1 : 3 : 4-*naphthoisotriazine*-6-*sulphonic acid*, sweet. None of the naphthoisotriazines described in the above series has m.p. <300°.

IX. The Na_2 salt of 1-p-*sulphobenzeneazo*-β-*naphthylamine*-6-*sulphonic acid* (prepared in the usual way), with AcOH and aldehydes gives 3-*phenyl*-, sweet, 3-o-*hydroxyphenyl*- and 3-p-*anisyl*-, both tasteless, 3-(4′-*hydroxy*-3′-*methoxyphenyl*)-, sweet with salt after-taste, and 3-*styryl*-2-(4′-*sulpho*-α-*naphthyl*)-1 : 2 : 4-*naphthoisotriazine*-8-*sulphonic acid*, tasteless. E. W. W.

Cobaltinitrites of hexamethylenetetramine. A. Hemmeler and (Signa.) M. Angelini (Gazzetta, 1937, **67**, 428—434; cf. A., 1936, 303).—$Na_3[Co(NO_2)_6]$ and $(CH_2)_6N_4$ (I) give the *compound*, $Na[(CH_2)_6N_4H]_2[Co(NO_2)_6],6H_2O$. De Koninck's reagent ($CoCl_2$ + $NaNO_2$ + AcOH, filtered) and (I) give a *compound* $CoO[(CH_2)_6N_4H]_4Co[Co(NO_2)_6]_2$. E. W. W.

Phosphorylation of mono*iso*propylideneadenosine and of diacetyladenosine. P. A. Levene and R. S. Tipson (J. Biol. Chem., 1937, **121**, 131—153).—In order to prepare an adenosine-5-phosphoric acid, the OH groups 2 and 3 were blocked as follows. Adenosine and CPh_3Cl in C_5H_5N give a mixture of 5-mono- (I), $[\alpha]_D^{23}$ −18° in C_5H_5N, and N : 5-*ditriphenylmethyladenosine* (II), m.p. 200—202°, $[\alpha]_D^{25}$ −19·2° in C_5H_5N. Heating (I) in C_5H_5N with $C_6H_4Me{\cdot}SO_2Cl$ yields N : 2 : 3-*tritoluenesulphonyl*-5-*triphenylmethyl*-, $[\alpha]_D^{25}$ −57·2° in $COMe_2$, hydrolysed by 80% AcOH to the *tritoluenesulphonyladenosine*, m.p. 195—196°, $[\alpha]_D^{26}$ −94·4° in $COMe_2$, the 5 position of which is free since it gives no cryst. derivative with NaI in $COMe_2$. With Ac_2O in C_5H_5N, (I) yields N : 2 : 3-*triacetyl*-5-*triphenylmethyl*-, $[\alpha]_D^{24}$ +14·0° in C_5H_5N, hydrolysed by 80% AcOH to 2 : 3-*diacetyladenosine*, m.p. 181—182°, $[\alpha]_D^{26}$ −78·7° in $COMe_2$ {also obtained from (II) via 2 : 3-*diacetyl*-N : 5-*ditriphenylmethyladenosine*, $[\alpha]_D^{26}$ −6·0° in $COMe_2$}, together with acetyladenine, m.p. 347—348°. Benzoylation of (I) in C_5H_5N gives N : 2 : 3-*tribenzoyl*-5-*triphenylmethyl*-, $[\alpha]_D^{25}$ −41·5° in C_5H_5N, hydrolysed by 80% AcOH to 2 : 3-*dibenzoyladenosine*, m.p. 132—134°, $[\alpha]_D^{25}$ −107·8° in $COMe_2$, together with benzoyladenine. Adenosine, $COMe_2$, and $ZnCl_2$ yield 2 : 3-iso*propylideneadenosine*, m.p. 200—204°, $[\alpha]_D^{26}$ −99·8° in C_5H_5N. Phosphorylation (cf. A., 1935, 1481) of this with 2 mols. of $POCl_3$, or of diacetyladenosine with 1 mol., and hydrolysis of the product with N-HCl gives adenosine-5-phosphoric acid, isolated as Ba salt. A. Li.

Absorption spectra of pyrrole colouring matters. Pyrromethenes and bilirubinoids.—See A., I, 548.

Morpholine alkanols.—See B., 1937, 1179.

Action of xanthhydrol on pyrroles. G. Illari (Gazzetta, 1937, **67**, 434—439).—Xanthhydrol (I) and pyrroles, in AcOH, give mono- and di-xanthylpyrroles. The following are described: 2 : 5-*dixanthyl*-, m.p. 200° (decomp.) (converted by KOH fusion into maleimide and xanthen), 5-*xanthyl*-2-*ethyl*-, m.p. 190—191°, 2-*acetyl*-5-*xanthyl*-, m.p. 221—224° (decomp.), 5-*xanthyl*-2 : 4-*dimethyl*-, m.p. 218—219° (decomp.), 3-*acetyl*-5-*xanthyl*-2 : 4-*dimethyl*-, m.p. 253° (decomp.), and 2 : 5-*dixanthyl*-1-*phenyl-pyrrole*, m.p. 256—259° (decomp.). 2 : 4-Dimethylpyrrole-3 : 5-dicarboxylic acid, 3 : 5-diacetyl-2 : 4-dimethyl-, 2 : 5-diethyl-, and 2 : 5-diacetyl-pyrrole do not condense with (I). It is suggested that (I) might be used as a reagent for identifying mixed pyrroles. E. W. W.

Pharmaceutical applications of furfuraldehyde. I. A. Mangini (Annali Chim. Appl., 1937, **27**, 386—392; cf. A., 1937, II, 428).—Furfuraldehyde and $AcCO_2H$ with *o*-, *m*-, and *p*-toluidine yield 2-2′-furyl-8-, m.p. 248—249° (decomp.) (*Na* salt), 7-, m.p. 272—272·5° (decomp.) (*Na* salt), and 6-*methylcinchonic acid*, m.p. 253—254° (decomp.) (*Na* salt), respectively. The acids are more or less active in the elimination of uric acid and are more tolerable and less toxic than atophan derivatives. L. A. O'N.

Oximinopyrroles. VII. Synthesis of phenylbenzylfurazan. T. Ajello (Gazzetta, 1937, **67**, 444—448).—$CH_2Ph{\cdot}CBz{:}N{\cdot}OH$ and NH_2OH give *Ph* CH_2*Ph diketone dioxime*, m.p. 217—218° (*Bz*$_2$ derivative, m.p. 146°; *Ni* salt), of which the *Ac*$_2$ derivative, amorphous, is converted by boiling 10% KOH into the substance $C_{15}H_{12}ON_2$, m.p. 98—99° (cf. A., 1935, 763; 1937, II, 264), which is thus shown to be 3-*phenyl*-4-*benzyl*-1 : 2 : 5-*oxadiazole*. E. W. W.

Hydroxyquinolines. III. Syntheses of diphenylquinolino*iso*oxazine and of its *N*-substituted derivatives. F. Pirrone (Gazzetta, 1937, **67**, 529—536).—8-Hydroxyquinoline (I) and $CHPh(N{:}CHPh)_2$ in C_6H_6 at 60° give 2 : 4-diphenyl-5 : 6-(7′ : 8′-quinolino)-1 : 3-*iso*oxazine (II) (A., 1936, 1526). In EtOH at 60°, (I), PhCHO, and $HCO{\cdot}NH_2$, NH_2Ac, NH_2Bz, or *p*-$OH{\cdot}C_6H_4{\cdot}CO{\cdot}NH_2$ give respectively the 3-*formyl*, m.p. 158—159°, 3-*acetyl*, m.p. 208—209° (*picrate*, m.p. 164—165°), 3-*benzoyl*, m.p. 198—199° (*picrate*, m.p. 186°), and 3-*salicoyl*, m.p. 171—172°, derivatives of (II). E. W. W.

Action of sulphuric acid on unsaturated thiocarbimides: thiolthiazolines. H. A. Bruson and J. W. Eastes (J. Amer. Chem. Soc., 1937, **59**, 2011—2013).—β-*Methylallylthiocarbimide* (I), b.p. 64°/10 mm., 169—170°/760 mm. (from $CH_2{:}CMe{\cdot}CH_2Cl$ and MeOH–NaCNS), and aq. 27% NH_3 give β-*methylallylthiocarbamide*, m.p. 92—94°, which is converted by aq. 35% HCl at 140° into 2-*amino*-5 : 5-*dimethylthiazoline hydrochloride*, m.p. 127—129·5°. 5 : 5-Dimethylthiazoline-2-diazonium chloride, decomp. violently about 140°, and H_2S in aq. KOH afford 2-*thiol*-5 : 5-*dimethylthiazoline* (II), m.p. 162·5—163° (*Ac*, m.p. 69·5°, *Bz*, m.p. 91°, and *ClHg*-derivatives), also prepared from 2-*thiol*-5 : 5-*dimethyloxazoline*, m.p. 107—109° (from $NH_2{\cdot}CH_2{\cdot}CMe_2{\cdot}OH$ and CS_2 in aq. EtOH–KOH), and P_2S_5 in C_6H_6. (II) is also obtained from (I) and 95% H_2SO_4 at <5°; (I) → $[CH_2{:}CMe{\cdot}CH_2{\cdot}NH{\cdot}CS_2H]$ → $\begin{matrix}CMe_2{\cdot}S\\ CH_2{\cdot}NH\end{matrix}>CS$ → (II). β-Methyl-α-ethylallyl alcohol (from MgEtBr and $CH_2{:}CMe{\cdot}CHO$), $SOCl_2$, and C_5H_5N at 65° give the chloride, b.p. 120—124°, and thence β-methyl-α-ethylallylthiocarbimide, b.p. 190—200°/760 mm., converted by 95% H_2SO_4 at 0° into 2-*thiol*-5 : 5-*dimethyl*-4-*ethylthiazoline* [or 2-*thiol*-5-*methyl*-5-*propylthiazoline* (cf. Billeter, A., 1925, i, 1051)], m.p. 115—118°. H. B.

Reactions in the thiazole series. I. Reactions of 2-chlorobenzthiazoles with thiocarbamides. Winfield Scott and G. W. Watt (J. Org. Chem., 1937, **2**, 148—156).—2-Chlorobenzthiazole (I) and $CS(NH_2)_2$ (II) in EtOH at the b.p. give 2-thiolbenzthiazole. This is also obtained from allyl- (III), phenyl- (IV), and *o*-tolyl-thiocarbamide (V), but not from *s*-diphenyl- (VI), *s*-di*cyclo*hexyl- (VII) [from

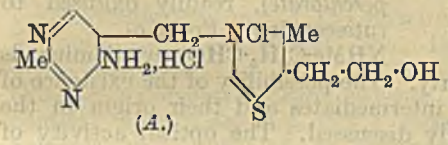
$(C_6H_{10}N)_2CH_2$ and S], *N*-phenyl-*N'N'*-dimethyl- (VIII), or *NN*-pentamethylene-*N'*-phenyl-thiocarbamide. With thiobenziminazolone, (I) gives an additive *compound*, $C_{14}H_{10}ClN_3S_2$, m.p. 233—234° (decomp.). 2-Chloro-6-nitrobenzthiazole and (II), (III), (IV), (V), (VI), or (VII) give 2-*thiol*-6-*nitrobenzthiazole* (IX), m.p. 225—227°; reaction with (VI) is very slow, whilst with (VII) some *s*-di*cyclo*hexylcarbamide is formed. With (VIII), no (IX) is identified, 6-*nitro*-2-*dimethylaminobenzthiazole*, m.p. 197·5—199°, and an unidentified product being formed. In general, thiocarbamides react the less readily as they are the more substituted. 1 : 1'-Dipiperidinomethane and S in xylene give *piperidine pentamethylenedithiocarbamate*, m.p. 172—173°. E. W. W.

5-Nitrobenzthiazyl dithiocarbamates.—See B., 1937, 1179.

1-Amino-5 : 6-tetramethylenebenzthiazole.—See B., 1937, 1179.

Pyrimidylthiazoles.—See B., 1937, 1270.

Synthesis of the antineuritic vitamin. H. Andersag and K. Westphal (Ber., 1937, 70, [*B*], 2035—2054). —The constitution *A* is established synthetically for vitamin-B_1 (I). γ-Acetopropyl acetate is brominated in anhyd. Et_2O and the crude product is converted by $Ba(CNS)_2$ in EtOH into *γ-thiocyano-γ-acetopropyl acetate*, isomerised in acid solution to 2-*hydroxy*-4-*methyl*-5-*acetoxyethylthiazole*, m.p. 89°. This is transformed by boiling $POCl_3$ into 2-*chloro*-4-*methyl*-3-*acetoxyethylthiazole*, b.p. 103—105°/0·7 mm., reduced by Zn dust and AcOH at 70° to 4-*methyl*-5-*acetoxyethylthiazole*, b.p. 112°/5 mm. (*picrate*, m.p. 133°), whence 4-*methyl*-5-*hydroxyethylthiazole*, b.p. 123—124°/3 mm. (*picrate*, m.p. 163—164°), identical with the basic product obtained by fission of (I) (Williams, A., 1935, 504, 668). Arising from the suggestions of Williams (*loc. cit.*) and Windaus *et al.* (A., 1936, 253) with regard to the pyrimidine portion of the mol. of (I) the synthesis of 4'-*methylthiazolo*-3' : 2'-1 : 2-*benziminazole*, m.p. 165°, from CH_2Cl·COMe, thiolbenziminazole, and Na in EtOH and of 4'-*methylthiazolo*-3' : 2'-1 : 2-5-*methyliminazole*, b.p. 150—160°/23 mm. (*hydrochloride*, m.p. 242°), from 2-thiol-4-methyliminazole and CH_2Cl·COMe, has been effected. These compounds as bases and salts are colourless and devoid of the fluorescence in the ultra-violet of the thiochrome obtained by the alkaline oxidation of (I). The previous suggestions for the constitution of (I) appear therefore inaccurate in this respect and further progress is made by the synthesis of all possible pyrimidine portions except the known 5 : 6-diamino-4-ethylpyrimidine. 4-Amino-2 : 6-dimethylpyrimidine could not be nitrated. Et benzeneazoacetoacetate, acetamidine hydrochloride (II), and Na in EtOH afford 5-*benzeneazo*-4-*hydroxy*-2 : 6-*dimethylpyrimidine*, m.p. 186°, reduced by $Na_2S_2O_4$ and NaOH to 5-*amino*-4-*hydroxy*-2 : 6-*dimethylpyrimidine*, m.p. 194°. This with PCl_5 in boiling $POCl_3$ affords 4-*chloro*-5-*amino*-2 : 6-*dimethylpyrimidine*, m.p. 80° (*picrate*, m.p. 169°), transformed by NH_3–MeOH at 238° into 4 : 5-*diamino*-2 : 6-*dimethylpyrimidine*, m.p. 248° [*monohydrochloride* (+0·5H_2O), m.p. 271°; *monopicrate*, m.p. 235°, condensation *product*, $C_{20}H_{16}N_4$, m.p. 207°, with benzil], which differs greatly from the degradation product of Windaus. Et_2 formylsuccinate, (II), and NaOEt in boiling EtOH give *Et* 4-*hydroxy*-2-*methylpyrimidyl*-5-*acetate*, m.p. 179°, whence Et 4-*chloro*-2-*methylpyrimidyl*-5-*acetate*, b.p. 110°/4 mm., m.p. 40—41°, converted by NH_3–MeOH into 4-*amino*-2-*methylpyrimidyl*-5-*acetamide*, (III), m.p. 250° (corresponding *acid*, m.p. 270°), and 4-*methoxy*-2-*methylpyrimidyl*-5-*acetamide* (IV), m.p. 201°. Treatment of (III) with Br and KOH and PhCHO successively and hydrolysis of the product with HCl yields 4-*amino*-2-*methyl*-5-*aminomethylpyrimidine*, m.p. 132° [*dihydrochloride*, m.p. 268—269°; *picrate*, m.p. 224—225°; *sulphate*, m.p. 276°; *formyl* derivative, (V), m.p. 224°], identical with the product of Windaus. P_2S_5 in boiling PhMe transforms (V) into 4-*amino*-2-*methyl*-5-*thioformamidomethylpyrimidine* (VI), m.p. 193°. Treatment of (IV) with Br and KOH gives 4-*methoxy*-2-*methyl*-5-*aminomethylpyrimidine*, b.p. 110—116°/? mm. (*picrate*, m.p. 188°), the *dihydrochloride*, m.p. 150—151°, of which is transformed by $NaNO_2$ into 4-*amino*-2-*methyl*-5-*hydroxymethylpyrimidine*, m.p. 194° (*hydrochloride*, m.p. 224°), whence (HBr in AcOH at 40°) 4-*amino*-2-*methyl*-5-*bromomethylpyrimidine dihydrobromide*, m.p. 213° (decomp.). This with 4-methyl-5-hydroxyethylthiazole at 120—130° gives 4-*methyl*-5-β-*hydroxyethyl*-N-4'-*amino*-2'-*methyl*-5-*pyrimidylmethylthiazolium bromide hydrobromide*, m.p. 220°, also obtained by treatment of *acetopropyl benzoate*, b.p. 138—140°/2 mm., with Br and then with (VI) and identical with vitamin-B_1 hydrobromide. This is transformed through the picrate, m.p. 201—202°, into the corresponding hydrochloride, m.p. 252°, chemically and physiologically identical with the natural material. 2 : 4-Dihydroxy-6-methyl-5-hydroxymethylpyrimidine and PCl_5 in boiling $POCl_3$ afford 2 : 4-*dichloro*-6-*methyl*-5-*chloromethylpyrimidine*, b.p. 120°/3 mm., m.p. 39°, which with NaI in $COMe_2$ affords 2 : 4-*dichloro*-6-*methyl*-5-*iodomethylpyrimidine*, m.p. 90°. This with AgOAc in $COMe_2$ yields 2 : 4-*dichloro*-6-*methyl*-5-*acetoxymethylpyrimidine*, b.p. 141°/4 mm., m.p. 55°, converted by NH_3–EtOH at 100° into 2-*chloro*-4-*amino*-6-*methyl*-5-*hydroxymethylpyrimidine*, m.p. 179°, which with Zn dust in boiling H_2O gives 4-*amino*-6-*methyl*-5-*hydroxymethylpyrimidine*, m.p. 166°. 4-*Amino*-6-*methyl*-5-*bromomethylpyrimidine hydrobromide* (VII), m.p. 210—212°, is condensed with the thiazole derivative at 120—130° to 4-*methyl*-5-*hydroxyethyl*-N-4'-*amino*-6'-*methyl*-5'-*pyrimidylmethylthiazolium chloride hydrochloride*, m.p. 242° (corresponding *hydrobromide*; *picrate*, m.p. 193°; *picrolonate*, m.p. 213°). This resembles (I) in giving an intense ultra-violet fluorescence when oxidised by alkaline $K_3Fe(CN)_6$ but is distinguished, *inter alia*, by less physiological activity. NH_3–MeOH at 100° transforms (VII) into 4-*amino*-6-*methyl*-5-*aminomethylpyrimidine* (VIII) (*picrate*, m.p. 238°; *hydrochloride*, m.p. 277°). Et_2 acetosuccinate, $CS(NH_2)_2$, and NaOEt in boiling EtOH afford 4-*hydroxy*-2-*thiol*-6-*methylpyrimidyl*-5-*acetic acid*, m.p. 295° (*Na* salt), the *Et* ester, m.p. 218°, of which is

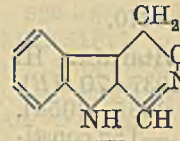


(*A.*)

transformed by $Pb(OAc)_2$ and H_2O_2 in AcOH at 30—40° into *Et* 4-*hydroxy*-6-*methylpyrimidyl*-5-*acetate*, b.p. 203—205°/0·5 mm., m.p. 153°. This with boiling $POCl_3$ gives *Et* 4-*chloro*-6-*methylpyrimidyl*-5-*acetate*, b.p. 116—117°/1·5 mm., whence (NH_3–MeOH at 120—130°) 4-*amino*-6-*methylpyrimidyl*-5-*acetamide*, m.p. 223°, and (VIII). H. W.

Oxidation of benzoylanabasine with potassium permanganate. G. Menschikov, J. Losik, and A. Orekhov (Chim. Farm. Prom., 1934, No. 6, 7—8).—dl-δ-*Benzamido*-δ-(3-*pyridyl*)*valeric acid*, m.p. 146°, is formed, and, with HCl, yields δ-*amino*-δ-(3-*pyridyl*)*valeric acid dihydrochloride*. Ch. Abs. (*r*)

Synthesis of natural substances, particularly alkaloids, under physiological conditions and its relationship to the question of the formation of vegetable compounds in the cell. C. Schöpf [with G. Lehmann, W. Arnold, K. Koch, H. Bayerle, K. Falk, F. Oechler, and H. Steuer] (Angew. Chem., 1937, **50**, 779—787, 797—805).—There is no evidence of any spontaneous chemical change in the animal cell. In the vegetable cell the reactions may be important for life and controlled at every stage by a sp. enzyme of the cell or may be accidental whether or not controlled by an enzyme. Far-reaching conclusions can seldom be drawn from the constitution of a single natural product but greater probability is attached to consideration of the "comparative anatomy" of a series of closely related compounds. The hypothetical method of biogenesis is then subjected to the criteria of physiological possibility and inherent probability with regard to initial materials. For the synthesis of the alkaloids of the *Angostura* bark, *o*-$NH_2{\cdot}C_6H_4{\cdot}CO_2H$ is too feebly reactive to serve as initial material. The condensation of *o*-$NH_2{\cdot}C_6H_4{\cdot}CHO$ with aldehydes or ketones requires too conc. alkali but its reaction with β-CO-acids at p_H 5—11, best at p_H about 7·0, takes place with loss of CO_2 and leads with suitable partners to quinoline, 2-methyl- and 2-*n*-amylquinoline. Condensation of *o*-$NH_2{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}CO_2H$ with $Me{\cdot}[CH_2]_4{\cdot}CHO$, $(OMe)_2C_6H_3{\cdot}[CH_2]_2{\cdot}CHO$, and $CH_2O_2{:}C_6H_3{\cdot}[CH_2]_2{\cdot}CHO$ is suggested for the biogenesis of the 4-hydroxyquinoline derivatives. Condensation of succindialdehyde (I) with NH_2Me and $CO(CH_2{\cdot}CO_2H)_2$ leads directly at p_H 3—11 to tropinone, whereas at p_H 13 tropinonedicarboxylic acid results. The alkaloids derived from tropinonecarboxylic acid may owe their origin to the condensation of (I) with NH_2Me and $CO_2H{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CO_2Me$. *meso*Tartardialdehyde, $CO(CH_2{\cdot}CO_2H)_2$, and NH_2Me give a homogeneous *ketone* (II), m.p. 192°, reduced to two stereoisomeric alcohols one of which is identical with teloidine. Hydroxytropine appears to be derived from maldialdehyde. ψ-Pelletierine is obtained directly at physiological p_H from glutardialdehyde (III), NH_2Me, and $CO(CH_2{\cdot}CO_2H)_2$ with loss of CO_2. Lobelanine is obtained in 80% yield from (III), NH_2Me, and $CH_2Bz{\cdot}CO_2H$ at p_H 4, the yield being dependent on p_H in an unusual degree. Examination of the probability of the synthesis of hygrine, cuskhygrine, and methyl*iso*-pelletierine from suitable amino-aldehydes is hampered by the difficulty of their prep., but the prep. of 2-β-phenylethylpyrrolidine from $CH_2Bz{\cdot}CO_2H$ and $NH_2{\cdot}[CH_2]_3{\cdot}CH(OEt)_2$ establishes its inherent possibility. The *iso*quinoline alkaloids are so complex that a complete suggestion of their biogenesis cannot yet be given, but it is shown that 6 : 7-dihydroxy-1-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline (precursor of carnegine and salsoline) is formed from a salt of β-3 : 4-dihydroxyphenylethylamine and MeCHO in dil. aq. solution at p_H 5. Tetrahydroharman results from tryptamine and MeCHO under physiological conditions; its further conversion into harmaline, harmalol, harmine, and harman is readily explained. Under physiological conditions the ring system of vasicine is rapidly formed from *o*-$NH_2{\cdot}C_6H_4{\cdot}CHO$ and $NH_2{\cdot}[CH_2]_3{\cdot}CHO$ and there is no reason to suppose that $OH{\cdot}CH(NH_2){\cdot}[CH_2]_2{\cdot}CHO$ behaves differently; the peculiarity is the reversibility of the change, irreversible stabilisation being attributed to an enzyme which displaces H from positions 1 : 2 to positions 3 : 4. Treatment of *o*-$NH_2{\cdot}C_6H_4{\cdot}CHO$ with dihydronorharman at p_H 5 gives the *substance* (IV) (isolated as the *perchlorate*), readily oxidised to rutæcarpine. From *o*-$NHMe{\cdot}C_6H_4{\cdot}CHO$ evodiamine is derived similarly. The possibility of the existence of the supposed intermediates and their origin in the cell is critically discussed. The optical activity of the alkaloids is considered. H. W.



(IV.)

Lupin alkaloids. XIV. Anisylsparteine. K. Winterfeld and E. Hoffmann (Arch. Pharm., 1937, **275**, 526—532; cf. A., 1937, II, 218).—*dl*-Lupanine and *p*-$OMe{\cdot}C_6H_4{\cdot}MgBr$ give p-*anisyldehydrosparteine*, b.p. 194—202°/0·1 mm., hydrogenated very slowly to *p-anisylsparteine* (I), b.p. 188°/0·3 mm. [*sulphate*, $+6H_2O$, m.p. 76°; *diauri-*, m.p. 193° (decomp.), and *platini-chloride*, $+2H_2O$, decomp. 246°; *picrate*, m.p. 206°]. Ethyl- and phenyl-sparteine sulphates, phenyldehydrosparteine sulphate, and (I) have 10, 20, 10, and 30 times, respectively, the effect of sparteine sulphate (II) on the frog's heart. The effect of (II) is equal to that of methylsparteine sulphate. R. S. C.

Rotatory power of some alkaloids derived from ecgonine. C. Lapp and A. Lévy (Bull. Sci. Pharmacol., 1937, **44**, 305—325).—The alteration of [α] with p_H is measured for cocaine, ecgonine, benzoyl-, methyl-, and nor-ecgonine. The changes which occur as the p_H is altered are discussed in the light of their absorption spectra. J. L. D.

Alkaloid of the Chinese drug, "Kuh-Seng." II. H. Kondo, E. Ochiai, and K. Tsuda (Arch. Pharm., 1937, **275**, 493—496; cf. A., 1928, 531).—The drug contains, besides matrine, *oxymatrine*, $C_{15}H_{24}O_2N_2$, $+H_2O$ (retained at 150°/vac.), m.p. 208°, $[\alpha]_D^{18}$ +29·8° in EtOH, and $+xH_2O$, m.p. 77—80° (*picrate*, decomp. 215°; *platini-*, decomp. 250°, and *auri-chloride*, decomp. 207°; *perchlorate*, decomp. 240°; *hydrobromide*, hygroscopic, m.p. 215°; *methoaurichloride*, decomp. 185°; *hydrochloride*, hygroscopic), unaffected by *p*-$NO_2{\cdot}C_6H_4{\cdot}COCl$; the latter

base contains one *tert.* N and one CO·N. The two alkaloids are not necessarily related. R. S. C.

Aconitine. II. Relationship between aconitine and atisine and some degradation products of the latter. A. LAWSON and J. E. C. TOPPS (J.C.S., 1937, 1640—1643).—Atisine (I), $C_{22}H_{33}O_2N$, m.p. 296° (decomp.), possesses CH_2O_2 and NMe groups (cf. Jowett, J.C.S., 1896, **69**, 1518; Chandrasena, A., 1933, 841). The hydrochloride of (I) is reduced (Pd–H_2) to the H_2-derivative [*hydrochloride*, m.p. 319° (decomp.)]. After removal of CH_2O_2, (I) with Zn gives a base, $C_{20}H_{31}ON$ (*picrate*, m.p. 173°). KOEt and (I) yield a *base*, $C_{21}H_{31}O_2N$, m.p. 147° [*hydrochloride*, m.p. 278° (decomp.)], dehydrogenated (Se) to a base, b.p. 150—160°/1 mm. (*picrate*, m.p. 206°), and a *hydrocarbon* (II), $C_{17}H_{16}$. Dehydrogenation of (I) gives a *base*, $C_{20}H_{29}ON$, b.p. 190—200°/1 mm. [*picrate*, m.p. 242—243° (decomp.); *hydrochloride*, m.p. 265°], a *substance*, $C_{19}H_{27}O_2N$, m.p. 240°, an oil, b.p. 170—200°/1 mm., and (II), b.p. 130—160°/1 mm. (*picrate*, m.p. 129°; $C_6H_3(NO_2)_3$ complex, m.p. 140°). The results indicate that (I) has a pentacyclic structure and is more closely related to lucidisculine than to aconitine. F. R. S.

Dihydrokurchine. J. C. CHOWDHURY and D. H. PEACOCK (J. Indian Chem. Soc., 1937, **14**, 486—488).—Kurchine (A., 1928, 1265), $C_{23}H_{38}N_2$, gives (PtO_2–H_2) *dihydrokurchine* [*sulphate*, m.p. 334° (decomp.); *hydriodide*, m.p. 222°; *picrate*, m.p. 176°; *sulphate*, m.p. 268°, of *Ac* derivative, m.p. 112°; *NO*-derivative, m.p. 109°; p-*toluenesulphonyl* derivative, m.p. 174°]. E. W. W.

Conessine series. III. Degradation of conessine and *iso*conessine hydriodides to a common hydrocarbon. IV. Action of nitric acid on conessine and the reduction of one of its two isomeric mononitro-derivatives to mono-oxy- and *iso*dioxy-conessine. S. SIDDIQUI and V. SHARMA (Proc. Indian Acad. Sci., 1937, **6**, **A**, 191—194, 199—206).—III. Conessine (I) and *iso*conessine hydriodides on heating at the m.p. in H_2 give NH_3 and about 70% yield of *conessene*, $C_{21}H_{30}$, b.p. 185—192°/3 mm., α_D^{31} +35·0°, which (bromination) appears to contain three double linkings.

IV. HNO_3 (1 part fuming : 1 part *d* 1·4) converts (I) into *nitroconessine*, m.p. 173°, $[\alpha]_D^{35·5}$ +11·0° in EtOH [*hydrochloride*, m.p. 253° (decomp.); *hydriodide*, m.p. 252° (decomp.); *hydrobromide*, m.p. 258° (decomp.); *platinichloride*, m.p. 267° (decomp.); *aurate*, m.p. about 167°; *picrate*, m.p. 216°; *dimethiodide*, m.p. 238° (decomp.); *dimethobromide*, m.p. 237° (decomp.)], which is reduced (Zn–HCl) to a mixture of *mono-oxyconessine*, $C_{24}H_{40}ON_2$, m.p. 202—203°, α_D^{30} +11·5° [*hydrochloride*, m.p. 273—275° (decomp.); *hydriodide*, m.p. 352° (decomp.); *hydrobromide*, m.p. 360° (decomp.); *platinichloride*, efferv. 297°; *picrate*, m.p. 249° (decomp.); *dimethiodide*, m.p. 298—300° (decomp.); *dimethobromide*, m.p. 308° (decomp.)], and iso*dioxyconessine*, $C_{24}H_{42}O_2N_2$, m.p. 279—280°, α_D^{24} −11·0° [*hydrochloride*, m.p. >360°; *platinichloride*, m.p. 288° (decomp.)]. With HNO_3 (3 parts fuming : 16 parts *d* 1·4) (I) affords iso*nitroconessine*, $C_{24}H_{39}N_2·NO_2$, m.p. 259—260°, α_D^{30} −45·5° in $CHCl_3$ [*hydrochloride* (+H_2O), m.p. 239—240° (decomp.); *hydriodide*, m.p. 295° (decomp.); *platinichloride*, m.p. 237° (decomp.); *dimethobromide*, m.p. 301° (decomp.)]. F. R. S.

Syntheses in the papaverine group. IV. Synthesis of 6-propoxy-1-(3′ : 4′ : 5′-trimethoxyphenyl)-7-methoxy*iso*quinoline. S. SUGASAWA and K. KAKEMI (J. Pharm. Soc. Japan, 1935, **55**, 1283—1288).—*iso*Vanillin, EtOH–KOH, and Pr^{n}Br yield 4-*methoxy*-3-n-*propoxybenzaldehyde*, b.p. 156—158°/4 mm., m.p. 51°, which, with galloylglycine Me_3 ether, NaOAc, and AcOH, yields 2-(3′ : 4′ : 5′-*trimethoxyphenyl*)-4-(4′-*methoxy*-3′-n-*propoxybenzylidene*)-5-*oxazolone*, m.p. 172°. With MeOH–Na_2CO_3, this affords α-*galloylamino*-4-*methoxy*-3-n-*propoxycinnamic acid* Me_3 *ether*, m.p. 213°, which, with Cu chromite and quinoline at 160—190°, yields ω-*galloylamino*-4-*methoxy*-3-n-*propoxystyrene* Me_3 *ether*, m.p. 133°, hydrogenated to β-3-(4-*methoxy*-n-*propoxyphenylethyl*)*galloylamide* Me_3 *ether*, m.p. 109°. With PCl_5 in $CHCl_3$ this affords 7-*methoxy*-6-n-*propoxy*-1-(3′ : 4′ : 5′-*trimethoxyphenyl*)-3 : 4-*dihydro*isoquinoline *hydrochloride*, m.p. 208—209° (free *base*, m.p. 104°), dehydrogenated to 7-*methoxy*-6-n-*propoxy*-1-(3′ : 4′ : 5′-*trimethoxyphenyl*)isoquinoline, m.p. 208—209°. The corresponding *Pr*$^\beta$ compounds are prepared similarly and have b.p. 132—134°/2 mm., and m.p. 188°, 137·5°, 137·5°, 102°, 217—218°, 96—97°, and 199°, respectively. CH. ABS. (*r*)

Synthesis of an isomeride of domesticine ethyl ether. H. SHISHIDO (Bull. Chem. Soc. Japan, 1937, **12**, 419—424).—3 : 4-OEt·C_6H_3(OMe)·CHO, $CH_2(CO_2H)_2$, and piperidine in C_5H_5N give 4-*methoxy*-3-*ethoxycinnamic acid*, m.p. 176—177·5°, reduced (H_2–Pd–C) to β-4-*methoxy*-3-*ethoxyphenylpropionic acid*, m.p. 104—106°. The *amide*, m.p. 123—124°, obtained from this acid by way of the chloride, with NaOEt gives β-4-*methoxy*-3-*ethoxyphenylethylamine* [*oxalate*, m.p. 226—227° (decomp.); *hydrochloride*, m.p. 166—168°]. This affords *homopiperon*-β-4′-*methoxy*-3′-*ethoxyphenylethylamide*, m.p. 129—131°, converted by $POCl_3$ in PhMe at 130—140° into 7-*methoxy*-4-*ethoxy*-1-*piperonyldihydro*isoquinoline [*oxalate*, m.p. 227—228° (decomp.)]; the *methiodide*, m.p. 142—144° (decomp.), of this base gives the methochloride, which with Zn–H_2SO_4 gives 7-*methoxy*-4-*ethoxy*-1-*piperonyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline, m.p. 154—154·5° [*oxalate*, m.p. 186—187° (decomp.); *hydrochloride*, m.p. 237—239° (decomp.); *sulphate*, m.p. 114—115° (decomp.)]. Conc. HNO_3 at <5° yields the 1-2′-*nitropiperonyl* compound, m.p. 128° after sintering at 123°, reduced by $SnCl_2$ to the 2′-NH_2-compound, m.p. 105—107° [*oxalate*, m.p. 186—188° (decomp.); *hydrochloride*, m.p. 220—222° (decomp.); *sulphate*, m.p. 179—181° (decomp.)], which with HNO_2–Cu–Zn–HCl gives dl-5-*methoxy*-6-*ethoxy*-2 : 3-*methylenedioxy*-N-*methylaporphine*, m.p. 136° [*hydrobromide*, m.p. 250—252° (decomp. from about 230°)], resolved by *d*- and *l*-tartaric acid into the d- and l-*isomerides*, m.p. 142—144°, $[\alpha]_D^{28}$ +90°, −90·9° in EtOH [*l*-base d-*tartrate* and *d*-base l-*tartrate*, m.p. 186—188° (decomp.); *hydrobromide*, m.p. 260—261° (decomp. from about 230°)]. The *d*-base depresses the m.p. of domesticine Et ether. R. S. C.

Synthetical experiments in the chelidonine–sanguinarine group of alkaloids. C. R. Noller, R. O. Denyes, J. W. Gates, and W. L. Wasley (J. Amer. Chem. Soc., 1937, **59**, 2079; cf. Richardson *et al.*, A., 1937, II, 356).—Various unsuccessful attempts to synthesise phenanthridines are indicated. Ring-closure of the *N*-piperonylamides of δ-piperonyl-*iso*crotonic and -propionic acid could not be accomplished. The synthesis of αγ-dipiperonylbutyric acid from Et piperonylmalonate and piperonylmethyl bromide is being attempted. Methylation of 2 : 3-$(OH)_2C_6H_3$·CHO has been effected. H. B.

Tylophorine salts.—See A., III, 246.

Haslerine, m.p. 237°, and quirandine, m.p. 218°.—See A., III, 331.

Organo-arsenic compounds. VI. Synthesis of 1-chloroarsindole from cinnamic acid. VII. Synthesis of arsindole derivatives. H. N. Das-Gupta (J. Indian Chem. Soc., 1937, **14**, 397—399, 400—405).—VI. *o*-Aminocinnamic acid, when diazotised and treated with Na_2CO_3, H_3AsO_3, and $CuSO_4$, gives *tris*-o-(β-*carboxyvinyl*)*phenylarsenic oxide*, m.p. >300°, which could not be converted into an indole derivative, but the Et ester on similar treatment yields *o*-(β-*carbethoxyvinyl*)-, m.p. >360°, hydrolysed to o-(β-*carboxyvinyl*)-*phenylarsinic acid*, m.p. 205—206°. HBr in glacial AcOH converts this into β-*bromohydrocinnamic*-, m.p. 185°, which with aq. Na_2CO_3 affords *styrene*-o-*arsinic acid*, m.p. 150°. Treatment with SO_2, conc. HCl, and a little KI yields the *arsenious chloride*, m.p. 55°, cyclised by $AlCl_3$ in CS_2 to 1-chloroarsindole.

VII. Neither β-*phenylvinylarsinic acid* [from ω-bromostyrene (I) and Na arsenite] nor *Hg distyrene*, m.p. 150° [obtained, together with *Hg styryl bromide*, m.p. >330°, from (I), Na, and $HgCl_2$], could be converted into $CHPh{:}CH{\cdot}AsCl_2$, but (I) with $AsCl_3$ and Na in C_6H_6–EtOAc gives *tri*-β-*phenylvinylarsine*, m.p. 82° (*picrate*, m.p. 100°; *methiodide*, m.p. 95°), which when heated with $AsCl_3$ yields 1-chloroarsindole, via the unstable dichloride. β-*Phenylvinyldimethylarsine*, b.p. 125—135°/5 mm. (*methiodide*, m.p. 155°; $HgCl_2$ *compound*, m.p. 131°) [from (I) and $AsBrMe_2$, using Na in C_6H_6–EtOAc or Mg in Et_2O], was treated with Cl_2 in CCl_4 and the product heated to 190°; this gave 1-methylarsindole. With $AsPhCl_2$ in cold EtOH (NaOH) (I) gives a compound which when distilled yields 1-phenylarsindole. A. Li.

Aromatic aurothiol-arsenic compounds. K. Burschkies (Arch. Pharm., 1937, **275**, 503—506).—*p*-$SH{\cdot}C_6H_4{\cdot}AsO_3H_2$, $KAuBr_2$, and Na_2SO_3 give *p*-*aurothiolphenylarsinic acid* (*Na* salt). 3-*Amino*- (*Na* salt) and 3-*acetamido*-4-*aurothiolphenylarsinic acid* (*Na* salt) and 3 : 3′-*diamino*-4 : 4′-*diaurothiolarsenobenzene* are similarly prepared. These compounds have no therapeutic advantage over the usual anti-tuberculosis drugs. R. S. C.

Arsenobenzenesulphoxylates.—See B., 1937, 1272.

Azo-dyes and immunobiology. Destruction of anaphylactic supersensitiveness to azoprotein by azo-dyes from *p*-aminophenylarsinic acid. H. E. Fierz, W. Jadassohn, and W. G. Stoll (Helv. Chim. Acta, 1937, **20**, 1059—1077).—Corresponding with Pauly's assumption, azoprotein (I) whether formed *in vitro* or *in vivo* contains the ·N:N· group. The dye which destroys the anaphylactic supersensitiveness to (I) in the Schultz–Dale experiment must contain the same N_2 group as the causative (I). 4′-*Sulphonyl*-2′-*carboxydiazoaminobenzene*-4-*arsinic acid* (Na_3 salt, decomp. 210°), 4′-*hydroxyazobenzene*-4-*arsinic acid*, the *compound*, $AsO(OH)_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3(OH){\cdot}N_2{\cdot}C_6H_4{\cdot}AsO(OH)_2$, and the *dye* from $p\text{-}NH_2{\cdot}C_6H_4{\cdot}AsO(OH)_2$ and $\beta\text{-}C_{10}H_7{\cdot}OH$ which exists in the quinonehydrazone (·NH·N:) and azo- (·N:N·) -forms are described. The azo-group can be fixed in the last-named compound by replacing OH by OMe, which can be effected nearly quantitatively by NaOH–Me_4SO_4. H. W.

Mercuriphenyl oleoxide and sodium ricinoleate mercuriphenyl ether.—See B., 1937, 1272.

Mercuriphenyl derivatives of aromatic acids.—See B., 1937, 1273.

Relative reactivities of organo-metallic compounds. XVII. Azo-linking. H. Gilman and J. C. Bailie (J. Org. Chem., 1937, **2**, 84—94; cf. A., 1937, II, 359).—Organo-metallic compounds form complexes with aromatic azo-compounds, large amounts (27—77%) of Ph_2N_2 being recovered after reaction with an excess of the reagent. Ph_2N_2 gives $(NHPh)_2$ by symmetrical addition to form $(\cdot NPh{\cdot}MgBr)_2$ etc. with $ZnEt_2$ (31), $BePh_2$ (55·4), MgEtBr (58), MgPhBr (62·5), LiPh (51·8), and NaPh (25·1%); it gives $NPh_2{\cdot}NHPh$ with CaPhI (18·5) and KPh (38·4%) by asymmetric addition to form $NPh_2{\cdot}NPhK$ etc.; it gives NH_2Ph with $ZnEt_2$ (16), ZnEtI (12·2), $ZnPh_2$ (6·8), and MnPhI (53·8%) by further reaction of $(NHPh)_2$ with the reagent. Asymmetric addition occurs only with the most reactive reagents and the above results are confirmed by exclusive 1 : 2-addition of the reactive CaPhI and KPh and partial 1 : 2-addition of LiPh and NaPh to ·CH:CH·CO·. Reaction of organo-Al compounds is accompanied by condensation and polymerisation. The mechanism of various apparently abnormal Grignard additions is discussed. R. S. C.

Reduction of lead organic nitro-compounds. K. A. Kotscheschkov and G. M. Borodina (Bull. Acad. Sci. U.R.S.S., Sér. Chim., 1937, 569—576).—$PbPh_2(NO_3)_2$ and fuming HNO_3 (7 hr. at 100°) yield $[m\text{-}C_6H_4(NO_2)]_2Pb(NO_3)_2$, converted by HBr into *Pb di*-m-*nitrophenyl dibromide*, reduction of which in acid, alkaline, or neutral solution leads to formation of amine, which immediately decomposes into NH_2Ph and $PbBr_2$. R. T.

Polarity of the co-ordinate link. II. Influence of aromatic substitution on the stability of the phosphinimines. F. G. Mann and E. J. Chaplin (J.C.S., 1937, 527—535).—The action of chloramine-*T* (I) on *tert.* phosphines (cf. A., 1932, 528) has now been investigated, each phosphine having been treated (*a*) with the anhyd. reagent in abs. alcoholic solution, and (*b*) with the hydrated reagent in rectified spirit. Under conditions (*a*), only a true phosphinimine, $R_3P{\rightarrow}N{\cdot}SO_2{\cdot}C_6H_4Me$, was

formed, whereas under (*b*) a phosphinimine or the hydroxyphosphinesulphonamide, $OH{\cdot}PR_3{\cdot}NH{\cdot}SO_2{\cdot}C_6H_4Me$, could be obtained according to the strength of the polarity of the co-ordinate link in the initial phosphinimine. PPh_3 and (I) give (*a*) *triphenylphosphine*-p-*toluenesulphonylimine*, m.p. 187°, and (*b*) NN-*bis*-(p-*toluenesulphonamido-triphenylphosphine*)-p-*toluenesulphonamide*, m.p. 138°. *Tri*-o-*tolylphosphine*, m.p. 125°, obtained from PCl_3 and o-$C_6H_4Me{\cdot}HgBr$, with (I) affords (*a*) *tri*-o-*tolylphosphine*-p-*toluenesulphonylimine*, m.p. 188°, and (*b*) the phosphinimine and *tri*-o-*tolylphosphine oxide* ($+0{\cdot}5H_2O$), m.p. 153°. $P(C_6H_4Me\text{-}p)_3$ and (I) yield (*a*) *tri*-p-*tolylphosphine*-p-*toluenesulphonylimine*, m.p. 174°, and (*b*) the phosphinimine and *hydroxytri*-p-*tolylphosphine*-p-*toluenesulphonamide*, m.p. 106°. *Tri*-m-*tolylphosphine*, m.p. 100°, with (I) forms (*a*) a syrup, from which a well-defined phosphinimine cannot be obtained and (*b*) *hydroxytri*-m-*tolylphosphine*-p-*toluenesulphonamide*, m.p. 98°, also obtained from *tri*-m-*tolylphosphine oxide*, m.p. 111°, and *p*-$C_6H_4Me{\cdot}SO_2{\cdot}NH_2$ (II). *Tri*-o-*anisylphosphine*, m.p. 204°, prepared from PCl_3 and o-$C_6H_4Br{\cdot}OMe$, with (I) gives (*a*) *tri*-o-*anisylphosphine*-p-*toluenesulphonylimine*, m.p. 273—274°, and (*b*) the phosphinimine and *hydroxytri*-o-*anisylphosphine*-p-*toluenesulphonamide*, m.p. 149°. *Tribromotri*-o-*anisylphosphine oxide*, m.p. 245°, is obtained by bromination of the phosphine, followed by alkaline hydrolysis. *Tri*-p-*anisylphosphine*, m.p. 131°, and (I) afford (*a*) *tri*-p-*anisylphosphine*-p-*toluenesulphonylimine*, m.p. 155°, and (*b*) *hydroxytri*-p-*anisylphosphine*-p-*toluenesulphonamide*, m.p. 121°, only. *Tri*-m-*anisylphosphine*, m.p. 115°, and (I) yield (*a*) a glass and (*b*) *hydroxytri*-m-*anisylphosphine*-p-*toluenesulphonamide*, m.p. 112°, easily converted into *tri*-m-*anisylphosphine oxide*, m.p. 151—152°, and (II).

Tri-o-*chlorophenylphosphine*, m.p. 185°, prepared from o-$C_6H_4Cl{\cdot}MgI$ and PCl_3 in H_2, and (I) give (*a*) *tri*-o-*chlorophenylphosphine*-p-*toluenesulphonylimine*, m.p. 235—236°, and (*b*) the phosphinimine and no hydroxy-sulphonamide, which could not be obtained from *tri*-o-*chlorophenylphosphine oxide* ($+0{\cdot}5H_2O$), m.p. 226—236°. *Tri*-p-*chlorophenylphosphine*, m.p. 103°, with (I) yields (*a*) *tri*-p-*chlorophenylphosphine*-p-*toluenesulphonylimine*, m.p. 232°, and (*b*) *tri*-p-*chlorophenylphosphine oxide*, m.p. 175°, and (II). *Tri*-m-*chlorophenylphosphine*, m.p. 67°, with (I) affords (*a*) and (*b*) $PO(C_6H_4Cl\text{-}m)_3$. $PPhMe_2$ and (I) do not give a cryst. product, whilst $PPhEt_2$ affords (*a*) and (*b*) *phenyldiethylphosphine*-p-*toluenesulphonylimine*, m.p. 82°. $PEt_2{\cdot}C_6H_4Mc\text{-}p$ and (I) yield (*a*) and (*b*) p-*tolyldiethylphosphine*-p-*toluenesulphonylimine*, m.p. 120°, and similarly obtained are *triethyl*-, m.p. 119°, *tri*-n-*propyl*-, m.p. 66°, and *tri*-n-*butylphosphine*-p-*toluenesulphonylimine*, m.p. 54°. *Triphenyl*-, m.p. 192—193°, *tri*-o-, m.p. 201—202°, and *tri*-p-*tolyl-arsine*-p-*toluenesulphonylimine*, m.p. 185°, are obtained from (I) and the corresponding arsine under conditions (*a*). The results are dependent on the fact that Me, OMe, and Cl are *op*-directing, and the theoretical significance is discussed.

F. R. S.

Magnetochemical investigations of organic compounds. XII. Potassium benzil and potassium phenanthraquinone. E. Müller and W. Wiesemann (Annalen, 1937, **532**, 116—126).—The product of the interaction of molar proportions of benzil (I) and K, Ph diphenylyl ketone (II), is converted by BzBr into (I) and (·CPh·OBz)$_2$. It is transformed by protracted agitation with Ph_2S_2 into (I) and PhSH which is oxidised to Ph_2S_2. It is hydrolysed to (I) and OH·CHPh·Bz. Gradual addition of increasing amounts of (I) to (II) (cf. Schlenk, A., 1913, i, 1205) and determination of the magnetic susceptibility of the product shows that free K benzil exists, but all materials previously mistaken for it are mixtures of it with (I) and K stilbenediol (II), in which (I) and (II) are united to a quinhydrone compound. Under the experimental conditions its prep. in the pure state is practically impossible and its existence as solid is very doubtful. Similarly, the material regarded as K phenanthraquinone is a mixture of this substance with phenanthraquinone and K phenanthraquinol. The so-called K xanthone and K benzanthrone are similar mixtures of compounds. The relative solubilities of the different components appear to determine the composition of the ppts. In the present instances definite mol. relationships between the quinhydrone or its constituents and the radical do not exist.

H. W.

Reaction between proteins and metaphosphoric acid. H. Herrmann and G. Perlmann (Nature, 1937, **140**, 807).—Analytical data obtained with the ppts. formed from egg-albumin (I) or clupein sulphate (II) and HPO_3 are recorded. The amount of P bound agrees with the no. of free NH_2 in (I) or with the no. of positively charged NH_2 in (II). L. S. T.

Simplified quantitative hydrogenation of milligrams and centigrams of substances. C. Weygand and A. Werner (J. pr. Chem., 1937, [ii], **149**, 330—336).—A simplified apparatus for rapidly and quantitatively hydrogenating (PtO_2) 3—5 or 30—50 mg. of substances is described. Errors in the hydrogenation of 10 substances with 1—9 ethylenic linkings were 0—1·6%. R. S. C.

Determination of alkyl- and aryl-halogen in presence of each other. W. H. Rauscher (Ind. Eng. Chem. [Anal.], 1937, **9**, 503—504; cf. A., 1937, II, 358).—The author's method gives results having errors <0·1%. F. R. G.

Micro-determination of organic sulphur. W. Saschek (Ind. Eng. Chem. [Anal.], 1937, **9**, 491—492).—A modification of Pregl's method. The combustion tube is washed out with 1 in 300 HCl into a crucible in which $BaSO_4$ is pptd. and the liquid removed by suction through a filter stick. Transference of ppt. is thus avoided. F. R. G.

Qualitative organic analysis. Identification of alkyl halides, amines, and acids. (Miss) E. L. Brown and N. Campbell (J.C.S., 1937, 1699—1701).—Primary and *sec.* alkyl bromides and iodides are identified by the formation with $CS(NH_2)_2$ of *S*-alkyl*iso*thiocarbamides; the following are described: n-, m.p. 181°, and iso-*propyl*-, m.p. 148°, n-, m.p. 180°, iso-, m.p. 174°, and sec.-*butyl*-, m.p. 190°,

n-, m.p. 154°, iso-, m.p. 179°, and sec.-*amyl*-, m.p. 143°, n-*hexyl*-, m.p. 157°, and *benzyl*-iso*thiocarbamide picrate*, m.p. 188°. $(\cdot CH_2Br)_2$ yields *ethylene bis*(iso*thiocarbamide*) (*picrate*, m.p. 270°). pp′-*Diphenylthiocarbanilide*, m.p. 233—235° (from p-$C_6H_4Ph\cdot NH_2$, CS_2, C_5H_5N, and I), is converted by Ac_2O into 4-*diphenylylthiocarbimide* (I), m.p. 70°. Aliphatic amines are identified by interaction with (I) or with β-naphthylthiocarbimide, and the following are described, the m.p. recorded being those of the N-*alkyl*- (or -*diakyl*-)N′-4-*diphenylylthiocarbamide*, and the *N*-alkyl (or dialkyl)-*N*′-β-naphthylthiocarbamide, respectively: *methyl*- (142°, 127°), *ethyl*- (165°, 142°), n-*propyl*- (156°, 114°), n- (155°, 119°) and iso-*butyl* (157°, 137°), n- (147°, 114°) and iso-*amyl*, (130°, 116°), n-*heptyl* (149°, 115°), *dimethyl*- (225°, 173°), *diethyl*- (114°, 90°), *dipropyl*- (117°, 109°), *diiso*butyl- (160°, 136°), *di*-n-*amyl*- (118°, 126°), *benzyl*- (147°, 173°), cyclo*hexyl*- (180°, 172°), *bornyl*- (167°, —), *camphyl*- (138°, 127°), and *ethylenebis*- (237° 223°). 2 : 4 : 5-$C_6H_2Me(NO_2)_3$ with the appropriate primary amine yields N-*ethyl*-, m.p. 126°, -n-*propyl*-, m.p. 101°, -n-, m.p. 96°, and -iso-*butyl*-, m.p. 112°, -n-, m.p. 99°, and -iso-*amyl*-, m.p. 82°, -n-*heptyl*, m.p. 50°, and -*benzyl*-4 : 6-*dinitro*-m-*toluidine*. $(CH_2\cdot NH_2)_2$ yields NN′-*bis*-(2 : 4-*dinitro*-5-*methylphenyl*)*ethylenediamine*, m.p. 280°. Org. acids are identified by formation of the 2-alkylbenziminazole with o-$C_6H_4(NH_2)_2$, and the following are described: 2-*methyl*-, m.p. 214°, -*ethyl*-, m.p. 120°, -n-, m.p. 124°, and -iso-*propyl*-, m.p. 136°, -amyl-, m.p. 282°, -*hydroxyethyl*-, m.p. 131°, -*hydroxymethyl*-, m.p. 214°, and -*phenylhydroxymethyl*-*benziminazole picrate*, m.p. 209°. Alkyl nitrites are identified by formation of 3-oximino-2-phenylindole with 2-phenylindole. An improved prep. of 2 : 4-dinitrobenzoic acid is described. J. D. R.

Determination of glycol or glycerol in dilute solutions containing oxidisable impurities. W. E. Shaefer (Ind. Eng. Chem. [Anal.], 1937, **9**, 449—450).—50 c.c. of solution containing <2·5 g. of $(CH_2\cdot OH)_2$ and free from mol. compounds are neutralised and distilled with a three-bulb Snyder column to 10 c.c.; 50 c.c. of dry C_5H_5N are added and the mixture is distilled to 110°, the residue being acetylated with 25 c.c. of 2·6N-Ac_2O in C_5H_5N, then diluted, and titrated, while shaking, with N-NaOH. The result is compared with a blank val. The method can be used for glycerol, and after applying a correction the accuracy is 1%. F. R. G.

Determination of βγ-butylene glycol. Y. Tomiyasu (J. Agric. Chem. Soc. Japan, 1937, **13**, 972—977).—Acetoin is first removed from the liquid by distillation (cf. A., 1937, II, 443). The residue is heated with Br and NaOAc, the excess of Br exactly removed by $Na_2S_2O_3$, and then the liquid is distilled into aq. $NiCl_2$ solution. Wt. of ppt. ×0·88 = βγ-butylene glycol. J. N. A.

Volumetric determination of polyhydric alcohols and reducing aldoses (monosaccharides) by means of periodate, and the determination of periodate and iodate in presence of each other. I. F. Rappaport, I. Reifer, and H. Weinmann (Mikrochim. Acta, 1937, **1**, 290—299).—I set free at p_H 4·4—7 from solutions of KIO_3 and KIO_4 in presence of KI corresponds with the KIO_4 present. Glucose (I), mannitol (II), and sorbitol (III) can be determined in acid or alkaline solution by means of the periodate method. (II) and (III) can be determined in presence of (I) by determining (I) by means of Fujita and Iwatake's method and the total sugar by means of periodate. Galactose and its admixture with (II) and (III) can similarly be determined but only in acid solution. C. R. H.

Quantitative acetylation of amines by acetyl chloride and pyridine. V. R. Olson and H. B. Feldman (J. Amer. Chem. Soc., 1937, **59**, 2003—2005).—Smith and Bryant's method (A., 1935, 369) of determination of OH, which gives inconsistent results with amines and amides, is modified. Using AcCl + C_5H_5N in Bu^{α}_2O at 70° and compounds which are sol. in the reagent, vals. >90% of the theoretical are generally obtained. H. B.

Effect of aldehydes on cystine and cysteine. W. C. Hess and M. X. Sullivan (J. Biol. Chem., 1937, **121**, 323—329).—Through formation of complexes, aldehydes have a marked effect on the determination of cysteine by the Sullivan method, the effect increasing with decreasing acidity, with increasing concn. of the reactants, and with increase in the val. of the ratio aldehyde : cysteine. Aldehydes do not affect the determination of cystine either in dil. or in conc. solutions. C. R. H.

Detection of thiocarbamide. E. Storfer (Mikrochim. Acta, 1937, **1**, 260—263).—The substance to be tested is gently heated for 2—4 min. with H_2O, mixed with dry $CuCl_2$ or other Cu salt, boiled for 1 min., and filtered. A drop of the filtrate, which must be neutral, is brought on to filter-paper soaked in $K_3Fe(CN)_6$. A violet-blue colour indicates the presence of $CS(NH_2)_2$. EtOH–H_2O and $COMe_2$–H_2O solutions sometimes give better results. High-mol. products, *e.g.*, resins, must first be decomposed by treatment with syrupy H_3PO_4 at 100—150° followed by neutralisation with NaOH. 0·00001 g. of $CS(NH_2)_2$ can be detected. C. R. H.

Micro-method for measuring rate of decomposition of diazoacetic esters. P. Gross, H. Steiner, and F. Krauss (Mikrochim. Acta, 1937, **1**, 87—91).—A micro-gas volumeter is described. J. S. A.

Quinone reactions. G. Woker and U. Antener (Helv. Chim. Acta, 1937, **20**, 1260—1270).—The complication in the detection of ascorbic acid caused by the development of colour by benzoquinone (I) and tissue only (A., 1937, II, 367) is not attributable to $\cdot C_6H_4\cdot OH$, carbohydrate group, or readily eliminated S but is given by the isolated NH_2-acids. This explanation is quantitatively inadequate; in the reaction of (I) and proteins the effect is due to the NH_2-acids, particularly histidine, lysine, arginine, ornithine, and proline, and also to NH_3 obtained by their deamination. The possible structures of the compounds thus formed are discussed. Similar reactions are afforded by triketohydrindene (cf. Cherbuliez, A., 1935, 102). H. W.