BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

JULY, 1940

Relative velocity of chloroalkylation of olefines. —See A., 1940, I, 260.

Grignard syntheses of halogen derivatives of ethylenic alcohols. G. I. Schtukin (J. Gen. Chem. Russ., 1940, **10**, 77—81).—CH_2AcCl and CH_2:CH·CH_2·MgBr in Et_2O at −10° afford *α-chloro-β-methyl-Δ^δ-penten-β-ol*, b.p. 159°, which with KCN in EtOH gives *α-cyano-β-methyl-Δ^δ-penten-β-ol*, b.p. 112°/17 mm. The following are obtained similarly: *α-chloro-β-chloromethyl-Δ^δ-penten-β-ol*, b.p. 82·5°/14 mm., from $CO(CH_2Cl)_2$, *γ-bromo-β-methyl-δ-allyl-Δ^ζ-hepten-δ-ol*, b.p. 115—116°/18 mm., from $CHPr^βBr·CO_2Et$, and *α-bromo-β-phenyl-Δ^δ-penten-β-ol*, decomp. at the b.p., from COPh·CH_2Br. R. T.

Preparation of esters in presence of magnesium chloride. P. A. Petiunin (J. Gen. Chem. Russ., 1940, **10**, 35—38).—Esters are obtained in 60—70% yield from aliphatic acid–alcohol mixtures in presence of anhyd. $MgCl_2$ (2 hr. at the b.p.). In these conditions BzOH gives only 20—27% yields of ester. R. T.

Direct esterification of higher fatty acids with glycerol. I. Formation of mono- and di-glycerides, and their separation. S. Kawai and H. Nobori (J. Soc. Chem. Ind. Japan, 1940, **43**, 59B).—Esterification was almost complete in 3 hr. with 1 mol. of fatty acid [lauric (I), stearic (II), oleic (III)] to 0·8—1·4 mol. of glycerol at 230—240°; prolonged heating (15—20 hr.) was necessary at 170—180°. Glycerides from (I) and (III) were mainly mono- and di- with a small amount of tri-glyceride. Those from (II) were mainly tri- and di- with a small amount of mono-glyceride. Glycerides obtained by prolonged heating at 170—180° contained less mono- and di-glyceride than those obtained at 230—240° for 3 hr. 85% EtOH was used to separate glycerides of (I) and (II) but 80% EtOH was more effective for those of (III). F. M. F.

Lactic esters: preparation and properties. L. T. Smith and H. V. Claborn (Ind. Eng. Chem., 1940, **32**, 692—694).—The prep. of lower alkyl lactates (cf. Bogin *et al.*, B., 1934, 637) is improved by using a large excess of alcohol, and removing this and H_2O at low temp. in vac. (column). Na or Ca lactate, the alcohol, and a slight excess of H_2SO_4 are used, for Bu^α to lauryl esters, with C_6H_6 or PhMe to remove H_2O. For higher esters, lactic acid without H_2SO_4 is used. The following are apparently new: *iso-amyl*, b.p. 82°/7 mm., n-*hexyl*, b.p. 75°/2 mm., *β-ethoxy-butyl*, b.p. 104°/12 mm., and *-hexyl*, b.p. 112°/3·6 mm., *lauryl*, b.p. 150—153°/4 mm., and *phenylethyl lactate*, b.p. 124°/4 mm. These with keten (cf. A., 1940, II, 5) give n-*hexyl*, b.p. 135°/17 mm., *β-ethyl-butyl*, b.p. 127°/14 mm., and *-hexyl*, b.p. 145°/13 mm., *lauryl*, b.p. 165°/4 mm., and *phenylethyl α-acetoxypropionate*, b.p. 139°/4 mm. The prep. of *glycol monolactate*, b.p. 140°/10 mm., and of glycerol monolactate, is described. *Stearyl lactate* has b.p. 180° (decomp.)/2 mm. E. W. W.

Action of sodium alkoxides on ethyl *s*-diethoxysuccinate. I. Isomerisation of ethyl *d*-*s*-diethoxysuccinate into ethyl *as*-diethoxysuccinate. S. Fukunaga (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1940, **37**, 137—142).—*d*-[CH(OEt)·CO_2Et]$_2$, b.p. 156—157°/26 mm., with warm NaOEt–EtOH gives Et *as*-diethoxysuccinate, b.p. 147—148°/25 mm., nearly quantitatively, hydrolysed (warm EtOH–NaOH) to the acid (*Ca*, $+H_2O$, and *Ba*, $+H_2O$, salts), which when heated (water-bath) alone, or with dil. HCl, or when kept in vac. gives $CO_2H·CO·CH_2·CO_2H$. J. L. D.

Determination of dehydroascorbic acid.—See A., 1940, III, 515.

Reaction of ortho-esters with aldehydes. H. W. Post (J. Org. Chem., 1940, **5**, 244—249).—Comparative data on the yields of acetals obtained by the interaction of an aldehyde with an aliphatic ortho-ester in presence of a little H_2SO_4 as catalyst show that polymerised aldehydes do not so react. The highest yields are obtained from PhCHO followed by MeCHO and EtCHO. $CH(OEt)_3$, $CH(OPh)_3$, and $CH(OBu)_3$ are decreasingly effective. $CMe(OEt)_3$ does not behave similarly. Aldehydes such as CHPh:CH·CHO and CHMe:CH·CHO polymerise under these conditions without perceptible further reaction. MeCHO yields the corresponding dithioacetals with HCO·SEt and HCO·SPr. H. W.

Gattermann synthesis of aldehydes. A. G. Mistretta and F. F. Nord (Nature, 1940, **145**, 387).—Yields obtained with C_6H_6, PhMe, PhEt, cumene, etc. as solvents in this synthesis, using $AlCl_3$, NaCN, and dry HCl, give an indication of a rule connecting solvent and yield. L. S. T.

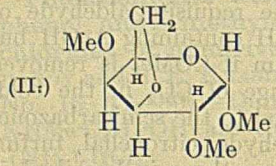
Preparation of semicarbazones by functional exchange. B. Angla (Ann. Chim. Analyt., 1940, [iii], **22**, 10—15).—Semicarbazones are obtained from CMe_2:N·NH·CO·NH_2 and the requisite aldehyde or ketone generally in aq. EtOH containing AcOH but frequently in neutral medium if $COMe_2$ is removed by evaporation or by passage of CO_2 in the cold. The application of the method to the semicarbazones of heptaldehyde, cinnamaldehyde, citronellal, furfuraldehyde, COMe·C_9H_{19}, and menthone is described. H. W.

Action of phosphate on hexoses. IV. Formation of lactaldehyde concurrently with acetol.

R. Goto (Bull. Chem. Soc. Japan, 1940, **15**, 103—106).—In the distillation of acidified K phosphate with glucose (I) (Nodzu *et al.*, A., 1938, II, 172), some OH·CHMe·CHO (II) is formed. The equilibrium acetol (III) $\rightleftharpoons$ (II) (shifted to the left, at least in the phosphate system) makes it uncertain whether (II) or (III) is the precursor in the cleavage of (I) to $AcCO_2H$. E. W. W.

Characterisation of carbohydrates. I. Oxidation of aldoses by hypoiodite in methanol. II. Identification of seven aldomonosaccharides as benziminazole derivatives. S. Moore and K. P. Link (J. Biol. Chem., 1940, **133**, 293—311).—Aldohexoses and -pentoses are converted into the aldonic acids by I–KOH in MeOH free from $COMe_2$ but containing a little H_2O at ~40°. When cold, nearly pure K salts are pptd. in the following yields: from glucose 92, galactose 85, arabinose 83, mannose 30, xylose 8, lyxose and rhamnose 0%. Addition of $BaI_2,2H_2O$ in MeOH ppts. the residual acid quantitatively as crude Ba salt. These salts are condensed separately with *o*-$C_6H_4(NH_2)_2$ by HCl–H_3PO_4 at 135° (with HCl–$ZnCl_2$ at 180° for xylose), giving 60—80% yields of benziminazoles, which, if sol., are pptd. as Cu derivatives and recovered therefrom by H_2S. These in conjunction with their derivatives are better suited than are osazones etc. for characterisation of the sugars. Benziminazoles are reported (if new, the sugar is italicised) from *l*-arabinose, m.p. 235° (decomp.), [α] +49·5° (hydrochloride, m.p. 230°; picrate, m.p. 158°), *d*-galactose, m.p. 245° (decomp.), [α] +43·3° (+44·4° in HCl) [hydrochloride, m.p. 202—204°; picrate, m.p. 217° (decomp.)], *d*-glucose, m.p. 215°, [α] +9·6° (+9·4° in HCl) [hydrochloride, m.p. 180°; picrate, 203° (decomp.)], d-*lyxose*, m.p. 189°, [α] −12·8° (*hydrochloride*, m.p. 191°; *picrate*, m.p. 95—99°), *d*-mannose, m.p. 227° (decomp.), [α] −22·0° [hydrochloride, m.p. 101—150°; picrate, m.p. 205° (decomp.)], l-*rhamnose*, m.p. 207°, [α] +27·4° (*hydrochloride*, m.p. 173—175°; *picrate*, m.p. 168°), and d-*xylose*, m.p. 224°, [α] +64·8° (*hydrochloride*, m.p. 200—202°; *picrate*, m.p. 191°). [α] are $[\alpha]_D^{25}$ in 5% aq. citric acid. Fructose gives only a little of the *d*-arabinose derivative. R. S. C.

Properties of 3 : 6-anhydrogalactose. W. N. Haworth, J. Jackson, and F. Smith (J.C.S., 1940, 620—632).—3 : 6-Anhydromethylgalactopyranosides and their methylation products are prepared. The stable 5-membered anhydro-ring is probably responsible for some of the peculiar properties of 3 : 6-anhydrogalactose and its derivatives. The 6-*p*-toluenesulphonate, new m.p. 188°, $[\alpha]_D^{17}$ +118° in C_5H_5N (cf. Ohle *et al.*, A., 1933, 492), of α-methyl-



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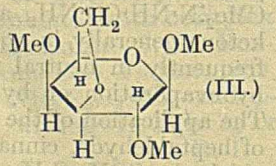
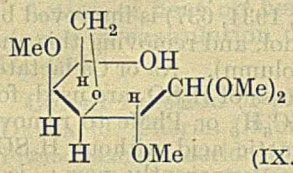


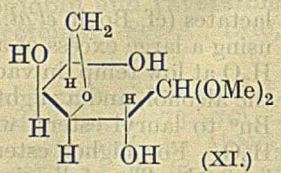
(III.)

galactopyranoside (*di*-p-*toluenesulphonate*, m.p. 148°, $[\alpha]_D^{16}$ +68° in C_5H_5N) with N-NaOH in EtOH at 60° followed by neutralisation with CO_2 gives 3 : 6-anhydro-α-methylgalactopyranoside (I) (*loc. cit.*). With MeI–Ag_2O–$COMe_2$, (I) gives liquid 2 : 4-*dimethyl*-3 : 6-*anhydro*-α-*methylgalactopyranoside* (II), b.p. 90° (bath)/0·01 mm., $[\alpha]_D^{15}$ +99° in Et_2O, which on keeping slowly changes (incompletely) into the β-*form* (III), m.p. 83°, $[\alpha]_D^{18}$ −77° in H_2O, −87° in $CHCl_3$. This α → β change, also effected by dry HCl, by HBr, by HCl in EtOH or Et_2O (cf. A., 1939, II, 99) or in MeOH, apparently does not involve intermediate formation of a free reducing group. *X*-Ray examination shows (III), and ebulliometry (II) and (III), to be monomeric. [The enantiomorph of (III) has been obtained by Hands *et al.* (A., 1939, II, 50) and by Percival *et al.* (*ibid.*, 142).] The structure of (III) is established (cf. Percival *et al.*, *loc. cit.*) by its prep. from Ag_2O–MeI and 3 : 6-*anhydro*-β-*methylgalactopyranoside* (IV), m.p. 119°, $[\alpha]_D^{18}$ −115° in H_2O. (IV) is obtained either (*a*) by conversion of galactose 6-*p*-toluenesulphonate, through its tetra-acetate, m.p. 107°, $[\alpha]_D$ +42° in $CHCl_3$ (cf. Ohle *et al.*, *loc. cit.*), into α-*acetobromogalactose* 6-p-*toluenesulphonate*, m.p. 149° (decomp.), $[\alpha]_D^{20}$ +165° in $CHCl_3$, which (Ag_2CO_3) gives β-*methylgalactoside* 2 : 3 : 4-*triacetate* 6-p-*toluenesulphonate*, $[\alpha]_D^{18}$ ~ +2·5° in $CHCl_3$, which gives (Na–MeOH) β-*methylgalactopyranoside* 6-p-*toluenesulphonate*, m.p. 137°, $[\alpha]_D$ ~ −3·5° in C_5H_5N, converted by N-NaOH–EtOH into (IV); or (*b*) from β-methylgalactoside 6-bromohydrin triacetate (Schlubach *et al.*, A., 1932, 369), which with Na–MeOH gives β-*methylgalactoside* 6-*bromohydrin*, m.p. (+dioxan) 106° (sinters at 75°), $[\alpha]_D^{20}$ +11° in H_2O, converted by N-NaOH at 80° into (IV).

With dil. acid, (II) and (III) are easily hydrolysed. With 0·1N-H_2SO_4 at 100°, (II) and (less rapidly) (III) give *aldehydo*-2 : 4-*dimethyl*-3 : 6-*anhydrogalactose* (V), m.p. 112° [in one prep. only, from (III)], b.p. 150° (bath)/0·03 mm., $[\alpha]_D^{16}$ +24° in H_2O. (V), which has the usual aldehydic properties, with NH_2Ph in boiling EtOH, gives its anilide, m.p. 123°, $[\alpha]_D^{18}$ → +56° in EtOH. Aq. Br oxidises (V) (in the presence of basic $PbCO_3$, followed by H_2S and Ag_2O) to 3 : 6-anhydrogalactonic acid (VI), m.p. 152°, $[\alpha]_D^{15}$ +66° [which with CH_2N_2 yields its Me ester (VII), m.p. 51°, $[\alpha]_D^{15}$ +67° in H_2O (cf. Forbes *et al.*, A., 1940, II, 35)], or (after treatment with Ag_2O and H_2S, and distillation) to a mixture of (VI) and the corresponding *lactone* (VIII), b.p. 140—150° (bath)/0·01 mm., $[\alpha]_D^{14}$ +4° (const.) in H_2O. Slow evaporation in air of a solution of (VIII) gives (VI) of m.p. 152°, $[\alpha]_D^{15}$ −66° in H_2O. With MeOH–NH_3 at −5°, (VII) or (VIII) gives the amide, m.p. 151°, $[\alpha]_D^{17}$ +81° in H_2O. (VI) heated above its m.p. (4 hr.) and distilled gives some



(IX.)



(XI.)

(VIII). The stability of the 3 : 6-anhydro-ring is shown by the prep. of (VI) from (II) and HNO_3 (*d* 1·42) at 50—80°.

With excess of 0·5—1% MeOH–HCl at room temp., (II) and (somewhat less readily) (III) both give the relatively strainless 2 : 4-*dimethyl*-3 : 6-*anhydrogalact*-

ose Me_2 *acetal* (IX), m.p. 36°, b.p. 95° (bath)/0·02 mm., $[\alpha]_D^{18}$ +36° in H_2O [purified through the p-*nitrobenzoate* (X), b.p. 215° (bath)/0·03 mm.]. With gaseous HCl or HBr, (IX) rapidly yields (III). Similarly, (I) or (IV) with MeOH–HCl, followed by Ag_2CO_3, gives 3 : 6-*anhydrogalactose* Me_2 *acetal* (XI), $[\alpha]_D^{18}$ +36·5° in H_2O [2 : 4 : 5-*tri*-p-*nitrobenzoate* (XII), m.p. 112°]. The open-chain structures are assigned to (IX) and (XI) because of the formation of (X) and (XII), and of the hydrolysis of (IX) and (XI) by 0·1N-H_2SO_4 respectively to (V) and to *aldehydo*-3 : 6-*anhydrogalactose* (XIII), a glass, $[\alpha]_D$ +24° in H_2O. This is also obtained from (I) or (IV) and 0·1N-H_2SO_4. (IX) is directly converted by HCl or HBr in air into (III) with the elimination of 1 Me. Both (IX) and (XI) on methylation (Ag_2O–MeI, MeOH–HCl, Ag_2CO_3) give 2 : 4 : 5-*trimethyl*-3 : 6-*anhydrogalactose* Me_2 *acetal* (XIV), b.p. 120° (bath)/0·03 mm., $[\alpha]_D^{12}$ +41·0° in H_2O. Hydrolysis (0·01N-H_2SO_4 at 100°) of (XIV) yields 2 : 4 : 5-*trimethylaldehydo*-3 : 6-*anhydrogalactose* (XV), b.p. 105° (bath)/0·02 mm., $[\alpha]_D^{19}$ +41° in H_2O. With aq. Br, (XV) gives 2 : 4 : 5-*trimethyl*-3 : 6-*anhydrogalactonic acid* (XVI), $[\alpha]_D^{17}$ +64° (*brucine* salt, m.p. 114°, $[\alpha]_D \sim -3°$ in H_2O). With Et_2O–CH_2N_2, (XVI) gives its *Me* ester, b.p. 115° (bath)/0·03 mm., $[\alpha]_D^{17}$ +67° in H_2O, also obtained by complete methylation of the *Me* ester, b.p. 160—170° (bath)/0·03 mm., $[\alpha]_D$ +38° in H_2O, of 3 : 6-*anhydrogalactonic acid*, $[\alpha]_D^{20}$ +33° in H_2O, prepared by Br oxidation of (XIII).

The above reactions are discussed in relation to the cyclic and dicyclic ring systems involved, and to the stability of these. E. W. W.

Crystalline β′-chloroethyl-β-*d*-glucoside. J. Compton (Contr. Boyce Thompson Inst., 1939, **11**, 21—23).—β′-Chloroethyl-β-*d*-glucoside tetra-acetate (I) (slightly modified prep.; cf. Jackson, A., 1938, II, 174) with $Ba(OMe)_2$ in MeOH for 20 hr. at 5°, followed by the calc. amount of H_2SO_4, gives (slowly from EtOAc) cryst. β′-*chloroethyl*-β-d-*glucoside* (II), m.p. 70—71°, $[\alpha]_D^{22}$ −29·0° in H_2O, reacetylated in C_5H_5N to (I). With Raney Ni in EtOH containing aq. NaOH, and H_2 at 3 atm., followed by CO_2 and acetylation of the product, (II) gives ethyl-β-*d*-glucoside tetra-acetate. E. W. W.

Synthesis of *o*-chlorophenol-β-*d*-glucoside. L. P. Miller (Contr. Boyce Thomson Inst., 1939, **11**, 25—27).—By the method of Helferich *et al.* (A., 1933, 379), *o*-C_6H_4Cl·OH (I), glucose penta-acetate, and *p*-C_6H_4Me·SO_3H at 115—125° give [after removing (I) in H_2O in vac. at <30°] the *tetra-acetate* (II), m.p. 150·5—151° (corr.), $[\alpha]_D^{23}$ −44·6° in $CHCl_3$, of *o-chlorophenol*-β-d-*glucoside* (III), m.p. 171—171·5°, $[\alpha]_D^{26}$ −65·3° in EtOH. $Ba(OMe)_2$–MeOH converts (II) into (III), which with Ac_2O–C_5H_5N gives (II). Emulsin hydrolyses (III), liberating (I). The product from gladiolus corms (cf. Miller, A., 1938, III, 966) and (I) gives on acetylation a product of m.p. ≫ m.p. of (II). E. W. W.

Acetolysis of carrageen mucilage. T. Dillon and P. O'Colla (Nature, 1940, **145**, 749).—Acetylation (AcOH and Ac_2O; catalyst, SO_2 and Cl_2) of the mucilage and removal of Ac yields two polymeric carbohydrates, $(C_6H_{10}O_5)_n$, probably galactans, one

sol. in cold and the other in hot H_2O. The latter gives a wine-red colour with I. L. S. T.

Methylation of chondrosamine hydrochloride. P. A. Levene (J. Biol. Chem., 1940, **133**, 767).—On methylation of chondrosamine penta-acetate with Me_2SO_4, the methylpyranoside is formed. E. M. W.

Amino-acid and peptide esters of choline as possible analogues of the oxytocic hormone of the posterior lobe of the pituitary gland. I. J. M. Gulland, M. W. Partridge, and S. S. Randall (J.C.S., 1940, 419—425).—Choline chloride (I) and glycyl chloride hydrochloride in vac. at 100° (4 hr.) give, via the *platinichloride*, m.p. 238°, glycylcholine chloride hydrochloride, m.p. 241—242° (cf. Dudley, J.C.S., 1921, **119**, 1259) (flavianate, rufianate, and picrolonate). With glycylglycyl chloride hydrochloride, (I) similarly gives, via the *picrolonate*, *glycylglycylcholine chloride hydrochloride* (+$3H_2O$), m.p. 128—130°. NEt_2·$[CH_2]_2$·OBz and MeI in C_6H_6 give *methyldiethyl*-β-*benzoyloxyethylammonium iodide*, m.p. 128° (corresponding *chloride*, m.p. 129°). Lauryl chloride (II) and NEt_2·$[CH_2]_2$·OH (III) in $CHCl_3$ give, after washing with $NaHCO_3$, β-*diethylaminoethyl laurate*, b.p. 194°/12 mm. (*hydrochloride*, m.p. 109°), which with MeI gives *methyldiethyl*-β-*lauryloxyethylammonium iodide*, m.p. 70°. NMe_2·$[CH_2]_2$·OBz (hydrochloride, new m.p. 151°) with MeI gives *benzoylcholine iodide*, m.p. 243—244° (decomp.), converted by AgCl in EtOH into the chloride, new m.p. 206—207° (decomp.) (cf. Fourneau *et al.*, A., 1914, i, 938). NMe_2·$[CH_2]_2$·OH (IV) and (II) give β-*dimethylaminoethyl laurate*, b.p. 193—194°/13 mm. (*hydrochloride*, m.p. 143—144°), which with MeI gives *laurylcholine iodide*, m.p. 161—162° (corresponding *chloride*, m.p. 54°). This has some oxytocic activity (tested by contraction of the isolated uterus of the virgin guinea-pig) at a dilution of 1/200,000, but larger doses appear to be toxic. PCl_5 and $(S{\cdot}CH_2{\cdot}CO_2H)_2$ (V) in Et_2O at <0° give *dithioglycollyl chloride*, an unstable oil, which with (IV) in $CHCl_3$ at 0° forms *di*-(β-*dimethylaminoethyl*) *dithioglycollate*, an oil [also obtained from (IV) and (V) with HCl in $C_2H_2Cl_4$], converted by MeI in C_6H_6 into the *dimethiodide* (*dithioglycollylcholine iodide*), $(S{\cdot}CH_2{\cdot}CO_2{\cdot}[CH_2]_2{\cdot}NMe_3I)_2$, m.p. 156—157°. The chloride of carbobenzyloxylglycine (VI) and (III) in $CHCl_3$ give the β-*diethylaminoethyl* ester (VII) of (VI). The methiodide of (VII) with PH_4I in AcOH with HCl (10 hr.) gives an *iodide hydriodide*, converted into *methyldiethyl*-β-*glycyloxyethylammonium dirufianate*, m.p. 259—260° (decomp.; darkening from 230—235°). Carbobenzyloxycystinyl chloride (VIII) and (IV) give an oily *ester*, converted by MeI in C_6H_6 into *di*-(β-*diethylaminoethyl*)*carbobenzyloxycystine dimethiodide*, $[S{\cdot}CH_2{\cdot}CH(NH{\cdot}CO_2CH_2Ph){\cdot}CO_2{\cdot}[CH_2]_2{\cdot}NEt_2MeI]_2$ (+$5H_2O$), deliquescent, m.p. 67—77° (evolves gas at ~92°; chars at 150°). With $OH{\cdot}[CH_2]_2{\cdot}Br$ and C_5H_5N, (VIII) in $CHCl_3$, first at room temp. and then at the b.p. (2 min.), gives β-*bromoethylcarbobenzyloxycystine* (IX), $[S{\cdot}CH_2{\cdot}CH(NH{\cdot}CO_2{\cdot}CH_2Ph){\cdot}CO_2{\cdot}[CH_2]_2{\cdot}Br]_2$, m.p. 86—88°, which with $NHMe_2$ in C_6H_6 at 60° yields β-*dimethylaminoethylcarbobenzyloxycystine* (X), an oil,

which forms a *dimethiodide* (*carbobenzyloxycystinylcholine iodide*) (XI), m.p. 140—142°, also obtained from the β-*iodoethyl* analogue of (IX) with NMe_3 in C_6H_6 [(IX) with NMe_3 gives the *dibromide*, m.p. ~235°], or, m.p. (+$2H_2O$) 70—79° (sinters 64°; chars at 150°), from (IV) and (VIII) in $CHCl_3$ at 0°, followed by treatment with aq. NH_4HCO_3, and action of MeI on the resulting (X). PH_4I and (XI) in $COMe_2$ with HCl at 40° give *cysteylcholine iodide hydriodide* (XII), m.p. 83—85° (decomp.) (sinters 74—75°; chars at 150°), which in EtOH with O_2 forms *cystinylcholine iodide hydriodide* (XIII), a glass. (XII) and (XIII) have slight oxytocic activity. Carbobenzyloxyphenylalanyl chloride with (IV) in Et_2O, followed by treatment with NH_4HCO_3, gives β-*dimethylaminoethylcarbobenzyloxyphenylalanine*, an oil, which with MeI gives the *methiodide* (*carbobenzyloxyphenylalanylcholine iodide*), m.p. 59—62° (sinters 45—48°; evolves gas at 169°; chars at 190°), which with PH_4I in $COMe_2$ (under H_2) gives *phenylalanylcholine iodide hydriodide*, m.p. 80—83° (evolving gas) (sinters 40—50°; chars at 200°), which with AgCl forms the *chloride hydrochloride*. Both these are very deliquescent. E. W. W.

Partial racemisation of glutamic acid in boiling hydrochloric acid solutions. L. E. Arnow and J. C. Opsahl (J. Biol. Chem., 1940, **133**, 765—766).—The extent of racemisation of *l*(+)-glutamic acid caused by boiling HCl is sufficient to account for the results of Johnson (A., 1940, III, 424) but not those of Kögl *et al.* (A., 1939, III, 489). E. M. W.

Preparation of *d*(−)-glutamic acid from *dl*-glutamic acid by enzymic resolution. J. S. Fruton, G. W. Irving, jun., and M. Bergmann (J. Biol. Chem., 1940, **133**, 703—705).—By the action of NH_2Ph on carbobenzyloxy-*dl*-glutamic acid in the presence of papain–cysteine, only the *l*-NH_2-acid forms an anilide. Pure *d*(−)-glutamic acid can be obtained from the filtrate by hydrogenation and recrystallisation of the hydrochloride. E. M. W.

Reactions of some high-mol. wt. fatty acid derivatives. M. R. McCorkle (Iowa State Coll. J. Sci., 1939, **14**, 64—66).—For thioamides cf. Ralston *et al.* (A., 1939, II, 204). β-*Imino*-α-n-*decylmyristonitrile*, b.p. 230—235°/3 mm. (from lauronitrile and NPhEtLi), is hydrolysed by EtOH–HCl to β-*keto*-α-n-*decylmyristonitrile*, m.p. 44—45°, and by conc. H_2SO_4 to β-*keto*-α-n-*decylmyristamide*, m.p. 114—115°, which yields laurone with EtOH–KOH. Similarly stearonitrile yields β-*imino*-, m.p. 54—55°, and β-*keto*-α-n-*hexadecylarachidonitrile*, m.p. 68—69°, and β-*keto*-α-n-*hexadecylarachidonamide*, m.p. 114—115°, hydrolysed to stearone. Fries rearrangement of p-*diphenylyl stearate*, m.p. 73—74°, yields 2-*hydroxy*-5-*phenyl*-, m.p. 63—64° [*Me ether* (also prepared from 2 : 5 : 1-OMe·C_6H_4Ph·MgBr and stearonitrile), m.p. 53—54°], and p-p′-*hydroxyphenyl-stearophenone*, m.p. 141—142°, the *Me ether*, m.p. 116—117° (also prepared from *p*-C_6H_4Ph·OMe, stearoyl chloride, and $AlCl_3$), of which is oxidised to *p*-$C_6H_4(CO_2H)_2$. Stearonitrile yields with β-$C_{10}H_7$·MgBr, β-*stearoylnaphthalene*, m.p. 65—66°, with *p*-C_6H_4PhLi, p-*phenylstearophenone* (I), m.p. 108—109°, and with MgMeBr, β-*keto*-n-*nonacosane*, m.p. 55—56°. Stearoyl chloride with Ph_2 and with Ph_2O yields (I) and p-*phenoxystearophenone* (II), m.p. 62—63°, respectively. Sulphonation of (I) yields 4-*sulpho*-4′-*stearoyldiphenyl*, m.p. 142—145°, oxidised to 4-*sulphodiphenyl*-4′-*carboxylic acid* (p-*toluidine* salt, m.p. 288—289°) (also obtained by sulphonating *p*-C_6H_4Ph·CO_2H), which on fusion with KOH yields 4 : 4′-OH·C_6H_4·C_6H_4·CO_2H. (I) with $ClSO_3H$ yields a trisulphonic acid, oxidised to 4 : 4′-SO_3H·C_6H_4·C_6H_4·CO_2H. Sulphonation of (II) yields p-p′-*stearoyl*-, m.p. 95—98°, oxidised (dil. HNO_3) to p-p′-*carboxy-phenoxybenzenesulphonic acid* (p-*toluidine* salt, m.p. 266—267°), which on fusion with KOH gives *p*-OH·C_6H_4·CO_2H. Hydrogenation (Adkin's Cu–Cr_2O_3 catalyst) of lauro- and stearo-nitriles yields *di*-n-*dodecyl*-, m.p. 52—53°, and -*octadecyl-amine*, m.p. 73—74°, respectively, which when heated with the corresponding chlorides (from the alcohols and $SOCl_2$) yield *tri*-n-*dodecyl*- (*hydrochloride*, m.p. 78—79°) and -*octadecyl-amine*, m.p. 54—55° (*hydrochloride*, m.p. 96—97°). Laurone and stearone are prepared by heating the acids with Fe powder. Reduction (Na + BuOH) of myristone and stearone yields $(C_{13}H_{27})_2$CH·OH and $(C_{17}H_{35})_2$CH·OH. Attempts to synthesise $[(C_{17}H_{35})_2CH]_2$ from σ-*iodopentatriacontane*, m.p. 43·5—45°, failed, but reduction of the latter yields *n*-$C_{35}H_{72}$. *n*-Octadecanol with HBr–conc. H_2SO_4 gives the bromide (87%). $C_{12}H_{25}$·MgBr with $CuCl_2$ gives 22% of *n*-$C_{24}H_{50}$, and with laurone yields μ-n-*dodecyltricosan*-μ-*ol*, b.p. 270—275°/2 mm. $C_{18}H_{37}$·MgBr (or the chloride, prepared in 64% yield) with stearone yields σ-n-*octadecylpentatriacontan*-σ-*ol* (III), m.p. 58—59°. The *iodide*, m.p. 29—32°, from (III) with Na gives an unsaturated mixture, m.p. 40—42°, and is reduced (Zn + HCl in AcOH) to σ-n-*octadecylpentatriacontane*, m.p. 45—46°. Dehydration (*p*-C_6H_4Me·SO_3H) of (III) gives a mixture of olefines, m.p. 42—44°. The prep. and reactions of these compounds showed no differences from lower members of the series. A. Li.

Structure of additive products of metal halides and unsaturated compounds. R. C. Freidlina and A. N. Nesmejanov (Compt. rend. Acad. Sci. U.R.S.S., 1940, **26**, 60—64).—$Hg(C_2H_2)Cl_2$ (I) (from $HgCl_2$ and C_2H_2 in dil. HCl) or $Hg(C_2H_2)_2Cl_2$ (II) [from (I) and NH_3 in $CHCl_3$] yields with $SnPh_2Cl_2$, in neutral solution, HgPhCl, and in alkaline solution, $HgPh_2$, with CH_2N_2, $Hg(CH_2Cl)Cl$, and with PPh_3, $Hg(PPh_3)_2Cl_2$, C_2H_2 being eliminated in each case, but with I in Et_2O, CHCl:CHI and HgClI are obtained. From these reactions and spectroscopic evidence it is suggested that (I) and (II) are resonance hybrids CHCl:CH·HgCl ⟷ $Hg(C_2H_2)Cl_2$ and $(CHCl:CH)_2Hg$ ⟷ $Hg(C_2H_2)_2Cl_2$. A. Li.

Action of organomagnesium compounds on trialkoxychlorosilanes. M. N. Kalinin (Compt. rend. Acad. Sci. U.R.S.S., 1940, **26**, 365—369).—$SiCl_4$ with EtOH, $Bu^{\beta}OH$, and *iso*-C_5H_{11}·OH in C_6H_6 at 0°, then at 50—60°, yields respectively $SiCl(OEt)_3$, *chlorotri*-iso*butoxy*-, b.p. 229—231°, and -iso*amyloxysilane*, b.p. 143—146°/12 mm. With MgEtBr and MgPhBr these yield respectively tri-ethoxy-, -iso*butoxy*-, b.p. 101—103°/8 mm., and -iso*amyloxyethylsilane*, b.p. 151—154°/17 mm., and tri-ethoxy-, -iso*butoxy*-, b.p. 154—157°/10 mm., and -iso*amyloxy*-

phenylsilane, b.p. 194—197°/18 mm. The physical properties of these compounds are tabulated.

A. Li.

Application of Meyer's reaction to lead. M. Lesbre (Compt. rend., 1940, **210**, 535—536; cf. A., 1935, 611).—RI (R = Me, Et, Pr$^{\alpha}$, Pr$^{\beta}$, Bu$^{\alpha}$, CH_2Ph, allyl) reacts slowly with a solution of $3PbO,H_2O$ in aq. NaOH (0·15 g.-mol. of Pb. per l.), giving the *alkylplumbonic acid*, $RPb(OH)_3$ or $RPbO_2H$ (I); traces of I catalyse the reaction. (I) is pptd. from the acidified solution by addition of aq. NH_3, and purified by repptn. from HBr solution with dil. KOH. The (I) are sol. in dil. acids and conc. alkalis, but insol. in aq. NH_3 and dil. alkalis; pyrolysis in a sealed tube gives PbO, H_2O, and ROH, $CH_2Ph{\cdot}Pb(OH)_3$ also affording $Pb(CH_2Ph)_4$. The metallic plumbonates are very unstable and readily hydrolysed.

A. J. E. W.

Hydroxylamine–thiocarbamide platinum compounds.—See A., 1940, I, 267.

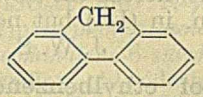
Dehydrogenation and irreversible catalysis of 1-vinyl-Δ^3-*cyclo*hexene. S. R. Sergienko (Compt. rend. Acad. Sci. U.R.S.S., 1940. **26**, 73—75; cf. A., 1939, II, 205).—With Cr_2O_3 at 400°, 1-vinyl-Δ^3-*cyclo*hexene (I) yields PhEt (99%) with a trace of styrene. Pd–C, but not Pt-black, catalyses the irreversible reaction: (I) (3 mols.) → $2PhEt + C_6H_{11}Et$.

A. Li.

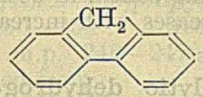
Fluorescence and oxidation in conjugated ring systems. J. Weiss (Nature, 1940, **145**, 744—745).—The essential conditions in these systems for fluorescence, which is due to highly mobile electrons, and the analogy to a metal of the structure and chemical reactivity of conjugated ring systems are discussed. The structures of hydrocarbon peroxides and of graphitic oxide are considered, and a mechanism for the action of carcinogenic hydrocarbons is suggested.

L. S. T.

Structure of aromatic compounds. II. N. Campbell, W. Anderson, and J. Gilmore (J.C.S., 1940, 446—451; cf. A., 1937, II, 407).—Polycyclic aromatic compounds are considered as resonance hybrids, the properties of which are explained by the non-equivalence of C–C linkings. This accounts for previous results (cf. also Lindner *et al.*, A., 1939, II, 448; Sandin *et al.*, *ibid.*, 541). As before, the halogen reactivity is measured by the piperidine method (Le Fèvre *et al.*, A., 1927, 653). The reactivity of 9-bromo-10-nitrophenanthrene and the non-reactivity of 3-bromo-4-nitroacenaphthene agree with the view that reactivity depends on a C:C or conjugated system. *o*-, *m*-, and *p*-$C_6H_4Cl{\cdot}CHO$ and $MeNO_2$ with aq. NaOH give o- (I), m.p. 47°, m- (II), m.p. 48—49°, and p-*chloro*-ω-*nitrostyrene* (III), m.p. 113—114°. *o*-$C_6H_4Br{\cdot}CHO$ (IV) (2 : 4-*dinitrophenylhydrazone*, m.p. 199—200°) with $MeNO_2$ gives o-*bromo*-ω-*nitrostyrene* (V), m.p. 86°. Of (I)—(III) and (V), only (II) is non-reactive. Attempts to prepare 2 : 1- and 4 : 1-$C_6H_4Br{\cdot}C(NO_2){:}CHPh$ were unsuccessful. $CH_2Ph{\cdot}NO_2$, NH_2Me,HCl, Na_2CO_3, EtOH, and (IV) when heated give a *diphenyl*-o-*bromophenyl*isooxazole, m.p. 135°; *p*-$C_6H_4Br{\cdot}CHO$ similarly gives an *isomeride*, m.p. 175° (180° after sublimation). The prep. of 1 : 4-$C_6H_4Ph{\cdot}NO_2$ is improved. 3 : 1 : 4-$NO_2{\cdot}C_6H_3Ph{\cdot}NH_2$ yields 4-*bromo*-3-*nitrodiphenyl*, m.p. 41—42°. 1 : 5 : 2-$C_6H_3PhBr{\cdot}NH_2$ yields 5-*bromo*-2-*nitrodiphenyl* (?), m.p. 230°. The non-reactivity of 2-bromo-4′-, 4-bromo-4′-, and 4-bromo-2′-nitrodiphenyl, and of 2-bromo-7-nitrofluorene shows that the influence of NO_2 is not transmitted from one ring to another. The slight reactivity of 4-bromo-5-nitrohydrindene, new m.p. ~20°, is confirmed. Reactivity of derivatives of fluorene (VI) suggests that (VI) has the structure (*A*), but it is probably a resonance hybrid of (*A*) and (*B*).



(*A*.)



(*B*.)

3-Nitro-2-amino- yields 2-*bromo*-3-*nitro*-*fluorene*, m.p. 120—121°. Attempts to prepare 1 : 2-substituted derivatives of (VI) are unsuccessful. 7-Bromo-2-aminofluorene (VII) with *p*-$C_6H_4Me{\cdot}SO_2Cl$ (VIII) and C_5H_5N yields 7-*bromo*-, m.p. 211°, which with Br–$CHCl_3$ gives 3 : 7-*dibromo*-2-p-*toluenesulphonamido*-*fluorene* (IX), m.p. 203°. 2-Amino- also yields 2-p-*toluenesulphonamido*-*fluorene*, m.p. 157—158°, which is brominated to (IX). On hydrolysis, (IX) gives 3 : 7-*dibromo*-2-*aminofluorene*, m.p. 135°, from which 3 : 7-*dibromofluorene*, m.p. 129°, is obtained. This is oxidised by $Na_2Cr_2O_7$–AcOH to 3 : 7-*dibromofluorenone*, m.p. 200°. With Ac_2O in boiling $C_{10}H_{12}$, (VII) gives its *Ac* derivative, m.p. 229—231°, brominated to 3 : 7-*dibromo*-2-*acetamidofluorene*, m.p. 272°. The pronounced reactivity of 3-bromo-2-nitroacenaphthene suggests that the acenaphthene nucleus has a resonance structure like that of $C_{10}H_8$. 1-Nitro- with boiling AcOH–Br gives 4(?)-*bromo*-1-*nitroacenaphthene*, m.p. 157°. Presence of Me decreases the reactivity of bromonitrotoluenes. 1 : 3 : 4-$C_6H_3MeBr{\cdot}NH_2$ yields 3-*bromo*-4-*nitrotoluene*, m.p. 36—37°. Bromination of 1 : 4 : 2′ : 1′-$C_6H_3Me{\cdot}SO_2{\cdot}NH{\cdot}C_6H_4Me$ (in an attempt to obtain 1 : 3 : 2-$C_6H_3MeBr{\cdot}NO_2$) gives 5-*bromo*-2-p-*toluenesulphonamidotoluene*, m.p. 136°, also obtained from (VIII) and 1 : 5 : 2-$C_6H_3MeBr{\cdot}NH_2$.

E. W. W.

Isomerisation accompanying alkylation. II. Alkylation of benzene with olefines, naphthenes, alcohols, and alkyl halides. V. N. Ipatiev, H. Pines, and L. Schmerling (J. Org. Chem., 1940, **5**, 253—263; cf. A., 1938, II, 130).—The alkylation of C_6H_6 with olefines, alcohols, and naphthenes in the presence of H_2SO_4 leads to the formation of alkylbenzenes different from those obtained when the reactions are catalysed by $AlCl_3$. In presence of H_2SO_4, Δ$^{\alpha}$-pentene gives a mixture of β- and γ-phenylpentane, and $CH_2{:}CHPr^{\beta}$ affords *tert.*-amylbenzene. Isomerisation does not occur in presence of $AlCl_3$; $CH_2{:}CHPr^{\beta}$ gives $CHPhMePr^{\beta}$. Pr$^{\alpha}$OH and C_6H_6 give $PhPr^{\beta}$ in presence of H_2SO_4 and $PhPr^{\alpha}$ in presence of $AlCl_3$. *cyclo*Propane (I) gives exclusively $PhPr^{\alpha}$ in presence of $AlCl_3$ but H_2SO_4 induces isomerisation if the temp. is sufficiently high; thus at 65° (I) and C_6H_6 afford $PhPr^{\beta}$. Alkyl halides with C_6H_6 and $AlCl_3$ give a mixture of isomerides; even at 35° much $PhPr^{\alpha}$ results from Pr$^{\alpha}$Cl and C_6H_6. The mechanism of the alkylations is discussed.

H. W.

Association of the nitrotoluenes. W. Hückel and M. von Schalscha-Ehrenfeld (J. pr. Chem.,

1940, [ii], **154**, 57—65).—The apparent mol. wts. (*M*) of *o*-, *m*-, and *p*-nitrotoluenes, 1-$C_{10}H_7$·NO_2, *trans*-β-decalol (I), and α-fenchol (II) have been determined cryoscopically and ebullioscopically in C_6H_6 and in *cyclo*hexane (III). For the nitrotoluenes, *M* increases almost equally with increasing concn., but the increase in C_6H_6 is ≫ in (III). It is inferred that the dipole moments do not determine the degree of association of these compounds. (II) shows similar association to *iso*borneol, the *M* increasing with increasing concn. in both solvents, whereas the *M* of (I) increases with increasing concn. in (III) but not in C_6H_6. J. W. S.

Catalytic dehydrogenation of ethylbenzene. S. R. Sergienko (Compt. rend. Acad. Sci. U.R.S.S., 1940, **26**, 69—72; cf. A., 1939, II, 205).—The dehydrogenation (Cr_2O_3) of PhEt to styrene begins at 425°, reaching 25—30% at 525°. At 525° some 1-ethylphenanthrene and PhMe are formed. A. Li.

Friedel and Crafts reaction. II. Condensation of *o*- and *m*-dichlorobenzene with chloroform and carbon tetrachloride. S. D. Wilson and Y. Y. Cheng (J. Org. Chem., 1940, **5**, 223—226; cf. A., 1936, 976).—$AlCl_3$ is added to a mixture of $CHCl_3$ and *o*-$C_6H_4Cl_2$ and the mixture is heated at 55—60° for 8 hr., thereby giving (probably) 3 : 4 : 3′ : 4′ : 3″ : 4″-*hexachlorotriphenylmethane*, m.p. 160·5—162°, in 15% yield. Similarly *m*-$C_6H_4Cl_2$ at 60—65° for 12—14 hr. affords 2 : 4 : 2′ : 4′ : 2″ : 4″-*hexachlorotriphenylmethane*, m.p. 227—228·5°, in 18% yield. CCl_4 and *o*-$C_6H_4Cl_2$ give (probably) 3 : 4 : 3′ : 4′-tetrachlorobenzophenone chloride, hydrolysed by hot, 95% EtOH to 3 : 4 : 3′ : 4′-*tetrachlorobenzophenone*, m.p. 141—142°. 2 : 4 : 2′ : 4′-Tetrachlorobenzophenone dichloride, m.p. 139—140·5°, is derived in 60% yield from *m*-$C_6H_4Cl_2$. H. W.

Organic selenium derivatives. V. Reaction products of selenium in [aqueous] sodium sulphide with benzyl derivatives. G. Speroni and G. Mannelli (Gazzetta, 1940, **70**, 246—253).—Se in conc. Na_2S with C_6H_4X·CH_2Cl gives a product (cf. A., 1940, II, 160) which is a solid solution of a disulphide in a diselenide (cf. Fromm *et al.*, A., 1913, i, 1323), as is shown by comparing the m.p. with that of mixtures of these. Products from CH_2PhCl, *m*- and *p*-NO_2·C_6H_4·CH_2Cl, and *o*- (I) and *p*-C_6H_4Cl·CH_2Cl (II) are examined. With Se in aq. Na_2Se, (I) and (II) give respectively *di*-o-, m.p. 105·5°, and *di*-p-*chlorobenzyl diselenide*, m.p. 82°. *Di*-p-*bromobenzyl diselenide*, m.p. 106°, is prepared similarly. With Na_2Se in $COMe_2$, *o*-NO_2·C_6H_4·CH_2Cl gives *di*-o-*nitrobenzyl diselenide*, m.p. 103·5°. K_2SSeO_3 and 5 : 2 : 1-NO_2·C_6H_3Cl·CH_2Cl (III) give *K* 2-*chloro*-5-*nitrobenzylseleniosulphate*. This with I–KI, or on heating with dil. HCl, gives *di*-2-*chloro*-5-*nitrobenzyl diselenide*, m.p. 171·5°, also obtained from (III) and aq. Na_2Se. E. W. W.

Synthesis of dialkylphenanthrenes. 3 : 5-Dimethyl-, 5-methyl-2-ethyl-, and 5-methyl-3-ethyl-phenanthrene. Abnormal selenium dehydrogenation of strophanthidin. E. E. Lewis and R. C. Elderfield (J. Org. Chem., 1940, **5**, 290—299).—If strophanthidin and Se are heated very rapidly in N_2 at 340° and then kept at 340—360° for 32 hr. small amounts of a *hydrocarbon* (I), $C_{17}H_{16}$ or $C_{16}H_{14}$, m.p. 131—132°, are obtained, not identical with the product of Elderfield *et al.* (A., 1934, 657, 1359). (I) gives a *picrate*, m.p. 142—144°, an additive *compound*, m.p. 168·5—170·5°, with *s*-$C_6H_3(NO_2)_3$, and a *quinone*, $C_{17}H_{14}O_2$ or $C_{16}H_{12}O_2$, m.p. 207—208°. *p*-C_6H_4Me·CH_2·CO_2K, 2 : 3 : 1-NO_2·C_6H_3Me·CHO, and Ac_2O at 105—110° yield 2-*nitro*-3-*methyl*-α-p-*tolylcinnamic acid*, m.p. 250·5—251·5°, reduced ($FeSO_4$–aq. NH_3) to the 2-NH_2-compound, m.p. 176·5—177·5°; this is transformed by diazotisation and treatment with $Na_2S_2O_4$ into 3 : 5-*dimethyl*-10-*phenanthroic acid*, m.p. 216—217°, which is decarboxylated (basic Cu carbonate in quinoline at 240—260°) to 3 : 5-*dimethylphenanthrene* (II), m.p. 53·5—54·5° (*picrate*, m.p. 139—139·5°; *styphnate*, m.p. 124—125°; 3 : 5-*dimethylphenanthraquinone*, m.p. 124·5—125·5°, and the corresponding *quinoxaline*, $C_{22}H_{16}N_2$, m.p. 173—173·5°). m-*Allylethylbenzene*, b.p. 88°/18 mm., from *m*-C_6H_4BrEt and CH_2:CH·CH_2Br, is oxidised (cold, dil. $KMnO_4$) to *m*-C_6H_4Et·CH_2·CO_2H, m.p. 62—63°, which is condensed with 2 : 3 : 6-NO_2·C_6H_3Me·CHO to 2-*nitro*-α-m-*ethylphenyl*-3-*methylcinnamic acid*, m.p. 144·5—145·5°. The corresponding NH_2-*acid* is cyclised to 5-*methyl*-2-*ethyl*-10-*phenanthroic acid*, m.p. 171·5—172·5°, which gives 5-methyl-2-ethylphenanthrene (III) [additive *compounds*, m.p. 111—112° and 49—50° respectively with *s*-$C_6H_3(NO_2)_3$ and 1 : 2 : 4 : 6-$C_6H_2Me(NO_2)_2$; unstable *picrate*, m.p. 101—102°], from which a cryst. quinone or quinoxaline could not be derived. *p*-C_6H_4EtBr, b.p. 86·88°/15 mm., is converted into p-*allylethylbenzene*, b.p. 94—95°/23 mm., and thence into *p*-C_6H_4Et·CH_2·CO_2H, m.p. 88—89°. This gives 2-*nitro*-, m.p. 182·5—184·5°, 2-*amino*-, m.p. 167—168°, -α-p′-*ethylphenyl*-3-*methylcinnamic acid* and 5-*methyl*-3-*ethyl*-10-*phenanthroic acid*, m.p. 186—187°, which is decarboxylated to 5-*methyl*-3-*ethylphenanthrene* (IV) [additive *compounds*, m.p. 124—125° and 74—76°, with *s*-$C_6H_3(NO_2)_3$ and 1 : 2 : 4 : 6-$C_6H_2Me(NO_2)_3$; *picrate*, m.p. 111°]. (I) is not identical with (II), (III), or (IV). The prep. of 2-*bromo*-5-*methyl*-, m.p. 122—123°, and 3-*bromo*-6-*methyl*-, m.p. 93·5—94·5°, -*phenylacetic acid* is described. The latter acid is transformed into 2-*nitro*-α-2′-*bromo*-5′-*methylphenyl*-3-*methylcinnamic acid*, m.p. 190—191°, reduced to the 2-NH_2-*acid*, which could not be satisfactorily cyclised. H. W.

Preparation of cholesterilene and various cholestadienes. R. L. Van Peursem (Iowa State Coll. J. Sci., 1939, **14**, 101—102).—The properties of cholesterilene and $\Delta^{3:5}$-cholestadiene are described again (cf. A., 1939, II, 105). Either of these with Cr_2O_3 yields Δ^4-cholestene-3 : 6-dione (identified as monophenylhydrazone). $\Delta^{4:6}$-Cholestadiene differs from 7-dehydrocholestene isomeride (Eck *et al.*, *ibid.*, 539). A. Li.

Derivatives of naphthyl- and tetrahydronaphthyl-oxamic acids, and preparation of 4-nitro-α-naphthylamine. S. I. Sergievskaja (J. Gen. Chem. Russ., 1940, **10**, 55—64).—NHPh·CO·CO_2Et and HNO_3 (*d* 1·53) yield *Et* 2 : 4-*dinitro-oxanilate*, m.p. 142—143°. Et α-naphthyl-

oxamate (I) and HNO_3 (*d* 1·4) (1 hr. at 15—20°) afford *Et* 4-*nitro*-α-*naphthyloxamate*, m.p. 158—159°, converted by heating at 70° with 10% NaOH into 4 : 1-NO_2·$C_{10}H_6$·NH_2; some 2-NO_2-derivative is also formed in this reaction. (I) and Br in $C_2H_4Cl_2$ (1·5 hr. at room temp.) yield *Et* 4-*bromo*-α-*naphthyloxamate*, m.p. 135—136°, which gives 4-*bromo*-α-*naphthyloxamic acid*, m.p. 180° (decomp.), with boiling 10% NaOH, and 4 : 1-$C_{10}H_6Br$·NH_2 with boiling 60% KOH. The following are prepared analogously: 1-*bromo*-β-*naphthyloxamic acid*, m.p. 156—157° (*Et* ester, m.p. 97°), and *Et* 1-*nitro*-β-*naphthyloxamate*, m.p. 135—137° (small amounts of 6- and 8-NO_2-derivatives, not isolated, are produced simultaneously). 5 : 6 : 7 : 8-Tetrahydro-α-naphthylamine and $Et_2C_2O_4$ (4 hr. at the b.p.) yield *Et* 5 : 6 : 7 : 8-*tetrahydro*-α-*naphthyloxamate* (II), m.p. 83·5—84°, together with *di*-(5 : 6 : 7 : 8-*tetrahydro*-α-*naphthyl*)*oxamide*, m.p. 258°. (II) is hydrolysed (10% NaOH at 100°) to 5 : 6 : 7 : 8-*tetrahydro*-α-*naphthyloxamic acid*, m.p. 156—157° [*amide*, m.p. 218—219°; 4-*Br*-derivative, m.p. 180—181° (decomp.) (*Et* ester, m.p. 135—136°); 4-NO_2-derivative, m.p. 163—164°]. 5 : 6 : 7 : 8-*Tetrahydro*-β-*naphthyloxamic acid*, m.p. 158° (decomp.) (*Et* ester, m.p. 81—82°; *amide*, m.p. 198—199°), is prepared analogously. R. T.

Derivatives of sulphonamides.—See B., 1940, 494.

N^4-Diethylaminoalkyl-N^1-dialkylsulphanilamides [*p*-diethylaminoalkylaminobenzenesulphondialkylamides] and related compounds. J. Walker (J.C.S., 1940, 686—692).—*p*-NHAc·C_6H_4·SO_2Cl (I) and $NHMe_2$–$COMe_2$–Et_2O give *p*-NHAc·C_6H_4·SO_2·NMe_2 (II), new m.p. 145—146° (solvated from aq. EtOH, m.p. 106—107°) (cf. Ganapati, A., 1939, II, 107), hydrolysed to *p*-NH_2·C_6H_4·SO_2·NMe_2 (III), new m.p. 169—170°. (II) and K in xylene at 140—150° (bath) give a K derivative, converted by NEt_2·$[CH_2]_2$·Cl into an oil, b.p. ~195°/0·05 mm., and p-N-β-*diethylaminoethylacetamidobenzenesulphondimethylamide*, b.p. 210°/0·05 mm., hydrolysed by 16% HCl to p-β-*diethylaminoethylaminobenzenesulphondimethylamide*, b.p. 195°/0·08 mm. (*hydrochloride*, m.p. 159—160°), also obtained in small yield from (III) and NEt_2·$[CH_2]_2$·Cl,HCl at 145—150°. (I) and piperidine in $COMe_2$ afford *p*-acetamidobenzenesulphonpiperidide, new m.p. 149—150°, converted through the K salt into the Ac derivative of *p*-β-diethylaminoethylaminobenzenesulphonpiperidide (*hydrochloride*, m.p. 201—203°).

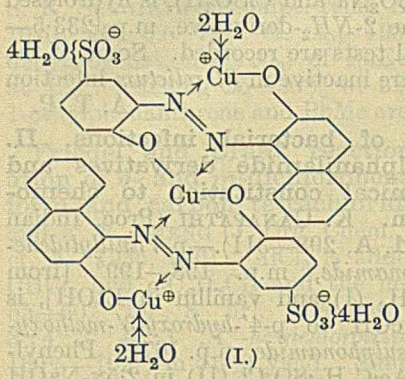
p-NHAc·C_6H_4·SO_2·NEt_2 (IV) (a gum from the monohydrate at 100°) is converted as above into *p*-NEt_2·$[CH_2]_2$·NH·C_6H_4·SO_2·NEt_2 (*hydrochloride*, m.p. 138—139°) and *p*-NH_2·C_6H_4·SO_2·NEt_2. NEt_2·$[CH_2]_3$·Cl and (IV) similarly afford *p*-NEt_2·$[CH_2]_3$·NH·C_6H_4·SO_2·NEt_2 (*dihydrochloride*, m.p. 180—181°). NAcPhEt or HCO·NPhEt and $ClSO_3H$, followed by aq. NH_3, give p-N-*acetyl*-, m.p. 126—127° (+H_2O, lost at ~102°) (low yield), or *p*-N-*formyl*-*ethylaminobenzenesulphonamide*, m.p. 188—189° (64% yield), respectively. The latter is hydrolysed by 16% HCl to p-*ethylaminobenzenesulphonamide*, m.p. 134—135·5°. (I) and NH_2Et–$COMe_2$–Et_2O afford p-*acetamidobenzenesulphonethylamide*, m.p. 153—155°, less readily obtained (impure) from *p*-NHAc·C_6H_4·SO_2·NH_2 and 95% EtOH–KOH–EtI. HCO·NNaPh and NEt_2·$[CH_2]_2$·Cl in C_6H_6 give *N*-β-diethylaminoethylformanilide (V), b.p. 143—144°/0·1 mm., converted by 22% HCl into *N*-β-diethylaminoethylaniline, b.p. 152—153°/18 mm. [Ac derivative (VI), b.p. 118—120°/0·1 mm.]. (V) or (VI) is unchanged by $ClSO_3H$. HCO·NNaPh and γ-bromopropylphthalimide at 100° (bath) afford N-γ-*phthalimidopropylformanilide*, m.p. 126°, converted by $ClSO_3H$ into N-γ-(o-*carboxybenzamido*)*propylaniline*-(?)p-*sulphonic acid*, m.p. 250—253°. 2-*Acetamidonaphthalene*-6-*sulphonamide*, m.p. 246—247° (intermediate chloride best obtained from 2 : 6-NHAc·$C_{10}H_6$·SO_3Na and $ClSO_3H$), is hydrolysed by 16% HCl to the 2-NH_2-derivative, m.p. 233·5—235°. Antimalarial tests are recorded. Some of the above compounds are inactive in *Pl. relictum* infection of canaries. A. T. P.

Chemotherapy of bacterial infections. II. Synthesis of sulphanilamide derivatives and relation of chemical constitution to chemotherapeutic action. K. Ganapathi (Proc. Indian Acad. Sci., 1940, **11**, A, 298—311).—p-*Vanillylideneaminobenzenesulphonamide*, m.p. 198—199° [from *p*-NH_2·C_6H_4·SO_2·NH_2 (I) and vanillin in EtOH], is reduced by Zn–AcOH to p-4′-*hydroxy*-3′-*methoxybenzylaminobenzenesulphonamide*, m.p. 167°. Phenylalanine and *p*-NHAc·C_6H_4·SO_2Cl (II) in 2·5N-NaOH afford, after hydrolysis (dil. HCl) of the *Ac* derivative, m.p. 205—206°, N-*sulphanilylphenylalanine*, m.p. 196—197° (decomp.). *dl*-Taurine affords N-*sulphanilyltaurine*. 1 : 3 : 6- or 2 : 5 : 7-NH_2·$C_{10}H_5(SO_3H)_2$ gives 1-*sulphanilamidonaphthalene*-3 : 6- or 2-*sulphanilamidonaphthalene*-5 : 7-*disulphonic acid*, respectively. 1- and 2-*Sulphanilamido*-8-*naphthol*-3 : 6-*disulphonic acid* are prepared. 6-Aminoquinoline and (II) in C_5H_5N give (after hydrolysis) 6-sulphanilamidoquinoline, m.p. 201° (cf. Bobrański, A., 1939, II, 179). (I) and PhNCS in EtOH afford p-*phenylthiocarbamidobenzenesulphonamide*, m.p. 189°. 4 : 4′-Diaminodiphenyl sulphone and CH_2:CH·CH_2·NCS in EtOH give 4 : 4′-*di*(*allylthiocarbamido*)*diphenyl sulphone*, m.p. 183°. Sulphanil-*p*-aminoanilide appears to have m.p. 137—138° or 155° (cf. lit.). (II) and *o*-NO_2·C_6H_4·NH_2 in C_5H_5N–$COMe_2$ yield *sulphanil*-o-*nitroanilide*, m.p. 167°. 2-Chloroquinoline-3-carboxylic acid and (I) at 165—170° afford N^4-(3-*carboxy*-2-*quinolyl*)*sulphanilamide*, m.p. >280°. 2 : 8-Diaminoacridine and (II) in C_5H_5N–$COMe_2$–H_2O give (after hydrolysis with aq. NaOH) 2 : 8-*di*(*sulphanilamido*)*acridine* (III). Similarly prepared is 2-p′-N^1-*sulphanilamidobenzenesulphonamidopyridine* (IV), m.p. 236—238°. 2-Aminothiazole affords 2-sulphanilamidothiazole, m.p. 197—198° (improved prep.) (cf. Fosbinder *et al.*, A., 1939, II, 525). The protective action of the latter and (III) in streptococcal and pneumococcal infections in mice is noted; (IV) has little effect. 4-Amino-uracil or -thiouracil (V) and diazotised (I) in aq. NaOH afford 4-*amino*-5-*benzeneazo-uracil*- or -*thiouracil*-4′-*sulphonamide*, respectively. Diazotised 2-sulphanilamidopyridine and (V) or *m*-$C_6H_4(NH_2)_2$ afford analogous dyes. Cholesteryl chloride does not react with (I). The relation between activity and chemical constitution is discussed. A. T. P.

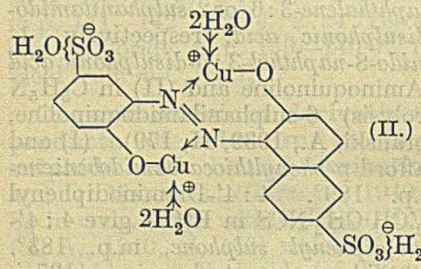
Reduction of dinitroveratrole with sodium sulphide. B. K. Nandi (Current Sci., 1940, **9**, 118—119).—1 : 2 : 4 : 5-$C_6H_2(OMe)_2(NO_2)_2$ with aq. EtOH–Na_2S yields 1 : 2 : 4 : 5-$C_6H_2(OMe)_2(NH_2)_2$ and the *Na* salt, m.p. 194°, of *5-nitro-4-hydroxylamino-veratrole*, m.p. 110°. F. R. G.

Manufacture of benzidine.—See B., 1940, 430.

Copper lakes of azo-dyes. Further types. W. F. Beech and H. D. K. Drew (J.C.S., 1940, 608—612; cf. A., 1938, II, 180).—1-2′-Hydroxy-5′-sulphobenzeneazo-β-naphthol (2 mols.) and aq. $CuCl_2,2H_2O$ (3 mols.) give a *Cu complex dodecahydrate* [probably (I)] (the *NH_4 salt*, $+8H_2O$, has 2 NH_3 co-ordinated to outer Cu atoms). Both azo-N are in the *anti*-form in both dye residues. This is the first case where both N of an azo-group are co-ordinated to metallic atoms at the same time, *i.e.*, are co-ordinatively saturated. 2 Cu of (I) are each singly ionised and co-ordinated with 3 other atoms. 1-2′-Hydroxy-5′-sulphobenzeneazo-β-naphthol-6-sulphonic acid and $CuCl_2,2H_2O$ in aq. EtOH afford the Cu complex (II), $+5{\cdot}5$ or $6H_2O$, sol. in H_2O. This is the first case of a lake where 2 atoms of a bivalent metal are combined with 1 azo-residue. In (I) and (II), the aromatic nuclei bearing *o*-OH have rotated to bring the OH on opposite sides of the azo-chain; the simple Cu lakes from dyes free from SO_3H have 2 OH on the same side of the azo-chain (*loc. cit.*). The Cu derivative, $C_{17}H_{10}O_3N_2Cu,Cu(OH)_2$, of benzeneazo-β-naphthol-2′-carboxylic acid (*loc. cit.*) is probably the *cupri-hydroxide complex* (formula given). Both types of lake can thus be prepared from the same azo-dye under different conditions of acidity. 2-2′-Carboxybenzeneazo-α-naphthol-4-sulphonic acid and aq. $CuCl_2,2H_2O$ yield a *Cu complex dihydrate*, $C_{17}H_{10}O_6N_2SCu,2H_2O$ (1 Cu : 1 azo-dye residue). Formation of the *NH_4* salt, $+4H_2O$, involves change of structure involving removal of one third of its azo-dye residues and co-ordination with NH_3 (formula suggested); left in air for 2 weeks, it loses $\sim$4 H_2O + 2 NH_3. 2-Benzeneazo-α-naphthol-4-sulphonic acid and aq. $CuCl_2$ afford the simple *Cu* salt, $+8H_2O$. Action of aq. NH_3 on the *Cu* salt, $+8H_2O$, from 1-3′-sulphobenzeneazo-β-naphthol causes the Cu to wander to the inner complex to give an *NH_4* salt of a *cupri-hydroxide complex* with loss of 1 dye residue.



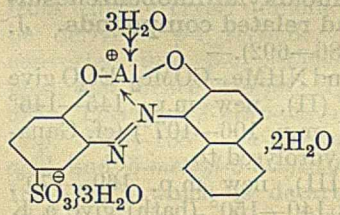
(I.)



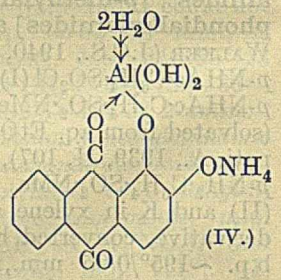
(II.)

1-2′-Hydroxy- or -carboxy-benzeneazo-β-naphthylamine yields anhyd. *Cu complexes*, $C_{16}H_{11}ON_3Cu$ (C_5H_5N derivative; base co-ordinated to Cu) or $C_{17}H_{11}O_2N_3Cu$ (III) [C_5H_5N derivative in moist air gives the *monohydrate* of (III)], respectively. The azo-dyes are able to adjust their configurations to conform with the structural requirements of substituents in the nuclei and with the valency of the lake-forming metal. A. T. P.

Structure of aluminium lakes of azo-dyes and of alizarin. W. F. Beech and H. D. K. Drew (J.C.S., 1940, 603—607; cf. A., 1939, II, 309).—As in case of Cr, no definite lakes of Al with *o*-monohydroxyazo-dyes are isolable; if formed they are unstable. *oo′*-Dihydroxyazo-compounds give lakes similar in structure to those of Cr^{III}, but much less stable to mineral and org. acids. 1-*o*-Hydroxybenzeneazo-β-naphthol (I) and $AlCl_3,6H_2O$ in 96% EtOH give the *aluminichloride pentahydrate* (II), $C_{16}H_{20}O_7N_2ClAl$, and a little of a *complex*, probably $[Al(C_{16}H_{10}O_2N_2)_2]H,2H_2O$. The aq. solution of (II) contains Cl′. At 150°, 5 H_2O and part of the Cl (as HCl) are lost. (II) and aq. NH_3 or K_2CrO_4, or (I)–$AlCl_3,6H_2O$–NaOH–96% EtOH afford the *oxide tetrahydrate*, $C_{32}H_{28}O_9N_4Al_2$, insol. in H_2O; 3 H_2O are lost at 120° to give probably the anhyd. hydroxide. 1-2′-Hydroxy-5′-sulphobenzeneazo-β-naphthol and $Al_2(SO_4)_3,18H_2O$ in aq. NaOH (+ a little EtOH) give the *alumini-sulphonate octahydrate* (III) (*NH_4 salt hexahydrate*), sol. in H_2O; at 180° it loses $\sim$7·5 H_2O and becomes almost insol. in H_2O; aq. HCl yields the azo-dye. 2′-Hydroxy-4′-sulphonaphthalene-1′ : 4-azo-1-phenyl-3-methylpyrazol-5-one and aq. $AlCl_3,6H_2O$ give the *alumini-sulphonate hexahydrate*, $C_{20}H_{25}O_{11}N_4SCl$ (*NH_4 salt pentahydrate*); it loses 5 H_2O at 180° but regains 2 H_2O in moist air. No pure Al lake is obtained from *o*-carboxybenzeneazo-β-naphthol or benzeneazosalicylic acid, although there is evidence of formation of lakes containing 1 Al : 1 dye residue. Alizarin and $AlCl_3,6H_2O$–NaOH in EtOH afford a *substance*, $C_{28}H_{19}O_{17}Al_5,13H_2O$ (formula suggested), converted by dil. aq. NH_3 into an insol. substance and a red *lake*, $C_{14}H_{21}O_{12}NAl_2$, or by aq. NH_3 (*d* 0·88) into *NH_4 Al alizarate dihydrate* [probably (IV)]; it loses $\sim$3 H_2O + 1 NH_3 at 170°; aq. HCl regenerates alizarin. Alizarin and $CaCO_3$ in boiling H_2O give Ca alizarate dihydrate. The structure of Turkey-red Al–Ca lake is discussed. A. T. P.



(III.)

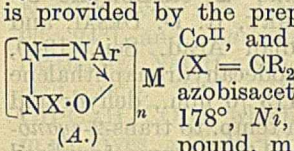


(IV.)

Method of diazotisation.—See B., 1940, 430.

Manufacture of stable diazo-salts.—See B., 1940, 430.

Azo-group as a chelating group. IV. Constitution of arylazobisoximes. (Miss) M. Elkins and L. Hunter (J.C.S., 1940, 653—655; cf. A., 1938, II, 483).—Support for Bamberger's hydroxytriazen structure for the arylazobisoximes is provided by the prep. of co-ordinated Cu^{II}, Ni, Co^{II}, and Fe^{III} complexes of type *A* (X = CR_2:N·O·CR_2). Thus, benzeneazobisacetoxime gives *Cu*^{II}, m.p. 175—178°, *Ni*, m.p. 166° (*dipyridino*-compound, m.p. ~108°, loses 2 C_5H_5N at ~80° or in air), *Co*^{II}, m.p. 148°, and *Fe*^{III}, m.p. 138°, compounds. *o*-Tolueneazobisacetoxime, m.p. 78—82°, yields *Cu*^{II}, m.p. 131°, *Ni*, m.p. 143°, *Co*^{II}, m.p. 128°, and *Fe*^{III}, m.p. 125°, compounds. *p*-Tolueneazobisacetoxime, m.p. 143°, affords *Cu*^{II} (*anhyd.*, m.p. 181°; *monohydrate*, m.p. 180°), *Ni*, m.p. 174° (*dipyridino*-compound loses 2 C_5H_5N at ~110°), and *Fe*^{III}, m.p. 136—137°, compounds. Benzeneazobismethylethylketoxime, m.p. 92—93°, yields *Cu*^{II}, m.p. 106°, *Ni*, m.p. 101° (*dipyridino*-compound, m.p. 80°), *Co*^{II} (+2H_2O), m.p. 115—118°, and *Fe*^{III}, m.p. 88—90°, compounds. m-*Tolueneazobismethylethylketoxime*, m.p. 50—51° (from *m*-C_6H_4Me·N_2Cl and COMeEt in alkali), yields *Cu*^{II} (+H_2O), m.p. 86—88° (*anhyd.*, m.p. 103—105°), *Ni*, m.p. 80—82°, *Co*^{II}, m.p. 80—85°, and Fe^{III}, m.p. ~50°, compounds. Benzeneazobisbenzaldoxime, new m.p. 132—134°, gives *Cu*^{II}, m.p. 187°, *Ni*, m.p. 168° (*dipyridino*-compound, m.p. 150—155°), *Co*^{II}, m.p. 80—85°, and *Fe*^{III} (impure), m.p. 110° (softens at 80°), compounds. There is only momentary formation of Co^{III} complexes. The complexes are decomposed by mineral acids but are stable to boiling aq. or alcoholic alkali. A. T. P.


(*A*.)

Apparatus for continuous automatic measurement of evolved gas.—See A., 1940, I, 302.

Ethers of phenylmethylcarbinol and its homologues.—See B., 1940, 431.

Resolution of β-naphthylmethylcarbinol. T. A. Collyer and J. Kenyon (J.C.S., 1940, 676—679).—*dl*-β-$C_{10}H_7$·CHMe·OH (Lund, A., 1937, II, 364) affords a *H phthalate* (I), m.p. 125°, and thence the *cinchonidine* salt, m.p. 167° (decomp.), $[\alpha]_{5893}$ −41·0° in $CHCl_3$, of d-β-*naphthylmethylcarbinyl H phthalate* (II), m.p. 101—102°. Decomp. of the mother-liquors and conversion into the *strychnine* salt, m.p. 200—202°, $[\alpha]_{5893}$ −45·3° in $CHCl_3$, affords l-β-*naphthylmethylcarbinyl H phthalate* (III), m.p. 101—102°. Hydrolysis (aq. EtOH–NaOH) of (II) and (III) gives *d*-, m.p. 71—72° (formate, m.p. 62—64°, $[\alpha]_{5893}$ +10·5° in EtOH; *acetate*, m.p. 36—37°, $[\alpha]_{5893}$ +124·2° in EtOH), and *l*-β-$C_{10}H_7$·CHMe·OH (IV), m.p. 71—72° (*benzoate*, m.p. 62—64°, $[\alpha]_{5893}$ −53·4° in EtOH), respectively. Both are optically pure. Vals. of [α] are compared with those of the corresponding derivatives of α-$C_{10}H_7$·CHMe·OH (cf. Pickard *et al.*, J.C.S., 1914, **105**, 2644). Both *l*-α- and *l*-β-derivatives of $C_{10}H_8$ are configuratively similar and optical behaviour of both series of compounds is dominated by $C_{10}H_7$· (III) and AcOH–NaOAc at 100° (bath) for ~40 hr. afford (I) + (III) and the acetate (activity 6·5% without inversion of configuration) of (IV); after ~20 hr. the *l* + *dl*-acetate, $[\alpha]_{5461}$ −8·8° in EtOH, and H phthalate, $[\alpha]_{5461}$ +27° in EtOH, are recovered. (III) and anhyd. HCO_2H rapidly afford *o*-$C_6H_4(CO_2H)_2$ and dl-β-*naphthylmethylcarbinyl formate*, m.p. 55—56°. A. T. P.

Hydrogenation of wood. H. P. Godard, J. L. McCarthy, and H. Hibbert (J. Amer. Chem. Soc., 1940, **62**, 988).—Hydrogenation (3·2 H_2 per 100 g.; Cu chromite; dioxan; 250—280°/333—400 atm.) of resin- and fat-free maple and spruce wood meal gives 60—70% and 35—40% (calc. on total lignin), respectively, of 4-*n*-propyl*cyclo*hexan-ol + -1 : 2-diol with oils of higher b.p. R. S. C.

Biochemistry of micro-organisms. LXV. (A) Chlorine metabolism by moulds. (B) Caldariomycin, $C_5H_8O_2Cl_2$, a metabolic product of *Caldariomyces fumago*, Woronichin. P. W. Clutterbuck, S. L. Mukhopadhyay, A. E. Oxford, and H. Raistrick (Biochem. J., 1940, **34**, 664—677).—A quant. survey of the Cl metabolism of 139 species or strains of moulds grown on Czapek–Dox 5% glucose solution containing 0·5 g. of KCl per l. as sole source of Cl shows that extensive conversion of inorg. chloride into org. metabolic products containing Cl is of rather rare occurrence although with a no. of species this conversion is by no means negligible. Under these conditions *C. fumago* affords fumaric acid and *caldariomycin* (I), m.p. 121°, $[\alpha]_{5461}^{20}$ +59·2° in H_2O, which is probably 2 : 2-*dichloro*cyclo*pentane*-1 : 3-*diol*. It does not contain OMe or Me as side-chain. The Cl atoms are very labile since they are completely removed when it is kept overnight in cold 0·1N-NaOH. It does not contain CO or CHO but since it has two active H (Zerevitinov) the probable presence of two actual or potential OH is indicated although no satisfactory derivatives proving the presence of these groups could be obtained. It is oxidised by CrO_3 to succinic acid, thus establishing the presence of :C·CH_2·CH_2·C:. It is reduced (H_2, Pd–C, H_2O) to *cyclo*pentanone. OH·C·C·OH cannot be present since it is not attacked by HIO_4. It is very stable to heat and does not lose H_2O or HCl at a moderate temp. Above 180° it gives H_2O, HCl, black resinous products, and two isomeric ketones, C_5H_5OCl, which yield *dinitrophenylhydrazones*, m.p. 226° (decomp.) and 238° (decomp.); the former is also obtained from the products of hydrolysis of caldariomycin by boiling 2N-H_2SO_4. It does not contain ·CH_2·CO· since it gives no ketonic reactions. This group is formed by treatment with dil. alkali hydroxide since the solution then gives a ppt. with Brady's reagent. Further, (I) does not immediately give Callow's modification of the Zimmermann reaction for active CH_2 although an alkaline solution after some time quickly gives an intense reaction. Finally, the reduction of cold Fehling's solution by (I) is apparent only after a considerable lag period during which a reducing substance is presumably formed. H. W.

Action of ephedrine on halogenated organic compounds.—See B., 1940, 493.

Reaction between dibenzyl disulphide and sulphuryl chloride. G. H. Elliott and J. B. Speakman (J.C.S., 1940, 641—649).—(CH_2Ph·S)$_2$ (I) and SO_2Cl_2 in H_2O-free Et_2O or C_6H_6 at 37—39° afford CH_2PhCl and SO_2, with some S (not formed with excess of SO_2Cl_2). In undried Et_2O, reaction is slow

at room temp. but at the b.p. similar fission may occur; (I) is partly oxidised to $CH_2Ph{\cdot}SO_2{\cdot}S{\cdot}CH_2Ph$ (II), the yield of which decreases with excess of SO_2Cl_2 since at 37—39° (II) and SO_2Cl_2 (excess) give CH_2PhCl (mainly), $CH_2Ph{\cdot}SO_2Cl$, and SO_2. Fission of (I) without conversion into (II) may occur. Dibenzyl disulphone could not be prepared, but di-*p*-tolyl disulphone is unchanged with SO_2Cl_2 in C_6H_6 at 58—60°, although the corresponding disulphide with SO_2Cl_2 in Et_2O affords *p*-C_6H_4ClMe. Mechanisms of reactions are discussed. H_2O may facilitate the action of SO_2Cl_2 on wool by swelling the fibres. Disulphide bond breakdown occurs; SO_2Cl_2, like Cl_2, renders wool unshrinkable probably by rupture of the cystine linkages between the peptide chains of the fibres. $SOCl_2$, unsuitable for making wool unshrinkable, has no significant action on (I) or (II) at 37—39°. A. T. P.

Separated auxo-enoid systems. X. Colour phenomena of nitrocinnamoyl derivatives of arylamines. E. A. Smirnov (J. Gen. Chem. Russ., 1940, **10**, 43—54).—$C_6H_4R{\cdot}CH{:}CH{\cdot}COCl$ and $NH_2{\cdot}C_6H_4R'$ give the following $C_6H_4R{\cdot}CH{:}CH{\cdot}CO{\cdot}NH{\cdot}C_6H_4R'$: R = H : R′ = m-, m.p. 115°, and p-*OMe*, m.p. 149°; R′ = m-, m.p. 218°, and p-*OH*, m.p. 213°; R′ = m-, m.p. 183·5°, and p-NMe_2, m.p. 173·5°; R = *m*-NO_2 : R′ = *H*, m.p. 199·5°; R′ = m-, m.p. 174°, and p-*OMe*, m.p. 192·5°; R′ = m-, m.p. 275·5°, and p-*OH*, m.p. 258·5° (N-*Me* derivative, m.p. 213°); R′ = m-, m.p. 194·5°, and p-NMe_2, m.p. 222°; R = *p*-NO_2 : R′ = *H*, m.p. 208·5°; R′ = m-, m.p. 178°, and p-*OMe*, m.p. 215·5°; R′ = m-, m.p. 254·5°, and p-*OH*, m.p. 279° (N-*Me* derivative, m.p. 226°); R′ = m-, m.p. 224·5°, and p-NMe_2, m.p. 238·5°. The intensity of coloration (yellow to dark red) of the compounds rises in the order R = H < *m*-NO_2 < *p*-NO_2, and R′ = H < *m*-OMe < *p*-OMe < *m*-OH < *p*-OH < *m*-NMe_2 < *p*-NMe_2. R. T.

Constitution of dihydroxy-homophthalic and -terephthalic acid derived from triethyl orcinol-tricarboxylate. Y. Asahina and H. Nogami (Proc. Imp. Acad. Tokyo, 1940, **16**, 119—121).—3 : 5-Dihydroxy-2-carboxyphenylacetic acid is converted by CH_2N_2 into the Me_2 ester, m.p. 77°, which with MeI and K_2CO_3 in $COMe_2$ affords Me 3 : 5-dimethoxy-2-carbomethoxyphenylacetate, m.p. 72—73°, hydrolysed (KOH–EtOH) to 3 : 5-dimethoxy-2-carbomethoxyphenylacetic acid, m.p. 147·5°. The corresponding chloride is condensed with $CHNaAc{\cdot}CO_2Et$ and the product is transformed by NH_3 into Et γ-3 : 5-dimethoxy-2-carbomethoxyphenylacetoacetate (I), m.p. 115°, which is converted by restrained action of KOH into 3 : 5-dimethoxy-2-carbomethoxybenzyl Me ketone, m.p. 100·5°, and thence by conc. H_2SO_4 into the corresponding acid, m.p. 139—140°, which is not readily lactonised. Successive treatments of (I) with BuI and EtOH–NaOEt, KOH–EtOH, and conc. H_2SO_4 or KOH–EtOH give a product, m.p. 137°, quite distinct from olivetonic acid Me_2 ether, m.p. 93°. Jerdan's orientation (J.C.S., 1899, **75**, 808) of the orcinoldicarboxylic acids must therefore be reversed. Et 3 : 5-dihydroxy-4-carboxy-2-carbethoxyphenylacetate has been converted into 6 : 8-dimethoxy-3-methyl*iso*coumarin and 3 : 5-dihydroxy-2-carbethoxyphenylacetic acid into olivetonic acid or olivetonide Me_2 ether. H. W.

Naphthalene series. II. Synthesis of *trans*-decahydronaphthalene-*trans*-2-carboxylic-3-acetic acid. N. A. Chaudhry, R. D. Desai, and G. S. Sahariya (Proc. Indian Acad. Sci., 1940, **11, A**, 145—148).—*trans*-2-Ketodecahydronaphthalene gives the *cyanohydrin*, b.p. 113°/6 mm., dehydrated by $SOCl_2$–C_5H_5N at 0°—room temp. to trans-2-*cyano*-Δ^2-*octahydronaphthalene*, b.p. 145°/6 mm. [oxidised by $KMnO_4$ to *cyclo*hexane-1 : 2-diacetic acid (I)]. Boiling conc. HCl then gives trans-Δ^2-*octahydronaphthalene*-2-*carboxylic acid*, m.p. 146° [oxidised to (I)], which with $CN{\cdot}CHNa{\cdot}CO_2Et$–EtOH at, successively, 0°, room temp., and the b.p. gives an ester, hydrolysed to trans-*decahydronaphthalene*-trans-2-*carboxylic*-3-*acetic acid*, m.p. 214—215°, and an impure acid, m.p. 160—180°. R. S. C.

Mechanism of aromatic side-chain reactions with special reference to polar effects of substituents.—See A., 1940, I, 295.

Naphthalene series. I. Properties of 2-acetyl-1-naphthol. Synthesis of 2-ethyl-1-naphthol. III. Properties of 4-acetyl-1-naphthol. Preparation of 4-ethyl-1-naphthol. IV. Preparation and properties of 2 : 4-diacetyl- and 2-acetyl-4-propionyl-1-naphthol. M. Akram and R. D. Desai (Proc. Indian Acad. Sci., 1940, **11, A**, 139—144, 149—155, 156—161).—I. Some (4 : 1-$OH{\cdot}C_{10}H_6)_2$, m.p. 300°, and 1 : 1′-*dihydroxy*-2 : 2′-*dinaphthyl oxide*, m.p. 183—184°, accompany (method : Clemo *et al.*, J.C.S., 1931, 1265) 2 : 1-$C_{10}H_6Ac{\cdot}OH$ (I) (blue-green $FeCl_3$ colour; *picrate*, m.p. 112°; *semicarbazone*, m.p. 306°; *phenylhydrazone*, m.p. 141°). Anhyd. $AlCl_3$ converts (I) in $PhNO_2$ into a *compound*, $C_{24}H_{18}O_4$, m.p. >300°. 2 : 4 : 1-$C_{10}H_5AcBr{\cdot}OH$, Ac_2O, and NaOAc at 180—185° give 6-*bromo*-3-*acetyl*-2-*methyl*-1 : 4-α-*naphthapyrone*, m.p. 206—207°, hydrolysed by 10% NaOH to 1 : 4 : 2-$OH{\cdot}C_{10}H_5Br{\cdot}CO_2H$ (II). Br and (I) in $CHCl_3$ give 4-*bromo*-2-*bromoacetyl*-1-*naphthol*, m.p. 150°, hydrolysed by NaOEt in boiling EtOH to 4-*bromo*-2-*hydroxyacetyl*-1-*naphthol*, m.p. 136—137°, and 4-*bromo*-α-*naphthacoumaranone*, m.p. 274°. 4-*Bromo*-2-*dibromoacetyl*-1-*naphthol* (similarly prepared), m.p. 199°, and NaOEt–EtOH give (II) and a neutral *substance*, m.p. 250°.

4 : 2 : 1-$NO_2{\cdot}C_{10}H_5Ac{\cdot}OH$ and NaOAc–Ac_2O at 100—140° give 6-*nitro*-3-*acetyl*-2-*methyl*-1 : 4-α-*naphthapyrone*, m.p. 242—243°, hydrolysed by hot 10% NaOH to 4 : 1 : 2-$NO_2{\cdot}C_{10}H_5(OH){\cdot}CO_2H$. Zn–Hg–HCl reduces (I) to 2 : 1-$C_{10}H_6Et{\cdot}OH$, m.p. 70° (lit. 68°) [picrate, m.p. 123° (lit. 118°); *Me ether*, b.p. 136°/6 mm. (*picrate*, m.p. 80°); 4-NO_2-, m.p. 88°, and PhN_2-derivative, m.p. 189°; with Br gives 2-β-*bromoethyl*-1-*naphthol*, m.p. 90° (with alkali gives a substance, m.p. 280° after sintering)], and 2-*ethyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthol*, b.p. 108°/8 mm.

III. 4 : 1-$C_{10}H_6Ac{\cdot}OH$ (III), m.p. 199—200° (*acetate*, m.p. 83—84°; Me ether, m.p. 71—72°; *picrate*, m.p. 160—161°; *semicarbazone*, m.p. 200°; *oxime*, m.p. 250°), with a little (I) is best obtained from α-$C_{10}H_7{\cdot}OH$ by AcCl and $ZnCl_2$ in $PhNO_2$ at

room temp. With $ZnCl_2$ and boiling $EtCO_2H$ it gives 1 : 2-OH·$C_{10}H_6$·COEt. With Br–$CHCl_3$ it gives 2-*bromo*-4-*acetyl*-, m.p. 134—135°, -4-*bromoacetyl*-, m.p. 140° [with warm EtOH gives (colour changes) a substance, m.p. 178—180°; with boiling 10% NaOH gives the 4-*hydroxyacetyl* derivative, m.p. 93—94°], and -4-*dibromoacetyl*-1-*naphthol*, m.p. 116° (with 10% NaOH gives 3-*bromo*-4-*hydroxy*-1-*naphthoic acid*, m.p. 208°). With NaOBr it gives 4 : 1-OH·$C_{10}H_6$·CO_2H, which in boiling H_2O or above the m.p. gives α-$C_{10}H_7$·OH and with Br–$CHCl_3$ gives 4 : 1-$C_{10}H_6Br$·OH. With HNO_3 (*d* 1·5) in AcOH it gives 2-*nitro*-4-*acetyl*-1-*naphthol* (IV), m.p. 145°, 2 : 1-NO_2·$C_{10}H_6$·OH, and 2 : 4 : 1-$(NO_2)_2C_{10}H_5$·OH [also obtained from (IV)]. With Zn–Hg–HCl it gives 4 : 1-$C_{10}H_6Et$·OH, m.p. 42°, b.p. 160—161°/7 mm. [with PhN_2Cl gives 2-*benzeneazo*-4-*ethyl*-1-*naphthol*, m.p. >300°, and (? cis- and trans-)*forms*, m.p. 111—112° and 180—181°, of 4-*ethyl*-1 : 2-*naphthaquinone*-2-*phenylhydrazone*], and 4-*ethyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthol*, b.p. 110—111°/10 mm.

IV. AcCl–$AlCl_3$ in $PhNO_2$ converts (I) or (III) into 2 : 4-*diacetyl*-1-*naphthol* (V), m.p. 141°, which yields (methods as above) 2-*acetyl*-4-*bromoacetyl*-, m.p. 164—165°, 2-*acetyl*-4-*hydroxyacetyl*-, m.p. 130°, and 2-*bromoacetyl*-4-*dibromoacetyl*- (VI), m.p. 136°, -1-*naphthol*. Boiling 10% NaOH converts (VI) into α-*naphthacoumaranone*-4-*carboxylic acid*, m.p. 207—209°. With HNO_3 (*d* 1·5) (1 mol.) in AcOH, (V) gives 4 : 2 : 1- and 2 : 4 : 1-NO_2·$C_{10}H_5Ac$·OH and 2 : 4 : 1-$(NO_2)_2C_{10}H_5$·OH, obtained also with a polynitro-compound, m.p. 215°, by use of 2 mols. of HNO_3. With $ZnCl_2$ in boiling AcOH or $EtCO_2H$, (V) gives 2 : 1-$C_{10}H_6R$·OH (R = Ac or EtCO, respectively), and with NaOAc–Ac_2O at 180—190° gives 3 : 6-*diacetyl*-2-*methyl*-1 : 4-α-*naphthapyrone*, m.p. 170—171°, hydrolysed by boiling 10% NaOH to 1-*hydroxy*-4-*acetyl*-2-*naphthoic acid*, m.p. 216° [decomp. to (III)]. With EtCOCl and $ZnCl_2$ in $PhNO_2$, (I) gives 2-*acetyl*-4-*propionyl*-1-*naphthol*, m.p. 131°, the *Br*-derivative, m.p. 141°, of which loses its Br to hot 5% NaOH, with $ZnCl_2$–AcOH gives (I), with $ZnCl_2$–$EtCO_2H$ gives 1 : 2-OH·$C_{10}H_6$·COEt, and with HNO_3 (1 mol.) gives 4 : 2 : 1-NO_2·$C_{10}H_5Ac$·OH with a little 2 : 1-NO_2·$C_{10}H_6$·OH and 2 : 4 : 1-$(NO_2)_2C_{10}H_5$·OH. R. S. C.

Preparation and properties of α- and β-naphthylglyoxal. L. N. Goldirev and I. J. Postovski (J. Gen. Chem. Russ., 1940, **10**, 39—42).—1- or 2-$C_{10}H_7$·COMe with SeO_2 in 80% AcOH (1 hr. at the b.p.) yields α- (I), an oil (+H_2O, m.p. 82°; *osazone*, m.p. 105°), or β-naphthylglyoxal (II) [+H_2O, m.p. 110° (lit. 98°); *osazone*, m.p. 134°], respectively. (I) and (II) with *o*-$C_6H_4(NH_2)_2$ yield the corresponding *quinoxalines*, m.p. 114° and 137°, respectively. (II) and CH_2O in aq. NH_3 [$Cu(OAc)_2$ catalyst] afford 4-β-*naphthylglyoxaline*, m.p. 168°. (I) and (II) give an intense green coloration when heated with 2-aminopyridine. R. T.

Derivatives of 2-phenyl*cyclo*hexanone. J. C. Bardhan (Chem. and Ind., 1940, 369).—CPhNa$(CO_2Et)_2$ and CH_2Ac·CH_2·$NMeEt_2I$ give Et δ-keto-α-carbethoxy-α-phenylhexoate, b.p. 182°/6 mm., hydrolysed and decarboxylated to δ-keto-α-phenylhexoic acid, b.p. 180°/4 mm., 185°/6 mm. [semicarbazone, m.p. 161—162°; Me ester, b.p. 149°/5 mm. (semicarbazone, m.p. 151—152°)]. The Et ester, b.p. 160°/9 mm. (semicarbazone, m.p. 119—120°), condenses with CN·CH_2·CO_2Et (piperidine) to Et_2 α-cyano-ε-phenyl-β-methyl-Δ^{α}-pentene-αε-dicarboxylate, b.p. 212°/7 mm., which when treated with KCN and then hydrolysed and esterified yields Et_3 α-phenyl-δ-methylpentane-αδε-tricarboxylate, b.p. 208°/7 mm. This is subjected to the Dieckmann reaction and the resulting β-CO-ester is condensed with CH_2Cl·CH_2·CO_2Et; the crude product is hydrolysed (conc. HCl) and purified through Et β-2-keto-4-carbethoxy-1-phenyl-4-methyl*cyclo*hexylpropionate. Similarly *p*-OMe·C_6H_4·$CH(CO_2Et)_2$ affords successively Et δ-keto-α-carbethoxy-α-anisylhexoate, b.p. 202°/6 mm., δ-keto-α-anisylhexoic acid, b.p. 200°/5 mm. (Et ester, b.p. 180°/8 mm.), Et_2 α-cyano-ε-anisyl-β-methyl-Δ^{α}-pentene-αε-dicarboxylate, b.p. 230°/6 mm., Et_3 α-anisyl-δ-methylpentane-αδε-tricarboxylate, b.p. 228°/6 mm., and Et β-2-keto-4-carbethoxy-1-anisyl-4-methyl*cyclo*hexylpropionate, b.p. 221°/5 mm. H. W.

Synthesis of β-phenylnaphthalene derivatives. M. Weizmann, E. Bergmann, and E. Bograchov (Chem. and Ind., 1940, 402—403; cf. Hey *et al.*, A., 1940, II, 168, 188).—Ph_2, $(CH_2$·$CO)_2O$, and $AlCl_3$ in $PhNO_2$ yield γ-*keto*-γ-p-*diphenylylbutyric acid*, m.p. 183°, reduced (Clemmensen–Martin; A., 1936, 1249) to γ-p-*diphenylylbutyric acid* (I), m.p. 118° (no 2-substituted product isolated), and a product, m.p. 328°. $SOCl_2$ followed by $AlCl_3$ in $PhNO_2$ converts (I) into 1-*keto*-7-*phenyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 70°, reduced as above and then dehydrogenated (Se) to 2-$C_{10}H_7Ph$. A. Li.

Production of polycyclic aromatic types through the *cyclo*dehydration of unsaturated ketones. W. S. Rapson and R. G. Shuttleworth (J.C.S., 1940, 636—641).—1-Keto-1 : 2 : 3 : 4-tetrahydronaphthalene (I) (cf. Hartmann *et al.*, A., 1933, 61) and PhCHO in 4% KOH–EtOH yield the 2-*CHPh*: derivative, m.p. 105°, b.p. 210—212°/2 mm., converted by P_2O_5 in xylene into 3 : 4-benzfluorene. 1-*Keto*-2-o-*tolylidene*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 68°, b.p. 213°/2 mm., affords (similarly or by $NaNH_2$) 8-*methyl*-3 : 4-*benzfluorene*, m.p. 104—105°, b.p. 203°/2 mm., purified through the *picrate*, m.p. 127—128°, and oxidised by $Na_2Cr_2O_7$–AcOH to the -*benzfluorenone*, m.p. 139·5—140·5°. *cyclo*Hexanone and *o*-C_6H_4Me·CHO in 4% aq. KOH give 2-o-*tolylidene*-, m.p. 66—67°, b.p. 151—154°/4 mm., and 2 : 6-*di*-o-*tolylidene*-cyclo*hexanone*, m.p. 138—139° (main product in KOH–EtOH); neither the former nor *o*-tolylideneacetophenone is dehydrated by P_2O_5 or $NaNH_2$. (I), 2 : 4 : 6 : 1-$C_6H_2Me_3$·CHO, and 4% KOH–EtOH afford 1-*keto*-2-(2′ : 4′ : 6′-*trimethylbenzylidene*)-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 92—92·5°, dehydrated by P_2O_5 in xylene to three *dihydro*-5 : 7-*dimethyl*-1 : 2-*benzanthracene*, m.p. 146—147° (II) (*picrate*, m.p. 190—191°), m.p. 114°, and m.p. 115·5—116·5° (picrate, m.p. 165°); one may be the 3 : 4-H_2-derivative. (II) and Se afford 5 : 7-*dimethyl*-1 : 2-

benzanthracene, m.p. 120—121°. 2-(2′ : 4′ : 6′-*Trimethylbenzylidene*)-α-*hydrindone*, m.p. 93·5—94·5°, could not be dehydrated. Tetrahydro-*o*-toluonitrile (III) and 95% H_3PO_4 (better than H_2SO_4) at 120—130° afford 6-*methyl*-Δ^1-*cyclohexenecarboxylic acid* (IV), m.p. 105·5° (not identical with that of Mazza *et al.*, A., 1927, 665), oxidised (O_3 followed by 0·1N-aq. $KMnO_4$ in CO_2) to α-methyladipic acid. Boiling aq. KOH–EtOH (9 days) and (III) give an *acid amide*, m.p. 128°, and (IV), but after 1 day yield an *amide*, m.p. 146°, and a (?) polymerised *amide*, m.p. >300°. The *anilide*, m.p. 106·5—107·5°, of (IV) is converted by PCl_5–PhMe at 100° (bath), then $SnCl_2$–HCl–Et_2O, into 6-methyl-Δ^1-*cyclo*hexenealdehyde, b.p. 66—68°/10 mm. (*semicarbazone*, m.p. 207—209°; 2 : 4-*dinitrophenylhydrazone*, m.p. 179°), converted by aq. $AgNO_3$–NH_3 into (IV). *cyclo*Hexanone, CHMe:CH·CHO (V), and 1% aq. KOH in EtOH at <30° give a resin and probably crotonylidene*cyclo*hexanone [*semicarbazone*, m.p. 191° (sinters at 187°)]; the total product and H_2 (Pd–$SrCO_3$) in MeOH at 1·5—2 atm. afford *cyclo*hexanol, 2-*n*-butyl*cyclo*hexanol, and a mixture, $C_{10}H_xO_2$. *cyclo*Pentanone and (V) yield a *product*, $(C_4H_6O)_n$, probably a polymeride from (V). Less alkali affords less resin and gives a product, b.p. 115—135°/10 mm.; the latter yields a *semicarbazone*, m.p. 215—216° (decomp.), probably from crotonylidene*cyclo*pentanone. Hydrogenation of the products affords 2-*n*-butyl*cyclo*pentanone (VI) (*semicarbazone*, m.p. 185—186°) and a mixture, $C_9H_{16}O_2$. α-n-*Butyladipic acid*, m.p. 59·5° (prepared from Et 5-*n*-butyl*cyclo*pentanone-2-carboxylate), on distillation with a little BaO, affords (VI). (V), $COMe_2$, and 1% aq. KOH (cold) yield crotonylideneacetone (*semicarbazone*, m.p. 164—166°); the total product was hydrogenated to Me *n*-amyl ketone and a product, $C_7H_{14\text{ or }16}O_2$ (2 reactive H). Probably the ketones react with (V) at the double linking and also at the CO group. A. T. P.

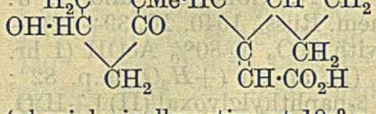
Dehydrogenation. V. S. C. Sen-Gupta (J. Indian Chem. Soc., 1940, **17**, 101—106; cf. A., 1939, II, 538).—*cyclo*Pentane-1-carboxylic-1-acetic anhydride (I), $C_{10}H_8$, and $AlCl_3$ in $PhNO_2$ give γ-*keto*-γ-α- (II), m.p. 140—141° (*Me* ester, m.p. 69—70°; oxidised by NaOBr to α-$C_{10}H_7$·CO_2H), and -β-*naphthyl*-αα-*tetramethylenebutyric acid*, m.p. 190—191° (*Me* ester, m.p. 109—110°; with NaOBr gives β-$C_{10}H_7$·CO_2H). Zn–Hg–HCl reduces (II) to 1-β-1′-*naphthylethyl*cyclo*pentane*-1-*carboxylic acid*, m.p. 108—109°, cyclised by H_2SO_4–H_2O (3 : 1 vol.) at 100° to 1-*keto*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-2 : 2-spirocyclo*pentane*, b.p. 215°/6 mm. Clemmensen reduction then gives 1 : 2 : 3 : 4-*tetrahydrophenanthrene*-2 : 2-spirocyclo*pentane*, b.p. 190—195°/8 mm., which with Se at 300—320° and later 340—350° gives chrysene. 1-$C_{10}H_7$Me and (I) give only γ-*keto*-γ-4-*methyl*-1-*naphthyl*-αα-*tetramethylenebutyric acid*, m.p. 176—177° (with NaOCl gives 4 : 1-$C_{10}H_6$Me·CO_2H), the *Me* ester, m.p. 56—57°, of which (but not the free acid) is reduced to Me 1-β-4′-methyl-1′-naphthylethyl*cyclo*pentane-1-carboxylate, b.p. 230—235°/5 mm. The derived *acid*, m.p. 112°, gives (as above) 1-*keto*-9-*methyl*-, m.p. 97°, and thence 9-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-2 : 2-spirocyclo*pentane*, m.p. 69—70°, which with Se gives 3-methyl-1 : 2-benzanthracene. R. S. C.

Structure of ethanolysis products of spruce and maple wood. L. Brickman, J. J. Pyle, W. L. Hawkins, and H. Hibbert (J. Amer. Chem. Soc., 1940, **62**, 986).—The "aldehyde fraction" obtained by ethanolysis of maple and spruce wood contains 4-*hydroxy*-3 : 5-*dimethoxyphenyl* and *guaiacyl Me diketone* and not the isomeric aroylacetaldehydes (cf. A., 1939, II, 516). R. S. C.

Sterol group. XL. Bromination of 7-keto-cholesteryl acetate. H. Jackson and E. R. H. Jones (J.C.S., 1940, 659—663; cf. A., 1938, II, 497).—7-Ketocholesteryl acetate (I) and Br (excess) in AcOH afford 5 : 6-*dibromo*-7-*ketocholestanyl acetate* (II), m.p. 146—147° (decomp.), converted by KI–$COMe_2$ into (I), or by KOAc–AcOH into an impure unsaturated bromo-ketone. Boiling $NPhMe_2$ and (II) afford 7-keto-$\Delta^{3:5}$-cholestadiene, also obtained from (I) and HBr–AcOH. (I) and Br–HBr–AcOH yield 3 : 4 : 6-*tribromo*-7-*keto*-Δ^5-*cholestene* (III), decomp. ~143°, which loses HBr by $AgNO_3$–C_5H_5N or KOAc–AcOH at 100°, or $NPhMe_2$ (less readily), to give 4 : 6-*dibromo*-7-*keto*-$\Delta^{3:5}$-*cholestadiene*, m.p. 189—190°. (III) and KI–$COMe_2$ afford 6-*bromo*-7-*keto*-$\Delta^{3:5}$-*cholestadiene*, m.p. 117°, unchanged by $NPhMe_2$, or C_5H_5N, or Zn dust in MeOH or AcOH. 6 : 6′-Dibromo-7-ketocholestanyl acetate or 7-bromo-6-ketocholestanyl acetate and boiling $NPhMe_2$ afford 7- or 6-ketocholestanyl acetate, respectively. The effect of substituent Br on light absorption of steryl ketones is discussed. A. T. P.

Hydroxy-ketones of the *cyclo*pentanopolyhydrophenanthrene series.—See B., 1940, 495.

Physiologically active oxidation product of ergosterol. A. F. von Christiani (Mikrochem., 1940, **28**, 183—185).—Cholesterol and Pr^aCOCl in C_5H_5N give a cholesteryl butyrate (I) which is biologically inactive (cf. A., 1939, III, 598). This is due to oxidation of ergosterol (II), present as impurity, to a product (III) which deactivates the (I). Passage of O_2 into ergosterol in EtOH–hæmatoporphyrin and light gives, *inter alia*, (III) as an acidic oil, probably having the annexed structure. Girard's reagent *P* separates (III) into an unreactive *cis*- (IV) (physiologically active at 10^{-9} g. per c.c.) and reactive *trans*-form (V) (physiologically much less active), transformed into one another by irradiation by Ra. Light changes (V) into (IV). At 180°/vac. (IV) gives (V). The known corresponding aldehyde (A., 1933, 500; 1939, II, 261) is oxidised to (III) by Ag_2O.



R. S. C.

α- and β-7-Hydroxy-3-ketocholanic acid. S. Miyazi and H. Isaka (J. Biochem. Japan, 1939, **30**, 297—302).—Chenodeoxycholic acid with C_5H_5N–Ac_2O at room temp. yields *diacetylchenodeoxycholic acid*, m.p. 230° (*Me* ester, m.p. 128°), and with abs. HCO_2H at 100° (bath) gives diformylchenodeoxycholic

acid, new m.p. 184° (*Me* ester, m.p. 56—86°), which, with 0·5N-NaOH at room temp. for 4 hr., affords *α-3-hydroxy-7-formylcholanic acid*, m.p. 147—149°, oxidised (AcOH–CrO_3) to the 3-*CO-acid*, m.p. 188—189°, hydrolysed (5% KOH in EtOH) to *α-7-hydroxy-3-ketocholanic acid*, m.p. 96°. Diformylursodeoxycholic acid (Iwasaki, A., 1937, II, 20), similarly yields β-3-*hydroxy*-, m.p. 135°, and β-3-*keto-7-formylcholanic acid*, m.p. 126—129°, and β-7-*hydroxy*-3-*ketocholanic acid*, m.p. 115—117°. F. O. H.

Manufacture of progesterone.—See B., 1940, 495.

Preparation of antihæmorrhagic compounds.—See A., 1940, III, 516.

Substituted anthraquinones and aroylbenzoic acids.—See B., 1940, 431.

Detoxication. VII. Biological reduction of *l*-menthone to *d*-neomenthol and of *d-iso*-menthone to *d-iso*menthol in the rabbit. Conjugation of *d*-neomenthol with glucuronic acid. R. T. Williams (Biochem. J., 1940, **34**, 690—697).—About 30—40% of *l*-menthone administered to rabbits is excreted as OH-derivatives conjugated with glucuronic acid (I); a part of the menthone mol. is therefore reduced at the CO group. *d-iso*Menthone is also reduced in the rabbit to *d-iso*menthol (II), isolated as the glucuronide. 67—68% of *d*-neomenthol fed to rabbits is excreted in the urine combined with glucuronic acid; this figure is of the same order as those found for *d*-menthol and (II). A method is described, using a Shaffer–Hartmann reagent, for the determination of conjugated (I) in 1 ml. of urine after feeding menthol derivatives. d-*Neomenthylglucuronide*, m.p. 146°, $[\alpha]_D^{22}$ −14·6° in EtOH, NH_4 d-*neomenthylglucuronate*, $[\alpha]_D$ −6·9° in H_2O or (+1H_2O) $[\alpha]_D$ −5·9° in H_2O, and d-*neomenthyl* 3 : 5-*dinitrobenzoate*, m.p. 155°, $[\alpha]_D^{22}$ +22·6° in $CHCl_3$, are new. H. W.

Condensation products from "α-terpinene" and the carenes with maleic anhydride. N. F. Goodway and T. F. West (J.C.S., 1940, 702—703).—The terpene mixture obtained by dehydration of terpineol with a solution of $H_2C_2O_4$ has been separated into five fractions, the first four of which with maleic anhydride give acids of m.p. 124—131°, and not 158° (cf. Diels *et al.*, A., 1938, II, 330). The hydrocarbon formulated by Diels is Δ^4- and not Δ^3-carene. F. R. S.

Syntheses in the camphane series. V. Synthesis of diethyl [1, 2, 2]di*cyclo*heptanedionedicarboxylate from diethyl *cyclo*pentanone-2 : 5-dicarboxylate. P. C. Guha and G. D. Hazra (J. Indian Chem. Soc., 1940, **17**, 107—110; cf. A., 1938, II, 13).—The Na_1 derivative of Et_2 *cyclo*pentan-1-one-2 : 5-dicarboxylate (improved prep.) and $CH_2Br{\cdot}CO_2Et$ in C_6H_6, first at room temp. and then at the b.p., give cis- and trans-*forms*, (I), b.p. 145—160° (145—202°)/3 mm., and (II), b.p. 202—208°/3 mm. or vice versa, of *Et*$_3$ cyclo*pentan*-1-*one*-2 : 5-*dicarboxylate*-2-*acetate*. When distilled, (I) slowly gives (II). Hydrolysis of (I) or (II) by 18% HCl gives Et *cyclo*pentan-1-one-2-acetate. With Na in boiling C_6H_6, (II) gives Et_2 1-keto-3 : 6-*endo*keto*cyclo*hexane-2 : 3-dicarboxylate (decomp. when distilled), which with boiling 18% HCl yields by decarboxylation 1-*keto*-3 : 6-endo*keto*-cyclo*hexane*-3-*carboxylic acid*, +H_2O, m.p. 212° [*Me* ester, m.p. 129° (*semicarbazone*, m.p. 209—210°); reduced (Clemmensen) to an acid, m.p. 118°], and a viscous acid, $C_7H_{10}O_3$ (*semicarbazone*, m.p. 192°). R. S. C.

Dependence of optical rotatory power on chemical constitution. XVII. Nitro- and carboxy-aryl derivatives of stereoisomeric methylenecamphors. B. K. Singh and T. P. Barat (J. Indian Chem. Soc., 1940, **17**, 1—18; cf. A., 1938, II, 149).—Many vals. of [α] in $CHCl_3$, C_6H_6, MeOH, EtOH, $COMe_2$, and C_5H_5N of the following compounds are determined: o-*nitroanilinomethylene*-d-, m.p. 157—158°, $[\alpha]_D^{35}$ +288·5°, -l-, m.p. 158°, $[\alpha]_D^{35}$ −288·0°, and -dl-*camphor*, m.p. 150°; *m*-nitroanilinomethylene-*d*-, new m.p. 181°, $[\alpha]_D^{35}$ +249·6° (cf. Rupe *et al.*, A., 1920, i, 327), -*l*-, m.p. 180—181°, $[\alpha]_D^{35}$ −248·0°, and *dl*-camphor, m.p. 167—168°; *p*-nitroanilinomethylene-*d*-, m.p. 154—155°, $[\alpha]_D^{35}$ +331·2° (cf. Pope *et al.*, J.C.S., 1909, **95**, 171; Rupe *et al.*), -*l*-, m.p. 154—155°, $[\alpha]_D^{35}$ −388·1° in MeOH, and -*dl*-camphor, m.p. 167—168°; o-*carboxyanilinomethylene*-d-, m.p. 166—167°, $[\alpha]_D^{35}$ +309·4°, -l-, m.p. 167—168°, $[\alpha]_D^{35}$ −309·7°, and -dl-*camphor*, m.p. 113° (cf. Rupe *et al.*); m-*carboxyanilinomethylene*-d-, m.p. 219—221°, $[\alpha]_D^{36}$ +310·9° in MeOH, -l-, m.p. 219—221°, $[\alpha]_D^{35}$ −311·2° in MeOH, and -dl-*camphor*, m.p. 215—217°; p-*carboxyanilinomethylene*-d-, m.p. 280—283°, $[\alpha]_D^{35}$ +335·0° in C_5H_5N, -l-, m.p. 280—282°, $[\alpha]_D^{35}$ −334·1° in C_5H_5N, and -dl-*camphor*, m.p. 283—285° (all above vals. of α are in C_6H_6 unless stated otherwise). Relation between rotatory power (*R*) and chemical constitution or solvent used follows no definite plan. The sequence of *R* of the isomerides of nitroanilino-derivatives is in general $p > o >$ unsubstituted $> m$ in all solvents; with carboxy-derivatives, the order in C_5H_5N is unsubstituted $> p > o > m$. Vals. of *R* of corresponding *d*- and *l*-forms in all solvents are equal and opposite. The compounds obey the simple dispersion law, $[\alpha] = K(\lambda^2 - \lambda_0^2)$. A. T. P.

Dependence of optical rotatory power on chemical constitution. XVI. Bromo- and iodoaryl derivatives of stereoisomeric methylenecamphors. B. K. Singh and B. Bhaduri (Proc. Indian Acad. Sci., 1939, **10**, **A**, 359—380).—The optical rotatory powers of *o*- (I), m.p., *l* and *d*, 88—89°, *dl*, 95—96°; *m*- (II), m.p., *l* and *d*, α-form, 162—163°, β-form, 111—113°; *dl*, 175—176°, and p-*bromo*-, m.p., *l* and *d*, 186—187°; *dl*, 186—187°, m-, m.p., *l* and *d*, 187—188°; *dl*, 182—183°, and p-*iodo*- (III), m.p., *l* and *d*, 185—186°; *dl*, 193—195°, *-anilinomethylenecamphor* in $CHCl_3$, $COMe_2$, C_6H_6, EtOH, MeOH, and C_5H_5N have been measured. *d*- and *l*-(II) exist in two interconvertible dimorphic forms with identical rotatory dispersion, m.p. 162—163° by slow crystallisation and m.p. 111—113° by rapid crystallisation from MeOH. *m*-Bromoanilinomethylene-*dl*-camphor exists in only one form. *o*-Iodoanilinomethylenecamphor could not be got solid. The effect of chemical constitution on the rotation is discussed. The rotatory power decreases in the order

of dielectric const. of the solvents, MeOH > EtOH > $COMe_2$ > C_5H_5N > $CHCl_3$ > C_6H_6. For position isomerides the sequence of rotatory power is no halogen > *p* > *m* > *o* in EtOH, $COMe_2$, and C_5H_5N, and no halogen > *o* > *m* > *p* in $CHCl_3$ and C_6H_6. The racemic forms of (I), (II), and (III) are true *dl* compounds. W. R. A.

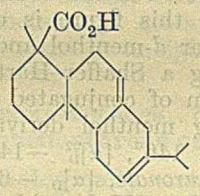
Pongamol, new crystalline compound from pongamia oil. S. Rangaswami and T. R. Seshadri (Current Sci., 1940, **9**, 179).—The isolation from pongamia oil of *pongamol*, $C_{17}H_{11}O_3$·OMe, m.p. 128—129°, a phenol which on reduction (Mg + HCl) yields a red anthocyanin, on oxidation or hydrolysis yields BzOH, and gives a *p*-nitrobenzoyl derivative, is described. A. Li.

Chemical constituents of lichens found in Ireland. *Lecanora gangaleoides*. II. T. J. Nolan and J. Keane (Sci. Proc. Roy. Dublin Soc., 1940, **22**, 199—209; cf. A., 1935, 550).—*L. gangaleoides* contains gangaleoidin (I), atranorin and chloratranorin (ratio 1 : 4), *d*-arabitol, endococcin (II), rhodophyscin (III) (*acetate*), and a *substance*, $C_{26}H_{21}O_{10}Cl_3$ (?) (containing OMe ?), m.p. 231—233° (*Me ether*, m.p. 143—144°), which gives a light purple colour with $FeCl_3$ and pale yellow with H_2SO_4; the presence of H_2O-sol. ester or lactone was not confirmed. (II) yields (III) when boiled with AcOH. (III), which contains no OMe, gives no ppt. with *o*-$C_6H_4(NH_2)_2$ in AcOH, and the resulting solution fails to give the colour reactions of (III). (I) is a lactone, $C_{16}H_7O_4Cl_2(OH)(OMe)_2$ (*Me ether*, m.p. 181°). MeOH–KOH opens the ring, giving a Me ester [*Me*$_1$ *ether*, m.p. 186—187°, obtained by hydrolysing the Me ether of (I); *Me*$_2$ *ether* (IV) (CH_2N_2), m.p. 141—142°], which when distilled under reduced pressure gives an *isomeride*, m.p. 184—185°. (I) with MeOH–KOH followed by H_2O yields *substances*, $C_{16}H_{10}O_6Cl_2(OMe)_2$, $+H_2O$, m.p. 197—198°, and $+2H_2O$, m.p. 161°, either of which with CH_2N_2 yields (IV). Hydrolysis (MeOH–KOH) of (IV) yields an *acid*, $C_{14}H_7OCl_2(CO_2H)_2(OMe)_3,H_2O$, m.p. 216—217°, which when heated alone or in HCO_2H gives an *acid*, $C_{14}H_8OCl_2(CO_2H)(OMe)_3$ (V), m.p. 138—139° (*Me* ester, m.p. 79—80°), when heated in glycerol at 220—225° for 5 hr. gives a *phenol* $C_{14}H_9OCl_2(OH)(OMe)_2$ (VI), m.p. 165—166° (*Me ether*, m.p. 112—113°), and when vac.-distilled gives (V), (VI), and a neutral *substance* (? a xanthone), $C_{15}H_7O_2Cl_2(OMe)_3$, m.p. 212—213°. It is concluded that (I) is a derivative of $C_6H_4<^{CO\cdot O}_{O\text{—}}>C_6H_4$, having as substituents 2 Me, 2 Cl, OH, OMe, and CO_2Me. A. Li.

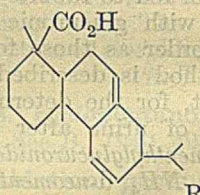
Constituents of higher fungi. I. Triterpene acids of *Polyporus betulinus*. Fr. L. C. Cross, C. G. Eliot, I. M. Heilbron, and E. R. H. Jones (J.C.S., 1940, 632—636).—Extraction of the fresh minced fungus by cold EtOH gives, after saponification, a mixture of sterols containing ergosterol and *polyporenic acid A*, $C_{30}H_{48}O_4$ or $C_{31}H_{50}O_4$, m.p. 194°, $[\alpha]_D^{20}$ +69° in C_5H_5N, which forms a *Me* ester, m.p. 142°, $[\alpha]_D^{20}$ +77° in $CHCl_3$ (*acetate*, m.p. 112°, $[\alpha]_D^{20}$ +88° in $CHCl_3$). Further extraction with $COMe_2$ and Et_2O under reflux affords *polyporenic acid B*, $C_{30}H_{48}O_4$, m.p. 300—310° (decomp.) (after drying in vac., m.p. 275—280°) (*Me* ester, m.p. 160°), and *C*, m.p. 270—275° (*Me* ester, m.p. 192—193°), the latter in small amount. Acids *A* and *B* appear to be isomeric, and both contain two OH and two ethylenic linkages. Acid *C* may be identical with gypsogenin. F. R. S.

Resin acids. II. Structure of abietic acid. V. Krestinski, A. Novak, and N. Komschilov (J. Appl. Chem. Russ., 1939, **12**, 1514—1528).—The isomeride (I) of abietic acid, m.p. 170—172°, is ozonised, and the diozonide is decomposed with H_2O at 100°, yielding a mixture of products, of which the following acids were identified: 1 : 3-*dimethyl*-2-*carboxymethyl*-3-(δ-*keto*-ε-*methyl*-α-*carboxymethylhexyl*)-cyclo*hexane*-1-*carboxylic acid*, 2-(1′-*carboxy*-1′ : 3′-*dimethyl*-2′-*carboxymethyl*-3′-cyclo*hexyl*)-4-iso*propyl*-cyclo*hexanone*-4 : 5-*ozonide*, and 1 : 3-*dimethyl*-2-*carboxymethyl*-3-(βδ-*diketo*-ε-*methyl*-α-*formylmethylhexyl*)-cyclo*hexane*-1-*carboxylic acid*. The isomeride (II) of m.p. 188—190° similarly yields 1 : 3-*dimethyl*-2-*carboxymethyl*-3-(αδ-*dicarboxy*-ε-*methylhexyl*)cyclo*hexane*-1-*carboxylic acid*, m.p. 209—213°, 1 : 3-*dimethyl*-2-*carboxymethyl*-3-(γδ-*dihydroxy*-αδ-*dicarboxy*-ε-*methylhexyl*)-cyclo*hexane*-1-*carboxylic acid* (oxidised by $KMnO_4$ to 1 : 3-*dimethyl*-3-*carboxymethyl*- and -3-*dicarboxymethyl*-cyclo*hexane*-1 : 2-*dicarboxylic acid*), 1 : 3-*dimethyl*-2-*formylmethyl*-3-(α-*formyl*-δ-*carboxy*-ε-*methyl*- and -3-(αδ-*dicarboxy*-ε-*methyl*-*hexyl*)cyclo*hexane*-1-*carboxylic acid*. The production of these acids is explicable on the assumption that the structures of (I) and (II) are:

(I.)



(II.)



R. T.

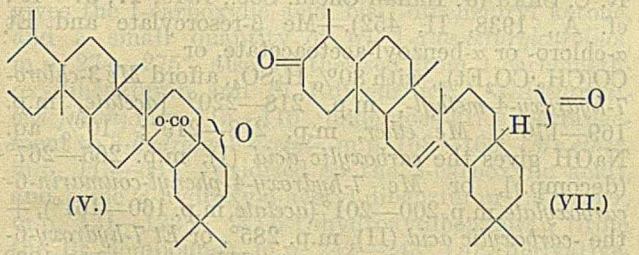
Miro resin. II. Resin acids. C. W. Brandt and L. G. Neubauer (J.C.S., 1940, 683—686).—Extraction of miro resin with 4% NaOH, followed by saturation with CO_2, yields *miropinic acid* (I) (85%), $C_{20}H_{30}O_2$, m.p. 160°, $[\alpha]_D^{16}$ −103·6° in 1 : 1 EtOH–$CHCl_3$, and iso*miropinic acid* (II), m.p. 284°, $[\alpha]_D^{17}$ +21·2° in dioxan. (I) forms a *Me* ester, b.p. 148°/0·3 mm., and is hydrogenated (Pd–C) in EtOAc to α-, m.p. 176°, $[\alpha]_D^{18}$ −10·5° in EtOH, and β-*dihydro-acids*, m.p. 115°, $[\alpha]_D^{18}$ +23·2° in EtOH. Further hydrogenation in AcOH of the H_2-acids gives respectively α-, m.p. 170°, $[\alpha]_D^{18}$ +15·2° in EtOH, and β-*tetrahydromiropinic acids*, m.p. 170°, $[\alpha]_D^{18}$ +30·5° in EtOH, along with γ-*dihydromiropinic acid*, m.p. 113°, $[\alpha]_D^{18}$ +46·2° in EtOH, in both cases. Se-dehydrogenation of (I) yields pimanthrene. Hydrogenation (PtO_2) in AcOH of (II) affords a *resin*, b.p. 200°/0·3 mm. (II) is also obtained by isomerisation of (I) with MeOH–HCl. F. R. S.

Colouring matters of the Chinese drug ta-chi, *Euphorbia pikinenis*, Rupr. J. H. Chu (Chinese J. Physiol., 1940, **15**, 151—157).—Extraction of the dried root skin with light petroleum gives *euphorbia* A, $C_{16}H_{10}O_5$, m.p. 217° [*Ba* salt, $+1H_2O$ and anhyd.; *semicarbazone*, m.p. 287° (decomp.)], converted by Ac_2O and anhyd. NaOAc at 140° into a *compound* $C_{15}H_8O_5$, m.p. 192°, *euphorbia* B, $C_{15}H_8O_5$ ($+0·5CHCl_3$),

m.p. 224°, converted by Ac_2O into a compound, $C_{14}H_{11}O_6$, m.p. 176°, and *euphorbia* C, m.p. 283°. The presence of a glucoside, $C_{37}H_{58}O_{12}$, could not be confirmed. H. W.

Acetyl content of marinobufagin, arenobufagin, and acetylmarinobufagin. V. Deulofeu, E. Duprat, and R. Labriola (Nature, 1940, **145**, 671).—Marinobufagin has a volatile acid content <1%; this excludes Ac and EtCO from its constitution. Jensen's formula, $C_{24}H_{32}O_5$, is confirmed. Acetylmarinobufagin (~18% Ac) probably has 2 Ac. A *compound*, $C_{24}H_{32}O_6$, m.p. 231—233°, Ac <1%, has been isolated from the crude venom of *Bufo arenarum*. L. S. T.

Sapogenins. VII. Structure of quillaic acid and its relation to echinocystic acid. D. F. Elliott, G. A. R. Kon, and H. R. Soper (J.C.S., 1940, 612—617; cf. A., 1939, II, 436).—The second OH of quillaic acid (I), which is not part of the group CH(OH)·CMe·CHO, is attached to a C immediately adjacent to the quaternary C carrying CO_2H, as in echinocystic acid (II) (cf. White *et al.*, A., 1939, II, 333). The following reactions suggest that (I) and (II) may be related in the same way as gypsogenin and oleanolic acid. The C_{30} acid (*loc. cit.*) and Kiliani's solution give small amounts of diketolactone (III), acid A_1 (probably $C_{27}H_{40}O_6$) and A_2, a ketohydroxy-acid, $C_{29}H_{44}O_6$, and acid B, $C_{31}H_{48}O_7$ (*loc. cit.*). The latter, crystallised from aq. MeOH, yields the (?) *hydrate* (IV), m.p. ~170—180°, which sublimes in high vac. to an unsaturated *acid*, $C_{29}H_{42}O_5$, corresponding with loss of ~AcOH + H_2O. (IV) and CH_2N_2 afford the Me ester, m.p. 210° [2 : 4-*dinitrophenylhydrazone*, m.p. 283° (decomp.)], of acid B, which is decomposed by MeOH–KOH to (IV). (III) and Zn–Hg in HCl–AcOH (cf. Jacobs *et al.*, A., 1926, 1250) yield the *keto-lactone* (V), m.p. 293—295°. Me quillaate and Cu-bronze at 270°, or Beckmann's



(V.) (VII.)

solution in aq. AcOH at 10°, afford the *diketo-ester* (VI), $C_{30}H_{44}O_4$, m.p. 193°, $[\alpha]_D$ +8·9° in $CHCl_3$, converted by 5% KOH–EtOH into the *diketone* (VII), m.p. 197° or m.p. 185° to an opaque liquid which clears at 210°; probably a mixture of stereoisomerides is formed. (VI) and Zn–Hg in AcOH–HCl (method : Reichstein, A., 1937, II, 449, or Jacobs *et al.*, *loc. cit.*) afford the *keto-ester*, m.p. 178° (formula given), $[\alpha]_D$ +5·2° in $CHCl_3$, hydrolysed to a *monoketone*, $C_{28}H_{44}O$, m.p. 185—187° [CO is no longer inert; 2 : 4-*dinitrophenylhydrazone*, m.p. 268° (decomp.)]. Attempts to reduce (Clemmensen) quillaic acid yielded the diacetyl-lactone, which is reduced by Zn–Hg in AcOH–HCl (cf. Jacobs *et al.*, *loc. cit.*) to an *isomeride*, m.p. 272—274°. Me quillaate (VIII) is reduced similarly to an impure (?) deoxy-ester. (VIII) and NH_2·NH·CO·NH_2,HCl in NaOAc–MeOH at room temp. afford a *semicarbazone*, sintering at 186°, m.p. 200—220°, converted by Na–EtOH at 160—170° into *deoxyquillaic acid* (IX), m.p. 302° (previous sintering), $[\alpha]_D$ +34° in EtOH. Its *Me* ester, m.p. 209—210°, is oxidised (method : White *et al.*, *loc. cit.*) to the *diketo-ester*, $C_{31}H_{46}O_4$, m.p. 152—153° (*oxime*, m.p. 246—247°). (IX) and its derivatives are probably not identical with, but very similar to, (II) and its derivatives. A. T. P.

Sapogenins. VIII. The sapogenin of fuller's herb. G. A. R. Kon and H. R. Soper (J.C.S., 1940, 617—620).—Saporubin, the saponin of fuller's herb (*Saponaria officinalis*, L.), is hydrolysed by aq. HCl to gypsogenin (I), m.p. 269—270° (previous sintering) [semicarbazone, m.p. 270—272° (decomp.)], also obtained directly from the root (method : Karrer *et al.*, A., 1924, i, 1091). (I) is purified by hydrolysing the acetate (II), m.p. 188—189° (sinters at 173°), $[\alpha]_D$ +79° in $CHCl_3$ (Me ester, m.p. 191°, $[\alpha]_D$ +80° in $CHCl_3$), with N-KOH at room temp. to the K salt, thence by dil. HCl to (I), which is sublimed in high vac. at 180°. (II) affords the Br-lactone, m.p. ~180° (decomp.), and *iso*acetylgypsogeninolactone, m.p. 330—332° (cf. Ruzicka *et al.*, A., 1937, II, 201); the latter and CrO_3–AcOH–H_2SO_4 yield the corresponding acid, and thence the *lactone*, $C_{30}H_{46}O_5$,H_2O, m.p. 353—355°, of gypsogenic acid (CH_2N_2 affords the *Me* ester, m.p. 344—345°, of the anhyd. acid). Further oxidation with Kiliani's solution in AcOH affords a monobasic *ketonic acid* (III), $C_{29}H_{44}O_5$, m.p. ~270—280° (*Me* ester, m.p. 191—192°; 2 : 4-*dinitrophenylhydrazone*, m.p. 246—247°), and hedragone lactone, m.p. 298—301°, clearing at 304° (decomp.) [bromide, m.p. 283° (cf. Kitasato *et al.*, A., 1934, 1223); 2 : 4-*dinitrophenylhydrazone*, m.p. 274—276° (decomp.)]. An impure specimen of (I) has probably been obtained from *S. rubra* by von Schulz (cf. A., 1898, i, 204). It is concluded that githagenin from corncockle (cf. Wedekind *et al.*, A., 1930, 1324) is identical with (I); githagonolic acid is probably identical with gypsogenic acid. The formation of githagic acid from githagenin is analogous to the formation of (III) (formulæ given). It appears that (I) is a characteristic constituent of saponins in the Caryophyllaceæ. A. T. P.

Anomalous Friedel–Crafts reactions. J. A. V. Turck (Iowa State Coll. J. Sci., 1939, **14**, 98—100).—Alkylation of Et 5-bromo-2-furoate is described again (cf. Gilman and Turck, A., 1939, II, 147, 172). >1 equiv. of $AlCl_3$ is required for these reactions, and no results are obtained using $PhNO_2$, PhCl, or petroleum as solvent. A. Li.

Pyrones and related compounds. I. Formation and structure of 2 : 6-dihydroxy-γ-pyrone. R. Kaushal (J. Indian Chem. Soc., 1940, **17**, 138—143).—Acid-free $CO(CH_2·CO_2H)_2$ (I) (*p*-nitrophenylhydrazone, m.p. 153°) and Ac_2O at <20° give acetonedicarboxylic anhydride (II), m.p. 136—137° (decomp.) (cf. Willstätter *et al.*, A., 1921, i, 92), but at 30° give 2 : 6-*dihydroxy-γ-pyrone* (III), m.p. 94°. Warm Ac_2O converts (II) into (III). (III) gives a p-*nitrophenyl*-

hydrazone, m.p. 215° [(II) does not react], and a $HgCl_2$ *compound*, m.p. 235°, and is unchanged by hot H_2O or EtOH or cold alkali. Hot alkali decomposes (III). H_2O or EtOH converts (II) into the acid or Et H ester, respectively. With a trace of HCl or H_2SO_4, (III) gives (I). With PCl_5 (2 mols.) at 100°, (III) gives 2 : 6-*dichloro-γ-pyrone*, m.p. 78—80° (*hydrochloride*, m.p. 105°). With NaOEt–EtOH, (III) gives a Na_2 salt, which with boiling EtI–EtOH gives 2 : 6-*diethoxy-γ-pyrone*, b.p. 65—70° [$HgCl_2$ *compound*, m.p. 265° (decomp.)], and with ArCOCl–C_6H_6 yields the *di*-3 : 5-*dinitrobenzoate*, m.p. 90°. PhNCO and (III) give only $CO(NHPh)_2$. AcCl or Ac_2O with a trace of H_2SO_4 converts (III) into dehydroacetocarboxylic acid. With NH_3–MeOH at 0°, (II) gives the $(NH_4)_2$ salt, +MeOH, sinters at 92°, m.p. 97°, of 2 : 6-dihydroxy-4-pyridone. R. S. C.

Anti-sterility factors (vitamin-*E*). VII. Red oxidation products of the tocopherols. W. John and W. Emte (Z. physiol. Chem., 1939, **261**, 24—34; cf. A., 1939, II, 175).—α- [absorption max. 270 mμ. (ε < 6800)] and β-tocopherol-red are obtained from the respective tocopherol by $AgNO_3$ in boiling EtOH, are reversibly reduced to colourless quinols by H_2–Pd-black, and are stable to acid but decomposed by alkali (rate of destruction depends on the solvent). The α-compound gives an oily quinol diacetate [absorption max. 278 mμ. (ε 1300)]. Chroman-red 141 (I) [prep. by HNO_3, Ag_2SO_4, or H_2SO_4; AgOAc gives only the quinone, m.p. 79° (best method of prep.); absorption max. 272 mμ. (ε 5200)] and chroman-red 109 behave similarly; the respective *quinol diacetates* have m.p. 82° [absorption max. 282 mμ. (ε 2100)] and 92°. Prep. of (I) by HNO_3 gives also a little (?) 7-*hydroxy*-2 : 6-*dimethylchroman*-5 : 8-*quinone*, m.p. 145° {absorption max. 294 mμ. (ε 22,400); *quinol diacetate*, m.p. 116° [absorption max. 280 mμ. (ε 630)]}, but too long oxidation gives a *product*, $C_{12}H_{14}O_3$, m.p. 129°. These reactions support formulæ previously suggested, but the red substances are bimol., although the quinol diacetates are unimol. R. S. C.

Synthesis of coumarins from *o*-hydroxyaryl alkyl ketones. D. Chakravarti and N. Dutta (J. Indian Chem. Soc., 1940, **17**, 65—71; cf. A., 1940, II, 50).—When there is an alkyl substituent in the β-position of the expected cinnamic ester, the coumarin is invariably formed, irrespective of the presence of any α-substituent. Thus 4-alkyl- and 3 : 4-dialkyl-coumarins are synthesised readily from the respective *o*-hydroxyaryl alkyl ketones; the presence of halogen or alkyl in the C_6H_6 nucleus of the ketone has little effect. 2 : 5 : 1-OH·C_6H_3Cl·COMe and MeI–NaOEt give 5-*chloro*-2-*methoxyacetophenone*, b.p. 135°/6 mm., converted by $CH_2Br·CO_2Et$–Zn wool in C_6H_6 into a OH-ester, and by $SOCl_2$–C_5H_5N–Et_2O into *Et* 5-*chloro*-2-*methoxy*-β-*methylcinnamate*, b.p. 155°/5 mm., and thence by H_2SO_4 at room temp. or HI (*d* 1·7) at 140° into 6-*chloro*-4-*methylcoumarin*, m.p. 184°. The following aceto- and propio-phenones are prepared from the corresponding Ac and EtCO derivatives of the phenols by $AlCl_3$ at 130—140° (it is not essential to convert the OH-esters into the unsaturated esters before forming coumarins): 5-*bromo*-2-*methoxy*- (I), b.p. 165°/12 mm., 2-*methoxy*-3-*methyl*- (II), b.p. 120°/3 mm., and -5-*methyl*-*acetopaenone* (III), b.p. 110°/6 mm.: 5-*chloro*-2-*methoxy*-3-*methyl*- (IV), b.p. 139°/8 mm., and 3-*chloro*-2-*methoxy*-5-*methyl*-*propiophenone* (V), b.p. 140°/8 mm.; 5-*chloro*-2-*methoxy*-3-*methyl*- (VI), b.p. 136°/8 mm., and -4-*methyl*- (VII), m.p. 81°, and 3-*chloro*-2-*methoxy*-5-*methyl*-*acetophenone* (VIII), b.p. 124°/4 mm. From (I): *Et* 5-*bromo*-2-*methoxy*-β-*methyl*-, b.p. 180°/8 mm., and -αβ-*dimethyl*-*cinnamate*, b.p. 169—170°/10 mm. (from CHBrMe·CO_2Et), respectively; from (II): *Et* 2-*methoxy*-3 : β-*dimethylcinnamate*, b.p. 140—142°/9 mm.; from (III): *Et* 2-*methoxy*-5 : β-*dimethylcinnamate*, b.p. 160°/12 mm., and *Et* β-*hydroxy*-αβ-*dimethyl*-β-(2-*methoxy*-5-*methyl*)*phenylpropionate*, b.p. 140—145°/8 mm.; from (IV): *Et* 5-*chloro*-2-*methoxy*-3 : α-*dimethyl*-β-*ethylcinnamate*, b.p. 164°/6 mm.; from (V): *Et* 3-*chloro*-2-*methoxy*-5 : α-*dimethyl*-β-*ethylcinnamate*, b.p. 160°/8 mm.; from (VI): *Et* 5-*chloro*-2-*methoxy*-3 : β-*dimethyl*-, b.p. 163°/5 mm., and -αβ-*dimethyl*-*cinnamate*, b.p. 165°/17 mm.; from (VII): *Et* 5-*chloro*-2-*methoxy*-4 : β-*dimethyl*-, b.p. 160°/5 mm., and -αβ-*dimethylcinnamate*, b.p. 160°/3 mm.; from (VIII): *Et* 3-*chloro*-2-*methoxy*-5 : β-*dimethyl*-, b.p. 160°/6 mm., and -αβ-*dimethyl*-*cinnamate*, b.p. 170°/9 mm. From the above are prepared: 6-*bromo*-4-*methyl*-, m.p. 187°, and 3 : 4-*dimethyl*, m.p. 169°; 4 : 8-*dimethyl*-, m.p. 114°, and 4 : 6-dimethyl-, m.p. 150° (cf. A., 1937, II, 160); 3 : 4 : 6-trimethyl-, m.p. 170° (cf. A., 1932, 519); 6-*chloro*-3 : 8-*dimethyl*-4-*ethyl*-, m.p. 126°; 8-*chloro*-3 : 6-*dimethyl*-4-*ethyl*-, m.p. 120°; 6-*chloro*-4 : 8-*dimethyl*-, m.p. 155°, and -3 : 4 : 8-trimethyl-, new m.p. 114°; 6-chloro-4 : 7-dimethyl-, m.p. 213°, and -3 : 4 : 7-trimethyl-, new m.p. 167°; 8-chloro-4 : 6-dimethyl-, m.p. 148°, and -3 : 4 : 6-trimethyl-coumarin, m.p. 153°, respectively. A. T. P.

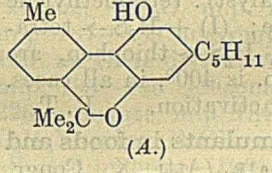
Pechmann condensation of methyl β-resorcylate with some β-ketonic esters. S. M. Sethna and R. C. Shah (J. Indian Chem. Soc., 1940, **17**, 37—40; cf. A., 1938, II, 452).—Me β-resorcylate and Et α-chloro- or α-benzoyl-acetoacetate, or $CO(CH_2·CO_2Et)_2$, with 80% H_2SO_4, afford *Me* 3-*chloro*-7-*hydroxy*-4-*methyl*-, m.p. 218—220° [*acetate*, m.p. 169—170°; *Me ether*, m.p. 218—219°; 10% aq. NaOH gives the *carboxylic acid* (I), m.p. 265—267° (decomp.)], or *Me* 7-*hydroxy*-4-*phenyl*-*coumarin*-6-*carboxylate*, m.p. 200—201° (*acetate*, m.p. 160—161°), + the -*carboxylic acid* (II), m.p. 285°, or *Et* 7-*hydroxy*-6-*carbomethoxycoumarin*-4-*acetate* (III), m.p. 194—196° (*acetate*, m.p. 148—149°), + the -*acetic acid* (IV), m.p. 184—186° (decomp.), respectively. (I) or (II) is decarboxylated with H_2O at 180—190° to 3-chloro-7-hydroxy-4-methyl-, new m.p. 240°, or 7-hydroxy-4-phenyl-coumarin, m.p. 242—244°, respectively; (IV) at its m.p. until effervescence ceases gives Me 7-hydroxy-4-methylcoumarin-6-carboxylate. (III) and 5% aq. NaOH at 100° (bath) afford 7-hydroxy-4-methylcoumarin-6-carboxylic acid, m.p. 285°. The 4-CO_2Me in the resorcinol nucleus has little retarding influence on the Pechmann condensation. A. T. P.

Kostanecki acylation of orcacetophenone. S. M. Sethna and R. C. Shah (Current Sci., 1940, **9**, 117—118).—A preliminary note.

γ-Substituted resorcinol derivatives. III. Synthesis of 5 : 6-dimethoxyflavone. K. NAKAZAWA (J. Pharm. Soc. Japan, 1939, **59**, 194—196).—1 : 2 : 6-$C_6H_3Ac(OH)_2$, MeI, and K_2CO_3 in $COMe_2$ yield 6-*hydroxy*-2-*methoxyacetophenone*, m.p. 58·5°, converted by oxidation by $K_2S_2O_8$ in alkaline solution and subsequent boiling with dil. H_2SO_4 into 3 : 6-*dihydroxy*-2-*methoxyacetophenone*, m.p. 91°. This is transformed by BzCl in C_5H_5N into the *dibenzoate*, m.p. 154°, which is converted by $NaNH_2$ in PhMe into 6-*hydroxy*-3-*benzoyloxy*-2-*methoxydibenzoylmethane*, m.p. 152·5°. The diketone is cyclised by conc. H_2SO_4 to 6-*hydroxy*-5-*methoxyflavone*, m.p. 185°, methylated (K_2CO_3 and MeI in $COMe_2$) to 5 : 6-*dimethoxyflavone*, m.p. 199°. H. W.

Derivatives of 1-, 4-, 6-, and 9-substituted dibenzfurans. J. SWISLOWSKY (Iowa State Coll. J. Sci., 1939, **14**, 92—94).—1-Aminodibenzfuran is obtained in 55% yield from the 1-carboxylic acid by a modification of Bywater's method, and in 45% yield from 1-hydroxydibenzfuran by a Bucherer reaction. Nitration of its Ac derivative yields, in Ac_2O at −10°, 2-nitro-1-acetamidodibenzfuran (Gilman *et al.*, A., 1939, II, 276), and in glacial AcOH, the *Ac* derivative, (I), m.p. 216°, of 4-*nitro*-1-*amino*-, m.p. 219—220°, converted by diazotisation and reduction with EtOH into 4-*nitro-dibenzfuran*, m.p. 120—121°. Catalytic reduction of (I) gives the Ac_1 derivative, m.p. 202°, of 1 : 4-*diaminodibenzfuran*, m.p. 86—87° (*dihydrochloride*, m.p. 322—323°), the Ac_2 derivative, m.p. 307—308°, of which is also prepared from 4-bromo-1-acetamidodibenzfuran. Nitration of (I) and of 2-nitro-1-acetamidodibenzfuran gives 4 : 7(?)-, m.p. 288°, and 2 : 6(?)-*dinitro*-1-*acetamidodibenzfuran*, m.p. 277—278°, respectively. 1-Bromodibenzfuran with $LiNEt_2$ and $LiNMe_2$ in Et_2O yields respectively 1-*diethyl*-, m.p. 68—69°, and -dimethyl-aminodibenzfuran, m.p. 98—99°, and with LiBu followed by CO_2 for 10—25 min. (cf. Gilman *et al.*, A., 1939, II, 441) gives the 1-carboxylic acid, bis-1-dibenzfuryl ketone, and a small quantity of *tris*-1-*dibenzfurylcarbinol*, m.p. 274—275°, also synthesised from 1-carbomethoxydibenzfuran and Li 1-dibenzfuryl. 3-*Acetoxydibenzfuran*, m.p. 115—116°, undergoes Fries rearrangement to 3-*hydroxy*-2-*acetyl*-, m.p. 168—169° (*Me ether*, m.p. 113—114°, oxidised to the 3-carboxylic acid), and some 3-hydroxy-4-acetyl-dibenzfuran (*Me ether*, m.p. 121—122°). 3 : 6-Dihydroxydibenzfuran (from the Br_2-compound), m.p. 242—243° (Ac_2 derivative, m.p. 150—151°), yields a Me_2 *ether* (II), m.p. 88—89° (*picrate*, m.p. 117—118°), which on mild hydrolysis gives 3-hydroxy-6-methoxydibenzfuran, m.p. 90—91° (*Ac* derivative, m.p. 110°). Bromination of (II) yields 4 : 5(?)-, m.p. 196—197°, and 2 : 7(?)-*dibromo*-3 : 6-*dimethoxydibenzfuran*, m.p. 260—261°. The former with LiBu in C_6H_6 followed by CO_2 gives the 4 : 5(?)-*dicarboxylic acid*, m.p. 271—272° [Me_2 ester (CH_2N_2), m.p. 129—130°], also obtained from (II) by direct metalation and carbonation. The latter similarly yields the 2 : 7(?)-*dicarboxylic acid*, m.p. 290° [Me_2 ester (MeOH–HCl), m.p. 183—184°], together with some BzOH, formed by the action of LiBu and CO_2 on C_6H_6. (II) with $(COCl)_2$ and $AlCl_3$ yields a *lactone* (*quinoxaline* derivative, m.p. 323—325°), probably 4′-*methoxybenzfurano*-(1′ : 2′ : 4 : 5)- or 4′-*methoxybenzfurano*-(2′ : 1′ : 3 : 4)-1 : 2-*diketo*-1 : 2-*dihydrobenzfuran*, which with CH_2N_2 gives *Me* 3 : 6-*dimethoxy*-2(or 4)-*dibenzfurylglyoxylate*, m.p. 206—207°. Bromination of 3 : 6-dihydroxydibenzfuran yields the 4 : 5(?)-Br_2-*compound*, m.p. 201—202° (Ac_2 derivative, m.p. 173·5—174°), the Me_2 ether of which (identical with that m.p. 196—197° described above) can be converted into the Me_2 *ether*, m.p. 106—107°, of 4 : 5(?)-*dimethyl*-3 : 6-*dihydroxydibenzfuran*, m.p. 168—169°. Attempts to convert this into 4 : 5-dimethyldibenzfuran via the 3 : 6-$(NH_2)_2$-compound were unsuccessful. 3 : 6-*Diaminodibenzfuran* (from the Br_2-compound) has m.p. 212—213° [*picrate*, m.p. 278° (decomp.)]; the Ac_2 derivative, m.p. 299—300°, on bromination yields 2-*bromo*-3 : 6-*diacetamido*-, m.p. 259—260°, hydrolysed and deaminated to 2-bromodibenzfuran. By the Bucherer reaction, 1 : 2-dihydroxydibenzfuran yields the *hydrochloride*, m.p. 275° (darkening at 200°), of 2-amino-1-hydroxydibenzfuran (?) (Ac_2 derivative, m.p. 209—210), whilst 4-bromo-3-hydroxy- yields only 3-amino-dibenzfuran. The (? 5 : 5)-dibromo-2 : 2′-dihydroxydiphenyl of Diels and Bibergeil (A., 1902, i, 219) gives a Me_2 *ether*, m.p. 128—129°, and a Ac_2 derivative, m.p. 105—106°. A. LI.

***Cannabis indica*. II. Isolation of cannabidiol from Egyptian hashish. Structure of cannabinol.** (MISS) A. JACOB and A. R. TODD (J.C.S., 1940, 649—653; cf. A., 1940, II, 185).—Approx. equal amounts of cannabidiol (I), $C_{21}H_{30}O_2$, b.p. 160—180°/0·003 mm., $[\alpha]_D^{18}$ −126·6° in EtOH, and cannabinol (II) (probably *A*; cf. Cahn, A., 1932, 747) are obtained by distilling the resin from Egyptian hashish. They are purified through their respective *p*-nitrobenzoates, m.p. ~70—80°, and 159—160°. (I) has probably the structure assigned to it by Adams *et al.* (A., 1940, II, 80); its di-3 : 5-dinitrobenzoate, m.p. 106—107°, $[\alpha]_D^{13}$ −76·2°, is identical with that obtained by Adams (from Minnesota wild hemp), and is hydrolysed to (I) by KOH–MeOH in N_2 or by liquid NH_3. No physiologically active material is isolable from the above resin by alkali extraction. (I) and (II) are inactive in the Gayer test in rabbits. From resin of Indian origin, no (I) has been isolated. (Cf. A., 1940, II, 215.) A. T. P.



(*A.*)

Furano-compounds. I. Synthesis of 3′-methyl- or -ethyl-5 : 6 : 4′ : 5′-furocoumarin. H. A. SHAH and R. C. SHAH (J. Indian Chem. Soc., 1940, **17**, 41—44; cf. A., 1939, II, 373).—5-Hydroxy-6-acetylcoumarin-3-carboxylic acid refluxed with H_2SO_4–EtOH gives the Et ester, converted by $CH_2Br{\cdot}CO_2Et$–K_2CO_3–$COMe_2$ into *Et* 3-*carbethoxy*-5-*carbethoxymethoxy*-6-*acetylcoumarin*, m.p. 113—115°, hydrolysed by 4% aq. NaOH to 5-*carboxymethoxy*-6-*acetylcoumarin*-3-*carboxylic acid*, m.p. 189—191° (decomp.), which with Ac_2O–NaOAc affords 3′-*methyl*-5 : 6 : 4′ : 5′-*furocoumarin*-3-*carboxylic acid*, m.p. 226—228°, and thence (quinoline–Cu-bronze) 3′-*methyl*-5 : 6 : 4′ : 5′-*furocoumarin*, m.p. 138—140°. Similarly, 5-hydroxy-6-propionylcoumarin-3-carboxylic acid yields the *Et*

ester, m.p. 152—154°, and thence *Et* 3-*carbethoxy*-5-*carbethoxymethoxy*-6-*propionylcoumarin*, m.p. 103—105°, 5-*carboxymethoxy*-6-*propionylcoumarin*-3-*carboxylic acid*, m.p. 194—196°, 3′-*ethyl*-5 : 6 : 4′ : 5′-*furocoumarin*-3-*carboxylic acid*, m.p. 157—158°, and 3′-*ethyl*-5 : 6 : 4′ : 5′-*furocoumarin*, m.p. 150—152°. A. T. P.

Constitution of rottlerin. J. N. Ray (Current Sci., 1940, **9**, 80).—Contrary to previous observation (A., 1940, II, 139), rottlerin is optically inactive in $CHCl_3$. Extraction of *Kamala* (I) with cold Et_2O and adsorption of the extract on Al_2O_3 gives a zone containing *iso*rottlerin (II). Contrary to Robertson *et al.* (A., 1939, II, 559) (II) is not formed during the extraction of (I) by hot PhMe. H. W.

Mol. wt. of the methyl ether of tetrahydrorottlerone. J. N. Ray, K. S. Narang, and B. S. Roy (Current Sci., 1940, **9**, 136—137).—The mol. wt. of the Me_2 ether of hydrogenated rottlerone, m.p. 101·5°, is 369·5—372 in C_6H_6, corresponding with $C_{20}H_{20}O_2(OMe)_2$ contrary to the val. obtained, and the diphenylmethane structure proposed, by McGookin *et al.* (A., 1939, I, 559). F. R. G.

Pentamethylene oxides and sulphides.—See B., 1940, 346.

Thioxanthones.—See B., 1940, 433.

Catalytic transformations of heterocyclic compounds. XV. Permanence of activity of the catalyst in the reactions of conversion of furanidin into pyrrolidine or thiophan. J. K. Juriev and V. A. Tronova (J. Gen. Chem. Russ., 1940, **10**, 31—34).—Optimum conditions for conducting the reactions (Al_2O_3 catalyst) : tetramethylene oxide (I) + NH_3 → pyrrolidine; (I) + H_2S → tetramethylene sulphide; furan + H_2S → thiophen, are described; the optimum temp. is 400°, in all cases. The catalyst does not suffer inactivation. R. T.

Physiologically-active stimulants in foods and their detection. W. Diemair (Atti X. Congr. Internaz. Chim., 1938, IV, 497—517).—See A., 1940, III, 592. N^a-Benzoylhistidine Me ester (I) (Erngross, A., 1921, i, 57) coupled with PhN_2Cl (accompanied by spontaneous de-esterification) yields 2 : 5-*dibenzeneazo*-N^a-*benzoylhistidine*, m.p. 145·5° (*Me* ester, m.p. 217°), whilst coupling with *p*-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ affords 2 : 5-*di*-p-*nitrobenzeneazo*-N^a-*benzoylhistidine*, m.p. 161—162°; N^a-benzoylhistamine with PhN_2Cl yields only 5-*benzeneazo*-N^a-*benzoylhistamine*, m.p. 186·5° (decomp.). Glyoxaline with $NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ gives 2-p-*nitrobenzeneazoglyoxaline*, m.p. 248°. With I (I) yields 2-*iodo*-N^a-*benzoylhistidine Me ester*, m.p. 189° (all m.p. uncorr.). The bearing of the formation and properties of these derivatives on the Pauly diazo-reaction is discussed. F. O. H.

3 : 3-Dimethylthiolindoline.—See B., 1940, 383.

β-Indolylacetic acids.—See B., 1940, 346.

***Coli*-tryptophan–indole reaction. III. Essential structural conditions for the enzymic degradation of tryptophan to indole.** J. W. Baker and F. C. Happold (Biochem. J., 1940, **34**, 657—663).—The breakdown of tryptophans to indoles by *E. coli* appears to require, *inter alia*, a free CO_2H, an unsubstituted α-NH_2, and a β-C capable of oxidative attack. The following appear new : l-p-*nitrobenzoyltryptophan*, m.p. 121° (decomp.) after softening at 114° (possibly +1EtOH); *Me* l-α-*methylamino*-β-3-*indolylpropionate hydriodide*, m.p. 192°; 3-*indolylacetamide*, m.p. 150—151°, by heating NH_4 3-indolylacetate with $(NH_4)_2CO_3$ at 200—210°; *indole*-3-*aldehydesemicarbazone*, m.p. 220° (decomp.). It is doubtful if *l*-tryptophan reacts simply with CH_2O. H. W.

Phenylpyridines.—See B., 1940, 346.

Benzacridones.—See B., 1940, 433.

Carcinogenic compounds. I. Synthesis of 9-azacholanthrene and of certain *meso*-alkyl derivatives of 1 : 2- and 3 : 4-benzacridine. I. J. Postovski and B. N. Lundin (J. Gen. Chem. Russ., 1940, **10**, 71—76).—*m*-$NH_2{\cdot}C_6H_4{\cdot}[CH_2]_2{\cdot}CO_2H$ and α-$C_{10}H_7{\cdot}OH$ heated with $ZnCl_2$ (5 hr. at 280—290°) yield 9-*azacholanthrene*, m.p. 187—188° [*picrate*, m.p. 222—224° (decomp.)]. α-$C_{10}H_7{\cdot}NHPh$ and AcOH or $EtCO_2H$ heated with $ZnCl_2$ (14 hr. at 230—240°), afford 5-*methyl*-, m.p. 126° [*hydrochloride*, m.p. 253°; *picrate*, m.p. 231° (decomp.)], or 5-*ethyl*-1 : 2-*benzacridine*, m.p. 123° [*hydrochloride*, m.p. 250°; *picrate*, m.p. 227° (decomp.)]. 5-*Methyl*-, m.p. 144° [*hydrochloride*, m.p. 266°; *picrate*, m.p. 239° (decomp.)], and 5-*ethyl*-3 : 4-*benzacridine*, m.p. 139°, are prepared similarly from β-$C_{10}H_7{\cdot}NHPh$. R. T.

Stabilised diazo-complexes with piperazine and other bases. P. J. Drumm, W. F. O'Connor, and J. Reilly (Sci. Proc. Roy. Dublin Soc., 1940, **22**, 223—227).—Diazonium salts with piperazine and with NHMe·OH give stable complexes which reproduce the diazonium salts in 55—98% yield when heated to 45° with 80% H_2SO_4. *Bis*-3-, m.p. 160·5° [reduced (Zn + EtOH–AcOH) to *NN′*-diaminopiperazine], and -4-*chloro*-6-*methyl*-, m.p. 184°, and -2 : 5-*dichlorobenzeneazopiperazine*, m.p. 146°, and 3-, m.p. 76°, and 4-*chloro*-6-*methyl*-, m.p. 84°, and 2 : 5-*dichlorobenzeneazo*-β-*methylhydroxylamine*, m.p. 112°, are described. A. Li.

Bis*iso*indolenylidenes.—See B., 1940, 349, 434.

Reaction of unsaturated halogen compounds of the types $CR_2{:}CX_2$ and $NR{:}CX_2$ with azides. I. Reaction of phenylcarbylamine chloride with sodium azide. P. S. Pelkis and C. S. Dunaevskaja (Mem. Inst. Chem. Ukrain. Acad. Sci., 1940, **6**, 163—180).—$NPh{:}CCl_2$ and NaN_3 in $COMe_2$ (at the b.p.) yield 5-azido-1-phenyl-1 : 2 : 3 : 4-tetrazole. R. T.

Magnetochemical investigations. XXXV. Heavy-metal complexes of phthalocyanine. H. Senff and W. Klemm (J. pr. Chem., 1940, [ii], **154**, 73—81).—The magnetic susceptibilities of the phthalocyanine complexes of Ni, Co, Fe, and Mn indicate a transition from penetration to normal complex in this series. In the V complex the metal is quadrivalent. The C_5H_5N and quinoline compounds of the Fe complex are diamagnetic. J. W. S.

Acylamidomorpholines.—See B., 1940, 431.

Biogenesis of vitamin-B_1. C. R. Harington and R. C. G. Moggridge (Biochem. J., 1940, **34**,

685—689).—The action of pressed top yeast on α-amino-β-(4-methylthiazole-5)-propionic acid (I) and sucrose in H_2O gives 4-methyl-5-β-hydroxyethylthiazole [picrate, m.p. 162°; picrolonate, m.p. 184° (decomp.); *p*-nitrobenzoate, m.p. 125°] and d(−)-α-*amino*-β-(4-*methylthiazole*-5)-*propionic acid*, $[\alpha]_D$ −9·0° in N-H_2SO_4, which appears homogeneous and gives a strongly positive ninhydrin reaction. The *Me ester hydrochloride*, m.p. 187° (decomp.), does not appear to react with $NHEt_2$, $ClCO_2CH_2Ph$, or AcCl. 4-Methylthiazole-5-aldehyde and acetylglycine yield the *azlactone*, $\begin{matrix}CH{-}S\\ \|\\ N{\cdot}CMe\end{matrix}\!\!>\!C{\cdot}CH{:}C\!<\!\!\begin{matrix}CO{\cdot}O\\ |\\ N{=}CMe'\end{matrix}$, m.p. 157·5°, converted by NaOMe–MeOH into *Me* α-*acetamido*-β-(4-*methylthiazole*-5)-*acrylate*, m.p. 160°. α-*Acetamido*-β-(4-*ethylthiazole*-5)-*propionic acid* has m.p. 191°. Attempts to condense 4-*amino*-2-*methyl*-5-*bromomethylpyrimidine hydrobromide* (II) with (I) were unsuccessful. α-Acetamido-β-(4-methylthiazole-5)-propionic acid and (II) at 160° afford the *acid*, $CMe\!<\!\!\begin{matrix}N{:}C(NH_2,HBr)\\ N\text{———}CH\end{matrix}\!\!>\!C{\cdot}CH_2{\cdot}NBr\!<\!\!\begin{matrix}CH{-}S\\ CMe{:}C{\cdot}CH_2{\cdot}CH{\cdot}CO_2H\end{matrix}\!\!>\!NHAc$ decomp. 260°, hydrolysed by HBr to the *NH_2-acid* [*tripicrate*, m.p. 164° (decomp.); *tribromide*, m.p. 233° (decomp.)]. H. W.

Synthesis of heterocyclic derivatives of sulphanilamide. K. Ganapathi and B. K. Nandi (Current Sci., 1940, **9**, 67—68).—5-Amino- and 2 : 8-diamino-acridine, 2-sulphanilamidopyridine, and 2-aminothiazole are condensed with *p*-NHAc·C_6H_4·SO_2Cl in $COMe_2$ or C_5H_5N and the products are hydrolysed (2·5N-NaOH or 4—5N-HCl) to 5-*sulphanilamido*- and 2 : 8-*disulphanilamidoacridine*, 2-p-*sulphanilamidobenzenesulphonamidopyridine*, and 2-*sulphanilamidothiazole* respectively. H. W.

Heterocyclic and other derivatives of sulphanilamide. B. K. Nandi and K. Ganapathi (Current Sci., 1940, **9**, 177; cf. preceding abstract).—Condensation of *p*-NHAc·C_6H_4·SO_2Cl with the appropriate NH_2-compounds in $COMe_2$ or C_5H_5N, followed by hydrolysis with NaOH or HCl, yields 2-N′-*sulphanilamido*-4-*methylthiazole*, -4-*phenylthiazole*, -*anthraquinone*, and -5-*hydroxy*-1 : 3 : 4-*thiodiazine*. A. Li.

Strychnine and brucine. III. Derivatives of dinitrostrychnic acid. R. H. Siddiqui (Proc. Indian Acad. Sci., 1940, **11**, **A**, 268—281).—Dinitrostrychnic acid nitrate (I) (the dinitrostrychnine hydrate nitrate of Tafel, A., 1898, i, 706) and MeOH–H_2SO_4 afford, through the *sulphate* (+MeOH) of (II), *Me dinitrostrychnate* (II), m.p. 210—211° (decomp.) (+MeOH, lost at 110° in vac.) [*hydriodide*, +MeOH (not lost at 140°), m.p. 245—246° (decomp.); hydrochloride, +H_2O, m.p. 245—247° (decomp.); picrate, chars at 275°; *methiodide* (III), +H_2O, m.p. 240—242° (decomp.) (shrinks at 215°)]. (III) and AgOH afford N(b)-*methyldinitrostrychnic betaine*, m.p. >310° [*picrate*, m.p. 276—277° (decomp.) (browns at 265°)]. (II) refluxed with piperidine affords dinitrostrychnic acid (IV), +1·5H_2O. *Et*, m.p. 226° (decomp.) [*sulphate*, +1·5EtOH; *hydrochloride*, +H_2O, m.p. 230° (decomp.) (softens at 190°); picrate], and *Pr dinitrostrychnate*, m.p. 246—247° (decomp.) [*sulphate*, m.p. 210°; *hydrochloride*, +H_2O, m.p. 230° (decomp.); picrate, chars from 254°], are prepared. (II) and $SnCl_2$–HCl or Zn–HCl afford diaminostrychnine (V), new m.p. 287° (decomp.), also obtained from (IV). (II) and N_2H_4,H_2O in Bu^{a}OH give *dinitrostrychnic acid hydrazide* (*dihydrochloride*, +H_2O; picrate; sulphate; perchlorate), converted by $NaNO_2$–AcOH at 7° and then boiling EtOH into a *substance*, $C_{21}H_{22}O_6N_4$, +0·5H_2O, m.p. 265° (softens at 175°, froths at 198°) (*hydrochloride*, +0·5H_2O), a *substance*, $C_{21}H_{23}O_6N_5$,H_2O, m.p. >320° [(?) amide of (IV)] (*hydrochloride*), and a *substance*, $C_{21}H_{22}O_6N_4$,H_2O, decomp. from 240° [(?) aldehyde related to (IV)] (*hydrochloride*, +H_2O). (IV) and aq. KOH yield an (?) isomeride (VI) [*hydrochloride*, $C_{21}H_{22}O_7N_4$,HCl; Me ester (VII), m.p. 165° (decomp.), then, after recrystallisation, 209°; cf. (II)]. (I) or (VI) and Ac_2O–NaOAc at 100° afford (after MeOH) (VII) and a base, decomp. from 235—248° (softens at 233°), probably α-dinitrostrychnine, converted by Bu^{a}OH–H_2O into (?) (IV), reduced to (V). (I) and HNO_3 (*d* 1·42) afford $H_2C_2O_4$, picric acid, dinitrostrycholdicarboxylic acid (cf. Ashley *et al.*, A., 1930, 625), an *acid*, $C_8H_6O_7N_2$, m.p. 182° (softens at 175°), two acids, m.p. 230—235° and 195°, respectively, and a K salt, m.p. 220°. The structure of strychnine is discussed. A. T. P.

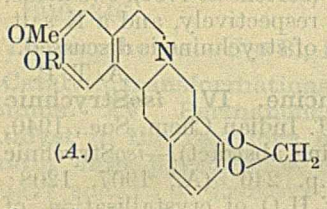
Strychnine and brucine. IV. *iso*Strychnic acid. R. H. Siddiqui (J. Indian Chem. Soc., 1940, **17**, 152—156; cf. preceding abstract).—*iso*Strychnic acid (I), $C_{21}H_{24}O_3N_2$, m.p. 240° (A., 1907, 1208; 231°), contains 1 mol. of H_2O of crystallisation, of which 0·5 mol. is lost at 135°/vac., gives a *hydrochloride*, +H_2O, m.p. 190—195° (decomp.), picrate, m.p. 187—189° (decomp. from 130°), and by Ac_2O at 100° an O-*Ac* derivative, +2H_2O (lost at 100°/vac.), m.p. 195—196° (decomp.) [*hydrochloride*, m.p. 225—226°; picrate, m.p. 184° (decomp.)], and with BzCl–C_5H_5N gives BzOH and *iso*strychnine. It is unaffected by hot 5—10% HNO_3, with 20% HNO_3 gives an amorphous powder, but with boiling 50% HNO_3 gives *dinitroisostrychnic acid*, $C_{21}H_{22}O_7N_4$, +1·5H_2O, m.p. >325° (hydrochloride; sulphate; resists reduction), and an amorphous acid, m.p. 260—271°. The structure of (I) is discussed. R. S. C.

Strychnine and brucine. V. Derivatives of dinitro*iso*strychnic acid. R. H. Siddiqui (J. Indian Chem. Soc., 1940, **17**, 233—238).—The *Me* ester, m.p. 225° (softens at 218°) [*sulphate*, chars at 280—290°; *hydrochloride*, softens at 194° and chars at 225—235°; *picrate*, m.p. 259° (decomp.)], of dinitro*iso*strychnic acid (I) with MeI in $CHCl_3$ yields the *methiodide*, m.p. 276—280° (decomp.), which with Ag_2O gives the *betaine*, m.p. ≮325° (*picrate*, decomp. 259°). The Et ester, m.p. 195° (softening at 192°) [*sulphate*, decomp. 250° (frothing at 150°); *hydrochloride*, decomp. 247°; *picrate*, m.p. 261° (decomp.)], of (I) is not affected by piperidine, and yields, with HNO_2, the *nitrite*, m.p. 198—199°, with Br in $CHCl_3$, a *Br*-derivative, m.p. 180°, and with N_2H_4,H_2O in BuOH, a mixture of the *hydrazide* (+0·25H_2O), m.p. ≮280°, with two *substances*, $C_{21}H_{23}O_6N_5$,H_2O, m.p. 221° [*picrate*, m.p. 225—235° (frothing)], and $C_{21}H_{23}O_5N_5$,0·25H_2O, m.p. 160° (frothing) [*picrate*,

m.p. 225—235° (frothing at 178°)]. The *Pr* ester of (I) has m.p. 118—122° [*sulphate*, m.p. 247—248° (decomp.); *hydrochloride*, m.p. 225° (frothing); *picrate*, m.p. 241—244° (decomp.)]. A. Li.

Alkaloids of fumariaceous plants. XXVI. *Corydalis claviculata* (L.), DC. XXVII. A new alkaloid, cheilanthifoline, and its constitution. R. H. F. Manske (Canad. J. Res., 1940, **18**, B, 97—99, 100—102).—XXVI. *C. claviculata* (L.), DC., contains cularine (I), suggesting the lack of any close relationship to *C. lutea* and *ochroleuca* (cf. A., 1939, II, 395). Protopine, partly racemised *l*-stylopine, and a phenolic base or mixture of bases, alkaloid F52, methylated to (I), are also present.

XXVII. *Cheilanthifoline* (alkaloid F13) (II), m.p. 184°, $[\alpha]_D^{20}$ −311° in MeOH, obtained from *C. cheilantheifolia*, and in smaller amounts from *C. scouleri* and *C. siberica* (A., 1937, II, 265), has the structure (*A*; R = H). With CH_2N_2 in MeOH (II) gives sinactine (III) (*A*; R = Me). With $CHMeN_2$ in MeOH–Et_2O, (II) gives its O-*Et ether*, m.p. 144°, which is oxidised by $KMnO_4$–Na_2CO_3 to 1-keto-6-methoxy-7-ethoxy-1 : 2 : 3 : 4-tetrahydro*iso*quinoline (cf. Gadamer *et al.*, A., 1928, 310) and 4-methoxy-5-ethoxyphthalic acid. The identity of alkaloid F36 from *Fumaria officinalis* (A., 1939, II, 190) with partly racemic (III) is confirmed. E. W. W.



(*A*.)

Salts of rubradinine. P. Denis (Bull. Acad. roy. Belg., 1939, [v], **25**, 177—182; cf. A., 1937, II, 266).—Rubradinine contains 1 OMe and its formula is therefore $C_{23}H_{25}O_3N_2$·OMe. The non-cryst. *hydrochloride*, *sulphate*, $C_{24}H_{28}O_4N_2,H_2SO_4,5H_2O$, m.p. 245° (block), *per-rhenate*, *platinichloride*, *aurichloride*, and *mercurichloride* are described. H. W.

Synthesis of lipophilic chemotherapeuticals. II. 4-Alkylaminoazobenzene-4′-arsonic acids. S. Adler, L. Haskelberg, and F. Bergmann (J.C.S., 1940, 576—578).—A series of dyes, R·NH·C_6H_4·N:N·C_6H_4·AsO_3H_2, has been prepared by coupling diazotised *p*-arsanilic acid with a solution of the substituted NH_2Ph, usually in AcOH. The lower members of the series are very toxic, the higher ones show a definite decrease in toxicity. The following are described: sec.-*butyl*-, b.p. 225°/759 mm., sec.-*butylcarbinyl*-, b.p. 236°/758 mm., β-*methylamyl*-, b.p. 138°/22 mm., *dodecyl*-, b.p. 140°/0·2 mm., *tetradecyl*-, b.p. 180°/4 mm., and *octadecylaniline*, b.p. 196°/0·6 mm., and 4-*dimethyl*-, m.p. 310° (decomp.), -*ethyl*-, m.p. 276° (decomp.), -n-*propyl*-, m.p. 286° (decomp.), -n-*butyl*-, -iso*butyl*-, m.p. 303° (decomp.), -sec.-*butyl*- (+EtOH), -n-*amyl*-, -sec.-*butylcarbinyl*-, m.p. 245° (decomp.), -n-*hexyl*-, m.p. 270° (decomp.), -β-*methylamyl*-, m.p. 265° (decomp.), -n-*heptyl*-, -n-*dodecyl*-, -n-*tetradecyl*-, -n-*octadecyl*-, -*cyclohexyl*-, m.p. 292° (decomp.), -*benzyl*-, m.p. 340° (decomp.), and -*cholesteryl-aminoazobenzene-4′-arsinic acid*, m.p. 237° (decomp.). F. R. S.

Mercuration of some simple derivatives of γ-pyrone. J. R. Files and F. Challenger (J.C.S., 1940, 663—670).—γ-Pyrone with $Hg(OAc)_2$ in H_2O–AcOH at 100° followed by HCl gives *dichloromercuri-γ-pyrone*. Dimethylpyrone with $HgCl_2$ and NaOAc affords a *trichloromercuri*-derivative. Meconic acid, NaOAc, and $HgCl_2$ yield *hydroxymercuricomenic anhydride*, CO_2, and Hg_2Cl_2; the pure anhydride is obtained by using HgO. This substance and HCl give *chloromercuricomenic acid*, which with Br affords 2-bromocomenic acid. Mercuration of comenic acid with $Hg(OAc)_2$ or $HgCl_2$ and NaOAc leads to the anhydride. Pyromeconic acid and $HgCl_2$ with $NaHCO_3$–glycerol give the *anhydride* of *hydroxymercuripyromeconic acid*, which with HCl forms *monochloromercuripyromeconic acid* (I); the acid with $HgCl_2$ and NaOAc yields *oxymercurichlorochloromercuripyromeconic acid*, which with HCl affords *dichloromercuripyromeconic acid*. With (I) and I, iodopyromeconic acid, with I in position 2, is obtained. Kojic acid with HgCl–NaOAc or $NaHCO_3$–glycerol gives *hydroxymercurikojic anhydride*, which with Me forms *chloromercurikojic acid*; treatment with Na_2S and NaI results in elimination of Hg. Almost all these mercurated products are amorphous, insol., infusible solids. F. R. S.

Organo-mercury compounds derived from quinine and cinchonine. N. V. S. Rao and T. R. Seshadri (Proc. Indian Acad. Sci., 1940, **11**, A, 289—297).—Quinine (I) (1 mol.) and $HgCl_2$ (1 mol.) in cold EtOH afford *quinine-monomercuri chloride* (II), m.p. ~140—170°; 2 or more mols. of $HgCl_2$ give the *-dimercuri chloride* (III), m.p. ~130—160°. (I) in H_2O, +HCl until just acid, and cold aq. $HgCl_2$ (1 or 2 mols.) afford the *monohydrochloride monomercuri chloride* (IV), m.p. 204° (chars); in hot aq. HCl, the *dihydrochloride monomercuri chloride* (V), m.p. 255° (decomp.), is formed. (V) and cold 10% aq. NaOH give (IV). (II), (III), or (IV) and boiling dil. HCl give (V). Hg is retained in solution as stable complex ions, probably of type $K^+(HgCl_3)'$ or $K_2^{++}(HgCl_4)''$, when (IV) or (V) is boiled with aq. KOH. (I) and aq. $Hg(OAc)_2$–AcOH–aq. NaOH afford *α-hydroxymercuri-β-hydroxydihydroquinine*, $+2H_2O$, decomp. 115° (freshly prepared) or 166° (dried in air), converted by AcOH into *α-acetoxymercuri-β-hydroxydihydroquinine acetate* (VI), $+2H_2O$. Cinchonine affords, as above, a *momomercuri*, m.p. 172° (decomp.) and *dimercuri chloride* (from 3 mols. of $HgCl_2$), m.p. 155—172°, a *mono-*, m.p. 120—166°, and *dihydrochloride monomercuri chloride*, m.p. ~95—128° (decomp.) ($+3H_2O$, lost at 100°), and *α-hydroxymercuri-β-hydroxydihydrocinchonine*, $+H_2O$, m.p. 235° (turns brown at 212°) (acetate). Formulæ are proposed for (II), (V), and (VI). A. T. P.

Organometallic compounds of group VIII elements. M. Lichtenwalter (Iowa State Coll. J. Sci., 1939, **14**, 57—59; cf. Gilman *et al.*, A., 1939, II, 53, 253).—Of the group VIII metals, only Pt could be made to yield organometallic compounds. Fe, Co, and Ni do not combine directly with org. halides. MgPhI with Fe, Co, or Ni halides (except FeF_3) in Et_2O–C_6H_6 gives the metal and Ph_2 in 100% yield. $FeCl_2$ or FeI_2 with α-$C_{10}H_7$·MgBr or α-$C_{10}H_7Li$ yields some (1-$C_{10}H_7)_2$; addition of CH_2PhBr before hydrolysis

gives no ketone. FeI_2 slowly yields Ph_2 with ZnPhCl, and a mixture of C_2H_4, C_2H_6, and C_4H_{10} with ZnEtI. $PbEt_4$ rapidly reduces $FeCl_3$ to $FeCl_2$. FeI_2 (with or without Fe powder) with $Pb(C_6H_4{\cdot}OMe\text{-}p)_3$ in Et_2O–C_6H_6 ppts. PbI_2 and $Pb(C_6H_4{\cdot}OMe\text{-}p)_4$; hydrolysis of the solution gives chiefly $PbI_2(C_6H_4{\cdot}OMe\text{-}p)_2$. $PtCl_4$ with MgPhI gives an amorphous mixture of Ph–Pt compounds containing 30—40% of Pt. $PtCl_2$ with MgMeI gives an amorphous *substance* analysing correctly for $PtMe_2I_2$, and with α-$C_{10}H_7{\cdot}MgBr$ gives *Pt di-α-naphthyl*, in presence of which (as of $PtCl_4$) BzBr and *m*-xylene give a 70—80% yield of 2 : 4 : 1-$C_6H_3Me_2{\cdot}COPh$. Anhyd. $PtCl_4$ with MgMeI yields $PtMe_3I$ (40%), together with a trace of $PtMe_3$, and compounds having compositions corresponding with $PtMeI_5$, $PtMe_3I$, and $PtMeI_3$. A. LI.

Organometallic radicals. J. C. BAILIE (Iowa State Coll. J. Sci., 1939, **14**, 8—10).—Some Pb triaryls are described again (cf. Gilman and Bailie, A., 1939, II, 233). *Pb tri*-p-*phenetylbenzyl* [from $PbNa(C_6H_4{\cdot}OEt\text{-}p)_3$ and CH_2PhCl] has m.p. 76—77°. When R = Ph, *p*-tolyl, *p*-$C_6H_4{\cdot}OMe$, *p*-$C_6H_4{\cdot}OEt$, or Et: $2PbR_3 + MgI_2 + Mg \rightarrow PbR_4 + Pb + 2MgRI$, probably with the intermediate formation of $PbR_3{\cdot}MgI$; the *o*-substituted Pb triaryls with MgI_2 and Mg yield PbR_3I, whilst $PbPh_4$ and $Pb(C_6H_4Me\text{-}p)_3$ do not react. $PbPh_3$ or $Pb(C_6H_4Me\text{-}p)_3$ with MgI_2 alone yields PbR_3I. PbR_3Na (R = aryl or alkyl) with NH_4X in liquid NH_3 yields PbR_3 and Pb, the colour changes indicating that the reaction is probably $PbR_3Na \rightarrow PbR_3H \rightarrow PbR_2 + RH$; $3PbR_2 \rightarrow 2PbR_3 + Pb$. $PbPh_3Cl$, $PbPh_3Br$, or $PbPh_3I$ with $CPh_3{\cdot}MgCl$ affords *Pb triphenyltriphenylmethyl* (?) (I), m.p. 196—197°, which in C_6H_6 dissociates appreciably, and is slowly oxidised to $PbPh_3$ and $(CPh_3)_2O_2$. The following reactions of (I) are recorded: thermal decomp. in xylene gives $PbPh_4$ and Pb; the reaction with HCl + I is inconclusive, but dry HCl yields, in $CHCl_3$, $CPh_3{\cdot}OH$, and in light petroleum (b.p. 60—66°), $PbPh_2Cl_2$; I in $CHCl_3$ gives PbI_2 and a trace of $PbPh_3I$; Na in liquid NH_3 gives a mixture of CPh_3Na and $PbPh_3Na$, which yields with NH_4Br, $CHPh_3$ and $PbPh_3$, and with CH_2PhCl, $CPh_3{\cdot}CH_2Ph$ and $PbPh_3{\cdot}CH_2Ph$. (I) could not be prepared by mixing CPh_3 and $PbPh_3$. *Sn triphenyltriphenylmethyl*, m.p. 272—273° (decomp.) (from $SnPh_3Cl$ and $CPh_3{\cdot}MgCl$), does not dissociate in C_6H_6. With Na followed by NH_4Br in liquid NH_3 it yields $CHPh_3$ and $SnPh_3$; the comparatively slow reaction with HCl to give *Sn diphenyltriphenylmethyl chloride*, m.p. 210°, shows that the C–Sn bond is more stable than the C–Pb. $PbI(C_6H_4{\cdot}OMe\text{-}o)_3$ and $CPh_3{\cdot}MgCl$ yield *Pb tri-o-anisyltriphenylmethyl*, m.p. 145—146°. $CPh_3{\cdot}MgCl$ with $PbCl_2$ in C_6H_6–Et_2O gives CPh_3 and Pb. A. LI.

Acridine derivatives. V. Aurothiol- and argentothiol-acridines. S. J. DAS-GUPTA (J. Indian Chem. Soc., 1940, **17**, 244—246).—5-Thiolacridines exist in two forms (? thio-ketonic and -enolic), one form yielding the other when dissolved in alkali and repptd. by acid. 7-*Methoxy*-5-*thiolacridine*, m.p. 231—232° (from the 5-chloroacridine and K xanthate in PhOH), in EtOH yields, with SO_2 followed by $KAuBr_4$, the 5-*aurothiolacridine*, m.p. 219—220° (decomp.), with $KAuBr_4$ followed by SO_2, *bis*-7-*methoxy*-5-*acridylthiolgold bromide*, m.p. 222—223°, and with NaOH followed by $AgNO_3$, 7-*methoxy*-5-*argentothiolacridine*, m.p. 261° (decomp.). The corresponding *compounds* from 2-*chloro*-7-*methoxy*-5-*thiolacridine*, m.p. 245°, have m.p. 247—248° (decomp.), 254—255° (decomp.), and 290° (decomp.), respectively. A. LI.

Structure of proteins. A. OLSEN (Tids. Kjemi, 1940, **20**, 45—52).—A review. M. H. M. A.

Cyclol hypothesis. D. WRINCH (Nature, 1940, **145**, 669—670).—Experiments cited as evidence against the hypothesis are accommodated with it. L. S. T.

Number and range of dissociation of ionogenic groups and the dissociation curve of proteins. I. LICHTENSTEIN (Biochem. Z., 1939, **303**, 13—31).—Acid- and base-binding capacities of gelatin, deaminated gelatin, and cryst. egg-albumin have been determined between p_H 1·5 and 12·5 in H_2O, in 80% EtOH, and in 1% CH_2O, and the curves obtained are compared with those derived from data on the constituent NH_2-acids and on the proportions of these in the respective proteins. The dissociation range of all single groups, and the no. of NH_2 and glyoxaline groups (corresponding respectively with the lysine and histidine content of gelatin), are in agreement with available analytical data, but the no. of free CO_2H is approx. twice that to be expected from the accepted content of dibasic NH_2-acids. A discrepancy also exists with regard to guanidino-groups calc. on the basis of the arginine content. Correct isoelectric points can be calc. from dissociation ranges and nos. of groups derived from the titration curves, but not from analytical data. F. L. U.

Simplified micro-determination of carbon and hydrogen in organic compounds. I. Combustion of compounds containing carbon, hydrogen, and oxygen. II. (FRLN.) A. DOMBROWSKI (Mikrochem., 1940, **28**, 125—135, 136—140).—I. Org. substances are burnt in O_2 in a shortened Pregl combustion tube using only Cu gauze therein. Shortened absorption tubes are more convenient.

II. With the above-mentioned apparatus, N oxides are absorbed in a tube, containing *p*-$NH_2{\cdot}C_6H_4{\cdot}N_2Ph$ and aq. H_3BO_3–$K_2Cr_2O_7$, placed between the H_2O- and CO_2-absorption tubes. S and halogen are absorbed by Ag (followed by CuO, $PbCrO_4$, and finally Ag). R. S. C.

Systematic qualitative organic micro-analysis. —See A., 1940, I, 301.

Semi-micro-Dumas method for difficult compounds. A. R. RONZIO (Ind. Eng. Chem. [Anal.], 1940, **12**, 303—304).—The method previously described (A., 1936, 578) is modified by using pptd. MnO_2 in the combustion tube, which burns CH_4 quantitatively to CO_2. A special nitrometer is described. J. D. R.

Bomb determination of organic chlorine by lime-fusion method. W. M. MACNEVIN and W. H. BAXLEY (Ind. Eng. Chem. [Anal.], 1940, **12**, 299—300).—A suitable bomb is described. The use of a sealed metal tube makes the process available

for volatile liquids, and is quicker than the Carius method. Procedure is detailed. J. D. R.

Determination of organic iodine by the micro-method of Leipert. A. BONOT (Bull. Soc. Chim. biol., 1940, **22**, 108—111).—Conditions to be observed for the determination of 0·1—1 mg. of I are described. A. L.

Determination of methylpropene by a modified Denigès reagent. A. NEWTON and E. J. BUCKLER (Ind. Eng. Chem. [Anal.], 1940, **12**, 251—254).—The normal determination of $CMe_2{:}CH_2$ by the Denigès reagent [$Hg(NO_3)_2$–HNO_3] is complicated by the solubility of the ppt. in HNO_3 and by changes in its wt. and composition on washing with H_2O. Use of a neutralised reagent and determination of the Hg in the ppt. (not the wt. of the ppt.), which is const. under the conditions of determination [7Hg ≡ $CMe_2{:}CH_2$], gives an accurate and rapid determination. C_2H_4, C_3H_6, $\Delta^{\alpha\gamma}$-butadiene, Δ^{α}- and Δ^{β}-butene, and β-methyl-Δ^{β}-butene do not interfere. Apparatus and procedure are detailed. J. D. R.

Equivalent weights of salts of organic acids. Micro-determination by electrodialysis. K. H. DITTMER and R. G. GUSTAVSON (Ind. Eng. Chem. [Anal.], 1940, **12**, 297—299).—The aq. salt solution is electrodialysed through a sintered glass membrane, the metal forming an amalgam with the Hg cathode and thence combining with a known excess of standard H_2SO_4 in the cathode vessel. Titration of the cathode acid after electrodialysis gives the equiv. wt. of the acid. Apparatus and procedure are detailed, and methods are described for prep. of sintered glass membranes. The error is ±3%. J. D. R.

Quantitative analysis by isotope dilution, with application to the determination of amino-acids and fatty acids. D. RITTENBERG and G. L. FOSTER (J. Biol. Chem., 1940, **133**, 737—744).—Palmitic acid (I) (*e.g.*) of known isotope content is added to the mixture to be analysed, and a small sample of the pure acid is isolated from the mixture. The (I) content of the mixture is calc. from the isotope concn. in the added and extracted samples. The method is also applied to glycine, glutamic acid, and aspartic acid in fibrin hydrolysates. R. L. E.

Determination of lactic and pyruvic acid with periodic acid. R. BOISSON (J. Pharm. Chim., 1940, [ix], **1**, 240—255; cf. A., 1940, II, 34).—Air is aspirated through boiling 0·1—1% lactic acid (I) (10 c.c.) containing 10% HIO_4 (10 c.c.) and 10N-H_2SO_4 (2 c.c.) and the MeCHO formed is absorbed in Nessler's reagent and determined titrimetrically (error −3%). 0·5—1 mg. is determined by a modified method. If glucose is mixed with (I), the latter is determined after extraction with ether. $AcCO_2H$ (II) interferes with the determination of (I) unless approx. equimol. amounts of the two substances are present. When (II) (5—30 mg.) is heated (boiling H_2O-bath/0·5—1 hr.) with 0·1N-$NaIO_4$ (5 c.c.), the excess of $NaIO_4$ determined titrimetrically is a measure of (II) present. J. L. D.

Polarographic analysis of mixtures of aldehydes and peroxides. V. SCHTERN and S. POLLJAK (J. Gen. Chem. Russ., 1940, **10**, 21—30).—The negative reduction potentials of certain peroxides and aldehydes in 0·1N-LiCl are: MeO_2H and EtO_2H 0·25—0·3, $(OH{\cdot}CH_2)_2O_2$ 0·35, Et_2O_2 0·5, H_2O_2 0·75, CH_2O 1·55—1·6, MeCHO and EtCHO 1·75—1·8. The polarographic determination of these substances and of their mixtures is described. R. T.

Identification of β-aminoethanol. B. KEISER (Ind. Eng. Chem. [Anal.], 1940, **12**, 284).—$NH_2{\cdot}[CH_2]_2{\cdot}OH$ (I) in H_2O is treated with o-$C_6H_4(CO)_2O$, evaporated to dryness, and heated at 210°/5 min.; o-$C_6H_4(CO)_2N{\cdot}[CH_2]_2{\cdot}OH$, m.p. 127°, is formed. Similarly, (I) with $H_2C_2O_4$ in H_2O yields the oxalate, m.p. 199—200°, which when heated to 220° gives *NN'*-bis-(β-hydroxyethyl)oxamide, m.p. 168°. J. D. R.

Biuret reaction. B. M. KOSOLAPOV (J. Appl. Chem. Russ., 1940, **13**, 314—316).—The biuret reaction is given by salts of Cu^{I}, Cu^{II}, and Ni^{II}. The violet complex obtained with Co^{II} is readily oxidised by atm. O_2 to a brownish-yellow Co^{III} complex. R. T.

Micro-determination of homocystine.—See A., 1940, III, 550.

Determination of creatinine with *m*-dinitrobenzoic acid.—See A., 1940, III, 619.

Determination of cholesterol.—See A., 1940, III, 620.

Determination of indole. Modification of Ehrlich's reaction. L. H. CHERNOFF (Ind. Eng. Chem. [Anal.], 1940, **12**, 273—274).—Indole in EtOH-free $CHCl_3$ is treated with p-$NMe_2{\cdot}C_6H_4{\cdot}CHO$ in 85% HPO_3, and AcOH added; the colour in the HPO_3 layer is compared with known standards. J. D. R.

Volumetric determination of acridines by methylene-blue. A. BOLLIGER (Quart. J. Pharm., 1940, **13**, 1—6).—Acridines are determined by pptn. from neutral or slightly acid solution with excess of picric acid (I); after removal of the picrate the excess of (I) is determined by titration with methylene-blue (A., 1939, II, 398). The determination of 2 : 8-diaminoacridine (*monopicrate*, decomp. 250°), 2 : 8-diamino-10-methylacridinium chloride [*monopicrate*, m.p. 244° (decomp.)], and their commercial forms proflavine, euflavine, and acriflavine is described. J. N. A.

Precipitating agents for alkaloids and amines. C. C. FULTON (Amer. J. Pharm., 1940, **112**, 51—64, 134—154; cf. A., 1932, 629).—A large no. of reagents are described which give characteristic cryst. ppts. with alkaloids. Pptn. is most satisfactory when the alkaloid is dissolved in 85% H_3PO_4. J. L. D.

Determination of nicotine and anabasine present together. A. SCHMUK and A. BOROZDINA (J. Appl. Chem. Russ., 1939, **12**, 1582—1585).—Total alkaloids are determined in a sample of tobacco by titration of the Et_2O extractives. A second portion of the aq. solution of extractives is made acid with H_2SO_4, filtered, and 3 ml. of 10% H_2SO_4 and 10 ml. of 5% $NaNO_2$ are added to 50 ml. of filtrate + washings. Nicotine is then pptd. as picrate (nitroso-anabasine is not pptd. under these conditions), and the ppt. is titrated in the usual way. Anabasine is given by difference. R. T.