BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

JANUARY, 1939.

Classification of chelating groups. H. M. HAENDLER and B. P. GEYER (J. Amer. Chem. Soc., 1938, **60**, 2813—2814).—An abbreviated nomenclature for chelating groups is detailed. R. S. C.

Selenious anhydride as an oxidising agent in organic chemistry. N. N. MEL'NIKOV (Uspechi Chim., 1936, **5**, 443).—The use of SeO_2 to oxidise paraffins, olefines, and alcohols to glycolaldehydes, substituted acetylenes to OH-acetylenes, terpenes to terpene ketones, aldehydes and ketones to keto-aldehydes, cyclic ketones to 1 : 2-diketones, mercaptans to disulphides, sulphides and disulphides to sulphoxides and sulphones, and *C*-methylamides to amide-aldehydes, is recommended. Amines, alcohols, and mercaptans give Se derivatives at low temp.
Ch. Abs. (*c*)

Nonanes. β-Methyloctane, γ-ethylheptane, βγ-dimethylheptane, and ββδδ-tetramethylpentane. F. C. WHITMORE and (MISS) H. A. SOUTHGATE (J. Amer. Chem. Soc., 1938, **60**, 2571—2573).—$CH_2Bu^{\gamma}\cdot CMe_2Br$, b.p. 75°/36 mm., or, better, $CH_2Bu^{\gamma}\cdot CMe_2Cl$, b.p. 53°/29 mm., with $ZnCl_2$ gives 18% of ββδδ-*tetramethyl*-n-*pentane*, b.p. 120—125°/730 mm., m.p. —66·9° to —67·1°. Dehydration of *n*-$C_6H_{13}\cdot CMe_2\cdot OH$, $CEt_2Bu^{\alpha}\cdot OH$, and $CMePr^{\beta}Bu^{\alpha}\cdot OH$ by heating with I and hydrogenating (Ni on Al_2O_3) the resulting olefines gives β-methyl-*n*-octane, b.p. 142·8°, m.p. —80·1°, *γ-ethyl*-n-, a glass, b.p. 143·1°, and βγ-*dimethyl*-n-*heptane*, b.p. 140·65°, respectively. *n*, *d*, and *η* are also determined. R. S. C.

Synthesis of tertiary hydrocarbons. F. C. WHITMORE and H. P. OREM (J. Amer. Chem. Soc., 1938, **60**, 2573—2574).—β-Methyl-*n*-hexane, b.p. 90·3°, m.p. —120·3°, β-methyl-*n*-octane, *γ*-ethyl-*n*-heptane, *γ*-methyl-*n*-nonane, b.p. 167·6°, m.p. —90°, and δ-methyl-*n*-decane, b.p. 188·1°, m.p. —92·9°, are obtained in 23·7—48·8% yield from $CMe_2Bu^{\alpha}\cdot OH$, *n*-$C_6H_{13}\cdot CMe_2\cdot OH$, $CEt_2Bu^{\alpha}\cdot OH$, *n*-$C_6H_{13}\cdot CMeEt\cdot OH$, and *n*-$C_6H_{13}\cdot CMePr^{\alpha}\cdot OH$, respectively, by passing in HI, then adding Zn, and passing in HCl at 70—80°. Prep. of the alcohols is also described, and *n* and *d* are determined. R. S. C.

Hexamethylethane and tetra-alkylmethanes. R. E. MARKER and T. S. OAKWOOD (J. Amer. Chem. Soc., 1938, **60**, 2598).—Addition of CuI to CR_3Hal and MgR'Hal in Et_2O gives 11—20% of CR_3R' ($R \neq H$). $Bu^{\gamma}Cl$ thus gives CMe_3Et, CMe_3Pr^{α}, CMe_3Bu^{α}, and *n*-$C_5H_{11}\cdot CMe_3$. CMe_2EtCl gives CMe_2Et_2, CMe_2EtPr^{α}, CMe_2EtBu^{α}, and *n*-$C_5H_{11}\cdot CMe_2Et$. $Bu^{\gamma}MgI$ and $Bu^{\gamma}Cl$ similarly give 16% of C_2Me_6, m.p. >99°. R. S. C.

Peroxide effect in the addition of reagents to unsaturated compounds. XVIII. Addition of and substitution by bisulphite. M. S. KHARASCH, E. M. MAY, and F. R. MAYO (J. Org. Chem., 1938, **3**, 175—192; cf. A., 1938, II, 345).—In presence of O_2 $NaHSO_3$ adds to olefines, $CR_2{:}CH_2$, giving the "abnormal" product, $CHR_2\cdot CH_2\cdot SO_3Na$. NO_3' or NO_2' also causes addition. Thus, C_3H_6, *iso*-C_4H_8, $CH_2{:}CH\cdot CH_2\cdot OH$, and $CHPh{:}CH\cdot CO_2H$ give $Pr^{\alpha}SO_3Na$, $Bu^{\beta}SO_3Na$, $OH\cdot CHEt\cdot SO_3Na$ (I), and $CO_2H\cdot CH_2\cdot CHPh\cdot SO_3Na$, respectively. $CHPh{:}CH_2$ gives similarly a little $CHPhMe\cdot SO_3Na$ (II), but mainly $CHPh{:}CH\cdot SO_3Na$ (III). (III) arises by substitution, since $CH_2Ph\cdot CH_2\cdot SO_3Na$ is unaffected by $NaHSO_3$–O_2. (I) is obtained also from $(CH_2)_3Br_2$ and aq. Na_2SO_3 and is identified by conversion by PCl_5 in CCl_4 into a lachrymatory chloride and thence by NH_3–Et_2O into *γ-chloropropane-α-sulphonamide*, m.p. 63°. $CH_2Ph\cdot CH_2Br$ gives β-phenylethane-sulphonic acid (*NHPh·NH*$_2$ salt, m.p. 154°), also obtained from $CH_2Ph\cdot CH_2\cdot SH$ (IV) (prepared from $Ph\cdot[CH_2]_2\cdot SO\cdot CH_2\cdot CO_2H$) and converted by PCl_5 into the chloride, m.p. 34°, and thence via the amide, m.p. 121°, into $CH_2Ph\cdot CH_2\cdot SO_2Na$ (V) and $CH_2Ph\cdot CH_2\cdot HgCl$, m.p. 165°. With $C_6H_3Cl(NO_2)_2$ (IV) gives 2 : 4-$(NO_2)_2C_6H_3\cdot S\cdot[CH_2]_2\cdot Ph$, m.p. 88°, and thence the corresponding sulphone, m.p. 131°, obtained also from (V). CHPhMeCl and Na_2SO_3–NaOH give α-phenylethane-α-sulphonic acid (VI) (*NHPh·NH*$_2$ salt, m.p. 115°), reconverted by PCl_5 into CHPhMeCl. Oxidation of $CHPhMe\cdot SH$ yields (VI), and $C_6H_3Cl(NO_2)_2$ gives 2 : 4-*dinitrophenyl CHPhMe sulphide*, m.p. 109° [corresponding *sulphone*, m.p. 161° (decomp.)]. $(CHPh{:}CH\cdot SO_3)_2Ba$ and PCl_5 give the acid chloride, m.p. 87°, and thence the amide, m.p. 142°, and *Zn β-phenylethylene-α-sulphinate*. *NHPh·NH*$_2$ *β-phenylethylene-α-sulphonate*, m.p. 148°, 2 : 4-*dinitrophenyl styryl sulphide*, m.p. 158°, and *styrylmercurichloride*, m.p. 207°, are described. These results correct those of Ashworth *et al.* (A., 1928, 994). Electronic reaction mechanisms for the addition and substitution are discussed. R. S. C.

Instability of liquid *iso*butene. E. E. ROPER (J. Amer. Chem. Soc., 1938, **60**, 2699—1701).—A liquid, probably a polymeride of relatively high b.p., with f.p. —100° to —120° and n_D^{20} 1·397—1·435, has been isolated from *iso*butene which has been kept for some time. Evidence points to dimerisation as the first step. At 0° this reaction causes a 0·6% lowering of the v.p. of pure *iso*butene. E. S. H.

Reactions in sulphuric acid. Destruction of acetylene.—See A., 1939, I, 33.

Effect of the triple linking on rate of reaction of ω-chlorides with potassium iodide in acetone. —See A., 1939, I, 31.

Influence of structure on the rate of racemisation of organic halogeno-compounds. H. BÖHME [with O. SIERING] (Ber., 1938, **71**, [*B*], 2372—2381; cf. Bodendorf *et al.*, A., 1935, 454).—CHPhMeCl (1 mol.) is completely racemised by $SnCl_4$ (0·001 mol.) in C_6H_6 within a few hr.; the addition of 0·001 mol. of HCl greatly retards racemisation, which is further retarded but not completely inhibited by 0·01 mol. of HCl. The effect is ascribed to the equilibrated production of an additive compound of $SnCl_4$ and HCl. Racemisation is ascribed to the formation of a complex between $SnCl_4$ and CHPhMeCl whereby the distance between C and Cl is increased and the intramol. electrical contrast is increased. The complex therefore dissociates into its ions which are configuratively labile. The alternative possibility of an equilibrium, $CHPhMeCl \rightleftharpoons CHPh{:}CH_2 + HCl$, is shown to be improbable. CHMeEtCl is not racemised by $SnCl_4$ (1 : 1) in C_6H_6 in one day. After several days CHMePrCl is unaffected by $HgCl_2$ in $COMe_2$ or by $SnCl_4$ in C_6H_6. $CH_2{:}CH{\cdot}CHMeCl$ is not racemised by $SnCl_4$ (1 : 0·001 mol.) in C_6H_6 after several hr. but with 0·01 mol. of $SnCl_4$ the change has a half-period of 126 min. The half-period of the action with $HgCl_2$ (1 : 1) is about 77 hr. The effect is more pronounced with $CHMe{:}CH{\cdot}CHMeCl$. $CH_2Ph{\cdot}CHMeCl$ is not racemised by $SnCl_4$. *α-cyclo*Hexylethyl chloride is unchanged by $SnCl_4$ (1 : 0·05) but with $SnCl_4$ (1 : 0·12) the half-period of racemisation is 3 hr. $CHMeCl{\cdot}CO_2Et$, $CO_2H{\cdot}CHCl{\cdot}CH_2{\cdot}CO_2H$, and $CO_2Et{\cdot}CHCl{\cdot}CH_2{\cdot}CO_2Et$ appear unchanged by $SnCl_4$ (1 : 1) after two days. $CHPhCl{\cdot}CO_2Et$ is not racemised by $SnCl_4$ (1 : 1). *Crotyl chloride*, b.p. −2°/18 mm., from crotyl alcohol, C_5H_5N, and PCl_3 at 0°, and *dl-methylvinylmethyl chloride*, b.p. −5°/26 mm., appear new. *(−)-Methylvinylmethyl chloride* has b.p. −5°/26 mm., α −2·52° (*l* = 0·5). H. W.

Complex between nitrobenzene and carbon tetrachloride.—See A., 1939, I, 26.

Primary active amyl halides. F. C. WHITMORE and J. H. OLEWINE (J. Amer. Chem. Soc., 1938, **60**, 2570—2571).—*d*-$CHMeEt{\cdot}CH_2{\cdot}OH$ (I) with $SOCl_2$–C_5H_5N or PBr_3 gives 77% of *d*-$CHMeEt{\cdot}CH_2Cl$, b.p. 50·5—51°/140 mm., $[\alpha]_D^{28\cdot5}$ +1·66°, and 29% of *d*-$CHMeEt{\cdot}CH_2Br$, b.p. 69·6°/140 mm., $[\alpha]_D^{29}$ +3·75°, respectively, reconverted by the Grignard reaction (O_2) into (I) with only 10% of racemisation during the complete cycle. Action of MgI_2 on the *d*-benzoate, b.p. 140·2°/20 mm., gives 17·5% of a largely racemised iodide, b.p. 47·1°/20 mm., $[\alpha]_D^{28}$ +4·84°, from which an active alcohol could not be regenerated. R. S. C.

Active atom in heptachloropropane. C. BRÜCKNER (Österr. Chem.-Ztg., 1938, **41**, 363; cf. A., 1938, II, 254).—Reaction of *n*-C_3HCl_7 with MgMeI can give only $CCl_3{\cdot}CCl{:}CHCl$ (I) + C_2H_6 or $CCl_3{\cdot}CCl{:}CCl_2 + CH_4$. (I) and CH_4 cannot be produced in the same direction. J. W. S.

Action of Grignard reagent on heptachloropropane. M. REBEK and G. MANDRINO (Österr. Chem.-Ztg., 1938, **41**, 363—364; cf. A., 1938, II, 254 and preceding abstract).—Addition of MgMeI (3 mols.) to *n*-C_3HCl_7 (1 mol.), followed by treatment with H_2O, yields a complex mixture of products, including C_3HCl_5, a liquid of higher b.p., about equal vols. of CH_4 and C_2H_6, and traces of MeCl. It is concluded that the reaction takes two courses, probably those suggested by Brückner and by the authors, respectively. Action of MgEtI on *n*-C_3HCl_7 yields C_4H_{10} as the principal gaseous product, whilst C_2HCl_5 reacts with MgMeI (1 mol.) yielding C_3HCl_3 and C_2H_6. J. W. S.

Nitromethane. Potential hazards in use. D. S. MCKITTRICK, R. J. IRVINE, and I. BERGSTEINSSON (Ind. Eng. Chem. [Anal.], 1938, **10**, 630—631).—$MeNO_2$, alone or with $OMe{\cdot}[CH_2]_2{\cdot}OH$, is liable to explode when subjected to high pressure or temp. F. N. W.

Reaction of esters with aluminium *iso*propoxide. R. H. BAKER (J. Amer. Chem. Soc., 1938, **60**, 2673—2675).—*Al* n-, b.p. 280—284°/12 mm., and sec.-*butoxide*, b.p. 165—166°/3 mm., allyloxide (impure), m.p. 145—150°, *n-hexadecoxide*, m.p. 44°, and *ethyleneglycoxide* are obtained by heating $Al(OPr^{\beta})_3$ with $Bu^{\alpha}OAc$, *sec.*-BuOAc, $CH_2{:}CH{\cdot}CH_2{\cdot}OAc$, *n*-$C_{16}H_{33}{\cdot}OAc$, and $(CH_2{\cdot}OAc)_2$, respectively, and allowing the $Pr^{\beta}OAc$ to distil. $Bu^{\gamma}OAc$ gives *Al* iso*propoxide di*-tert.-*butoxide*, m.p. 165—167°, sublimes at 160°/14 mm. $OEt{\cdot}CH_2{\cdot}OAc$ and $Al(OPr^{\beta})_3$ give the products of decomp. of $Al(OPr^{\beta})_2{\cdot}O{\cdot}CH_2{\cdot}OEt$, namely, MeOAc, (?) HCO_2Pr^{β}, EtOAc, $Pr^{\beta}OAc$, and $COMe_2$. R. S. C.

Synthesis of *cis*-Δ$^{\gamma}$-hexenol (natural hexenol). M. STOLL and A. ROUVÉ (Helv. Chim. Acta, 1938, **21**, 1542—1547).—COMeEt and PCl_5 give $CMeEtCl_2$ (yield scarcely 50%) which when dissolved in vaseline and added to $NaNH_2$ in the same medium at 170° gives $CEt{:}CH$. This is dried by distillation over $MgClO_4$ and then over KOH and treated successively with MgEtBr and $(CH_2)_2O$, giving $CH_2Br{\cdot}CH_2{\cdot}OH$ and Δ$^{\gamma}$-*hexinol*, b.p. 65·5—66°/12 mm. This is hydrogenated (colloidal Pd) to cis-Δ$^{\gamma}$-*hexenol*, b.p. 59—61°/12·5 mm. (3 : 5-*dinitrobenzoate*, m.p. 44·5—46°). The 3 : 5-dinitrobenzoate obtained from natural hexenol prepared from its phenylacetate derived from Japanese peppermint oil has m.p. 48—48·5° and does not depress the m.p. of the synthetic product. The two hexenols are very similar but not identical in odour. H. W.

Influence of branched chains on optical activity. Configuration of propyl*tert.*-butylcarbinol. Relation between rotatory power and chemical character. P. G. STEVENS, W. E. HIGBEE, and R. T. ARMSTRONG (J. Amer. Chem. Soc., 1938, **60**, 2658—2660).—The factor controlling [*M*] in carbinols is the chemical effect due to branching of the chain and is paralleled by the amount of rearrangement occurring on dehydration or conversion into the chloride. *d*-$CHMeBu^{\gamma}{\cdot}OH$ (I), b.p. 120°, $[M]_D$ +7·8° (benzoate, $[M]_D$ +93·4°, +86·3° in $CHCl_3$; phthalate, $[M]_D$ +159·7° in $CHCl_3$), and *l*-$CHPr^{\alpha}Bu^{\gamma}{\cdot}OH$ are configuratively related to *d*-$CHMeBu^{\alpha}{\cdot}OH$, but the [*M*] of (I) is abnormally low, as (I) is the first member of its series. d-n-*Propyl*tert.-*butylcarbinol* [ββ-*dimethyl*-n-*hexan*-γ-*ol*], b.p. 74·5—75°/36 mm., $[M]_D$ +55·2°

(almost the max.) [*acetate*, b.p. 73—73·5°/20 mm., $[M]_D^{23}$ +59·3° (max.); *benzoate*, b.p. 117·5—117·8°/4 mm., $[M]_D^{23}$ +19·9° (max.), +20·7° (max.) in $CHCl_3$], is obtained from $MgBu^{\gamma}Cl$ and $Pr^{\alpha}CHO$ and by resolution of its *H phthalate*, $[M]_D$ −8·4° in $CHCl_3$, by strychnine. CHMe:CH·CHBu$^{\gamma}$·OH has max. $[M]_D$ +23·5° and gives a H phthalate, $[M]_D^{23}$ −16·2° in $CHCl_3$. R. S. C.

Periodate oxidation of αβ-glycols.—See A., 1939, I, 32.

α-Alkoxybutadienes. O. Wichterle (Coll. Czech. Chem. Comm., 1938, **10**, 497—509).—β-Chlorobutaldehyde Me_2 acetal and KOH give a small amount of *α-ethoxy-Δ$^{\alpha\gamma}$-butadiene*, b.p. 37—38°/41 mm., which with acraldehyde (I) affords 2(5 ?)-*ethoxy*-Δ^3-*tetrahydrobenzaldehyde*, b.p. 90°/10·7 mm., and with crotonaldehyde yields the 2(5 ?)-*ethoxy*-6-*methyl* compound, b.p. 93—96°/10·5 mm. β-Chlorobutaldehyde Pr^{α}_2 acetal and KOH form a mixture of *α-propoxybutadiene* (III), b.p. 35·5—36·5°/13 mm., *crotonaldehyde Pr^{α}_2 acetal*, b.p. 75—77°/13 mm., and *ααγ-tripropoxybutane*, b.p. 116—118°/13 mm. (I) and (III) give 2(5 ?)-*propoxy*-, b.p. 103—104°/10·8 mm., and (II) and (III) form 2(5 ?)-*propoxy*-6-*methyl*-Δ^3-*tetrahydrobenzaldehyde*, b.p. 112—115°/12 mm. The following are similarly obtained: α-n-*butoxybutadiene*, b.p. 53·5—54·5°/13·2 mm.; *crotonaldehyde Bu^{α}_2 acetal*, b.p. 103—104°/12 mm.; 2(5 ?)-n-*butoxy*-6-*methyl*-Δ^3-*tetrahydrobenzaldehyde*, b.p. 127—129°/13 mm.; α-iso*butoxybutadiene*, b.p. 53—56°/13 mm.; *crotonaldehyde Bu^{β}_2 acetal*, b.p. 103·5—104·5°/12·3 mm.; and 6-*methyl*-2(5 ?)iso*butyl*-Δ^3-*tetrahydrobenzaldehyde*, b.p. 127—130°/13·5 mm. Mol. refractions of the compounds have been determined. F. R. S.

Preparation of the higher aliphatic glycol ethers from crotonaldehyde. R. Kuhn and C. Grundmann (Ber., 1938, **71**, [*B*], 2274—2277; cf. A., 1937, II, 306).—In the presence of alcohols the condensation of crotonaldehyde (I) gives alkoxypolyene aldehydes (II), as dark red to violet, cryst., very sparingly sol. ppts. which belong mainly to the C_{20} series but contain in addition to C_{16} compounds substances derived from 6 or 7 mols. of (I). The solvent is involved in the change. Thus MeOH yields a methoxypolyene aldehyde, hydrogenated to the *glycol ether*, OH·$C_{20}H_{40}$·OMe, m.p. 42—43°; oxidation with CrO_3 leads to methoxy-fatty acids. The colour and position of the absorption bands of (II) proves that the addition of alcohol has not caused any marked interruption in the conjugation of the double linkings. With piperidine acetate as catalyst the best yields are obtained in EtOH and $Bu^{\alpha}OH$; reaction proceeds less favourably in alcohols with an odd no. of C atoms and does not appear to occur in CS_2 or C_6H_6. Comparatively few amines or their salts are efficient as catalysts, the most suitable being piperidine, piperazine, and morpholine, the performance of which depends greatly on the quality. H. W.

Phosphoric oxide as catalyst of the polymerisation of olefines. I. Existence of "benzenedimetaphosphoric acids." F. Jostes and J. Cronjé (Ber., 1938, **71**, [*B*], 2335—2341).—The product obtained by the action of P_4O_{10} on C_6H_6 at 120° does not induce the union of C_6H_6 and Δ$^{\alpha}$-heptene to *n*-heptylbenzene and gives only a small proportion of dimeric heptene. When P_4O_{10} and C_6H_6 are heated at 110—120° according to Giran (A., 1898, i, 407; 1900, i, 147) the product has nearly the same wt. as the original P_4O_{10}; similar observations are made at 200°. Treatment of it (without removal of C_6H_6) with EtOH and neutralisation with BaO appears to give *Ba Et$_2$ pyrophosphate*; the presence of Giran's Ba benzenedimetaphosphate or Ba tetradimetaphosphate is excluded. Contrary to Giran, the action of NH_3 on the product from P_4O_{10} and C_6H_6 does not lead to NH_4 benzenemonodimetaphosphate but probably to a partial *anhydride* of iminopyrophosphoric acid, O:P(OH)$_2$·NH·PO$_2$, which yields a non-hygroscopic *Ba* salt, probably, O:P(OH)$_2$·NH·PO$_3$Ba. The colour produced during the action of P_4O_{10} on C_6H_6 is due to the presence of thiophen. It appears, therefore, that Giran's benzenedimetaphosphoric acids do not exist; this is true also in the cases of PhMe and xylene. Giran's hypotheses on the course of the condensation of olefines and aromatic compounds in presence of P_4O_{10} are therefore irrelevant. H. W.

Reactions of trialkyl phosphates, alkyl acetates, and *tert.*-butyl hypochlorite in the Friedel–Crafts syntheses. N. Berman and A. Lowry (J. Amer. Chem. Soc., 1938, **60**, 2596—2597).—With $AlCl_3$ and C_6H_6, Et_3PO_4 gives PhEt, *Pr^{β}_3 phosphate* (b.p. 122—125°/15—16 mm.) or $Pr^{\beta}OAc$ gives $PhPr^{\beta}$, Bu_3PO_4 or *sec.*-BuOAc gives *sec.*-BuPh, $Bu^{\gamma}OCl$ gives $PhBu^{\gamma}$, and $CHMeBu^{\beta}$·OAc gives $CHPhMeBu^{\beta}$. $Pr^{\beta}OAc$ and $AlCl_3$ at 15—50° react, but $Pr^{\beta}Cl$ was not isolated. R. S. C.

Vinyl halide polysulphones. Peracetic acid as a catalyst for the reaction between sulphur dioxide and olefines. C. S. Marvel and F. J. Glavis (J. Amer. Chem. Soc., 1938, **60**, 2622—2626).—AcO_2H (which may be present in paracetaldehyde) causes reaction of CH_2:CHCl and SO_2 to give an amorphous *polymeride*, $(C_4H_6Cl_2{-}SO_2)_x$, darkens at 135—140°, m.p. 250—275°, which with liquid NH_3 gives, not a cyclic product as usual, but a *substance*, $(C_4H_{12}Cl_2N_2{-}SO_2)_x$, with NH_2Ph gives a *product*, $(C_{10}H_{12}NCl{-}SO_2)_x$, slowly loses SO_2 in boiling dioxan, and is decomposed by hot aq. NaOH, giving a small amount of an *aldehyde*, $(C_3H_5O)_x$ [2 : 4-*dinitrophenylhydrazone*, m.p. 127—129°]. CH_2:CHBr gives similar products. Ascaridole causes formation of a 1 : 1 : 2 *co-polymeride*, m.p. 200—225°, of CH_2:CHCl, Δ$^{\alpha}$-C_5H_{10}, and SO_2, and a 2 : 1 : 2 *co-polymeride*, m.p. about 280—285° (decomp.), of CH_2:CHCl, CPh:CH, and SO_2. Allyl chloride gives a *product*, $(C_3H_4Cl{-}SO_2)_x$, m.p. 185—215°, decomp. 225—275°, in presence of AcO_2H, but CH_2:CH·CH_2Br, CHCl:CCl·CHMeCl, and *n*-C_5H_{11}·CH:CHBr give no polymeride. Cryoscopy of SO_2 and CH_2:CHCl reveals a compound containing 60% of SO_2, but Δ$^{\alpha}$-C_5H_{10}, CHPh:CH_2, and CH_2:CH·$[CH_2]_8$·CO_2H form no compound. R. S. C.

Formation of large ring monosulphides from halogenated sulphides with extended carbon chains. G. M. Bennett and H. Gudgeon (J.C.S., 1938, 1891—1897; cf. A., 1938, II, 200).—The poly-

merisation and ring-closure of ω-halogenoalkyl sulphides, obtained ($SOCl_2$) from the hydroxysulphides derived from glycol chlorohydrins and KSMe, is studied. For ring-closure (observed in C_{14}, C_{14}, and C_{18} compounds), the halogenosulphide was heated at high dilution in a polar solvent; hydroxylic solvents [$Bu^{\alpha}OH$, $(CH_2{\cdot}OH)_2$, PhOH] were discarded as yielding alkoxy- or phenoxy-compounds, and in AcOH reaction was very slow; COPhMe was the most satisfactory. *Me* 7-*hydroxy*-, b.p. 133—134°/10 mm., gives *Me* 7-*chloro-heptyl sulphide*, b.p. 100—102°/3 mm. [*mer.* (= mercurichloride), m.p. 60—61°]. *Me* 8-*hydroxy*-, m.p. 12°, b.p. 135—138°/10 mm., gives *Me* 8-*chloro-octyl sulphide*, b.p. 113—116°/3 mm. (*mer.*, m.p. 75°). *Me* 9-*hydroxy*-, m.p. 22°, b.p. 138—142°/9 mm., gives *Me* 9-*chloro-nonyl sulphide*, b.p. 118—124°/2 mm. (*mer.*, m.p. 60—62°). *Me* 10-*hydroxy*-, m.p. 25°, b.p. 170—172°/13 mm., gives *Me* 10-*chloro-decyl sulphide* (I), b.p. 128—131°/1 mm. (*mer.*, m.p. 75—78°). *Me* 12-*hydroxy*-, m.p. 49°, gives *Me* 12-*chloro-dodecyl sulphide*, m.p. 3—4°, b.p. 140°/1 mm. (*mer.*, m.p. 62—64°). *Me* 14-*hydroxy*- (II), m.p. 38°, gives *Me* 14-*chloro-tetradecyl sulphide* (III), m.p. 13—14°, b.p. 155°/1 mm. (*mer.*, m.p. 66°). *Me* 16-*hydroxy*-, m.p. 54—56°, gives *Me* 16-*chloro-hexadecyl sulphide* (IV), m.p. 22° (*mer.*, m.p. 72—76°). *Me* 18-*hydroxy*-, m.p. 62°, gives *Me* 18-*chloro-octadecyl sulphide* (V), m.p. 31° (*mer.*, m.p. 91—94°). With PBr_5 in C_6H_6, (II) gives *Me* 14-*bromotetradecyl sulphide* (VI) (*mer.*, m.p. 69—70°). When heated in AcOH, (I) is little changed; in $C_2H_2Cl_4$ (VII), a *compound*, $C_6H_2Cl_6$ (1 : 3 : 5-*trichlorobenzene trichloride* ?), m.p. 104—106°, b.p. 90°/10 mm., derived from (VII), is formed. In $(CH_2{\cdot}OH)_2$ (VIII), (I) gives *Me* 10-(β-*hydroxyethoxy*)*decyl sulphide* (*mer.*, m.p. about 60°). In (VII) or (VIII), (II) gives no pure product. With KI in $Bu^{\alpha}OH$, or NaI in boiling PhOH, (II) gives *Me* 14-*butoxy*-, m.p. 60—68°, and 14-*phenoxy-tetradecyl sulphide*, m.p. 46—59°. When boiled in AcOH for 1 day, (VI) gives a small amount of a sulphonium salt, but after 1 week gives *polymeric tetradecamethylene sulphide*, and, after addition of $HgCl_2$, the *mercurichloride*, m.p. 167°, of tetradecamethylene sulphide (IX) (cf. *loc. cit.*). When heated for 24 days in AcOH, (III) gives small quantities of a sulphonium chloride, a substance, m.p. 115—118°, and (IX). The last is obtained most readily from (III) and NaI in boiling COPhMe. MeI formed is removed in vac.; unless this is done, highly polymerised substances are formed during subsequent distillation. Treated similarly, (IV) gives *polymeric hexadecamethylene sulphide*, and, after addition of $HgCl_2$, the *mercurichloride*, m.p. 164—166°, of *hexadecamethylene sulphide*, m.p. 61° (extinction angle, of one of three forms, 5°). Similarly (V) gives a *polymeric sulphide*, m.p. 60—77° (mixed di- and tri-polymerides ?), and the *mercurichloride*, m.p. 121—125°, of *octadecamethylene sulphide*, m.p. 74°, b.p. 186°/16 mm. Chlorosulphides with 7, 8, 9, 10, and 12 C atoms and NaI in COPhMe give no monomeric or H_2O-sol. products, but only di- to tri-polymerides. Higher polymerides are produced by heating without solvent. The cyclic sulphides described have a musk-like odour. E. W. W.

Esters of chlorosulphonic acid. W. W. Binkley with E. F. Degering (J. Amer. Chem. Soc., 1938, 60, 2810—2811).—The b.p., 48·1°/29 mm., 42·3°/10 mm., 53·2°/10 mm., and 69°/10 mm., *d*, and *n* for $ClSO_3R$ (R = Me, Et, Pr^{α}, and Bu^{α}, respectively) (improved prep.) are reported. R. S. C.

Optical crystallographic studies with the polarising microscope. II. Identification of the *p*-bromoanilides of lower aliphatic acids. W. M. D. Bryant and J. Mitchell, jun. (J. Amer. Chem. Soc., 1938, 60, 2748—2751; cf. A., 1938, II, 344).—M.p. (quoted in parentheses) and optical crystallographic data are recorded for Bu^{α} (112·0°), Bu^{β} (155·0°), *n*-valeric (I) (107·1°), *iso*valeric (II) (126·7°), *dl*-α-methylbutyric (III) (122·3°), αα-dimethylpropionic (155·7°), Δ^{α}-butenoic (IV) (116·0°), methoxyacetic (85·3°), and pyruvic (167·8°) *p*-bromoanilides. Metastable, cryst. modifications of (I), (II), (III), and (IV) have been obtained from the molten substances. E. S. H.

Kolbe's synthesis in the electrolysis of butyric acid.—See A., 1939, I, 35.

Reversibility of the reaction between triglycerides and glycerol. H. H. Young, jun., and H. C. Black (J. Amer. Chem. Soc., 1938, 60, 2603—2605).—With boiling glycerol and a trace of Na_3PO_4 trilaurin (I) gives a little α-monolaurin (II); in absence of a catalyst reaction is slower and gives also αα′-dilaurin (III); with Na_2CO_3 (III) is formed. When (I) is distilled at 0·5 mm. (190°), some glycerol and (II) are formed; steam at 2·2 mm. causes the same disproportionation. Only traces of soap are obtained. Similar reactions with palmitins, stearins, ethylene dipalmitate, and $OH{\cdot}[CH_2]_2$ palmitate are described. R. S. C.

Catalytic action of selenium on unsaturated compounds. M. Yokoyama and M. Kotake (J. Chem. Soc. Japan, 1936, 57, 183—186; cf. A., 1935, 829).—Heating oleic acid (I) with 3% of Se at 300° for 3 hr. (also in CO_2 or H_2) caused 70% reduction. The behaviour of elaidic, ricinoleic, linoleic, and erucic acids (II) and the isomerisation of (I) and (II) (with Se at 180°) were also studied. Ch. Abs. (c)

Fatty acids. IV. Purification of linolenic acid by fractional crystallisation of the fatty acids of linseed and perilla oils. Properties of this acid prepared by crystallisation and by debromination. G. Y. Shinowara and J. B. Brown (J. Amer. Chem. Soc., 1938, 60, 2734—2738; cf. A., 1938, II, 82).—Linolenic acid, obtained 84·5—99% pure by crystallisation of the fatty acids of linseed and perilla oils from $COMe_2$ and light petroleum at −23°, −45°, −60°, and −75°, differs slightly in its consts. from α-linolenic acid regenerated from the hexabromide, and is probably a mixture although its m.p. (about −11·5°) is sharp. Determination of the acid by its Br_6 no. is discussed. R. S. C.

Kinetic examination of cyclisation problems and the preparation of lactones. M. Stollet and A. Rouvé (Parfum. mod., 1935, 29, 207—215; Chem. Zentr., 1937, i, 1121).—The lactonisation of ν-hydroxytetradecanecarboxylic acid in presence of $PhSO_3H$ was studied in C_6H_6, PhMe, Et_2O, Bu_2O, and C_2HCl_3. (Monomeric) cyclisation in C_6H_6 is favoured by low concn. of OH-acid, small activation energy, and

increase in temp. (for the unimol. reaction). The quantity of catalyst has no direct influence.
A. H. C.

Aqueous hydrolysis of β-butyrolactone.—See A., 1939, I, 32.

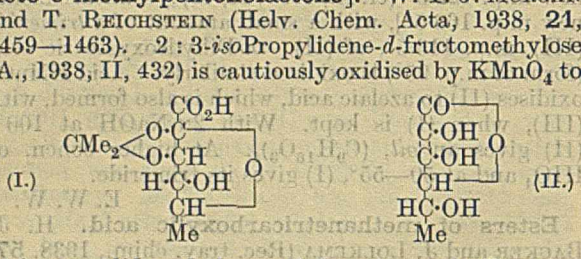
Odour and constitution in the series of deca- and undeca-lactones. M. Stoll and P. Bolle (Helv. Chim. Acta, 1938, **21**, 1547—1553).—Contrary to the experience of Stoll and Rouvé (A., 1937, II, 240) with compounds containing large rings, the double linking does not produce a marked augmentation of the intensity of the odour in the present instances. The odour of the γ-decalactone is considerably modified by the *cis*-double linking and its intensity is somewhat increased by ramification of the chain. Lactones obtained by dehydration with H_2SO_4 which are consequently mixtures of structural and spatial isomerides have more penetrating and less refined odours. Hexyl*cyclo*hexanone is transformed by $K_2S_2O_8$, H_2SO_4, and K_2SO_4 at 0—10° into δ-*hydroxyundecolactone*, b.p. 152—155°/10·5 mm. The Mg derivative from *cis*-hexenyl chloride and iodide in Et_2O transforms $CH_2Ac{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Et$ into γ-*hydroxy-γ-methyl-*Δ^{δ}*-undecenolactone*, b.p. 136·5—137°/8·5 mm., and converts Et β-formylpropionate into γ-*hydroxy-*Δ^{ζ}*-undecenolactone*, b.p. 80—81°/0·08 mm. $CHNa(CO_2Et)_2$ and *cis*-$\Delta^{\beta\zeta}$-nonadienyl chloride afford *Et*$_2$ *nonadienylmalonate*, b.p. 100—101°/0·03 mm., hydrolysed and decarboxylated to $\Delta^{\gamma\eta}$-*undecadienoic acid*, b.p. 104—107°/0·12 mm., which is lactonised by boiling 80% H_2SO_4 to cis-γ-*hydroxy-*Δ^{η}*-undecenolactone*, b.p. 95—98°/0·15 mm., the position of the double linking in which is established by the formation of EtCHO on ozonolysis. $CHNa(CO_2Et)_2$ and *cis*-Δ^{γ}-hexenyl iodide yield *Et*$_2$ cis-Δ^{γ}-*hexenylmalonate*, b.p. 131—133°/8·5 mm., which with $CH_2{:}CH{\cdot}CH_2Br$ affords *Et*$_2$ *allyl*-cis-Δ^{γ}-*hexenylmalonate*, b.p. 144—146°/9 mm., hydrolysed and decarboxylated to α-*allyl-*Δ^{δ}*-octenoic acid*, b.p. 95—96°/0·05 mm.; this is transformed by Fittig's method into γ-*hydroxy-*α-Δ^{γ}-cis-*hexenylvalerolactone*, b.p. 80°/0·18 mm. H. W.

Introduction of substituted vinyl groups. I. *iso*Propenylalkylmalonic esters. A. C. Cope and (Miss) E. M. Hancock (J. Amer. Chem. Soc., 1938, **60**, 2644—2647).—$CMe_2{:}C(CO_2Et)_2$ (prep. described), best with $NaNH_2$ in liquid NH_3, gives $CH_2{:}CMe{\cdot}CNa(CO_2Et)_2$, which with the alkyl halide or sulphate gives *Et*$_2$ *methyl-*, b.p. 110—111°/12 mm., *ethyl-*, b.p. 117—119°/13 mm., *allyl-*, b.p. 122—123°/10 mm., *propyl-*, b.p. 132—133°/17 mm., iso*propyl-*, b.p. 114—116°/10 mm., *butyl-*, b.p. 137—138°/13 mm., iso*butyl-*, b.p. 131—132°/12 mm., n-*amyl-*, b.p. 147—148·5°/12 mm., and iso*amyl-*, b.p. 140—141°/11 mm., -iso*propenylmalonate*. Yields are good for introduction of primary, but moderate for that of *sec.*, alkyl. *n* and *d* are given. With Na in Et_2O much reduction occurs. R. S. C.

Oxidation of θι-dihydroxystearic acids by periodic acid. η-Aldehydo-octoic acid. G. King (J.C.S., 1938, 1826—1828).—θι-Dihydroxystearic acid (form of m.p. 132°) in EtOH is oxidised by KIO_4 in N-H_2SO_4 to nonaldehyde (I) and η-aldehydo-octoic acid (azelaic semialdehyde) (II) [*p*-nitrophenylhydrazone, new m.p. 144°; 2 : 4-dinitrophenylhydrazone, new m.p. 122·5° (cf. A., 1937, II, 48); semicarbazone, new m.p. 166·5°], with a small amount of a *trimeride* (III), m.p. 113·5°, of (II). θι-Dihydroxystearic acid (form of m.p. 95°) is oxidised similarly. Acid $KMnO_4$ oxidises (II) to azelaic acid, which is also formed, with (III), when (I) is kept. With 2N-NaOH at 100°, (II) gives an *oil*, $(C_9H_{16}O_3)_4$. At higher concn. of HIO_4 and at 50—55°, (I) gives its trimeride.
E. W. W.

Esters of methanetricarboxylic acid. H. J. Backer and J. Lolkema (Rec. trav. chim., 1938, **57**, 1234—1248).—The following *diesters* of $CH_2(CO_2H)_2$ (I) are prepared: sec.-*Bu*, b.p. 118°/12 mm.; *Bu*$^{\gamma}$, m.p. −14°, b.p. 101·5—102°/15 mm., from Bu$^{\gamma}$OH–$CH_2(COCl)_2$–$PhNMe_2$ (cf. Gallus and Macbeth, A., 1938, II, 41); *CHEt*$_2$, b.p. 136—137°/11—12 mm.; n-*decyl*, m.p. 17·5—18°, b.p. 216—217°/2·5 mm., from *n*-decyl alcohol, H_2SO_4, and $CN{\cdot}CH_2{\cdot}CO_2K$ at 150° for 3 hr.; *benzyl*, b.p. 187°/1·5—2 mm., from (I), $CH_2Ph{\cdot}OH$, and H_2SO_4 at 120° for 2 hr.; p-*nitrophenyl*, m.p. 202—203° (decomp.), from $CH_2(COCl)_2$ and *p*-$OH{\cdot}C_6H_4{\cdot}NO_2$ (water-bath), or from HNO_3 and $CH_2(CO_2Ph)_2$ at 0° for 10 min.; p-*tolyl*, m.p. 69°. The following *triesters* of *methanetricarboxylic acid* are prepared from the corresponding alkyl-malonate and -chloroformate in PhMe, *e.g.*, $CHNa(CO_2Me)_2$–$ClCO_2Me$ (boil for 4 hr.) afford $CH(CO_2Me)_3$, m.p. 46—47°, b.p. 132°/12 mm. (cf. Scholl and Egerer, A., 1913, i, 588) [*C-Ac* derivative, b.p. 149—150°/11—12 mm.; *C-Bz* derivative, m.p. 83°, b.p. 182—183°/2·5 mm. (cryst. form examined)]; *Pr*$^{\alpha}$ (prepared in Et_2O–C_6H_6), b.p. 160—161°/10 mm. (*Na* derivative); *Pr*$^{\beta}$, b.p. 139—140°/9—10 mm. [*Na* derivative and BzCl at 120° for 3 hr. give the *Bz* derivative, m.p. 88° (cryst. form examined)]; *Bu*$^{\alpha}$, b.p. 147°/1—2 mm., 181—183°/11 mm. (*Na* derivative, m.p. 184°); *Bu*$^{\beta}$ (II), b.p. 143°/2 mm., 171°/10 mm.; sec.-*Bu*, b.p. 139°/2·5 mm.; n-*amyl*, b.p. 173—174°/2 mm. (prepared at 130°), together with some amyl methanetetracarboxylate; iso*amyl* (III), b.p. 175—176°/2·5—3 mm.; *CHEt*$_2$, b.p. 145—146°/2 mm.; n-*decyl* (prepared in xylene), m.p. 14·5—15°, b.p. 208—210°/0·0015 mm.; cyclo*hexyl* (in xylene at 100° for 7 hr.), b.p. 163—164°/0·0004 mm.; the *Me Pr*$^{\beta}_2$ ester, b.p. 106·5—107°/2 mm., is prepared from $CH_2(CO_2Pr^{\beta})_2$ and $ClCO_2Me$ (4 hr. at 100°). (II) and (III) with NaOMe–Et_2O do not give Na derivatives, but afford $CH_2(CO_2Me)_2$ and *iso*butyl and *iso*amyl alcohols respectively; the *n*-amyl ester shows similar partial decomp., although it yields a Na derivative. The *Ph*$_3$ ester, m.p. 168° (HNO_3 at −5° affords the p-*nitrophenyl* ester, m.p. 199—120°), is prepared by the above method (at 80° for 3 hr.), but also from $CHNa(CO_2Ph)_2$–Mg–CCl_4–Et_2O [$OEt{\cdot}Mg{\cdot}CH(CO_2Ph)_2$] and EtOH–$ClCO_2Ph$ and decomp. the $MgCl{\cdot}C(CO_2Ph)_3$ with dil. H_2SO_4; some $CO(OPh)_2$ and $OPh{\cdot}CO{\cdot}OEt$ are formed also (cf. Lund, A., 1934, 869). The latter method is adopted to prepare the *tri*-p-*tolyl*, m.p. 109—110·5°; *Ph*$_2$ *mono*-p-*tolyl*, m.p. 110° [from $CH_2(CO_2Ph)_2$–$ClCO_2{\cdot}C_6H_4Me$-*p*], and *Ph di*-p-*tolyl*, m.p. 109—110° [from $CH_2(CO_2{\cdot}C_6H_4Me$-*p*$)_2$–$ClCO_2Ph$], *methanetricarboxylate*. $OEt{\cdot}Mg{\cdot}CH(CO_2Ph)_2$ and BzCl–Et_2O afford *benzoyldiphenylmalonate*, m.p. 126·5—127·5°. A. T. P.

6-Deoxy-*d*-araboascorbic acid [*d*-erythro-3-keto-6-methylpentonolactone]. W. T. J. MORGAN and T. REICHSTEIN (Helv. Chem. Acta, 1938, **21**, 1459—1463). 2 : 3-*iso*Propylidene-*d*-fructomethylose (A., 1938, II, 432) is cautiously oxidised by $KMnO_4$ to



(I.) (II.)

αβ-*isopropylidene*-d-*glucomethylosonic acid* (I), m.p. 147—148° (corr.), $[\alpha]_D^{24}$ +10·7°±0·5° in H_2O (*K* salt; *Me* ester, m.p. 95—96°). This is converted by EtOH–conc. HCl at 100° into $COMe_2$ and 6-*deoxy*-d-*arabo-ascorbic acid* (II) (*Pb* salt), which is 100—150 times less active than ascorbic acid towards guinea-pigs.

H. W.

Dismutation of the carbonyl oxygen atom of aldehydes and ketones. N. BORGHELLO (Atti R. Ist. Veneto Sci. Lett., 1936, **95**, II, 321—327; Chem. Zentr., 1937, i, 1404).—The view that carbonyl compounds contain, relative to O, a bivalent C united by secondary valencies or co-ordinatively to H and one or two univalent radicals is examined in the light of decomp. experiments. The decomp. of $COMe_2$ and EtCHO over catalysts into CO (180°) and its further conversion into CO_2 and C (>200°) proceeds equally easily so that the secondary linkings are of the same nature in both (cf. spectroscopic evidence, Henri, A., 1935, 10). A. H. C.

Preparation and use of copper-chromium oxide catalysts for dehydrogenations. R. E. DUNBAR (J. Org. Chem., 1938, **3**, 242—245).—Prep. of Cu–Cr_2O_3 on an inorg. support (best "celite," a clay) (a convenient form) and a simple apparatus for its use for the prep. of aldehydes from alcohols are described. 56·7 g. of Pr^aCHO are obtained from 100 g. of Bu^aOH. R. S. C.

Photo-decomposition of aldehydes and ketones. —See A., 1939, I, 35.

Dynamic isomerism of acetaldehyde-2 : 4-dinitrophenylhydrazone. W. M. D. BRYANT (J. Amer. Chem. Soc., 1938, **60**, 2814—2815).—The forms, m.p. 168·5—170° and 156—157°, of $CHMe{:}N{\cdot}NH{\cdot}C_6H_3(NO_2)_2$-2 : 4 (A., 1937, II, 5) are now considered to be dynamic isomerides. When cooled, the melt often gives a (?) equilibrium mixture, m.p. 148°. R. S. C.

β-Chlorobutyric acetals. O. WICHTERLE and I. VAVRECKA (Coll. Czech. Chem. Comm., 1938, **10**, 493—496).—MeOH, HCl, and crotonaldehyde give *β-chlorobutaldehyde Me₂ acetal*, b.p. 55—57°/19 mm.; the Pr^a_2, b.p. 102—104°/13 mm., Bu^γ_2, b.p. 130—131°/17 mm., and Bu^β_2 compounds, b.p. 129—130·5°/16 mm., are similarly prepared. F. R. S.

Oxidation of semiacetals. L. SCHULZ (Schimmel & Co. Ann. Rept., 1938, 119—123).—Mol. proportions of *n*-C_9H_{19}·CHO and BzOH yield with CrO_3, *n*-$C_9H_{19}{\cdot}CO_2Bz$ in 20% yield via the semiacetal; BzOBz is absent since PhCHO forms no semiacetal. *n*-$C_{12}H_{25}$·OH and *n*-C_9H_{19}·CHO give both dodecyl decoate and decyl dodecoate in 50% yield since the semiacetals involved hydrolyse less readily. Semiacetals oxidise less readily than free alcohols and chloral-decylalcoholate gave (solid CrO_3 and C_6H_6) only 1·3% of decyl decoate with 17·7% of decyl trichloracetate. CrO_3 may be replaced by other H-acceptors (peroxides, peracids, etc.) capable of addition to the newly formed dipole of the semiacetals suggested as occurring thus: $OH{\cdot}CHR{\cdot}O{\cdot}CH_2R' + X \rightarrow H{\cdots}X{\cdots}O{\cdot}CHR{\cdot}O{\cdot}CH_2R' \rightarrow O{:}CR{\cdot}O{\cdot}CH_2R' + XH_2$, but experiments to prove this mechanism in which X = R″CHO were only partly successful since ester formation is accompanied by functional interchange. T. F. W.

Enol acylates. H. SCHMIDT (Schimmel & Co. Ann. Rept., 1938, 124—126).—Boiling mol. proportions of the aldehyde and Ac_2O afforded *citral enol acetate*, a limpid oil with odour of geranyl acetate, *citronellal enol acetate*, a colourless oil with fresh odour, b.p. 110°/7mm., iso*decaldehyde enol acetate*, a colourless oil, pleasant odour, and *hydrocinnamaldehyde enol acetate*, a limpid oil, pleasant odour. The action of Ac_2O (2·5 mols.) and 100% H_3PO_4 (1 mol.) on the ketone (1 mol.) at −5° gave *pulegone enol acetate*, mint odour, having α_D +53° 57′, and iso*pulegone enol acetate*, odour of menthyl acetate, α_D +22° 16′; both *l*-menthone, α_D −24°, and *d*-*iso*-menthone, α_D +84°, yield the same *menthone enol acetate* with an odour of menthyl acetate, α_D +64°. Piperitone and carvone yield phenol acetates with the enol acetates; no enol acetates were obtained from aliphatic or aromatic ketones and camphor. Enol acetates of saturated cyclic ketones give with Br and HBr, in most cases, bimol. products with loss of HBr, and catalytic hydrogenation is not possible. With Na and EtOH hydrolysis occurs, followed by reduction of the CO group. T. F. W

Interaction between methylene radicals and hydrogen. C. ROSENBLUM (J. Amer. Chem. Soc., 1938, **60**, 2819—2820).—When irradiated by a "hot" Hg arc, keten gives CO and C_2H_4. Mixtures of keten and H_2, similarly irradiated at 35° and 200°, give 1 and 9·6%, respectively, of CH_4 and large amounts of saturated and polymerised hydrocarbons, indicating the reaction, $CH_2 + H_2 \rightarrow Me + H$. R. S. C.

Bromination of aliphatic ketones. S. V. SHAH and D. G. PISHAWIKAR (Current Sci., 1938, **7**, 182—183).—With an excess of liquid Br (4 days) $COMe_2$ gives a Br_5-, m.p. 72—73°, COMeEt and Ac_2 give Br_2- (m.p. 54° and 94°, respectively), $COEt_2$, $COPr_2$, $COBu^a_2$, $COBu^\beta_2$, and $CO(C_6H_{13})_2$ give Br_3- (b.p. 90—93°/4 mm., 120—123°/4 mm., 121—123°/4 mm., 129—132°/4 mm., and 162—165°/4 mm., respectively), $(CH_2Ac)_2$ gives a Br_8-, m.p. 181°, and $COMeBu^\gamma$ gives a Br_2-derivative, m.p. 69°. The reaction, initially slow, is catalysed by HBr produced. If *x* = no. of H on the C adjacent to CO and *y* = no. of CO in the compound, then *x* − *y* = no. of Br introduced. R. S. C.

Keto-ethers. III. β-Halogenoethoxyethyl alkyl ketone derived from ethylene bromohydrin. H. R. HENZE (J. Org. Chem., 1938, **3**, 287).—Corrections (cf. A., 1938, II, 348). R. S. C.

Steroids and sex hormones. XLVI. Syntheses with αβ-diacetylethylene. M. W. Goldberg and P. Müller (Helv. Chim. Acta, 1938, **21**, 1699—1705).—CHAc:CHAc [improved prep. from $(CH_2Ac)_2$ and SeO_2 (cf. Armstrong and Robinson, A., 1934, 1337)] and CH_2:CMe·CMe:CH_2 in boiling C_6H_6 smoothly give 1 : 2-*diacetyl*-4 : 5-*dimethyl*-Δ^4-cyclo*hexene*, b.p. 135°/10 mm., m.p. 36—37° [*disemicarbazone*, m.p. 214·5° (corr.; decomp.)], slowly converted by boiling 0·1N-NaOMe into 3 : 5 : 6-*trimethyl*-4 : 7 : 8 : 9-*tetrahydroindone*, b.p. 145°/10 mm. [*semicarbazone*, m.p. 222—223° (corr.; decomp.)]. CNaMeAc·CO_2Et and COMe·CH_2Cl in Et_2O at 0° and subsequently at room temp. yield *Et* αβ-*diacetylisobutyrate* (I), b.p. 120—121°/10 mm. *Et* αβ-*diacetyl*-n-*butyrate* (II), b.p. 121—124°/10 mm., is derived similarly from CHNaAc·CO_2Et and COMe·CHBrMe. (III) when preserved and then warmed gives H_2O and *Et* 3-*keto*-2 : 5-*dimethyl*-Δ^4-cyclo*pentenecarboxylate*, b.p. 108°/15 mm., which is not sol. in alkalis and does not give a colour with $FeCl_3$. Hydrolysis of (II) is accompanied by extensive cyclisation whereas (III) is converted by boiling 20% aq. K_2CO_3 into αβ-diacetylpropane, b.p. 73—74°/11 mm. This is transformed by aq. H_2SeO_3 into αβ-*diacetylpropene* [*γ-methyl*-Δ^γ-*propene*-βε-*dione*] (IV), b.p. 83—84°/10 mm., which does not give a colour with $FeCl_3$, and δ-*hydroxy*-*γ*-*methyl*-Δ^γ-*propene*-βε-*dione*, b.p. 135°/15 mm., which rapidly becomes brown on contact with air, gives a violet-red colour with $FeCl_3$, and yields Ac_2 when ozonised. (IV) and CH_2:CMe·CMe:CH_2 afford 1 : 2-*diacetyl*-1 : 4 : 5-*trimethyl*-Δ^4-cyclo*hexene*, b.p. 141°/10 mm. H. W.

Quantitative formation of furfuraldehyde from xylose. E. E. Hughes and S. F. Acree (J. Res. Nat. Bur. Stand., 1938, **21**, 327—336).—Examination of various methods of formation of furfuraldehyde (I) by distillation of xylose with 12% HCl shows that sources of error in determination of xylose by this method are decomp. and volatilisation of (I), effect of rubber stoppers, incompleteness of distillation, formation of (I) from hexuronic acid, and substances other than (I) and methylfurfuraldehyde in the distillate. A 100% yield of (I) is obtained by use of special apparatus with only glass in contact with hot vapours, and with a trap to prevent losses by evaporation from the distillate. 12% HCl saturated with NaCl is used and (I) removed by steam-distillation. J. D. R.

Behaviour of anhydromethylhexosides towards alkaline reagents. Preparation of derivatives of 3-aminoglucose and 2-aminoaltrose. S. Peat and L. F. Wiggins (J.C.S., 1938, 1810—1815).—Further examples are given of hydrolytic fission of a sugar anhydro-ring in two alternative directions. The glucose derivative formed rarely exceeds 10% of the product. 4 : 6-Benzylidene-2 : 3-anhydro-α-methylalloside (A., 1938, II, 349) with dry NH_3–MeOH at 150° gives, after 35 hr., a product, m.p. 162—166°, $[\alpha]_D^{20}$ +119° (all rotations in $CHCl_3$ unless otherwise stated), and after 3 days a mixture acetylated to 4 : 6-*benzylidene*-3-*acetamido*-α-*methylglucoside* 2-*acetate* (I) (1 part), m.p. 270°, $[\alpha]_D^{18}$ +44·6°, and -2-*acetamido*-α-*methylaltroside* 3-*acetate* (10 parts), m.p. 184°, $[\alpha]_D^{18}$ +52·5°. With 0·5% MeOH–HCl at 55°, followed by Ac_2O–NaOAc, (I) gives 3-*acetamido*-α-*methylglucoside triacetate* (II), m.p. 178°, $[\alpha]_D^{20}$ +101·9°, of which the structure is established by prep. by other routes (see below). The mixed 3 : 4-anhydro-α-methylalloside and 3 : 6-anhydro-α-methylglucoside (III) [from the alkaline hydrolysis product of α-methylglucoside triacetate 3-*p*-toluenesulphonate (IV), from which the 2 : 3-anhydromethylalloside is removed as the :CHPh derivative (cf. *loc. cit.*)] with MeOH–NH_3 at 150° give 3-*amino*-α-*methylglucoside*, m.p. 167—168°, $[\alpha]_D^{18}$ +144·4° in H_2O [acetylated to (II)], and (III); the gulose derivative, presumably also formed, was not isolated. The hydrolysis product of β-methylglucoside triacetate 3-*p*-toluenesulphonate, freed as before from the 2 : 3-anhydro-β-methylglucoside, and thus containing the 3 : 4-anhydro-β-methylalloside, gives with MeOH–NH_3 3-amino-β-methylglucoside (hydrochloride, new m.p. 185°, new $[\alpha]_D^{20}$ −35° in H_2O), which with Ac_2O–NaOAc yields 3-*acetamido*-β-*methylglucoside triacetate*, m.p. 160°, $[\alpha]_D^{18}$ −21·4°, converted by 2% MeOH–HCl into (II). With MeOH–NH_3 at 150°, (IV) gives (II), which with 6% HCl gives 3-aminoglucose (4-methylgulose not isolated), and with Me_2SO_4–NaOH–CCl_4 gives 3-*acetamido*-2 : 4 : 6-*trimethyl*-α-*methylglucoside*, m.p. 156° (decomp.), $[\alpha]_D^{17}$ +131·1°. With MeOH–NH_3 at 130°, dimethyl-3 : 4-anhydro-β-methylalloside (*loc. cit.*) gives 3-*acetamido*-2 : 6-*dimethyl*-β-*methylglucoside* 4-*acetate*, m.p. 142°, $[\alpha]_D^{21}$ −50·9°, which with Me_2SO_4–NaOH–CCl_4 forms 3-*acetamido*-2 : 4 : 6-*trimethyl*-β-*methylglucoside*, m.p. 134—135°, $[\alpha]_D^{21}$ −82·9°. Dimethyl-2 : 3-anhydro-β-methylalloside (V) with 5% MeOH–NaOMe gives 3 : 4 : 6-trimethyl-β-methylglucoside (5%) and 2 : 4 : 6-*trimethyl*-β-*methylaltroside*, a syrup (66%) (hydrolysed to 2 : 4 : 6-altrose, new $[\alpha]_D^{18}$ +38·2°). With 5% aq. KOH, (V) yields 4 : 6-*dimethyl*-β-*methylaltroside*, m.p. 118°, $[\alpha]_D^{19}$ −49·3°, further hydrolysed to 4 : 6-dimethylaltrose. 4 : 6-Benzylidene-2 : 3-anhydro-β-methylalloside and boiling 5% MeOH–NaOMe give 4 : 6-*benzylidene*-3-*methyl*-β-*methylglucoside* (VI) (12%), m.p. 166°, $[\alpha]_D^{17}$ −46·0°, and -2-*methyl*-β-*methylaltroside* (72%), m.p. 127—129°, $[\alpha]_D^{18}$ −48·0°. The glucosidic character of (VI) is shown by its giving, with Purdie's reagents, 4 : 6-benzylidene-2 : 3-dimethyl-β-methylglucoside. With aq. KOH, dimethyl-2 : 3-anhydro-β-methylalloside gives 4 : 6-*dimethyl*-β-*methylaltroside*, m.p. 118°, $[\alpha]_D^{19}$ −49·3° (from which a cryst. 4 : 6-dimethylaltrose was not obtained by acid hydrolysis), and 4 : 6-dimethyl-β-methylglucose. E. W. W.

Syntheses with 5 : 6-anhydro*iso*propylideneglucose. VII. Glucose 6-phenyl ether. H. Ohle, E. Euler, and R. Voullième (Ber., 1938, **71**, [*B*], 2250—2259).—5 : 6-Anhydro*iso*propylideneglucose (I) and PhOH in presence of a trace of C_5H_5N at 110° give *isopropylideneglucose* 6-*Ph ether* (II) (+1H_2O), m.p. 61—62°, $[\alpha]_D^{21}$ −2·81° in $CHCl_3$, $[\alpha]_D^{20}$ −11·17° in MeOH, −11·9° in 50% AcOH [*diacetate* (III), m.p. 109°, $[\alpha]_D^{20}$ −10·16° in $CHCl_3$, −10·07° in AcOH; non-cryst. *dibenzoate*; 3 : 5-*di*-p-*toluenesulphonate*, m.p. 131°, $[\alpha]_D^{20}$ +29·62° in $CHCl_3$]. (II) is converted by $COMe_2$–$CuSO_4$–H_2SO_4 into iso*dii*so*propylideneglucose* 6-*Ph ether*, m.p. 133°, $[\alpha]_D^{20}$ +31·40° in $CHCl_3$. 50% AcOH at 100° hydrolyses (II) to

α-*glucose* 6-*Ph ether* (III), m.p. 180°, $[\alpha]_D^{18}$ +140·5° to +88·32° in C_5H_5N in 6 days, $[\alpha]_D^{20}$ +63·85° in H_2O–C_6H_5N (1 : 1) (equilibrium after 2 min.); the *phenylhydrazone* is resinous whereas the *phenylosazone* has m.p. 174°, $[\alpha]_D^{19}$ −125·4° to −73·4°. (III) and Ac_2O in C_5H_5N at −10° and then at 37° yield a mixture from which α-*glucose* 6-*Ph ether* 1 : 2 : 3 : 4-*tetra-acetate*, m.p. 127°, $[\alpha]_D^{20}$ +117·4° in $CHCl_3$, is isolated. The mixture is transformed by HBr–AcOH at 20° into α-1-*bromoglucose* 6-*Ph ether* 2 : 3 : 4-*triacetate*, m.p. 93—94°, $[\alpha]_D^{20}$ +204° in $CHCl_3$, converted by AgOAc in AcOH into β-*glucose* 6-*Ph ether* 1 : 2 : 3 : 4-*tetra-acetate*, m.p. 142·5°, $[\alpha]_D^{24}$ +28·37° in $CHCl_3$, and by Ag_2CO_3 in boiling MeOH into β-*methylglucoside* 6-*Ph ether* 2 : 3 : 4-*triacetate*, m.p. 122—123·5°, $[\alpha]_D^{21·5}$ −2·66° in $CHCl_3$; the latter compound is hydrolysed by NH_3–MeOH at 20° to β-*methylglucoside* 6-*Ph ether*, m.p. 135—136°, $[\alpha]_D^{21}$ −16·88° in $COMe_2$, also obtained by direct glucosidification of (IV). (III) and boiling 50% AcOH give a mixture of the α- and β-forms of *glucose* 6-*Ph ether* 3 : 5-*diacetate*. (I) and *p*-C_6H_4Br·OH give iso*propylideneglucose* 6-p-*bromophenyl ether*, m.p. 63°, $[\alpha]_D^{20}$ −4·64° in $CHCl_3$, hydrolysed by boiling 50% AcOH to α-*glucose* 6-p-*bromophenyl ether*, m.p. 166°, $[\alpha]_D^{20}$ +91·36° to +58·18° in C_5H_5N in 92 hr. [*phenylosazone*, m.p. 200—201° (decomp.); $[\alpha]_D^{20}$ −101·94° to −55·80° in C_5H_5N]. The mixture of stereoisomeric *glucose* 6-p-*bromophenyl ether tetra-acetates*, m.p. 119·5—122°, becoming transparent at 127°, is converted by HBr–AcOH into α-1-*bromoglucose* 6-p-*bromophenyl ether* 2 : 3 : 4-*triacetate*, m.p. 140—141°, $[\alpha]_D^{20}$ +169·7° in $CHCl_3$, whence (Ag_2CO_3 in boiling MeOH) β-*methylglucoside* 6-p-*bromophenyl ether* 2 : 3 : 4-*triacetate*, m.p. 142·5°, $[\alpha]_D^{20}$ +3·02° in $CHCl_3$. *p*-OH·C_6H_4·OBz at 160° gives iso*propylideneglucose* 6-p-*benzoyloxyphenyl ether*, m.p. 166°, $[\alpha]_D^{18}$ −2·50° in $CHCl_3$ (3 : 5-*diacetate*, m.p. 166°, $[\alpha]_D^{20}$ −15·83° in $CHCl_3$). *o*-NO_2·C_6H_4·OH at >140° without catalyst yields iso*propylideneglucose* 6-*o*-*nitrophenyl ether*, m.p. 105°, or (+0·5H_2O) m.p. 98—99°, $[\alpha]_D^{19}$ +7·16° in $CHCl_3$, but cryst. compounds could not be obtained from *m*- or *p*-NO_2·C_6H_4·OH. β-$C_{10}H_7$·OH at 140° affords iso*propylideneglucose* 6-β-*naphthyl ether*, m.p. 116—117°, $[\alpha]_D^{19}$ −80° in $CHCl_3$ (3 : 5-*diacetate*, m.p. 131—132°, $[\alpha]_D^{19}$ −12·55° in $CHCl_3$), whence α-*glucose* 6-β-*naphthyl ether*, m.p. 170—171°, $[\alpha]_D^{19}$ +98° (const.) in C_5H_5N, $[\alpha]_D^{19}$ +88° to +59° in C_5H_5N–H_2O (95 : 5) in 4 hr. [*phenylhydrazone*, m.p. 165°, $[\alpha]_D^{19}$ −8·75° in C_5H_5N–EtOH (4 : 6); *phenylosazone*, m.p. 187°, $[\alpha]_D^{19}$ −109·7° to −103·9° in C_5H_5N–EtOH (4 : 6) in 30 min.]. α-*Glucose* 6-β-*naphthyl ether* 1 : 2 : 3 : 4-*tetra-acetate*, m.p. 162°, $[\alpha]_D^{19}$ +107·5° in $CHCl_3$, is transformed by HBr–AcOH at 20° into α-*bromoglucose* 6-β-*naphthyl ether* 2 : 3 : 4-*triacetate*, m.p. 141° [α_D^{20} +177·0° in $CHCl_3$. This is converted by C_5H_5N and Ag_2SO_4 into the *pyridinium sulphate*, $C_{49}H_{52}O_{20}NS$, m.p. 151°, $[\alpha]_D^{20}$ +14·23° in $CHCl_3$, by AgOAc in AcOH into β-*glucose* 6-β-*naphthyl ether* 1 : 2 : 3 : 4-*tetra-acetate*, m.p. 165—166°, $[\alpha]_D^{20}$ +28·5° in $CHCl_3$, and by Ag_2CO_3 and boiling MeOH into β-*methylglucoside* 6-β-*naphthyl ether* 2 : 3 : 4-*triacetate*, m.p. 151°, $[\alpha]_D^{20}$ +6·0° in $CHCl_3$. H. W.

Synthesis of 2 : 4 : 6-trimethylglucose and its relationship to yeast glucan. K. Freudenberg and E. Plankenhorn (Annalen, 1938, **536**, 257—266).—3-Benzyldi*iso*propylideneglucose is converted into 3-benzylglucose and thence by Ac_2O and C_5H_5N at 30° into β-3-*benzylglucose* 1 : 2 : 4 : 6-*tetra-acetate* (I), m.p., 107°, $[\alpha]_D^{20}$ −1·23° in $CHCl_3$. This is hydrogenated (Pd–C in AcOH) to β-*glucose* 1 : 2 : 4 : 6-*tetra-acetate*, m.p. 127°, $[\alpha]_D^{20}$ −13·5° in $CHCl_3$ (whence β-glucose penta-acetate and 1 : 2 : 4 : 6-tetra-acetate 3-*p*-toluenesulphonate, m.p. 174°), and converted in presence of Pt into β-3-*hexahydrobenzylglucose* 1 : 2 : 4 : 6-*tetra-acetate*, m.p. 123°, $[\alpha]_D^{20}$ +1·1° in $COMe_2$. Repeated methylation of (I) in $COMe_2$ by 50% KOH and Me_2SO_4 at room temp. and then at 50° gives 3-*benzyl*-2 : 4 : 6-*trimethyl*-αβ-*methylglucoside* (II), b.p. 149°/0·4 mm., $[\alpha]_D^{20}$ +43·50° in EtOH (separation of α- and β-forms not attempted), from which by hydrolysis (5% HCl–MeOH at 70°) 3-*benzyl*-2 : 4 : 6-*trimethylglucose*, m.p. 127—128°, $[\alpha]_D^{20}$ +54·6° in $CHCl_3$, is obtained. With Na at 100° (II) gives 2 : 4 : 6-trimethyl-β-methylglucoside, m.p. 70—71°, $[\alpha]_D^{20}$ −19·3° in H_2O (whence 2 : 4 : 6-*trimethyl*-β-*methylglucoside* 3-p-*toluenesulphonate*, m.p. 104°, $[\alpha]_D^{20}$ −47·45° in $CHCl_3$), hydrolysed (5% HCl at 100°) to 2 : 4 : 6-trimethylglucose, m.p. 123°, $[\alpha]_D^{20}$ +108° in MeOH, identical with the products of Haworth and Sedgwick (A., 1926, 1228) and Zechmeister and Tóth (A., 1934, 810). The following compounds are incidentally described: 3-*benzylglucose* 1 : 2 : 4 : 6-*tetrabenzoate*, m.p. 203°, $[\alpha]_D^{20}$ +8·6° in $CHCl_3$; 3-*nitrobenzylglucose* 1-*nitrate* 2 : 4 : 6-*triacetate*, m.p. 116°, $[\alpha]_D^{20}$ +80·0° in $CHCl_3$, from (I) and fuming HNO_3 in $CHCl_3$; 3-*hexahydrobenzyl*-1 : 2-*acetonylglucose* 5 : 6-*diacetate*, m.p. 66°, $[\alpha]_D^{20}$ −21·1° in $CHCl_3$, by hydrogenation (Pt sponge in AcOH) of the corresponding 3-CH_2Ph compound; 3-*benzyl*-6-*triphenylmethylglucose* 1 : 2 : 4-*triacetate* (mixture of isomerides), m.p. 200° after softening at 145°, $[\alpha]_D^{20}$ +50·3° in $CHCl_3$; *dimethylanhydro*-β-*methylhexoside*, b.p. 85°/0·1 mm., m.p. 47—48°, $[\alpha]_D^{20}$ −158·0° in H_2O, by methylation of β-methylglucoside triacetate 3-*p*-toluenesulphonate (III) with NaOH and Me_2SO_4; *anhydro*-β-*methylhexoside diacetate*, liquid, $[\alpha]_D^{20}$ −120° in $CHCl_3$, by the successive treatment of (III) with NaOEt in $CHCl_3$ and Ac_2O in C_5H_5N; 3 : 6-*anhydro*-β-*methylglucoside* 2 : 4-*diacetate*, m.p. 78—79°, $[\alpha]_D^{20}$ −107° in $CHCl_3$.

H. W.

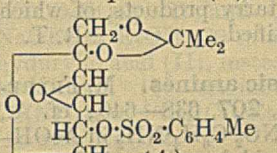
Acetone [*iso*propylidene] derivatives of the sugars and their transformations. XXII. New conversion of *iso*propylideneglucose into 3 : 6-anhydroglucose. Stereochemistry of ethylene oxides. H. Ohle and H. Wilcke [with, in part, K. Tessmar] (Ber., 1938, **71**, [*B*], 2316—2327).—Addition to ethylene oxides occurs in three phases. The first consists of the union by the adding ions at the ends of the dipole of the mols., the second in the fission of a C·O· linking of the ethylene oxide ring to the zwitterion which in the third phase reacts with the adding ions. The first and third phases are, as ionic reactions, instantaneous and involve liberation of energy whereas the second requires energy and controls the rate of reaction. If the oxide contains no other polar group and the space fulfilment of the substituents permits an adequate approach of the adding ions to one of the two C atoms

of the ethylene oxide ring in the direction of its dipole, addition is invariably accompanied by Walden inversion. If other polar groups are present their mutual influence changes the position of the dipole moment of the ethylene oxide group and the orientation of the adding ions is determined by the total moment of the mol. resulting from the combination of the individual moments. In these circumstances the addition of the anion can occur without Walden inversion and prediction of the course of addition is impossible.

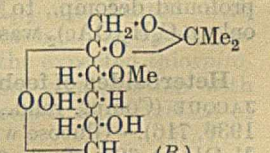
*iso*Propylideneglucose 5 : 6-diacetate 3-*p*-toluenesulphonate is hydrolysed by N-NaOH in boiling $COMe_2$ to *iso*propylideneglucose (I) in 83% yield; formation of an inner ether cannot be detected. Gradual addition of N-KOH to β-methylglucofuranoside 2 : 5 : 6-triacetate 3-*p*-toluenesulphonate in boiling aq. $COMe_2$ gives 3 : 6-*anhydro*-β-*methylglucofuranoside*, b.p. 141—142°/0·08 mm., m.p. 98°, $[\alpha]_D^{20}$ −49·5° in H_2O (2 : 5-*dibenzoate*, m.p. 99°, $[\alpha]_D^{20}$ +2·8° in $CHCl_3$; 2 : 5-*di*-p-*toluenesulphonate*, m.p. 130·5°, $[\alpha]_D^{20}$ +55·7° in $CHCl_3$); it is hydrolysed by 0·03N-H_2SO_4 at 100° to 3 : 6-anhydroglucose, m.p. 110°, $[\alpha]_D^{20}$ +49·1° in H_2O. *iso*Propylideneglucose 5 : 6-dibenzoate 3-*p*-toluenesulphonate is transformed by HBr–AcOH followed by addition of Et_2O into 1-*bromo*-β-*glucofuranose* 2-*acetate* 5 : 6-*dibenzoate* 3-p-*toluenesulphonate*, m.p. (indef.) 123—135°, $[\alpha]_D^{20}$ −101° in $CHCl_3$. Gradual addition of N-KOH to a boiling solution of β-methylglucofuranoside 2-acetate 5 : 6-dibenzoate 3-*p*-toluenesulphonate in aq. $COMe_2$ leads mainly to the non-cryst. 2 : 3-*anhydro*-β-*methyl*-α-*allofuranoside* 5 : 6-*dibenzoate*, $[\alpha]_D^{20}$ −96·2° in EtOH, hydrolysed by boiling 2N-NaOH to 3 : 6-anhydro-β-methylglucofuranoside, m.p. 98°, $[\alpha]_D^{20}$ −49·6° in H_2O. (I) and *p*-$C_6H_4Me{\cdot}SO_2Cl$ in C_5H_5N–$CHCl_3$ at 40° give *iso*propylideneglucose tri-*p*-toluenesulphonate, m.p. 129°, $[\alpha]_D^{20}$ −5·4° in $CHCl_3$. Titration of β-methylglucofuranoside 2-acetate 3 : 5 : 6-tri-*p*-toluenesulphonate in boiling $COMe_2$ with N-NaOH (phenolphthalein) affords 2 : 3-*anhydro*-β-*methylallofuranoside* 5 : 6-*di*-p-*toluenesulphonate*, m.p. 115·5—116°, $[\alpha]_D^{20}$ −26·3° in $CHCl_3$, in 78% yield. Under similar conditions β-methylglucofuranoside 2-acetate 6-benzoate 3 : 5-di-*p*-toluenesulphonate yields 2 : 3-*anhydro*-β-*methylallofuranoside* 6-*benzoate* 5-p-*toluenesulphonate*, m.p. 111°, $[\alpha]_D^{20}$ −45·0° in $CHCl_3$, in 66% yield. Hydrolysis of the pyroid β-methylglucoside 2 : 4 : 6-triacetate 3-*p*-toluenesulphonate (II) appears to give exclusively 3 : 4-anhydromethylalloside or a transformation product thereof. (II) is converted by $TiCl_4$ in $CHCl_3$ into α-*methylglucopyranoside* 2 : 4 : 6-*triacetate* 3-p-*toluenesulphonate*, m.p. 95—96° $[\alpha]_D^{20}$ +84·1° in $CHCl_3$.

H. W.

Acetone [*iso*propylidene] derivatives of the sugars and their transformations. XXI. Transformation of 1 : 2-*iso*propylidene-β-*d*-fructose into 3-methyl-*d*-sorbose. Stereochemistry of the ethylene oxides. H. Ohle and C. A. Schultz (Ber., 1938, **71**, [*B*], 2302—2315; cf. A., 1935, 735).—1 : 2-*iso*Propylidene-β-*d*-fructose 3-benzoate (I), m.p. 197—199°, $[\alpha]_D$ −151·8°, is obtained in 90—95% yield by the action of 80% AcOH at 40° on 1 : 2 : 4 : 5-di*iso*propylidene-β-*d*-fructose 3-benzoate, into which it is re-converted by $COMe_2$ containing $CuSO_4$. 1 : 2-*iso*Propylidene-β-*d*-fructose 3-acetate (II), m.p. 152—153°, is best prepared (yield 70%) from the 1 : 2 : 4 : 5-di*iso*propylidene compound and 0·33N-H_2SO_4 in $Pr^{\beta}OH$ at 40°. (I) and *p*-$C_6H_4Me{\cdot}SO_2Cl$ in C_5H_5N at 40° slowly yield 1 : 2-iso*propylidene*-β-d-*fructose* 3-*benzoate* 4 : 5-*di*-p-*toluenesulphonate* (III), m.p. 164—165° (subsequent decomp.), $[\alpha]_D^{20}$ −175·0° in $CHCl_3$, from which a monotoluenesulphonate could not be prepared conveniently. 1 : 2-iso*Propylidene*-β-d-*fructose* 3-*acetate* 4 : 5-*di*-p-*toluenesulphonate*, prepared similarly, has m.p. 127—128°, $[\alpha]_D^{24}$ −119·5° in $CHCl_3$. 1 : 2-iso*Propylidene*-β-d-*fructose* 3-*benzoate* 4 : 5-*di*-2′-*naphthalenesulphonate*, decomp. about 150°, $[\alpha]_D^{21}$ −121·2° in $CHCl_3$, is described. (II) and 2-$C_{10}H_7{\cdot}SO_2Cl$ (in suitable proportion) in C_5H_5N at about 40° give 1 : 2-iso*propylidene*-β-d-*fructose* 3-*acetate* 4 : 5-*di*-2′-*naphthalenesulphonate*, m.p. 132—133°, $[\alpha]_D^{20}$ −100° in $CHCl_3$. Reduction of the relative amount of 2-$C_{10}H_7{\cdot}SO_2Cl$ permits the isolation of (after subsequent acetylation) 1 : 2-iso*propylidene*-β-d-*fructose* 3 : 5-*diacetate* 4-2′-*naphthalenesulphonate* (IV), m.p. 142·5—143°, $[\alpha]_D^{22}$ −116·1° in $CHCl_3$, and 1 : 2-iso*propylidene*-β-d-*fructose* 5-*acetate* 3-*benzoate* 4-2′-*naphthalenesulphonate*, m.p. 135—136°, $[\alpha]_D^{20}$ −160·0° in $CHCl_3$. Attempts to remove the Bz group catalytically or with a mol. amount of NaOMe from (IV) were unsuccessful but it is converted by the gradual addition of N-NaOH to it in EtOH into 3 : 4-*anhydro*-1 : 2-iso*propylidene*-β-d-*tagatose* 5-p-*toluenesulphonate* (*A*), m.p. 117—118°, $[\alpha]_D^{25}$ −27·0°



(*A*.)



(*B*.)

in $CHCl_3$. (IV) is converted by the successive action of NaOMe and Ac_2O–C_5H_5N into 3 : 4-*anhydro*-1 : 2-iso*propylidene*-β-d-*tagatose* 5-*acetate* (V), m.p. 80—81°, $[\alpha]_D^{23}$ −28·6° in $CHCl_3$, whence 3 : 4-*anhydro*-1 : 2-iso*propylidene*-β-d-*tagatose*, m.p. 81—82°, $[\alpha]_D^{20}$ −80·7° in $CHCl_3$, $[\alpha]_D^{22}$ −60·0° in H_2O, which is hydrolysed by 0·1N-H_2SO_4 to 3 : 4-*anhydro*-β-d-*tagatose*, m.p. 142—145° (subsequent decomp.), $[\alpha]_D^{20}$ −56·0° to +16·8° in H_2O in 21 hr. (V) is transformed by Ac_2O, AcOH, and C_5H_5N at 100° into 1 : 2-*iso*propylidene-β-d-fructose triacetate, m.p. 98·5—99·5°, $[\alpha]_D^{20}$ −135·7° in EtOH, and converted by NaOMe in boiling MeOH into 3-*methyl*-1 : 2-iso*propylidene*-β-d-*sorbose* (*B*), m.p. 121—122°, $[\alpha]_D^{20}$ −66·3° in EtOH [with (?) 4-*methyl*iso*propylidenefructose*, b.p. 129—131°/0·08 mm., $[\alpha]_D^{20}$ −98·7° in EtOH], which is transformed with difficulty into the *Me*$_3$ *ether*, b.p. 99—101°/0·2 mm., $[\alpha]_D^{20}$ −59·6° in H_2O. 3-*Methyl*-d-*sorbose* has m.p. 152—153°, $[\alpha]_D^{20}$ −28·3° in H_2O. 3 : 4-*Anhydro*-1 : 2-iso*propylidene*-β-d-*tagatose* 5-2′-*naphthalenesulphonate*, decomp. 140°, $[\alpha]_D^{22}$ −38·7° in $CHCl_3$, is described. The fission of the syrupy iso*propylidene*-*fructose* 3-*acetate* *mononaphthalenesulphonate* is discussed.

H. W.

Tritylation of α-*l*-sorbose. Y. Khouvine and F. Valentin (Compt. rend., 1938, **207**, 636—638).—

α-*l*-Methylsorboside with CPh_3Cl in C_5H_5N, followed by AcCl in C_5H_5N, affords 1-*triphenylmethyl*-α-l-*methylsorboside* 3 : 4 : 5-*triacetate*, m.p. (block) 185°, $[\alpha]_{5578}^{20}$ +76·8° in C_6H_6, converted by AcOH–HBr into α-l-*methylsorboside* 3 : 4 : 5-*triacetate*, m.p. (block) 81°. 1 : 6-Ditriphenylmethyl-2 : 3-*iso*propylidene-α-*l*-sorbofuranose 4-acetate (cf. Ohle, A., 1938, II, 173) treated as above affords 2 : 3-iso*propylidene*-α-l-*sorbofuranose* 4-*acetate*, m.p. (block) 100°, $[\alpha]_{578}^{20}$ +23·0° in $CHCl_3$. 2 : 3 : 4 : 6-Di*iso*propylidene-α-*l*-sorbofuranose with CPh_3Cl affords 1-*triphenylmethyl*-2 : 3 : 4 : 6-*di*iso-*propylidene*-α-l-*sorbofuranose*, m.p. (block) 182°, $[\alpha]_{578}^{20}$ −29·6° in $CHCl_3$. J. L. D.

Thermal decomposition of certain glucosides. Z. Jerzmanowska and S. Kłosówna (Rocz. Chem., 1938, **18**, 234—244).—Hyperin [from *Hypericum perf.*; identical with Sando's 3-galactosidylquercetin (A., 1937, II, 206)] and Ac_2O (2 hr. at the b.p.) yield *hyperin octa-acetate*, amorphous, m.p. 100—105°. This, when heated at 200°/0·001 mm., yields 2-hydroxy-*d*-galactal tetra-acetate and quercetin 5 : 7 : 3′ : 4′-tetra-acetate (I), m.p. 159—160°. Quercetin hepta-acetate decomposes analogously, at 250°/0·001 mm., to yield (I) and 2-*hydroxy*-l-*rhamnal triacetate*, m.p. 74°, $[\alpha]_D^{20}$ +65° in $CHCl_3$. The thermal decomp. of phloridzin hepta-acetate proceeds differently, the products being β-glucose penta-acetate and 5-*hydroxy*-7-*acetoxy*-4-[β-(4′-*acetoxyphenyl*)*ethyl*]*coumarin*, m.p. 120—121°. Arbutin acetate distils unchanged at 200—250°/10 mm., whilst at higher pressures it undergoes profound decomp., to yield tarry products, of which only *p*-$C_6H_4(OAc)_2$ was identified. R. T.

Heterosides of feebly basic amines. M. Frère-Jacque (Compt. rend., 1938, **207**, 638—640; cf. A., 1936, 716).—Glucose with *p*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$ in AcOH–MeOH at 60° affords β-*glucosidyl*-p-*nitroanilide*, m.p. about 175° (*Ac*$_4$, m.p. ~155°, and *Ac*$_5$, m.p. ~161°, derivatives). The following are prepared similarly: β-*mannosidyl*-, m.p. ~209° (*Ac*$_4$ derivative, m.p. ~184°), β-*galactosidyl*-, m.p. ~203° (*Ac*$_4$ and *Ac*$_5$ derivatives, m.p. indefinite and ~140°, respectively), and β-*rhamnosidyl*-, m.p. ~208° (*Ac*$_3$ derivative, m.p. ~209°), -p-*nitroanilide*; β-*glucosidyl*-, m.p. ~175° (*Ac*$_4$ derivative, m.p. ~136°), β-*mannosidyl*-, m.p. ~199°, and β-*rhamnosidyl*-, m.p. ~150°, m-*nitroanilide*; β-*mannosidyl*-o-*nitroanilide*, m.p. ~196° (*Ac*$_4$ derivative, m.p. ~126°). Vals. for $[\alpha]_D^{20}$ are listed. Solutions of the above compounds in C_5H_5N or H_2O are not mutarotatory. The heterosides with cold Ac_2O–C_5H_5N afford Ac$_3$ or Ac$_4$ derivatives; in the presence of $ZnCl_2$ at 100°, Ac$_5$ derivatives are formed. J. L. D.

Hemicelluloses from cottonseed hulls. E. Anderson, J. Hechtman, and M. Seeley (J. Biol. Chem., 1938, **126**, 175—179; cf. A., 1932, 47).—By fractional pptn. and chlorination or bromination of the unknown impurity (I), white hemicelluloses are obtained from cottonseed hulls in two fractions, having 1 mol. of *d*-glucuronic acid (II) combined with 10 and 15 mols. of *d*-xylose. In the unhalogenated products, (I) and (II) bear a const. ratio. A. Li.

Macromolecular compounds. CCII. Oxidative degradation of celluloses in phosphoric acid. H. Staudinger and I. Jurisch (Ber., 1938, **71**, [*B*], 2283—2289).—The viscosity of solutions of cellulose (I) in H_3PO_4 is determined before and after addition of so much $KMnO_4$ as is necessary to cause fission of the mol. of (I) to half its degree of polymerisation. The amount of O required for this purpose does not depend greatly on the type of (I) and is somewhat greater for the more highly polymerised than for the somewhat degraded products. Marked chemical change is caused in 7·5 g. of (I) by 1 mg. of O. Since the amount of (I) is not appreciably altered by degradation it follows that O attacks the glucose residues within the chain and not at the ends. Possibly the thread mols. of (I) are not quite uniformly constructed and at certain points possess reactive groups which the oxidising agent attacks with particular readiness. H. W.

Structure of cellulose ethers obtained by the methylation of cellulose materials dispersed in quaternary ammonium bases. J. Compton (J. Amer. Chem. Soc., 1938, **60**, 2823).—Dispersions of wood pulp or viscose rayon in $(CH_2Ph)_2NMe_2{\cdot}OH$ with Me_2SO_4 gives a product (I) (OMe 12—16%), converted by Ac_2O–C_5H_5N and subsequent heating with MeOH at 125° in 30—35% yield into α- (mainly) and β-methylglucoside and a syrup, which with Ac_2O–C_5H_5N gives methyltrimethylglucoside acetate, methyldimethylglucoside diacetate, α-methyl-2-methylglucoside triacetate, and β-methylglucoside tetra-acetate. Acetolysis of (I) gives 5% of cellobiose octa-acetate. (I) is thus similar to the product obtained by $Cu(OH)_2$–NaOH etc. Cellulose is thus dispersed in $(CH_2Ph)_2NMe_2{\cdot}OH$ as particles, confirming the fact that particles of about 1 μ. diameter are made visible by the slit ultra-microscope. R. S. C.

Relative rate of ring-closure reactions.—See A., 1939, I, 32.

ββ′β″-Trichlorotriethylamine. J. P. Mason and D. J. Gasch (J. Amer. Chem. Soc., 1938, **60**, 2816—2817).—$N(CH_2{\cdot}CH_2Cl)_3$, b.p. 143—144°/5 mm., prepared in 92% yield, is rather unstable. R. S. C.

Time factor in the interaction of amino-acids with sugars. M. Frankel and A. Katchalsky (Biochem. J., 1938, **32**, 1904—1907; cf. A., 1937, II, 402; Balson and Lawson, A., 1938, II, 120).—At 20° and varying initial p_H no decrease in p_H occurs in aq. mixtures of non-aldehydic sugars (sucrose, fructose) and glycine to which NaOH is added, and the potentiometric titration curve is not affected by the length of the intervals between the additions of NaOH. When aldehydic sugars (glucose, galactose) are used the p_H is decreased, the extent of the rapid and marked decrease increasing when the intervals between additions of NaOH are increased. The decrease is not due solely to the acidity of the sugars. W. McC.

Synthesis of *dl*-glutamic acid. C. S. Marvel and M. P. Stoddard (J. Org. Chem., 1938, **3**, 198—203).—*dl*-Glutamic acid (I) is obtained in 70—75% yield from *o*-$C_6H_4(CO)_2N{\cdot}CH(CO_2Et)_2$ (II), $CH_2{:}CH{\cdot}CO_2Me$ (III), and NaOEt–EtOH, or in 57%

yield from (II), $CH_2Cl{\cdot}CH_2{\cdot}CO_2Et$, and slightly >1 mol. of NaOEt in EtOH [by way of (III)]. $CHNa(CO_2Et)_2$ and (III) give *Me γγ-dicarbethoxy-n-butyrate*, b.p. 156—162°/18 mm., converted by Br–CCl_4 into the *γ-Br*-ester, b.p. 129—133°/2 mm., which with NH_3–MeOH gives Br′ but very little NH_2-acid, and with *o*-$C_6H_4(CO)_2NK$ gives compounds, hydrolysed mainly to glutaric acid. $CO_2H{\cdot}[CH_2]_2{\cdot}CBr(CO_2H)_2$ and aq. NH_3 give γ-carboxy-γ-butyrolactone.

R. S. C.

Rotatory power of citrulline. Synthesis of the optically active product. R. Duschinsky (Compt. rend., 1938, **207**, 735—737).—Citrulline from the press juice of the water-melon (A., 1930, 1224) has m.p. 219—220°, $[\alpha]_D^{20}$ +3·7° in H_2O. *l*(+)-Ornithine treated by Kurtz's method yields *l*(+)-citrulline, m.p. 220—221°, $[\alpha]_D^{20}$ +3·4° in H_2O. $[\alpha]_D^{20}$ varies with p_H, as in the case of all α-NH_2-acids (cf. *ibid.*, 460).

J. L. D.

Methionine. I. Interaction of methionine and other amino-acids with mercuric chloride. G. Toennies and J. J. Kolb (J. Biol. Chem., 1938, **126**, 367—379).—The ppt. obtained by the interaction of methionine (I) and $HgCl_2$ is $[SMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2]_2Hg + 4HgCl_2$. Complete pptn. is favoured by neutrality, absence of Cl′, presence of EtOH, and removal with $Hg(OAc)_2$ of Cl′ produced by the interaction. Basic NH_2-acids yield ppts. with $HgCl_2$, and acid NH_2-acids with $Hg^{\cdot\cdot}$ [from $Hg(OAc)_2$] and hence should be removed before pptn. of (I). Neutral NH_2-acids yield sol. compounds with $HgCl_2$ with liberation of HCl, the effect of which is counteracted by using excess of $HgCl_2$ and adding $Hg(OAc)_2$ and alkali. W. McC.

Differences in the reactivity of thiol and disulphido-groups in organic compounds. A. Schöberl and F. Krumey (Ber., 1938, **71**, [*B*], 2361—2371).—The method used for the determination of cystine (I) and cysteine (II) by phosphotungstic acid (III) (A., 1938, II, 211) can be extended immediately to SS- (IV) but not to SH- (V) -glutathione. In acetate buffer at p_H 5·2 (IV) reacts smoothly with Na_2SO_3: $G{\cdot}S{\cdot}S{\cdot}G + Na_2SO_3 = G{\cdot}SNa + G{\cdot}S{\cdot}SO_3Na$, and (V) thus produced can be oxidised by (III). Since the S·S· groups of (I) and (IV) have the same reduction equiv. towards (III) the determination of the purity of preps. of (IV) is simply effected by comparative measurements. At p_H 5·2 (V) does not reduce (III) as strongly as (II) and under these conditions the two compounds have not the same reduction equiv. but at p_H 7·3 the reducing power of (V) is equal to that of (II) at p_H 5·2. *iso*Cysteine and $SH{\cdot}CH_2{\cdot}CO_2H$ completely reduce (III) at p_H 5 and have high extinction coeffs. at p_H 4. The max. p_H for (I) is ~5. $SH{\cdot}[CH_2]_2{\cdot}CO_2H$ and (V) exhibit full reducing power at p_H 6. When the max. of a thiol is reached it is little influenced by further increase in alkalinity. α-SH acids display reducing power at lower p_H than do the corresponding β-SH acids. The experiments are not independent of the particular buffer used. Thus a PO_4''' buffer with p_H about 5·9 gives much smaller colour intensities with (V) and $SH{\cdot}[CH_2]_2{\cdot}CO_2H$ than does an acetate buffer of like p_H whereas with α-SH acids this influence is not observed. The action of Na_2SO_3 on S·S compounds also depends greatly on p_H, the yield of SH-compound increasing very rapidly with increase of p_H from 3·5 to 5·0; differences are encountered in different systems. $(\cdot S{\cdot}CH_2{\cdot}CO_6H)_2$ cannot be determined by (III) at p_H 5·2 but this is readily done at greater p_H, suitably in presence of $NaHCO_3$. $(\cdot S{\cdot}CHMe{\cdot}CO_2H)_2$ is not attacked by Na_2SO_3 at p_H 12 and its colorimetric determination by means of (III) shows the firmness of the S·S linking. Even at p_H 13 the completion of the reaction remains uncertain. At higher temp. the colour intensities attain the expected vals. but there is a danger of hydrolysis of the S·S linking. H. W.

Decomposition of cystine in aqueous solution. J. I. Routh (J. Biol. Chem., 1938, **126**, 147—154; cf. Shinohara *et al.*, A., 1934, 761).—Cystine when boiled with H_2O in air or N_2 gives H_2S and S (ratio ~2 : 1 after long boiling) and cysteine. The concn. of cysteine (determined by Shinohara's method) rises to a max. and then falls. Traces of acidic products are formed, but no NH_3. A. Li.

Behaviour of carbamide on heating. J. Krustinsons (Z. Elektrochem., 1938, **44**, 790—791).—NH_3 is absorbed rapidly by $CO(NH_2)_2$ at 104—139°; at higher temp. the absorbed NH_3 is freed.

E. S. H.

Condensation of esters of unsaturated acids with carbamide. IV. Z. Jerzmanowska and I. Gamota (Rocz. Chem., 1938, **18**, 245—249).—$[:C(CO_2Et)_2]_2$ (I) and $CS(NH_2)_2$ are heated with NaOEt in EtOH (30 min. at the b.p.), to yield thiohydurylic acid (II), instead of the expected thio*spiro*hydantoin. (II) originates from condensation with $CS(NH_2)_2$ of $[\cdot CH(CO_2Et)_2]_2$, formed by reduction of (I) with NaOEt. R. T.

Carbonyl cyanide. II. R. Malachowski and H. Pisarska (Ber., 1938, **71**, [*B*], 2239—2240; cf. A., 1937, II, 282).—$CO(CH{:}N{\cdot}OH)_2$ is transformed by $(EtCO)_2O$ at 60—65° into its *dipropionate* (I), m.p. 84—85°, which passes at 100—110°/1 mm. into $EtCO_2H$ and *propionoximinoacetonitrile*, b.p. 115°/1 mm., m.p. 43—44°; at 160—180°/130—140 mm. this gives $CO(CN)_2$ in 31·2% yield. (I) is therefore not preferable to the corresponding acetate for the prep. of $CO(CN)_2$. An improved prep. of $OAc{\cdot}N{:}CH{\cdot}CO{\cdot}CN$ is described. H. W.

Formation of α-amino*iso*butyronitrile.—See A., 1939, I, 32.

Synthesis of creatinephosphoric acid. K. Zeile and H. Meyer (Z. physiol. Chem., 1938, **256**, 131—140; cf. A., 1938, II, 157).—Methylallylaniline, from $CH_2{:}CH{\cdot}CH_2Br$ and NHPhMe, with HCl and $NaNO_2$ yields the corresponding NO-compound which, hydrolysed with alkali, gives methylallylamine (I). (I) with the sulphate of *iso*methylthiocarbamide gives *methylallylguanidine* [*sulphate* (II) with $0{\cdot}5H_2SO_4$, decomp. 245°; *picrate*; *diphenylphosphate*, m.p. 77°, from (II) and $(OPh)_2POCl$]. (II) with $Ba(MnO_4)_2$ gives creatine in 14% yield. The Ca salt of creatinephosphoric acid (III) with dry HCl at 103° for 3 hr. yields creatinine, inorg. PO_4''', and a substance similar to or identical with the phosphate of methyl-

hydantoic acid (Ca salt). Na creatininephosphate with 0·1N-NaOH at 100° for 10 min. gives an approx. 100% yield of (III). *iso*Creatinephosphoric acid is identical with natural (III). The results and electrochemical data confirm the view that (III) is $CO_2H{\cdot}CH_2{\cdot}NMe{\cdot}C(NH){\cdot}NH{\cdot}PO(OH)_2$. W. McC.

Optical rotation of a Grignard reagent. F. C. Whitmore and B. R. Harriman (J. Amer. Chem. Soc., 1938, **60**, 2821—2822).—CHMeEtBr, $[M]_D^{25}$ −4·35°, in Bu^{α}_2O gives a Grignard reagent, which after removal of excess of bromine, has $[M]_D^{25}$ +5·36°. R. S. C.

Reducing action of primary Grignard reagents with trimethylacetyl chloride. F. C. Whitmore, R. E. Meyer, G. W. Pedlow, jun., and A. H. Popkin (J. Amer. Chem. Soc., 1938, **60**, 2788—2789).—Addition of $Bu^{\gamma}COCl$ to an excess of MgRCl gives $CH_2Bu^{\gamma}{\cdot}OH$ (if R = Et 0, Pr^{α} 20, Pr^{β} 23, Bu^{β} 28, Bu^{β} 61, *n*- 20, and *iso*-amyl 71%) and $CHBu^{\gamma}R{\cdot}OH$ (if R = Et 69, Pr^{α} 76, Pr^{β} 53, Bu^{α} 71, Bu^{β} 26, *n*- 75, and *iso*-amyl 71%). If R = Et, 20% of $CEt_2Bu^{\gamma}{\cdot}OH$, and, if R = *iso*amyl, 7% of olefine, are formed. R. S. C.

Action of primary Grignard reagents with *tert.*-butylacetyl chloride. II. F. C. Whitmore, J. S. Whitaker, K. F. Mattil, and A. H. Popkin (J. Amer. Chem. Soc., 1938, **60**, 2790—2792; cf. A., 1938, II, 476).—Addition of MgRBr (R = Et, Pr^{α}, Bu^{α}, and *n*-amyl) to a slight excess of $CH_2Bu^{\gamma}{\cdot}COCl$ gives $CH_2Bu^{\gamma}{\cdot}COR$ (51, 37, 34, and 29%, respectively) and $CH_2Bu^{\gamma}{\cdot}CHR{\cdot}O{\cdot}CO{\cdot}CH_2Bu^{\gamma}$ (7, 20, 23, and 21%, respectively). R. S. C.

Complex cuprohydrocyanide of hexamethylenetetramine. P. Mesnard (Bull. Trav. Soc. Pharm. Bordeaux, 1936, **74**, 157—161; Chem. Zentr., 1937, i, 1212).—The complete analysis of the complex $CuCN,5[(CH_2)_6N_4,HCN]$ (cf. A., 1938, II, 341) is described. A. H. C.

Cuprohydrocyanide reagent as a precipitant for methylene-blue. P. Mesnard (Bull. Trav. Soc. Pharm. Bordeaux, 1936, **74**, 161—164; Chem. Zentr., 1937, i, 1212).—The compound $2CuCN,13(C_{16}H_{18}N_3SCl,HCN),5HCN$ (yield 60—70%) (analysis described) forms a violet-blue ppt. which becomes cryst. on boiling and again amorphous on drying. Unlike the compounds of alkaloids, it is insol. in the reagent on boiling. A. H. C.

Electronegativities of highly branched aliphatic groups. F. C. Whitmore and H. Bernstein (J. Amer. Chem. Soc., 1938, **60**, 2626—2628).—By reaction of HgRR′ with HCl the following relative electronegativities are established: Ph > Me > Et > Pr^{α} > Bu^{α}, *n*-C_6H_{13}, $CH_2Bu^{\gamma}{\cdot}CH_2$, $Bu^{\gamma}[CH_2]_3$ > *sec.*-Bu > $CHMeBu^{\gamma}$; CH_2Ph > Bu^{γ} > CH_2Bu^{γ}, which is remarkable, since CH_2Ph is less electronegative than other alkyl groups. *tert.*-Butyl-, m.p. 122—123° (decomp.), β-methyl*iso*butyl-, m.p. 117—118°, *γ-methyliso*amyl-, m.p. 133—133·5°, pinacolyl-, m.p. 89—90°, *δδ-dimethyl*-n-*amyl*-, m.p. 104—105°, and n-*octyl*-, m.p. 115—115·5°, *-mercuric chloride* are prepared. $CH_2Bu^{\gamma}{\cdot}CH_2Cl$, b.p. 115°, is obtained from the alcohol by $SOCl_2$–C_5H_5N. R. S. C.

Improved preparation of lead triethyl and lead trimethyl. F. Hein and A. Klein [with, in part, E. Nebe] (Ber., 1938, **71**, [*B*], 2381—2384).—Restricted passage of HCl into a dil. solution of $PbEt_4$ in Et_2O yields a ppt. (I), $PbEt_3Cl,HCl,1{\cdot}5Et_2O$, readily sol. in 2N-KOH; continued passage gives a product, approx. $PbEt_3Cl$, which is very unstable and sparingly or slowly sol. in EtOH. $PbEt_3$ is readily obtained by electrolysing a solution of (I) in the necessary amount of 2N-KOH between Pb electrodes under N_2 or CO_2 in a glass vessel the bottom of which is drawn out to a narrow tube and provided with a tap. $PbEt_3$ collects at the bottom of the vessel and is obtained as a lemon-yellow liquid by filtration after desiccation over Na_2SO_4. Zn electrodes are less serviceable. $PbEt_3Br$ can replace $PbEt_3Cl$. Alternatively, the solution of $PbEt_3Cl$, prepared as above, is heated with fine Al wire at 100°. The change proceeds also at room temp. if Al activated by preheating with alkali hydroxide, Pb pretreated with dil. HNO_3, or Zn pretreated with HCl is used. $PbMe_3$ is obtained similarly. H. W.

Formation of organometalloidal and similar compounds by micro-organisms. VI. Further studies on the fission of the disulphide linkage. S. Blackburn and F. Challenger (J.C.S., 1938, 1872—1878).—Air aspirated through aq. bread cultures of *Penicillium brevicaule*, Saccardo (Baarn strain A), containing $(Bu^{\alpha}S)_2$ and passed through aq. $Hg(CN)_2$ and $HgCl_2$ gives small amounts of Hg di-*n*-butylthiol (also obtained, with *chloromercury* n-*butylthiol*, m.p. 177—177·5°, from $Bu^{\alpha}SH$ and $HgCl_2$) and *Me* n-*butyl sulphide dimercurichloride*, m.p. 115—116·5° (also prepared from $MeBu^{\alpha}S$). With *di*-n-*amyl disulphide*, b.p. 140·5—142°/17 mm. (from *n*-$C_5H_{11}Br$, EtOH, and $Na_2S_2O_3$, followed by KOH), and the culture, *Me* n-*amyl sulphide*, b.p. 144·5—145·5°/? mm. [*mercurichloride*, $3SMe{\cdot}C_5H_{11},7HgCl_2$ (?), m.p. 126—127°], and probably *n*-$C_5H_{11}{\cdot}SH$ are formed. With $(MeS)_2$ (new prep., free from mono- and poly-sulphide, from MeI, MeOH, and $Na_2S_2O_3$, followed by KOH) and the culture, a product, m.p. 135—141°, decomp. 156°, consisting of *chloromercury methylthiol mercurichloride*, $SMe{\cdot}HgCl,xHgCl_2$, and Me_2 sulphide mercurichloride, is formed. Without the culture, $(EtS)_2$ and aq. $HgCl_2$ give $SEt{\cdot}HgCl,HgCl_2$ (cf. A., 1937, II, 271), and a filtrate which after removal of $Hg^{\cdot\cdot}$ and neutralisation gives $EtSO_2Na$, converted into *p*-$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}SO_2{\cdot}Et$. $(MeS)_2$ similarly gives *p*-$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}SO_2{\cdot}Me$. MeSH and aq. $HgCl_2$ give a *product*, m.p. 141°, decomp. 156°, and a *product*, (MeS·HgCl?), m.p. ≮260°. Me_2S_3 gives a mixture of the compounds, $SMe{\cdot}HgCl,xHgCl_2$ and $HgCl_2,2HgS$, and $(Bu^{\alpha}S)_2$ the *compound*, $SBu^{\alpha}{\cdot}HgCl$. (*n*-$C_5H_{11}{\cdot}S)_2$ gives *chloromercury* n-*amylthiol*, m.p. 180·5°, also obtained, with di-*n*-amylthiol, from *n*-$C_5H_{11}{\cdot}SH$ and $HgCl_2$. E. W. W.

Stereoisomeric hexaethyl*cyclo*hexanes. H. Koch and H. Steinbrink (Brennstoff-Chem., 1938, **19**, 407—408).—Fractions, b.p. 153·3—154°, 154—155°, and 155—156°/16 mm., of the previously described hexaethyl*cyclo*hexane (A., 1938, II, 354) have yielded 2·5, 6·9, and 7·9%, respectively, of a cryst. *form* (I), m.p. 104·7—105° (corr.). Comparison

of the sp. refractions of the fractions before and after separation of (I) indicates that the liquid part is the *cis*- and that (I) is, therefore, the *trans*-form. A. B. M.

Diene synthesis. VIII. Simple method in the di*cyclo*-[1 : 2 : 3]-octane series. K. ALDER and E. WINDEMUTH (Ber., 1938, **71**, [*B*], 2404—2409).—Addition of AcOH to a solution of 2 : 5-*endo*-methylenehexahydrobenzylamine hydrochloride (A., 1938, II, 488) and $NaNO_2$ through which steam is passing gives di*cyclo*-[1 : 2 : 3]-octan-2-ol, m.p. 183° (phenylurethane, m.p. 130°; *H phthalate*, m.p. 116—117°), oxidised (cold $K_2Cr_2O_7$ and dil. H_2SO_4) to di*cyclo*-[1 : 2 : 3]-octan-2-one, m.p. 129° (*semicarbazone*, m.p. 171°; *monoanisylidene* compound, m.p. 91—92°). This is oxidised by HNO_3 (*d* 1·4) to *cyclo*pentane-1-carboxylic-3-acetic acid, m.p. 139°; its Pb salt when dry distilled in CO_2 gives norcamphor. Di*cyclo*-[1 : 2 : 3]-octane has m.p. 141° (sealed capillary). H. W.

Use of liquid amalgams in the analysis of nitro-derivatives of benzene homologues. M. I. PERRIER (Bull. Sci. Univ. Kiev, 1937, **3**, No. 3, 37—41).—Minor improvements in the technique of the method previously described (A., 1937, II, 268) are recommended. R. T.

Reversible replacement of aromatic halogen atoms. G. M. BENNETT and I. H. VERNON (J.C.S., 1938, 1783—1786).—Conditions are given for interchange of Cl, Br, and I in halogeno-2 : 4-dinitrobenzenes. 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$ (I) and NaI (5 mols.) in boiling $(CH_2{\cdot}OH)_2$ for ½ hr. give 30% of 1 : 2 : 4-$C_6H_3I(NO_2)_2$ (II), reconverted into (I) by excess of anhyd. LiCl in $(CH_2{\cdot}OH)_2$. (I) and (II) with NaBr–$(CH_2{\cdot}OH)_2$ afford some 1 : 2 : 4-$C_6H_3Br(NO_2)_2$, which gives (I) with LiCl. (I) and AgF, or dinitrophenyl *p*-toluenesulphonate and a chloride in $(CH_2{\cdot}OH)_2$, give only 2 : 4 : 1-$(NO_2)_2C_6H_3{\cdot}OH$. 1 : 3 : 4 : 6-$C_6H_2Cl_2(NO_2)_2$ and NaI in boiling $(CH_2{\cdot}OH)_2$ for 5 min. give some 1 : 3 : 4 : 6-$C_6H_2I_2(NO_2)_2$. 1 : 3 : 4 : 6-$C_6H_2MeCl(NO_2)_2$ and NaI–$(CH_2{\cdot}OH)_2$ for 5—30 min. also show incomplete conversion, yielding 70% of 3-*iodo*-4 : 6-*dinitrotoluene*, m.p. 108° (also prepared from *m*-C_6H_4MeI and HNO_3–H_2SO_4). The reaction $C_6H_3I(NO_2)_2 + Cl' \rightleftharpoons C_6H_3Cl(NO_2)_2 + I'$ [in $(CH_2{\cdot}OH)_2$ at 175° (cf. A., 1932, 26)] is shown to be reversible and bimol. With mol. quantities, it proceeds from either side towards an equilibrium at 68 mols. % of $C_6H_3Cl(NO_2)_2$, but some subsidiary reaction occurs. Velocity measurements are recorded. With 1 : 2 : 4-$C_6H_3Br(NO_2)_2$ and Cl' in $(CH_2{\cdot}OH)_2$ at 175° (190°, 195°), the equimol. mixture tends from either side to an equilibrium with 23 mols. % of Br-compound. A. T. P.

Thermal decomposition of toluene; exclusive formation of benzyl radicals. F. HEIN and H. I. MESÉE (Naturwiss., 1938, **26**, 710).—Decomp. of PhMe at 900—1100°/0·1—0·5 mm. yields only H and $CH_2Ph{\cdot}$ [identified by reaction with Hg vapour and subsequent conversion into $CH_2Ph{\cdot}HgBr$ (I)]. The absence of $C_6H_4Me{\cdot}HgBr$ in (I) is proved by quant. conversion into CH_2PhI and thence $CH_2Ph{\cdot}NEt_3I$. A. LI.

Aromatic nitro-derivatives. XV. 3 : 4-Dinitrotoluene: reactivity and nuclear configuration. A. MANGINI and M. COLONNA (Gazzetta, 1938, **68**, 543—554).—In 1 : 3 : 4-$C_6H_3Me(NO_2)_2$ (I), the 3-NO_2-group is the more reactive. On the Bonino formulation, the prevailing structure (*A*) is assigned to (I), in which, however, Me has a less powerful orienting influence than Cl or Br in 1 : 3 : 4-$C_6H_3Hal(NO_2)_2$, in agreement with the respective dipole moments. With NaOMe in boiling MeOH, (I) gives 4 : 1 : 3-$NO_2{\cdot}C_6H_3Me{\cdot}OMe$, with a phenolic substance, m.p. 120—127°, and an insol. product, m.p. 180—200°; the crude residue when reduced (Sn–HCl) and acetylated gives only 4 : 1 : 3-$NHAc{\cdot}C_6H_3Me{\cdot}OMe$. There is no evidence that any 3 : 1 : 4-$NO_2{\cdot}C_6H_3Me{\cdot}OMe$ is formed. With NH_2Me–EtOH, however, (I) gives 4 : 1 : 3- (85%) and 3 : 1 : 4-$NO_2{\cdot}C_6H_3Me{\cdot}NHMe$ (15%) (new prep. from 3 : 1 : 4-$NO_2{\cdot}C_6H_3Me{\cdot}NH_2$ and Me_2SO_4). With $NHMe_2$–EtOH, (I) gives 4-nitro-*NN*-dimethyl-*m*-toluidine (*picrate*, m.p. 125·5—126·5°), reduced (Sn–HCl) to 3-dimethylamino-*p*-toluidine (*picrate*, m.p. 136—137°; *Ac* derivative, m.p. 105—106°), which differs from 3 : 1 : 4-$NH_2{\cdot}C_6H_3Me{\cdot}NMe_2$. With NH_2Et–EtOH, 4 : 1 : 3-$NO_2{\cdot}C_6H_3Me{\cdot}NHEt$ is formed. E. W. W.

Reactions of paraffins with aromatic hydrocarbons. I. Various paraffins with benzene. A. V. GROSSE, J. M. MAVITY, and V. N. IPATIEV (J. Org. Chem., 1938, **3**, 137—146).—Paraffins and C_6H_6 in presence of $AlCl_3$, when saturated with HCl and heated, usually at 135—175°, react mainly thus: $RR' + HCl \rightarrow RCl + R'H$; $RCl + ArH \rightarrow ArR + HCl$. The main intermediate RCl is EtCl, but many other fissions also occur. C_5H_{12} (*n*- and *iso*-) gives $PhEt + C_3H_8$ and $PhMe + C_4H_{10}$. *n*-C_6H_{14} and $CHMe_2Pr^{\alpha}$ give $C_4H_{10} + PhEt$. *n*-C_7H_{16} gives $PhMe + C_6H_{14}$, $PhEt + C_5H_{12}$, and $PhPr + C_4H_{10}$. *n*-C_8H_{18} gives $PhEt + C_6H_{14}$ and $PhPr + C_5H_{12}$, but $CHMeEtBu^{\gamma}$ gives (readily at 80—90°, and even at 0°) only $C_4H_{10} + PhBu^{\gamma}$. *n*-$C_{10}H_{22}$ and *n*-$C_{16}H_{34}$ suffer fission at many places, giving C_4—C_{11} hydrocarbons. The products are often isomerised during the reaction, *e.g.*, *n*- to *iso*-C_4H_{10}, and PhR may give $C_6H_6 + C_6H_4R_2$, $C_6H_3R_3$, etc. Further, the reaction, $RR' + 2C_6H_6 \rightarrow RH + R'H + Ph_2$, occurs, leading to extra yields of paraffin fission products. Slight decomp. of C_6H_6 itself to PhEt and other products occurs at 125—175°, but this decomp. is a main factor in the reaction with CH_4, C_2H_6, and C_3H_8, which occurs only at much higher temp. R. S. C.

Derivatives of *s*-triethylbenzene. W. B. DILLINGHAM and E. E. REID (J. Amer. Chem. Soc., 1938, **60**, 2606).—*s*-$C_6H_3Et_3$, b.p. 211·2°, is separated from the products of reaction of C_6H_6, C_2H_4, and $AlCl_3$ at 60—80° by virtue of its relative inertness to H_2SO_4 at 60—70° and liberation from its sulphonic acid at 110—125°. It is converted by standard methods into 2-*nitro*-1 : 3 : 5-*triethylbenzene*, b.p. 141·2°/7 mm., 2 : 4 : 6-*triethyl-aniline*, b.p. 135·5°/6 mm. (*Ac*, m.p. 149·5°, and *Bz* derivative, m.p. 181·3°), -phenol, b.p. 126·5°/mm. (*Me ether*, b.p. 100·8°/3 mm.), -*benzonitrile*, b.p. 108·5°/2 mm., and -*benzeneazo*-β-*naphthol*,

and 2 : 4 : 6 : 2′ : 4′ : 6′-*hexaethyldiphenylthiocarbamide*, m.p. 196·5°. R. S. C.

Polymerisation of styrene.—See A., 1939, I, 31.

Dimerisation of 3-phenylindene. C. S. MARVEL and H. A. PACEVITZ (J. Amer. Chem. Soc., 1938, **60**, 2816).—3-Phenylindene with 47% HI or $SnCl_4$ gives a *dimeride*, m.p. 156—157°. The compound, m.p. 210—211°, of Blum-Bergmann (A., 1931, 208) could not be prepared. R. S. C.

Dimerisation of 3-phenylindene. E. BERGMANN (J. Amer. Chem. Soc., 1938, **60**, 2816).—The dimerides, m.p. 210—211° and 156—157°, of 3-phenylindene (cf. preceding abstract) are not allyl-isomeric forms, as they are not interconverted by NaOEt–EtOH. R. S. C.

Normal and destructive hydrogenation of naphthalene.—See B., 1938, 1389.

Reduction of nitronaphthalene with liquid zinc amalgam, for determination of nitro-groups. M. I. PERRIER and M. M. LOBUNETZ (Bull. Sci. Univ. Kiev, 1937, **3**, No. 3, 43—48).—$C_{10}H_7{\cdot}NO_2$ is reduced by Zn–Hg in acid aq. EtOH or $COMe_2$, or in dil. HCl, and the resulting $C_{10}H_7{\cdot}NH_2$ is titrated with standard $NaNO_2$. The error is ±3%. R. T.

Diene syntheses. IX. 1 : 4 : 5 : 8-Di*endo*-methylenedecahydronaphthalene. K. ALDER and E. WINDEMUTH (Ber., 1938, **71**, [*B*], 2409—2414).—2 : 5-*endo*Methylene-Δ^3-tetrahydrobenzaldehyde and *cyclo*pentadiene at 170—175° give 1 : 4 : 5 : 8-di*endo*-methylene-Δ^6-octahydronaphthalene-2-aldehyde, b.p. 142—143°/18 mm., hydrogenated (colloidal Pd in EtOH) to 1 : 4 : 5 : 8-di*endo*methylenedecahydronaphthalene-2-aldehyde (semicarbazone, m.p. 205°), the enol acetate, b.p. 155—165°/14 mm., of which is oxidised ($KMnO_4$–$COMe_2$–$MgSO_4$) to 2-keto-1 : 4 : 5 : 8-di*endo*methylenedecahydronaphthalene, b.p. 139—140°/11 mm. [*semicarbazone* (I), m.p. 206°]. The constitution of the ketone is established by its oxidation to *cis*-4 : 7-*endo*methylenehexahydrohydrindene-1 : 3-dicarboxylic acid (Alder *et al.*, A., 1932, 938). NaOEt–EtOH converts (I) at 190—200° into 1 : 4 : 5 : 8-*di-endomethylenedecahydronaphthalene*, m.p. 36—37°, which appears sterically homogeneous. 1 : 4 : 5 : 8-Di*endo*methylene-2-decahydronaphthol, m.p. 93—95° and its *phenylurethane*, m.p. 117—119°, are described. H. W.

Action of benzaldehyde on *o*-, *m*-, and *p*-xylenes in presence of aluminium chloride. H. ELLISON and D. H. HEY (J.C.S., 1938, 1847—1853; cf. A., 1935, 344).—Dry CO passed into boiling C_6H_6–$AlCl_3$ for 6 hr. gives only a trace of $CHPh_3$, but CO + HCl (1 : 2) afford some anthracene (also obtained by using CO–$AlBr_3$). The yields are very small compared with those using PhCHO. The production of PhCHO is not an essential stage in forming the anthracene mol. (cf. Dewar and Jones, J.C.S., 1904, **85**, 212; Egloff *et al.*, Chem. Rev., 1937, **20**, 388). *o*-Xylene, PhCHO, and $AlCl_3$ at 60° for 6 hr. give 2 : 3 : 6 : 7-tetramethylanthracene, m.p. 304° (corr.) (cf. Morgan *et al.*, A., 1931, 1282). *m*-Xylene, similarly, or with CH_2Cl_2–$AlCl_3$ at room temp., then at 60—80°, gives a mixture (*A*), m.p. 163—164° (const. val. after several crystallisations), of 1 : 3 : 5 : 7- and 1 : 3 : 6 : 8-tetramethylanthracenes, with (in first case) traces of a (?) *trimethylanthracene*, m.p. 233—235°. Oxidation (CrO_3–AcOH) of (*A*) gives a mixture, m.p. 160—162°, of the corresponding anthraquinones; fractionation affords an impure quinone, m.p. ~200° (cf. Seer, A., 1912, i, 276; Friedel and Crafts, A., 1887, 1102). Similarly, *p*-xylene and PhCHO or CH_2Cl_2 give 1 : 4 : 5 : 8-*tetramethylanthracene*, m.p. 270° (corr.) (*-anthraquinone*, m.p. 258—260°). Oxidation of a crude hydrocarbon from the mother-liquors (CH_2Cl_2 reaction) also gives a *tetramethylanthraquinone*, m.p. 223—226°, probably resulting initially owing to migration of Me. Ph_2, PhCHO, and $AlCl_3$ in CS_2 at 35° for 5 hr., then 40° for 1 hr., or with CH_2Cl_2–$AlCl_3$ at 25° (4 hr.) and 45° (2 hr.), give a mixture, m.p. 312° (corr.), of 2 : 6- and 2 : 7-diphenylanthracene, oxidised by CrO_3–AcOH to the corresponding mixed anthraquinones, m.p. 194—196°. The view (*loc. cit.*) that PhCHO supplies only the *meso*-C in the anthracene nucleus is substantiated; the linking uniting CHO to Ph is broken, and CO (active form) or HCOCl may be formed. A. T. P.

Dissociable anthracene oxides. Photo-oxides of 9-*cyclo*hexyl- and 10-*cyclo*hexyl-9-phenylanthracene. A. WILLEMART (Compt. rend., 1938, **207**, 536—538; cf. A., 1938, II, 226).—Anthrone and 9-phenylanthrone with Mg *cyclo*hexyl chloride afford 9-cyclo*hexyl*- (I), m.p. 135—136°, and 10-cyclo*hexyl*-9-*phenyl-anthracene* (II), m.p. 231—232°, respectively. The absorption spectra of these substances in $CHCl_3$ are analogous to those of 9-alkyl- and 9-phenyl-10-alkyl-anthracene. (I) and (II) with maleic anhydride form 1 : 1 adducts, m.p. ~315° and ~340°, respectively. Insolation of (I) and (II) affords *photo-oxides*, $C_{20}H_{20}O_2$ and $C_{26}H_{24}O_2$, respectively; the former is stable when heated, whereas the latter gives 48% of O_2 (cf. A., 1936, 1101; 1937, 374). J. L. D.

Unsaturated steroids. IV. Preparation and photochemical oxidation of $\Delta^{2:4}$-cholestadiene. E. L. SKAU and W. BERGMANN (J. Org. Chem., 1938, **3**, 166—174; cf. A., 1937, II, 289).—A modified prep. and purification gives pure $\Delta^{2:4}$-cholestadiene (I), m.p. 68·5°, $[\alpha]_D^{23}$ +168·5° in Et_2O (cf. *loc. cit.*), and a *cholestadiene* (II), m.p. 80—80·5°, $[\alpha]_D^{23}$ −51·3° in Et_2O, which has an absorption max. at 234 mμ., and thus contains conjugated ethylenic linkings extending over two rings. Higher reaction temp. gives mainly (II). Pure (I) has absorption max. only at 267 and 275 mμ. and is not carcinogenic. In EtOH–eosin and light with O_2 it gives the 2 : 5-peroxide (III), m.p. 113—114°, $[\alpha]_D^{24}$ +48·3° in $CHCl_3$ (cf. A., 1938, II, 227), which changes in m.p. and [α] when recrystallised; in EtOH–eosin and sunlight it gives [as does (I)] a (? non-peroxidic) *isomeride*, m.p. 166—168°, $[\alpha]_D^{23}$ +141° in $CHCl_3$ (cf. Butenandt *et al.*, A., 1938, II, 270). The structure of (III) follows from its hydrogenation (PtO_2) to a *diol*, $C_{27}H_{48}O_2$, m.p. 155°, $[\alpha]_D^{27}$ +19·6° in $CHCl_3$, which is unaffected by $Pb(OAc)_4$ and gives only a *monoacetate*, m.p. 141—142°, $[\alpha]_D^{27}$ −9° in Et_2O. R. S. C.

Symmetrical derivatives of chrysene. II. Elimination of methyl groups during dehydrogenation in attempt to prepare 1 : 10-dimethyl-

chrysene. W. E. Jones and G. R. Ramage (J.C.S., 1938, 1853—1858; cf. A., 1938, II, 228).—Et *meso*-βγ-diphenylbutane-ααδδ-tetracarboxylate, new m.p. 86°, heated with 85% H_2SO_4 for 3 hr. gives *trans*-2 : 11-diketo-1 : 2 : 9 : 10 : 11 : 18-hexahydrochrysene (cf. A., 1933, 828). Benzil, $CHMeBr{\cdot}CO_2Me$, and Zn–C_6H_6 with a trace of MgMeI in Et_2O at 100°(bath)/3 hr. give β-*benzoyl*-α-*methylcinnamic acid* (I), m.p. 235°, and *Me* β-*hydroxy*-β-*benzoyl*-β-*phenyl*-α-*methylpropionate*, m.p. 83°; dehydration of the latter with $KHSO_4$ and hydrolysis of the resultant ester with KOH–EtOH gives (I). *cyclo*Hexene and EtCOCl–$SnCl_4$ in CS_2 at −10° afford 1-*propionyl*cyclo*hexene* (II), b.p. 101—102°/14 mm. (*oxime*, m.p. 78°; *semicarbazone*, m.p. 189°). $CH_2Ph{\cdot}COMe$ gives (Reformatsky) Et β-hydroxy-β-benzyl-*n*-butyrate, b.p. 160—165°/15 mm. (corresponding *Me* ester, b.p. 151—152°/15 mm.), which with $KHSO_4$ at 180° for 4 hr. gives an unsaturated *Et* ester, b.p. 155—157°/14 mm. (*Me* ester, b.p. 140—141°/14 mm.), reduced slowly (H_2, Pd–C, EtOH, atm. pressure) to *Et* β-*benzyl*-n-*butyrate*, b.p. 133°/12 mm. This and H_2SO_4–H_2O at 100° (bath)/2 hr. give 1-keto-3-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 138°/11 mm. (semicarbazone, new m.p. 189°; 2 : 4-*dinitrophenylhydrazone*, m.p. 242°), the Na derivative (prep. with $NaNH_2$ in Et_2O) of which with (II) and 1-acetylcyclohexene in Et_2O gives 2-*keto*-1 : 10-*dimethyl*- (III), m.p. 104°, and 2-*keto*-10-*methyl*- (IV), m.p. 132°, -2 : 3 : 4 : 5 : 6 : 7 : 8 : 9 : 10 : 11-*decahydrochrysene*, respectively; in the prep. of (IV), an *isomeride*, m.p. 165°, is obtained. (III) does not give a semicarbazone, but affords a 2 : 4-dinitrophenylhydrazone. (IV) gives a *semicarbazone*, m.p. 227°, and a 2 : 4-*dinitrophenylhydrazone*, m.p. 210°. (III) and (IV) are reduced (Clemmensen) to unsaturated products, converted by Se at 280—360° into chrysene and a little of a *methylchrysene*, m.p. 151° [$C_6H_3(NO_2)_3$ *compound*, m.p. 184—185°; unstable picrate, m.p. 162°]. A. T. P.

Synthesis of mescaline. H. Jensch (Med. u. Chem., 1936, **3**, 408—411; Chem. Zentr., 1937, i, 881).—Contrary to Hahn (A., 1934, 886) the synthesis of mescaline (β-3 : 4 : 5-trimethoxyphenylethylamine) (I) according to G.P. 526,172 is suitable for laboratory use as only the prep. of 3 : 4 : 5-$(OMe)_3C_6H_2{\cdot}CH_2{\cdot}CN$ (II) from the chloride gives >60% yield, and syringa alcohol is a readily accessible starting material. Reduction (Ni) of (II) yields (I) and *di*-β-*trimethoxyphenylethylamine*; hydrolysis affords 3 : 4 : 5-$(OMe)_3C_6H_2{\cdot}CH_2{\cdot}CO_2H$. β-3 : 5-*Dimethoxy*-4-*butoxyphenylethylamine* (*hydrochloride*, m.p. 153°) and 6 : 7 : 8-*trimethoxy*-3 : 4-*dihydro*isoquinoline *methochloride* (*base*, m.p. 97—98°) [from (I)] are described. A. H. C.

Reactions of isomeric nitroanilines with hydrogen peroxide in hydrochloric acid solution. R. Garzuly-Janke (Magyar Chem. Fol., 1936, **42**, 169—172; Chem. Zentr., 1937, i, 3479).—$NO_2{\cdot}C_6H_4{\cdot}NH_2$ (I) undergo nuclear chlorination when treated with 80% H_2O_2 in EtOH–conc. HCl at 30—40°; prolonged reaction also affords $(NO_2{\cdot}C_6H_4{\cdot}N{:})_2$ (II). Possible intermediates are $NO_2{\cdot}C_6H_4{\cdot}NCl_2$; these can rearrange and react with (I) [to give (II)]. 4 : 6-*Dichloro*-2-, m.p. 101°, 2 : 6-*dichloro*-4-, m.p. 191°, and 2 : 4 : 6-*trichloro*-3-, m.p. 98°, *-nitroanilines*, and 4 : 6-*dichloro*-o-, m.p. 60°, and 2 : 6-*dichloro*-p-, m.p. 123° *-phenylenediamines* appear to be new. H. B.

Reactivities and basic strengths of *p*-alkyldimethylanilines.—See A., 1939, I, 25.

Rearrangement of 1-naphthylhydroxylamine. O. Neunhoeffer and H. G. Liebich (Ber., 1938, **71**, [*B*], 2247—2249).—1-$C_{10}H_7{\cdot}NH{\cdot}OH$ (I) is almost quantitatively obtained by reduction of 1-$C_{10}H_7{\cdot}NO_2$ by solid $(NH_4)_2S$ and saturated NH_3–EtOH at 0°. Under varied conditions of temp. and concn. it is resinified by H_2SO_4. In 70% EtOH it is transformed by 20% H_2SO_4 into 4 : 1-$OEt{\cdot}C_{10}H_6{\cdot}NH_2$ (sulphate, m.p. 240°). Gradual addition of (I) in $COMe_2$ to 17% H_2SO_4 at 55° gives 1 : 4-$OH{\cdot}C_{10}H_6{\cdot}NH_2$ in 77% yield. H. W.

Fluorene compounds. Nitrogen derivatives. F. E. Ray and G. Rieveschl, jun. (J. Amer. Chem. Soc., 1938, **60**, 2675—2677).—2-Aminofluorene hydrochloride and $COCl_2$ in PhMe give 2-*carbimidofluorene* (I), m.p. 69—70°, converted by the appropriate alcohol into *Me*, m.p. 118°, *Et*, m.p. 121—122°, and *Pr*$^{\alpha}$ 2-*fluorenylcarbamate*, m.p. 113°, by NH_3–Et_2O into 2-*fluorenylcarbamide*, m.p. >360°, by NH_2Ph into s-*phenyl*-2-*fluorenylcarbamide*, m.p. 305° (block), and by 2-aminofluorene (II) into s-*di*-2-*fluorenylcarbamide*, m.p. >360°, which is also obtained from (II) by $COCl_2$ or from (I) by H_2O. 2-Benzoylfluorene, *iso*-$C_5H_{11}{\cdot}O{\cdot}NO$, and KOMe in a little MeOH in Et_2O–C_6H_6 give the α-, m.p. 213—214° (*acetate*, m.p. 144—145°), and β-, m.p. 207—208° (*acetate*, m.p. 150—151°), *forms* of 2-*benzoyl*-9-*fluorenoneoxime*. The β-form was obtained by Fortner's method (A., 1903, i, 177), but his compound, m.p. 199°, was a 1 : 1 mixture of the two forms. R. S. C.

Preparation of thiocarbamides and thiuram disulphides. H. S. Fry and B. S. Farquhar (Rec. trav. chim., 1938, **57**, 1223—1233; cf. A., 1934, 60). —The method of prep. of thiocarbamides and thiuram disulphides from primary and *sec.* amines, respectively, CS_2, I, and C_5H_5N (*loc. cit.*) is re-examined for extent of completion and effect of substituents. The use of 100% excess of C_5H_5N usually gives quick and good results. The times required for the conversion of $C_6H_4Hal{\cdot}NH_2$ into $CS(NH{\cdot}C_6H_4Hal)_2$ are in the order: *o*-Br > *o*-Cl ≫ *m*-Cl > *m*-Br > *p*-Cl > *p*-Br, *p*-I (almost instantaneous); all except *o*-Br give yields >92%. Conversion of *sec.* amines into thiuram disulphides is fast with NHPhMe (0·33 hr.; 92% conversion) and slower with NHPhEt (11·5 hr.; 97%); $NHPh_2$ gives only 20% conversion in 10 weeks. Conversion of *p*-$C_6H_4Me{\cdot}NHMe$ (1·5 hr.; 86%) occurs more readily than the *m*- (2 hr.; 62%) and *o*- (12·5 hr.; 93%) isomerides. Unlike *m*-$NO_2{\cdot}C_6H_4{\cdot}NHMe$ (3 hr.; 83%), the *o*- and *p*-isomerides do not react. The following are described: *s*-di-*o*-chloro-, new m.p. 131·5°, *-o*-bromo-, new m.p. 154°, *-m*-bromo-, new m.p. 132°, and -p-*iodo*-, m.p. 188—189° (decomp.), -phenylthiocarbamides; *tetraphenyl*-, m.p. 217·6° (decomp.), *di*-o-, m.p. 200·2°, -m-, m.p. 170·5°, and -p-*tolyl*-, m.p. 183° (decomp.), and *di*-m-*nitrophenyl*-, m.p. 172° (decomp.), *-dimethylthiuram disulphides*. PhNCS and *o*-, *m*- and *p*-$C_6H_4Me{\cdot}NHMe$ afford N-*phenyl*-N′-*methyl*-N′-o-, m.p. 89—90°, -m-, m.p. 67·6—

67°, and -p-, m.p. 89·4°, *-tolylthiocarbamides*, respectively. A. T. P.

Guanidine structure and hypoglycæmia. Carbocyclic diguanidines. C. E. Braun, J. D. Erit, and G. C. Crooks (J. Org. Chem., 1938, **3**, 146—152).—*p*-$C_6H_4(NH_2,HCl)_2$ and $NH_2{\cdot}CN$ in abs. EtOH give p-*diguanidinobenzene* (I), m.p. 258—259° (decomp.) [*dihydrochloride*, m.p. 315°; *picrate*, m.p. >317° (darkens at 290°)]. (*p*-$C_6H_4{\cdot}NH_2,HCl)_2$ and $CH_2(C_6H_4{\cdot}NH_2,HCl\text{-}p)_2$ similarly give 4 : 4′-*diguanidinodiphenyl* (II), m.p. 234—236° (decomp.) [*picrate*, decomp. 308°; *dihydrochloride*, m.p. >300°; *sulphate*, m.p. 318—320° (decomp.)], and *di*-(p-*guanidinophenyl*)*methane* (III), m.p. 199—200° (decomp.) [*picrate*, m.p. 229—230° (darkens at 200—202°); *sulphate*, m.p. 254—256° (decomp.)]. p-*Bromo*-, m.p. 121—123° [*hydrochloride*, m.p. 175°; *carbonate*, m.p. 145—149° (decomp.)], and p-*iodo-phenylguanidine* (*carbonate*, m.p. 147—149°; *picrate*, m.p. 235°; *hydrochloride*, m.p. 151—153°), similarly prepared, could not be converted (Ullmann reaction) into (II). (I), (II), and (III) possess less hypoglycæmic activity than $[CH_2]_6[N{\cdot}C(NH){\cdot}NH_2]_2$, and (II) and (III) are much more toxic. R. S. C.

Thermal persistence of crystalline liquid phases. C. Weygand and R. Gabler (Ber., 1938, **71**, [*B*], 2399—2403).—Only very small differences exist between the groups ·N(:O):N·, ·N:N· and ·CH:N· in their action on the existence of cryst. liquid phases if attention is paid to cryst. solid phases when the strength of the cryst. liquid properties is estimated. Apparently their common factor, the double linking, is of outstanding importance for the occurrence of cryst. liquid phases. The actual series of persistencies is that of mol. wts. not only qualitatively but nearly quantitatively. The clearing temp. of the azoxy-series differ more from those of the azo-series than do the latter from those of the azomethine series, corresponding with the difference of 16 mol. wt. units between the first two and of 1 unit between the second and third. The persistent differences between the three series can therefore be referred to the same causes as the differences in m.p. observed in morphologically comparable homologous series (chloride, bromide, and iodide of higher alcohols), that is, as a first approximation, to the inertia of the different heavy individual mols. The following are described incidentally: p-*nitrophenyl Bu*^{a}, b.p. 160—163°/7 mm., m.p. 31—32° (from *p*-$NO_2{\cdot}C_6H_4{\cdot}OK$ and Bu^aBr in EtOH at 170—190°), and n-*amyl ether*, b.p. 162—163°/5 mm. 4 : 4′-*Dibutoxy*-, m.p. 134°, and 4 : 4′-*diamyloxy-azoxybenzene*, m.p. 81—82° (turbid), clear at 119°, are obtained by electrolytic reduction (Pb cathode and Ni anode in 96% EtOH saturated with NaOAc) of the NO_2-ethers. Further reduction to the azo-stage is not secured under more drastic conditions. 4 : 4′-*Dibutoxy*-, m.p. 135°, and 4 : 4′-*diamyloxy-azobenzene*, m.p. 112°, are obtained from the $(OH)_2$-derivative, KOH, and the requisite alkyl iodide in boiling MeOH. H. W.

Spectrochemical study of complex colouring matters. I. Metallic complexes of 2 : 2′-dihydroxyazobenzene. T. Uémura and Y. Inamura (Bull. Chem. Soc. Japan, 1938, **13**, 623—630).—(*o*-$OH{\cdot}C_6H_4{\cdot}N{:})_2$ (I) and some salts of Cr, Co, and Ni in aq. KOH give the *complexes*, $[CrR_2(H_2O)_2]K,2H_2O$, $[CoR_2(H_2O)_2]K$, and $[NiR_2(H_2O)_2]K_2,3H_2O$ (R = $C_{12}H_8O_2N_2$). The absorption spectra, in aq. and H_2SO_4 solutions, indicate that in the latter, the complexes undergo decomp. to (I) and metallic sulphates. The absorption curves indicate a ratio 1 : 2 of the metal to (I) in the new complexes. W. R. A.

Phenols from cornstalk alkali-lignin.—See B., 1938, 1389.

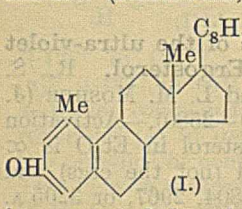
Physico-chemical study of reactions in organic solution.—See A., 1939, I, 26.

Hydroxy-by-products in aromatic nitration. G. M. Bennett and P. V. Youle (J.C.S., 1938, 1816—1818; cf. A., 1938, II, 401).—Literature on the formation of OH-by-products during aromatic nitration is reviewed, and new cases are also examined. Mechanisms are discussed and it is concluded that the by-products (much larger with *m*-directing substituents) are derived from OH-compounds in which OH enters the mol. according to the normal orientation law; polynitration then occurs, and in some cases the original substituent is lost, to yield the final by-product. C_6H_6 and 96% H_2SO_4–HNO_3 (*d* 1·42) at 65° afford 2 : 4 : 1-$(NO_2)_2C_6H_3{\cdot}OH$ (0·03%); PhMe gives 3 : 5-dinitro-*p*-cresol (0·7%). $PhNO_2$ and HNO_3 (*d* 1·42, 1·52, with or without H_2SO_4) or KNO_3–H_2SO_4 give, through *m*-$NO_2{\cdot}C_6H_4{\cdot}OH$ and 2 : 3 : 4 : 6 : 1-$(NO_2)_4C_6H{\cdot}OH$, small amounts of styphnic acid (max. yield 5·5—6·5% by KNO_3–H_2SO_4 at 90° for 2 hr.). $PhSO_2Cl$ affords (cf. *ibid.*, 313) 2 : 4 : 6-trinitro-3-hydroxybenzenesulphonyl chloride (1·7%); $PhSO_2Me$ (KNO_3–H_2SO_4) and Ph_2SO_2 [HNO_3 (*d* 1·52) at 90°] give styphnic acid (1·3 and 2·2%, respectively). Nitrations catalysed by Hg must be considered independently (cf. Davis *et al.*, A., 1921, i, 338). A. T. P.

Hydroxy- and methoxy-phenyldihydroanthracenes. F. F. Blicke and R. A. Patelski (J. Amer. Chem. Soc., 1938, **60**, 2636—2638).—9 : 9-Diphenyl-10-anthrone (in C_6H_6) and *p*-$OMe{\cdot}C_6H_4{\cdot}MgI$ (in Et_2O) give 10-*hydroxy*-9 : 9-*diphenyl*-10-p-*anisyl*-9 : 10-*dihydroanthracene*, m.p. 142—144°, which with HCl–MeOH gives the 10-*OMe*-compound, m.p. 191—193°, and with PhOH or PhOMe and a little H_2SO_4 at 100° gives 9 : 9-*diphenyl*-10-p-*hydroxyphenyl*-10-p-*anisyl*-(I), m.p. 250—252°, and 9 : 9-*diphenyl*-10 : 10-*di*-p-*anisyl*-9 : 10-*dihydroanthracene* (II), m.p. 233—235°, respectively. With HBr (I) yields 9 : 9-*diphenyl*-10 : 10-*di*-p-*hydroxyphenyl*-9 : 10-*dihydroanthracene*, m.p. 343—345° [(m-$C_6H_4Br{\cdot}CO)_2$ derivative, m.p. 231—233°], which with Me_2SO_4 gives (II) [also obtained from (I) by Me_2SO_4]. 9 : 9-Di-*p*-hydroxyphenylanthrone and Me_2SO_4 give 9-p-*hydroxyphenyl*-9-p-*anisyl*-, m.p. 232—233° (also obtained from 9-hydroxy-9-*p*-anisyl-10-anthrone, PhOH, and H_2SO_4), and 9 : 9-di-*p*-anisyl-10-anthrone (III). With *p*-$OMe{\cdot}C_6H_4{\cdot}MgI$, (III) gives 10-*hydroxy*-9 : 9 : 10-*tri*-p-*anisyl*-9 : 10-*dihydroanthracene* (IV), m.p. 226—228° (*Me ether*, m.p. 205—206°), converted by PhOH and H_2SO_4 into 9-p-*hydroxyphenyl*-9 : 10 : 10-*tri*-p-*anisyl*-9 : 10-*dihydroanthracene*, m.p. 310—312°, which with HBr and Me_2SO_4 yields 9 : 9 : 10 : 10-*tetra*-p-*hydroxy*-

phenyl-, m.p. 371—374° [(m-C_6H_4Br·*CO*)$_4$ derivative, m.p. 163—168°], and *-tetra*-p-*anisyl*-9 : 10-*dihydroanthracene*, m.p. 329—331° [also obtained from (IV) by PhOMe and H_2SO_4], respectively. R. S. C.

Conversion of sterols into aromatic compounds. III. Aromatisation of $\Delta^{1:4}$-cholestadien-3-one. H. H. Inhoffen and Huang-Minlon (Naturwiss., 1938, **26**, 756; cf. A., 1937, II, 147).—$\Delta^{1:4}$-Cholestadien-3-one with Ac_2O and H_2SO_4 yields a *phenol*, m.p. 145·5° [probably (I)] [*dinitrobenzoate*, m.p. 178°; *benzeneazo*-, m.p. 182°, and Br_2-derivative (II), m.p. 83—84°; *Me ether*, m.p. 104·5—105°]. The formula (I) is supported by the fact that (II) couples with PhN_2Cl, indicating two free *o*-positions in (I).



(I.)

J. D. R.

Reaction of aliphatic olefines with thiophenol. V. N. Ipatiev, H. Pines, and B. S. Friedman (J. Amer. Chem. Soc., 1938, **60**, 2731—2734).—Olefines add "abnormally" to thiophenols at 50—120° alone or in presence of H_3PO_4, but according to Markovnikov's rule in presence of H_2SO_4. $CHPr^{\beta}{:}CH_2$ is isomerised during the latter reaction, giving the *tert.*-amyl product. Thus are obtained *Ph Pr*$^{\alpha}$, b.p. 218·5—219·5°/750 mm., *Pr*$^{\beta}$, b.p. 206·5—207·5°/750 mm., Bu$^{\alpha}$, b.p. 94·5—97°/4 mm. [$PdCl_2$ compound, m.p. 106—106·5° (lit., 118°)], Bu$^{\beta}$, b.p. 107—108°/13 mm. [$PdCl_2$ compound, m.p. 92·5—93·5° (lit., 96°)], *Bu*$^{\gamma}$, b.p. 73°/5 mm. ($PdCl_2$ compound, m.p. 84° and >250° when recryst.; *sulphone*, m.p. 98—99°), n-, b.p. 117—118°/8 mm. ($PdCl_2$ *compound*, m.p. 75—76°), and iso-*amyl*, b.p. 100—100·5°/6 mm. ($PdCl_2$ *compound*, m.p. 96—97°), *CHMePr*$^{\beta}$ (I), b.p. 99—100°/5 mm., and *CMe*$_2$*Et sulphide* (II), b.p. 91—91·5°/6 mm. [*sulphone*, m.p. 29—30°; $PdCl_2$ *compound*, m.p. 72—73° and >250° when recryst.]. Structures are proved by prep. also from PhSNa and AlkBr, except that (II) could not be thus obtained; this method gives also Ph *sec.*-Bu, b.p. 90—91°/4 mm., *CHMePr*$^{\alpha}$, b.p. 91—92·5°/4·5 mm., *CHEt*$_2$, b.p. 107—107·5°/9 mm., and active *amyl sulphide*, b.p. 99—101°/4·5 mm. *m*-Nitrophenyl *n*-, m.p. 78·5—79°, and *iso*-propyl sulphone, m.p. 112—113°, and m-*aminophenyl* α-*methyl*isobutyl *sulphone*, m.p. 93—94°, are incidentally prepared. The compound, termed (I) by Posner (A., 1905, i, 279) was really (II), and his $PhSO_2$·CMe_2Et was really $PhSO_2H$. R. S. C.

Unsymmetrical aryl sulphides. N. E. Foss, J. J. Stehle, H. M. Shusett, and D. Hadburg (J. Amer. Chem. Soc., 1938, **60**, 2729—2730).—(*m*-NO_2·C_6H_4·S)$_2$ (prep. from *m*-NO_2·C_6H_4·SO_2Cl by HI) and Cl_2 give *m*-NO_2·C_6H_4·SCl, which with the appropriate phenol gives m-*nitrophenyl* p-*hydroxyphenyl*, m.p. 83—83·5° (*Ac*, m.p. 66—67°, Br_2-, m.p. 136—137°, *Bz*, m.p. 102—102·5°, and O-CH_2Ph derivative, m.p. 105—106°), 2 : 4-*dihydroxyphenyl*, m.p. 150·5—151·5° (Ac_2, m.p. 77—78°, and Br_2-derivative, m.p. 128—130°), and 2-*hydroxy*-1-*naphthyl sulphide*, m.p. 106° (*Ac*, m.p. 85—85·5°, *Bz*, m.p. 110—110·5°, and O-CH_2Ph derivative, m.p. 136—137°), and 2 : 4-*dihydroxy*-1 : 3-*phenylene bis*-(m-*nitrophenyl sulphide*), m.p. 179—180° (Ac_2, m.p. 109·5—110·5°, and *Br*-derivative, m.p. 189—190°). Hydrogenation (PtO_2) gives m-*aminophenyl* p-*hydroxyphenyl*, m.p. 84—84·5°, and 2-*hydroxy*-1-*naphthyl sulphide*, m.p. 193° (ON-Ac_2 derivative, m.p. 163—164°). R. S. C.

Cumyl alcohol. R. G. Cooke, D. T. Gillespie, and A. K. Macbeth (J.C.S., 1938, 1825—1826).—*p*-$C_6H_4Pr^{\beta}$·CH_2·OH (I), b.p. 91°/0·7 mm. (p-*nitro*-, m.p. 39—39·5°, and 3 : 5-*dinitro*-, m.p. 107°, *-benzoates*; phenyl-, m.p. 62°, and α-*naphthyl*-, m.p. 112—112·5°, *-urethanes*; *H phthalate*, m.p. 61—62°), is best prepared (70% yield) by reduction [H_2 (1340 lb.), Cu–Ba–Cr oxide catalyst, EtOH, 120°] of *p*-$C_6H_4Pr^{\beta}$·CHO (II). A cross-Cannizzaro reaction with (II) and CH_2O gave 42% of (I). A. T. P.

Reactions of αβ-unsaturated cyclic aldehydes and ketones. III. Reduction of cryptone. *cis*- and *trans*-dihydrocryptol. D. T. C. Gillespie, A. K. Macbeth, and T. B. Swanson (J.C.S., 1938, 1820—1824).—Reduction (Ponndorf, Al–Pr$^{\beta}$OH) of cryptone affords *l*-cryptol (*l*-4-*iso*propyl-Δ^2-*cyclo*hexen-1-ol) (I), b.p. 82—83°/2 mm., $[\alpha]_D^{20}$ −45·4° (*phenyl*-, m.p. 105°, and α-*naphthyl*-, m.p. 118°, *-urethanes*), which when purified through the *p*-nitrobenzoate is stereochemically pure and has b.p. 72°/2 mm., $[\alpha]_D^{20}$ −133° (homogeneous), −142° in EtOH. It is dehydrated by $KHSO_4$ at 120° to *l*-1-*iso*propyl-$\Delta^{2:4}$-*cyclo*hexadiene (II), b.p. 30°/4 mm., which with maleic anhydride in Et_2O forms an *adduct*, m.p. 133°, $[\alpha]_D^{20}$ −29·16° in $CHCl_3$. (II) and $KMnO_4$–H_2O–$COMe_2$, then PbO_2 in dil. H_2SO_4, give *iso*propylsuccinic acid. Reduction of either of the above *l*-cryptols with Pd–C–EtOH affords dihydrocryptol (III) (4-*iso*propyl*cyclo*hexan-1-ol), b.p. 84—85°/5 mm. (p-*nitrobenzoate*, m.p. 75·5°; 3 : 5-*dinitrobenzoate*, m.p. 124·5°; *phenylurethane*, m.p. 114°; α-*naphthylurethane*, m.p. 159·5°), converted by *o*-$C_6H_4(CO)_2O$ at 110° for 15 hr. into a *H phthalate*, m.p. 115°. (III) is obtained also by Ponndorf reduction of dihydrocryptone. Electrolytic reduction (Pt anode, Ni cathode) of cryptone in 95% EtOH–$NiSO_4$–10%H_2SO_4 at 34—36°, gives an isomeric (cis- or trans-)*dihydrocryptol* (IV), b.p. 60°/1·9 mm. (p-*nitrobenzoate*, m.p. 69·5°; 3 : 5-*dinitrobenzoate*, m.p. 112°; *phenylurethane*, m.p. 87—88°; α-*naphthylurethane*, m.p. 113°; *H phthalate*, m.p. 129°). Both (III) and (IV) are oxidised ($K_2Cr_2O_7$–H_2SO_4 at 30°) to dihydrocryptone (cf. A., 1937, II, 345). A. T. P.

Derivatives of 4-*spiro*heptane [*cyclo*butane-*spirocyclo*butane] identically substituted in the 2 : 6 [3 : 3′]-positions. H. J. Backer and H. G. Kemper (Rec. trav. chim., 1938, **57**, 1249—1258; cf. A., 1938, II, 324).—*cyclo*Butane*spirocyclo*butane-3 : 3′-dicarboxylic acid (I) gives the *dichloride* (II), b.p. 158—160°/15 mm., converted by PhOH in boiling C_5H_5N–$CHCl_3$ into the *Ph*$_2$ ester, m.p. 96—96·5°, of (I), which is reduced (Na–EtOH) to 3 : 3′-*bishydroxymethyl*cyclo*butane*spirocyclo*butane*, m.p. 167°/16 mm. The *di-H phthalate*, m.p. 139—139·5°, is resolved through the brucine or neutral *strychnine* salt. The Me$_2$ ester, m.p. 14°, b.p. 141°/11 mm., of (I), with MgMeI affords 3 : 3′-*bis*-(α-*hydroxy*isopropyl)-, m.p. 75—76°, and with MgPhBr gives 3 : 3′-*bis*-(α-*hydroxy*-

benzhydryl)cyclo*butane*spirocyclo*butane* (III), m.p. 105—105·5° (+2C_5H_5N), ~56° (decomp.) (+2Et_2O) (cryst. form examined), and 138·5—139° (" anhyd. "). (III) is dehydrated (AcOH–I) to the 3 : 3′-*bisdiphenylmethylene* derivative, m.p. 116—116·5°, oxidised (O_3–AcOH) to $COPh_2$ and a *compound*, $C_{10}H_{18}O_3$, m.p. 190—190·5°. (II) and $AlCl_3$–CS_2–C_6H_6 afford 3 : 3′-*dibenzoyl*cyclo*butane*spirocyclo*butane*, m.p. 73·5—74°, b.p. 263°/6 mm. [converted by MgPhBr into (III)], which does not react with HCN–C_5H_5N. A. T. P.

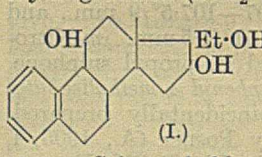
Oxidising action of selenium dioxide. Oxidation of acenaphthene. (Signa.) L. Monti (Gazzetta, 1938, **68**, 608—612).—Acenaphthene with SeO_2 at 150—170° gives acenaphthylene (15—25%) and *cis*- and *trans*-acenaphthylene glycol (cf. A., 1938, II, 138) (15—16%). E. W. W.

Interaction of β-hydroxyethylamine and halogenonitrobenzenes. K. F. Waldkötter (Rec. trav. chim., 1938, **57**, 1294—1310).—NH_2·$[CH_2]_2$·OH (I) reacts with halogenonitrobenzenes with elimination of labile group(s) to form derivatives of β-hydroxyethylaniline. (I) with 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$ and picryl chloride (±NaOAc), in EtOH, gives respectively 2 : 4-dinitro- (II), new m.p. 90° (*N-Ac* derivative, m.p., 130°), and 2 : 4 : 6-trinitro- (III), m.p. 110° (ON-Ac_2 derivative, m.p. 117°), -β-hydroxyethylanilines. (II) or (III) in abs. HNO_3 at −15° gives *N*- nitro - *N* - 2 : 4 : 6 - trinitrophenyl - β - aminoethyl nitrate [" pentryl "], m.p. 129° or >188° (block), ignites at 250°. (I) and 1 : 4 : 2-$C_6H_3Cl_2$·NO_2 in EtOH at 140—145° for 5 hr. give 4-*chloro*-2-*nitro*-β-*hydroxyethylaniline*, m.p. 107° (Ac_2 derivative, m.p. 48°), converted by HNO_3 at −15° into N-*nitro*-N-4-*chloro*-2 : 6-*dinitrophenyl*-β-*aminoethyl nitrate* (IV), forms, m.p. 81° (? 84°) and 92° (block), decomp. 105°, ignites 296°. (I) and 4-chloro-2 : 6-dinitroanisole in boiling EtOH give 4-*chloro*-2 : 6-*dinitro*-β-*hydroxyethylaniline*, m.p. 102°, which with HNO_3 yields (IV). 4-*Bromo*-2-*nitro*-, m.p. 106° (Ac_2 derivative, m.p. 53°), and 4-*bromo*-2 : 6-*dinitro*-, m.p. 114°, -β-*hydroxyethylanilines* are similarly prepared; they are both nitrated to N-*nitro*-N-4-*bromo*-2 : 6-*dinitrophenyl*-β-*aminoethyl nitrate*, m.p. 95°, decomp. 180°, ignites 256°. (I) and 1 : 3 : 4-$C_6H_3Cl(NO_2)_2$ in EtOH afford 5-*chloro*-2-*nitro*-β-*hydroxyethylaniline*, m.p. 116° (Ac_2 derivative, m.p. 94°), which with HNO_3 at −10° gives N-*nitro* - N-5 - *chloro* - 2 : 4 - *dinitrophenyl* - β - *aminoethyl nitrate* (V), decomp. 180°, ignites 253°, also formed similarly from 5-*chloro* - 2 : 4 - *dinitro* - β - *hydroxyethylaniline*, forms, m.p. 132° and 116° (Ac_2 derivative, m.p. 96°). 5-*Bromo*-2-*nitro*-β-*hydroxyethylaniline*, m.p. 126° (Ac_2 derivative, m.p. 75°, hydrolysed by boiling H_2O to the N-*Ac* derivative, m.p. 109°), and HNO_3 at −10° give N-*nitro*-N-5-*bromo*-2 : 4-*dinitrophenyl*-β-*aminoethyl nitrate* (VI), m.p. 114°, decomp. 173°, ignites 262°. (I) (4 equivs.) and 1 : 3 : 4 : 6-$C_6H_2Cl_2(NO_2)_2$ afford 4 : 6-*dinitro*-1 : 3-*bis*-(β-*hydroxyethylamino*)*benzene*, m.p. 211° [NN′-Ac_2 derivative, m.p. 149°; (?) 2 : NN′-$(NO_2)_3$-derivative, decomp. violently at 98°, ignites at 230°]. Equiv. amounts of (I) and 1 : 3 : 4 : 5-$C_6H_2Cl_2(NO_2)_2$ in EtOH (3 hr.) give 4 : 6-*dichloro*-2-*nitro*-β-*hydroxyethylaniline*, m.p. 51° (Ac_2 derivative, m.p. 82°), whence N-*nitro*-N-4 : 6-*dichloro*-2-*nitrophenyl*-β-*aminoethyl nitrate*, m.p. 88°, decomp. 187°, ignites 305°. 4 : 6-*Dibromo*-2-*nitro*-β-*hydroxyethylaniline*, m.p. 71° (Ac_2 derivative, m.p. 86°), and HNO_3 yield N-*nitro*-N-4 : 6-*dibromo*-2-*nitrophenyl*-β-*aminoethyl nitrate*, m.p. 69°, decomp. 178°, ignites 305°. (V) and (VI) with EtOH–NH_2Ph appear to give the same (?) 5-*NHPh*-derivative, m.p. ~60°. A. T. P.

Diaryl(dimethylaminomethyl)carbinols. — See B., 1938, 1502.

Quantitative measurement of the ultra-violet activation of sterols. I. Ergosterol. R. S. Harris, J. W. M. Bunker, and L. M. Mosher (J. Amer. Chem. Soc., 1938, **60**, 2579—2580).—Activation (measured biologically) of ergosterol in Et_2O is ∝ the quanta of energy absorbed (not the ergs) and equal for light of 2537, 2652, 2804, 2967, or 3205 A. Possibly, however, 2804 is the most effective λ. R. S. C.

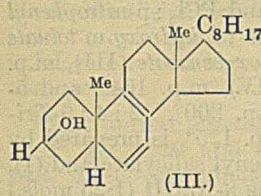
Coffee. IV. Elucidation of the constitution of cafesterol. K. H. Slotta and K. Neisser (Ber., 1938, **71**, [*B*], 2342—2346).—The formula $C_{20}H_{28}O_3$ is confirmed for cafesterol (I) by the examination of its *monoacetate* (II), m.p. 163·5—165°, $[\alpha]_D^{20}$ −134·6° in $CHCl_3$, obtained by use of NaOAc and boiling Ac_2O. More drastic conditions do not lead to a more highly acetylated product so that only 1 O of (I) is present as acetylatable primary or *sec.* OH. CO and phenolic OH are absent. One of the outstanding O atoms must be present in a *tert.* OH group vicinal to the acetylatable OH since Zn dust transforms (I) or (II) at 160—190°/0·01 mm. into *anhydrocafesterol* (III), m.p. 126—128° [*semicarbazone*, m.p. 227—229° (decomp.)]. The nature of the third O could not be elucidated and its presence is suggested as an unreactive *sec.*-OH such as has been proved present in corticosterone. (II) is very rapidly hydrogenated (PtO_2) to *hexahydrocafesteryl acetate*, m.p. 101—105° (among other compounds). The three double linkings appear equiv.; they cannot be saturated with Na and EtOH and therefore are not present in an aliphatic conjugated system; hence one ring is probably aromatic. Hydrogenation (PtO_2 in AcOH) of (III) yields octahydroanhydrocafesterol. (I) has probably the structure shown. Further examination shows substance *A* (A., 1938, II, 449) to be a mixture (1 : 1) of (I) and γ-sitosterol. Substance *S* is probably a paraffin alcohol not closely related to (I). Substance *I*, $C_{27}H_{48}O$, is nearly allied to the true sterols; it cannot be acetylated and does not react with NH_2·CO·NH·NH_2. H. W.



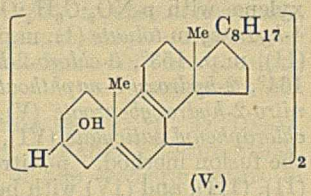
(I.)

Product of the irradiation of $\Delta^{6:8}$-cholestadienol. A. Windaus and G. Zühlsdorff (Annalen, 1938, **536**, 204—216; cf. A., 1938, II, 185).—The first preparatively established, photochemical transformation product of $\Delta^{6:8}$-cholestadienol (I) is due to a steric rearrangement at $C_{(5)}$ which corresponds exactly with the first photochemical transformation of $\Delta^{5:7}$-cholestadienol (II) at $C_{(10)}$, since in accordance with the rule of double linkings the union between $C_{(5)}$ and $C_{(10)}$ in (I) is loosened in the same manner as that between $C_{(9)}$ and $C_{(10)}$ in (II). Exposure of (I) in pure C_6H_6 to a Mg spark light leads to $\Delta^{6:8}$-

coprostadienol (III), m.p. 92° [*acetate* (IV), m.p. 101°, $[\alpha]_D^{20}$ +176·5° in $CHCl_3$; *benzoate*, m.p. 125°, $[\alpha]_D^{20}$



(III.)



(V.)

+167° in $CHCl_3$; 3 : 5-*dinitrobenzoate*, m.p. 192°, $[\alpha]_D^{20}$ +127° in $CHCl_3$], which gives a sparingly sol. additive *compound* with digitonin and strongly resembles (I) in its absorption spectrum, indicating the presence of conjugated double linkings in a ring. This view is confirmed by the isolation of an *adduct*, $C_{33}H_{48}O_5$, m.p. 242—244°, $[\alpha]_D^{18}$ +47·3° in $CHCl_3$, from (IV) and maleic anhydride, and by oxidation [HNO_3 (*d* 1·4)] of (III) to $C_6HMe(CO_2H)_4$. Photochemical dehydrogenation of (I), (II), or (III) in presence of eosin gives the dihydric alcohol (V), [*diacetate* (VI), m.p. 202° (decomp.), $[\alpha]_D^{20}$ −133·5° in $CHCl_3$; *dipropionate*, m.p. 197° (decomp.), $[\alpha]_D^{20}$ −125·5°; *diisobutyrate*, m.p. 184—185°, $[\alpha]_D^{20}$ −114·5°]. (VI) is transformed by hot Ac_2O into the norsteryl acetate $C_{26}H_{39}$·OAc (corresponding *dinitrobenzoate*, m.p. 207°, $[\alpha]_D^{18}$ +2·5° in $CHCl_3$). Hydrogenation (Pt sponge in AcOH) at room temp. and, after addition of conc. HCl, at 60° of (IV) yields coprosteryl acetate, m.p. 88—90° (corresponding *dinitrobenzoate*, m.p. 214—215°). Oxidation of (IV) with BzO_2H in $CHCl_3$ gives unidentified crystals, m.p. 73—78°, and material which is acetylated (Ac_2O, C_5H_5N) to Δ^8-*coprostene*-3 : 6 : 7-*triol diacetate benzoate*, m.p. 200—201°, $[\alpha]_D^{20}$ +32° in $CHCl_3$, hydrolysed to Δ^8-*coprostene*-3 : 6 : 7-*triol*, m.p. 191—192° (*triacetate*, m.p. 150—151°). (III) is reduced by Na and PrOH to δ-*coprostenol* [$\Delta^{8:9}$-*coprostenol*], m.p. 80—83°, $[\alpha]_D^{21}$ +15·0° in $CHCl_3$ (*dinitrobenzoate*, m.p. 195—196°, $[\alpha]_D^{21}$ +33·5° in $CHCl_3$); the corresponding *acetate*, m.p. 107—108°, $[\alpha]_D^{21}$ +43·5° in $CHCl_3$, is isomerised by H_2–Pd to α-*coprostenyl acetate*, m.p. 114—115°, $[\alpha]_D^{16}$ +30·5° in $CHCl_3$ (corresponding *dinitrobenzoate*, m.p. 181°, $[\alpha]_D^{20}$ +27·3° in $CHCl_3$), also obtained by hydrogenation (Pd sponge in EtOAc at room temp.) of (IV). HCl and (IV) in $CHCl_3$ at 0° give an *isomeride*, m.p. 80—81°, $[\alpha]_D^{19}$ −49·3° in $CHCl_3$, of the type of ergosterol *B* and containing its conjugated double linkings in two rings. It is hydrolysed to *coprostadienol* B, m.p. 75°, $[\alpha]_D^{20}$ −48° (*dinitrobenzoate*, m.p. 169°). Catalytic perhydrogenation transforms it into coprosterol. When heated with maleic anhydride it is re-converted into (III). H. W.

α-Theosterol, $C_{30}H_{50}O_3$, m.p. 113—114° [acetate, m.p. 113—115°; digitonide, m.p. 222—224° (decomp.)], from cacao germ oil.—See A., 1939, III, 109.

Separation of the antirachitically acting components of irradiated 7-dehydrocholesterol.—See B., 1938, 1502.

Transmission of substituent influences in ester hydrolysis.—See A., 1939, I, 31.

Reactivity of the ω-halogen atom in *p*-alkoxybenzyl halides: preparation of phenylacetic acids. R. G. Naik and T. S. Wheeler (J.C.S., 1938, 1780—1783).—6-Chloro- (I) and -bromo-piperonal (II) (prepared in AcOH), and 3-chloro- (III) and -bromo- (IV) -*p*-anisaldehyde with NH_2Ph at 100° give the corresponding *anils*, m.p. 112°, 131—132°, 85°, and 96—97°, respectively. (I), (II), (III), and (IV), with 50% aq. NaOH–EtOH at 50° (cf., Ahmad *et al.*, A., 1938, II, 337), afford 6-*chloro*-, m.p. 73—74°, and -*bromo*-, m.p. 90°, -3 : 4-*methylenedioxybenzyl*, and 3-*chloro*-, b.p. 178—180°/10 mm., and -*bromo*-, m.p. 63—64°, -4-*methoxybenzyl alcohols*, respectively, converted by HCl–C_6H_6 at 0° or HBr (*d* 1·69) into 6-*chloro*-3 : 4-*methylenedioxybenzyl chloride*, m.p. 65°, and *bromide*, m.p. 75—76°; 6-*bromo*-3 : 4-*methylenedioxybenzyl chloride*, m.p. 64—65°, and *bromide*, m.p. 94° (also from 3 : 4-methylenedioxybenzyl alcohol or Me ether and 1 mol. of Br); 3-*chloro*-4-*methoxybenzyl chloride* (V), b.p. 145—147°/6 mm., and *bromide*, m.p. 52—53°; 3-*bromo*-4-*methoxybenzyl chloride*, m.p. 51—52°, and *bromide*, m.p. 61—62°. The chlorides and KI–$COMe_2$–H_2O at 100° for 1½ hr. give the corresponding *iodides*, m.p. 95—96°, 90—91°, 61—62°, and 64—65°, respectively. The chlorides and KCN–EtOH for 24 hr. afford respectively 6-*chloro*-, m.p. 70—71°, and -bromo-, m.p. 71—72°, piperonylacetonitrile, and 3-*chloro*-, m.p. 54—55°, and -*bromo*-, m.p. 56—57°, -p-*anisylacetonitriles*, hydrolysed by aq. NaOH–EtOH at 100° for 8 hr. to 6-*chloro*-, m.p. 174—175° (*Me*, m.p. 69—70°, and *Et* ester, m.p. 60—61°), and -bromo-, m.p. 190° (*Et* ester, m.p. 69—70°), -piperonylacetic acid, and 3-*chloro*-, m.p. 95—96°, and -bromo-, m.p. 114—115°, -*p*-anisylacetic acid, respectively. (V) and MeOH or EtOH at 100° for 2 hr. give 3-*chloro*-4-*methoxybenzyl Me*, b.p. 135—140°/5 mm., and *Et*, b.p. 150—155°/10 mm., *ethers*. 3-*Bromo*-4-*methoxybenzyl Et ether* boils at 155—160°/10 mm. The ethers with HCl–C_6H_6 or HBr (*d* 1·69) are reconverted into the halides. 3 : 4-Methylenedioxybenzyl bromide (VI) and hot MeOH (EtOH) give 2 : 3 : 6 : 7-bismethylenedioxy-9 : 10-dihydroanthracene, m.p. >360°, but (VI) and MeOH + Na_2CO_3 at 100° for 1½ hr. afford 3 : 4-*methylenedioxybenzyl Me ether*, b.p. 120°/10 mm. (cf. Kobayashi, A., 1928, 169). The 6-halogeno-3 : 4-methylenedioxybenzyl halides react with alcohols without forming dihydroanthracene derivatives, but the resultant oils contain more halogen than the expected ethers; 6-nitro-3 : 4-methylenedioxybenzyl chloride does not react. 6-Chloro- and -bromo-3 : 4-methylenedioxybenzyl halides and PCl_5 at 120° for 4 hr. give the unstable 6-*chloro*-, b.p. 150—154°/10 mm., and -*bromo*-, b.p. 155—157°/10 mm., -3 : 4-*dichloromethylenedioxybenzyl chloride* (cf. Ewins, J.C.S., 1909, **95**, 1482), HCO_2H then giving 6-*chloro*-, m.p. 64°, and -*bromo*-, m.p. 80—81°, -3 : 4-*carbonyldioxybenzyl chloride*, respectively. A. T. P.

Reactivity of the methylene group in derivatives of phenylacetic acid. G. D. Parkes and B. C. Aldis (J.C.S., 1938, 1841—1845; cf. A., 1936, 1497).—The actions of HNO_2 and diazonium salts respectively on derivatives of phenylacetic acid are recorded (cf. Meyer, A., 1889, 516). The Me ester of 2 : 4-dinitrophenylacetic acid (I) (*benzyl* ester, m.p. 98°) with *p*-$C_6H_4Hal{\cdot}N_2Cl$ or 2 : 4-$C_6H_3(Hal)_2{\cdot}N_2Cl$ in NaOAc–EtOH affords respectively *Me* p-*chloro*-, m.p. 155°, p-*bromo*-, m.p. 182°, 2′ : 4′-*dichloro*-, m.p. 181°,

and 2′ : 4′-*dibromo-*, m.p. 199°, *-benzeneazo-*2 : 4-*dinitrophenylacetate*. Me benzeneazo-2 : 4-dinitrophenylacetate and Br–AcOH–NaOAc afford ω-bromo-2 : 4-dinitrobenzaldehyde-*p*-bromophenylhydrazone (cf. Chattaway *et al.*, A., 1931, 1416), probably through the unstable Me *p*-bromobenzeneazo-2 : 4-dinitrophenylacetate. (I) and PhN_2Cl-aq. NaOAc give *formazyl*-2 : 4-*dinitrobenzene*, 2 : 4 : 1-$(NO_2)_2C_6H_3$·C(N:NPh):N·NHPh, m.p. 198°; similarly prepared are pp′-*dibromo-* (II), m.p. 220°, 2′: 2″: 4′: 4″-*tetrachloro-*, m.p. 206° (darkens at 150°), and *-tetrabromo-*, m.p. 201° (darkens at 150°), *-formazyl*-2 : 4-*dinitrobenzene*, stable to boiling HCl. (II) and Sn–HCl afford 6(or 7)-*bromo*-3-2′ : 4′-*diaminophenyl*-1 : 2 : 4-*benztriazine*, m.p. 180° (darkens at 160°). (I)–aq. $(NH_4)_2S$–H_2S, boiled for 5—6 hr., give 2-nitro-4-aminophenylacetic acid (III), m.p. 185° [*Ac* (IV), m.p. 205°, and *Bz*, m.p. 223°, derivatives], which at 190° for a few min. gives 2-*nitro*-4-2′-*nitro*-4′-*aminophenylacetamidophenylacetic acid*, m.p. 213° (some 2-nitro-*p*-toluidine is formed also if reaction is at 270°) (cf. Gabriel and Meyer, A., 1881, 729). (IV) is stable to HNO_2, but with $KMnO_4$–$MgSO_4$–H_2O, refluxed for 7 hr., it gives 4 : 2 : 1-NHAc·$C_6H_3(NO_2)$·CO_2H. Diazotisation of (III) followed by CuCl affords 4-chloro-2-nitro-benzaldehyde and -phenylacetic acid; thus even in the cold, HNO_2 attacks the CH_2. (III) and Br–AcOH at 60° for a few min. give impure 5-bromo- [Ac derivative, oxidised to 4 : 5 : 2 : 1-NHAc·$C_6H_2Br(NO_2)$·CO_2H, m.p. 246°] and 3 : 5-dibromo-2-nitro-4-aminophenylacetic acid [*Ac* derivative, m.p. 240° (decomp.)]. (I) does not react with HNO_2 and no reaction occurs between NO_2·C_6H_4·CH_2·CO_2H and HNO_2 or ArN_2Cl. 6-Amino-oxindole [*Ac*, m.p. 324° (stable to HNO_2), and *Bz* derivative, m.p. 273°] with C_5H_{11}·O·NO–HCl followed by CuCl gives 6-*chloro-oximino-oxindole*, m.p. 240°, and (impure) 6-chloro-oxindole. 6-Nitro-oxindole and *p*-C_6H_4Br·N_2Cl–NaOAc give 6-*nitro*-3-p-*bromobenzeneazo-oxindole*, m.p. 281° (decomp.) (cf. Borsche and Meyer, A., 1922, i, 53). A. T. P.

Derivatives of salicylic acid. XIII. Chlorosalicylic acids and their methyl ethers. N. W. Hirwe, K. N. Rana, and K. D. Gavankar (Proc. Indian Acad. Sci., 1938, **8**, A, 208—213).—5-Sulphosalicylic acid with Cl_2 in glacial AcOH or with $KMnO_4$ in conc. HCl, and subsequent decomp. with superheated steam, yields 3-chlorosalicylic acid (I) [*K*, *Ca* (+$3H_2O$), and *Ag* salts; *amide*, m.p. 174—176°], also obtained by hydrolysis of *chloral*-3-*chlorosalicylamide*, m.p. 159—160° (from chloralsalicylamide and Cl_2 in AcOH). Methylation (Me_2SO_4–KOH) of (I) yields 3-*chloro*-2-*methoxybenzoic acid*, m.p. 120—121° [*Na* (+H_2O), *Ba* (+$4H_2O$), and *Ag* salts; *amide*, m.p. 99—100°]. *o*-OH·C_6H_4·CO_2H in AcOH at 0° yields with 1 mol. of Cl_2, 5-chloro-, and with 2 mols. 3 : 5-dichloro-salicylic acid [*Ca* (+$4H_2O$) salt]. *o*-OMe·C_6H_4·CO_2H under the same conditions yields 5-chloro- (*Ag* salt; *amide*, m.p. 137—138°) and 3 : 5-dichloro-2-methoxybenzoic acid [*Na* (+$2H_2O$), *Ba* (+$5H_2O$), and *Ag* salts; *amide*, m.p. 152—153°]. A. Li.

Rearrangement of aryl salicylates. B. T. Tozer and S. Smiles (J.C.S., 1938, 1897—1900; cf. A., 1936, 716).—The following are prepared from the appropriate acid by fusion at 140°, or better in boiling xylene, with *p*-NO_2·C_6H_4·OH and PCl_5: p-*nitrophenyl* 4-*hydroxy*-m-*toluate* (I), m.p. 136°, 2-*hydroxy*-m-*toluate* (II), m.p. 153°, 5-*chloro*-2-*hydroxybenzoate* (III), m.p. 164°, 2-*hydroxy*-3-*naphthoate* (IV), m.p. 164°, and 5-*nitro*-2-*hydroxybenzoate* (V), m.p. 200°. 2 : 4 : 6-*Trichlorophenyl salicylate* (VI), m.p. 125°, is prepared by the fusion method. *p*-Nitrophenyl salicylate and (I), (II), (III), and (IV) with boiling N-NaOH (1·25 mols.) for 1¼ hr. afford respectively 4′-*nitro*-2-*carboxydiphenyl ether*, m.p. 161° (70% yield), p-*nitrophenyl* 3-*carboxy*-p-, m.p. 173°, and -o-, m.p. 143° (*Me* ester, m.p. 99°), *-tolyl ethers*, 4-*chloro*-4′-*nitro*-2-*carboxydiphenyl ether*, m.p. 174—175°, and p-*nitrophenyl* 3-*carboxy*-β-*naphthyl ether*, m.p. 208°. The last could not be decarboxylated. Under the above conditions, (V) and (VI) show no evidence of rearrangement. *o*-NO_2·C_6H_4·OK and *O*-carbethoxy-*p*-cresol-3-sulphonyl chloride (VII) at 100° for ½ hr. give a product, decarbethoxylated with N-NaOH–EtOH at 15° to o-*nitrophenyl* 4-*hydroxytoluene*-3-*sulphonate*, m.p. 88°. This is rearranged by boiling 0·25N-NaOH–EtOH for ½ hr. to *o*-nitrophenyl 3-sulpho-*p*-tolyl ether, which with PCl_5 at 130° for 1 hr. gives 4-o-*nitrophenoxytoluene*-3-*sulphonyl chloride*, m.p. 132° (*sulphanilide*, m.p. 157°), also prepared from *o*-nitrophenyl 3-sulphino-*p*-tolyl ether and 6% NaOCl. (VII) and PhOH in boiling $COMe_2$ + K_2CO_3 form a product, decarbethoxylated to Ph 4-hydroxytoluene-3-sulphonate, new m.p. 57° (*Na* derivative, m.p. 220—230°, readily sol. in cold $CHCl_3$). The *Na* derivative of Ph salicylate melts at 193—195° (cf. A., 1938, II, 320). The tendency to form covalent Na derivatives may assist the rearrangements. A. T. P.

Stability of esters of *p*-hydroxybenzoic acid. F. Reimers (Dansk Tidsskr. Farm., 1938, **12**, 240—247).—Hydrolysis of esters of *p*-OH·C_6H_4·CO_2H (I) by alkalis can be followed by bromometric titration, the esters giving Br_2-derivatives and (I) giving 2 : 4 : 6-$C_6H_2Br_3$·OH (cf. A., 1938, II, 409). No hydrolysis occurs on boiling with H_2O. Na salts of esters of (I) are hydrolysed slowly on storage and rapidly in aq. solution. *Pr*$^{\alpha}$, m.p. 106—109°, and *benzyl*, m.p. 109—110°, 3 : 5-*dibromo*-4-*hydroxybenzoates* have been prepared. M. H. M. A.

1-Amino-4-hydroxynaphthalene-8-carboxylic acid.—See B., 1938, 1390.

Reduction and autoxidation products of 7 : 7-di(hydroxyaryl)acenaphthenones. I. Matei and E. Bogdan (Ber., 1938, **71**, [*B*], 2296—2300).—Reduction of 8-keto-7 : 7-di-4′-hydroxy-3′-methylphenylacenaphthene by Zn dust and NaOH under H_2 or CO_2 yields 7 : 7-*di*-4′-*hydroxy*-3′-*methylphenylacenaphthen*-8-*ol* (I), m.p. 117°, converted by air in the presence of alkali into the *compound*, 1 : 8-$C_{10}H_6<\begin{matrix}CH(OH)\\CR_2\end{matrix}>O$ (R = 4 : 3-OH·C_6H_3Me·), m.p. 230—235° (decomp.) (*dibenzoate*, m.p. 230°). Exhaustive autoxidation of (I) leads to *di-o-cresolnaphthalein*, m.p. (indef.) <100°, which dissolves in alkali to an intense violet solution. Reduction of 8-keto-7 : 7-di-*p*-hydroxyphenylacenaphthene by Zn dust and NaOH followed by passage of air through

the solution gives *di*-p-*hydroxyphenyl*-8-*carboxy*-1-*naphthylcarbinol*, m.p. 239—240°. *Di*-4′-*hydroxy*-2′ : 5′-*dimethylphenyl*-, m.p. 233° (decomp.) (*dibenzoate*, indef. m.p.), and *di*-4-*hydroxynaphthyl*- (dibenzoate, indef. m.p.) -8-*carboxy*-1-*naphthylcarbinol* are obtained analogously. H. W.

Multiplanar *cyclo*hexane rings. R. D. Desai, R. F. Hunter, and G. S. Saharia (Nature, 1938, **142**, 798).—Bromination of the isomeric forms of 1-carboxy-4-methyl*cyclo*hexane-1-acetic acid (A., 1936, 846) gives Br_1-acids, hydrolysed (hot aq. Na_2CO_3) to the corresponding OH-acids, which are oxidised (alkaline $KMnO_4$) to isomeric forms of 4-methyl*cyclo*hexane-1 : 1-dicarboxylic acid. Similar observations have been made in the 3-methyl*cyclo*hexane series. L. S. T.

Octa- and deca-hydronaphthalene-9 : 10-dicarboxylic acid. P. Brigl and R. Herrmann (Ber., 1938, **71**, [*B*], 2280—2282; cf. Alder *et al.*, A., 1938, II, 491).—Butadiene and Δ^1-tetrahydrophthalic acid at 160—170° give (after hydrolysis) octahydronaphthalene-9 : 10-dicarboxylic acid, m.p. 190° [anhydride, m.p. 68°; *imide*, m.p. 176°; *hydrazide*, $C_{10}H_{14}\langle^{CO}_{CO}\rangle N{\cdot}NH_2$, m.p. 98° (*Ac* derivative, m.p. 225°)]. It is hydrogenated (PtO_2 in AcOH) to decahydronaphthalene-9 : 10-dicarboxylic acid (I), decomp. 192° (block) when slowly heated [anhydride, m.p. 96°; Me_2 ester, m.p. 63°; *imide*, m.p. 188—189°; *hydrazide*, m.p. 137—138° (Ac_1 derivative, m.p. 170°)]. The Et_2 ester, m.p. 48°, of (I), obtained from the Ag_2 salt and EtI, is transformed by very energetic hydrolysis into the *Et H ester*, m.p. 120—121°, which is very resistant towards boiling 2N-NaOH. (I) therefore resembles $(CMe_2{\cdot}CO_2H)_2$ rather than o-$C_6H_4(CO)_2O$. H. W.

Lactone formation of the addition product of maleic anhydride and di*cyclo*hexenyl. R. Adams and E. E. Gruber (J. Amer. Chem. Soc., 1938, **60**, 2792—2794).—$\Delta^{12:13}$-Dodecahydrophenanthrene-9 : 10-dicarboxylic acid (I) (A., 1936, 331) or its anhydride (II) [prep. from (I) and Ac_2O] with HCl–abs. EtOH gives the *lactone*, m.p. 109—110°, of 12-hydroxy-10-carbethoxytetradecahydrophenanthrene-9-carboxylic acid, converted by 5% NaOH into Na_2 12-*hydroxytetradecahydrophenanthrene*-9 : 10-*dicarboxylate*, from which acid ppts. the 9 : 12-*lactone-acid*, m.p. 246—247°, also obtained from (I) by hot, conc. HCl–$COMe_2$ or, with (II), by heating alone at 200—210°. With EtOH–NaOEt (II) gives *Et H* $\Delta^{12:13}$-*dodecahydrophenanthrene*-9 : 10-*dicarboxylate*, m.p. 127—128°, hydrolysed to (I) by alkali. The unsaturated compounds, but not the lactones or Na_2 salt, absorb Br. Oily by-products are formed in all the above reactions. R. S. C.

Syntheses in the hydroaromatic series. III. (A) Further diene syntheses from 6-methoxy-1 acetylenyl- and -1-vinyl-3 : 4-dihydronaphthalene. (B) Condensation of *cyclo*pentadiones with acetylene. (Frl.) E. Dane, O. Höss, K. Eder, J. Schmitt, and O. Schön (Annalen, 1938, **536**, 183—196; cf. A., 1937, II, 500).—(A) Me_2 7-*hydroxyoctahydrophenanthrene*-1 : 2-*dicarboxylate* has m.p. 174—175°. The constitution of 7-methoxy-1 : 2 : 9 : 10-tetrahydrophenanthrene-1 : 2-dicarboxylic anhydride (I) (*loc. cit.*) (free acid, new m.p. 216°) is established by its dehydrogenation (Pt-black at 280°) to 7-methoxyphenanthrene-1 : 2-dicarboxylic anhydride, m.p. 253—254°. *p*-Benzoquinone in boiling PhOMe converts (I) into 7-methoxy-1 : 2-dihydrophenanthrene-1 : 2-dicarboxylic anhydride, m.p. 221—221·5° (corresponding acid, m.p. 221°, and its Me_2 ester, m.p. 138°), hydrogenated (Pd–C) to the 1 : 2 : 3 : 4-H_4-anhydride. Similarly di-6-methoxy-3 : 4-dihydro-1-naphthylacetylene is transformed into *di*-6-*methoxy*-1-*naphthylacetylene*, m.p. 195°, hydrogenated (Pd–C in dioxan) to *di*-6-*methoxy*-1-*naphthylethane*, m.p. 154°. 3 : 6-Diketo-10-methoxytetrahydrochrysene (*loc. cit.*) is hydrogenated (Pd–$CaCO_3$ or Pd–C in PhOMe) to 3 : 6-*diketo*-10-*methoxydodecahydrochrysene* (II), m.p. 130—132° or 145—148° (according to the catalyst used), which gives non-cryst. products when treated with HBr–AcOH; when reduced in presence of PtO_2 in AcOH or PhOMe it yields a *compound*, (?) $C_{18}H_{20}O_2$, m.p. 194° or 183—184° according to the solvent used. Hydrogenation (PtO_2 in AcOH) of (II) affords 3 : 6-*dihydroxy*-10-*methoxydodecahydrochrysene*, m.p. 163°, the *diacetate*, m.p. 153°, of which is transformed by HBr–AcOH into 10-*methoxyoctahydrochrysene*, m.p. 148—149°. Boiling Et propiolate and 6-methoxy-1-acetylenyl-3 : 4-dihydronaphthalene in N_2 give, after hydrolysis, re-esterification (CH_2N_2), and adsorption (Al_2O_3) 7-*methoxy*-9 : 10-*dihydrophenanthrene*-2-*carboxylic acid*, m.p. 206—207° [as *Me* ester (III), m.p. 86°], which does not absorb H_2 in presence of Pd–$CaCO_3$ or PtO_2 in *cyclo*hexane or EtOH, and 7-*methoxy*-9 : 10-*dihydrophenanthrene*-1-*carboxylic acid*, m.p. 152—153°; the constitution of the former follows from its dehydrogenation (Se at 300°) to 7-*methoxy*-2-*methylphenanthrene*, m.p. 143—144° (whence 7-*hydroxy*-2-*methylphenanthrene*, m.p. 146°), not identical with the known 1-Me product. 7-*Hydroxy*-9 : 10-*dihydrophenanthrene*-2-*carboxylic acid* (+0·5MeOH) (*Et* ester, m.p. 146°) has m.p. 246°. *p*-Benzoquinone and (III) at 200° give *Me* 7-*methoxyphenanthrene*-2-*carboxylate*, m.p. 134°.

(B) *cyclo*Pentane-1 : 2-dione and CH:C·MgBr yield 2-*hydroxy*-2-*acetylenyl*cyclo*pentanone*, b.p. 50°/0·1 mm., which does not give a coloration with $FeCl_3$ or react with dinitrophenylhydrazine. 2-Hydroxy-5-methyl-2-acetylenyl*cyclo*pentanone, b.p. 65°/0·2 mm., gives a colourless Ag derivative which rapidly becomes brown. H. W.

Benzaldehyde reaction of deoxycholic acid. T. Shimada (J. Biochem. Japan, 1938, **28**, 169—174).—Whilst free deoxycholic acid gives a green colour (A., 1938, II, 365), the conjugated acid, *e.g.*, glycodeoxycholic, produces a blue colour. The reaction indicates that the acid is conjugated in rabbit's bile and mainly free in the bile of ox and dog. Anthropo- and hyo-deoxycholic acid give a violet colour with the reagent. F. O. H.

Action of concentrated hydrochloric acid on chenodeoxycholic acid. K. Yamasaki and K. Takahashi (Z. physiol. Chem., 1938, **256**, 21—27; cf. A., 1938, II, 492).—Chenodeoxycholic acid with AcOH–conc. HCl gives a *hydroxycholenic acid* (I),

$C_{24}H_{38}O_3$, m.p. 185°, $[\alpha]_D^{20}$ +96° in EtOH, which with PtO_2–H_2 in EtOH gives lithocholic acid (II) and β-apo*chenodeoxycholic acid* (III), $C_{24}H_{38}O_3$, m.p. 196°, $[\alpha]_D^{20}$ +77° in EtOH (*acetate*, m.p. 164°). (III) in a high vac. at 250—280° for 30 min. and then at 350—360° gives a *choladienic acid*, $C_{24}H_{36}O_2$, m.p. 163°, $[\alpha]_D$ +41·9° in EtOH, which with PtO_2–H_2 in AcOH gives δ-*cholenic acid*, $C_{24}H_{38}O_2,H_2O$, m.p. 173° (decomp. 170°), $[\alpha]_D^{20}$ +43·6° in EtOH. Oxidation (CrO_3, AcOH) of (III) gives a *ketocholenic acid*, $C_{24}H_{36}O_3$, m.p. 137° (*oxime*, decomp. 227°). (I) is probably a mixture of a 3-hydroxy-$\Delta^{7:8}$-cholenic acid [reduced to (II)] and (III) (which has a double linking at 8 : 14 or 8 : 9 and is not reducible). W. McC.

Autoxidation of benzaldehyde in presence of didiphenylene-ethylene. G. Wittig and W. Lange (Annalen, 1938, **536**, 266—284; cf. A., 1937, II, 284).—The inhibitor action of tetraphenylpolyenes towards the autoxidation of PhCHO increases with the no. of C:C linkings and the hydrocarbons, which are otherwise stable towards O_2, become oxidised in an increasing degree. The products are, however, intractable mixtures wherefore the study is restricted to didiphenylene-ethylene (I). In non-polar solvents this is stable to light and air for months but in polar media (EtOH, Et_2O, dioxan) it is autoxidised to fluorenone (II); the change occurs very much more rapidly in presence of PhCHO. BzO_2H is not an intermediate in the change since it does not attack (I) under the experimental conditions and oxidises (I) to (II) only at 80—90° and in presence of a large excess of BzO_2H without detectable intermediate production of the ethylene oxide. Evidence is adduced that OH or other radical is not the carrier of a chain reaction and that therefore the hypothesis of Haber and Willstätter (A., 1932, 352) must be discarded. It is considered that PhCHO first adds O_2 to a very reactive "mol. adduct" PhCHO···O=O; this either may become stabilised to BzO_2H (which is unimportant for the further autoxidation of PhCHO) or may react with a second mol. of PhCHO with formation of 2 mols. of BzOH. The energy thereby liberated activates a further mol. of PhCHO which adds O_2 and continues the autoxidation as a chain reaction; the further possibility of intermediate formation of 2 equivs. of $CHPh\langle^{O}_{O}\rangle$ is suggested by the production of some CHPh: ether of *cis*-diphenylacenaphthylene glycol from 7 : 8-diphenylacenaphthylene [used instead of (I)]. If the "mol. adduct" encounters a mol of (I) instead of PhCHO there is production of (II) whereby PhCHO is regained or formation of BzOH occurs. Since the energy thus liberated is inadequate to activate a fresh mol. of PhCHO, the oxidation of 1 mol. of (I) inhibits that of a complete chain of PhCHO mols. The possibility that labile mol. adducts can evolve O in an activated form is established by the observation that, whereas dioxan is not appreciably affected by prolonged exposure to O_2, solutions of (I) in this solvent absorb more O_2 than is required for the transformation of (I) into (II). The behaviour of autoxidising PhCHO in presence of hydrocarbons at higher concn. is thus readily explained. H. W.

Preparation of *m*-bromobenzaldehyde. F. T. Tyson (J. Amer. Chem. Soc., 1938, **60**, 2821).—*m*-C_6H_4Br·CHO, prepared from *m*-NO_2·C_6H_4·CHO by $SnCl_2$–HCl and diazotisation (Sandmeyer) (NH_2-compound not isolated) and previously regarded as pure, contains both Cl and Br. R. S. C.

γ-Substitution in the resorcinol nucleus. I. Synthesis of γ-resorcylaldehyde. R. C. Shah and M. C. Laiwalla (J.C.S., 1938, 1828—1832; cf. Limaye, A., 1937, II, 258).—Me β-resorcylate and $Zn(CN)_2$–$AlCl_3$ in dry Et_2O–HCl give *Me* 2 : 4-*dihydroxy*-3-*formylbenzoate* (I), m.p. 138—140° [2 : 4-*dinitrophenylhydrazone*, m.p. 291—293° (decomp.); *semicarbazone*, decomp. 260—265°; *oxime*, m.p. 164—165°; *anil*, m.p. 131—132°], reduced (Zn–Hg, dil. HCl–EtOH at 100°) to *Me* 2 : 6-*dihydroxy*-m-*toluate* (II), m.p. 134—135°, which is converted by MeI–NaOMe–MeOH into Me 2-hydroxy-6-methoxy-*m*-toluate, new m.p. 77—79°. (I) and $CH_2(CO_2Et)_2$ in C_5H_5N–piperidine at 100° for 1 hr. give *Et* 5-*hydroxy*-6-*carbomethoxycoumarin*-3-*carboxylate*, m.p. 157—158°. (I) and Br–AcOH afford *Me* 5-*bromo*-2 : 4-*dihydroxy*-3-*formylbenzoate*, m.p. 133—134° (2 : 4-*dinitrophenylhydrazone*, m.p. 294—295°); MeI–K_2CO_3–$COMe_2$ yields *Me* 2-*hydroxy*-4-*methoxy*-3-*formylbenzoate*, m.p. 121—122°, whereas Me_2SO_4–KOH–MeOH at 100° gives 2 : 4-*dimethoxy*-3-*formylbenzoic acid*, m.p. 185—187°, reduced (Clemmensen) to 2 : 6-*dimethoxy*-m-*toluic acid*, m.p. 146—147°. The latter is obtained also from 2-hydroxy-6-methoxy-*m*-toluic acid, new m.p. 214—215°, and Me_2SO_4–20% KOH–$COMe_2$. (II) and 2N-NaOH at 100°, or 2-methylresorcinol and aq. $KHCO_3$ (100°/4 hr., then reflux for ½ hr.) give 2 : 6-*dihydroxy*-m-*toluic acid*, m.p. 200—201° (decomp.). (I) and N-NaOH at room temp. for 45 hr. afford 2 : 4-*dihydroxy*-3-*formylbenzoic acid*, m.p. 193—194° (decomp.), which with H_2O at 100—110° (sealed tube) for 10 hr. gives γ-resorcylaldehyde (III), new m.p. 155—156° (2 : 4-*dinitrophenylhydrazone*, m.p. 288—291°; *semicarbazone*, m.p. 245°), reduced (Clemmensen) to 2-methylresorcinol. (III) and $CH_2(CO_2Et)_2$ (piperidine) give *Et* 5-*hydroxycoumarin*-3-*carboxylate*, m.p. 229—230°. 3-Substitution in β-resorcylic acid or ester is not recorded previously. It is suggested that chelation between OH and CO_2Me in Me β-resorcylate leads to a fixation of the double linkings in the resorcinol nucleus, and a stabilisation of one of the Kekulé forms (cf. Baker *et al.*, A., 1937, II, 198). A. T. P.

Interaction between Grignard compounds and maleic acid derivatives. C. Weizmann and F. Bergmann (J. Amer. Chem. Soc., 1938, **60**, 2647—2650).—Me_2 maleate (I) and CH_2Ph·MgCl give αζ-*diphenyl*-γ-*benzylhexane*-βε-*dione* m.p. 136°, which gives no semicarbazone, but with MgPhBr yields αβζ-*triphenyl*-δ-*benzylhexan*-β-*ol*-ε-*one*, m.p. 202°. MgEtI and (I) give δ-*ethyloctane*-γζ-*dione*, b.p. 110°/1 mm. $MgBu^aBr$ and (I) give ζ-n-*butyldodecane*-εθ-*dione* (II), b.p. 136°/0·05 mm., and a little ε-n-*butyl*-Δ^5-*dodecen*-ε-*ol*-θ-*one* (III), b.p. 115—120°/0·1 mm. With MgPhBr, (II) gives εθ-*diphenyl*-ζ-n-*butyl*-n-*dodecane*-εθ-*diol*, m.p. 122—123°, and (?) dehydration products. (:CH·CO)$_2$O with CH_2Ph·MgCl, $MgBu^aBr$, and MgEtBr gives γ-*hydroxy*-δ-*phenyl*-γ-*benzyl*-Δ^a-*pentenoic* (p-

phenylphenacyl ester, m.p. 142—143°), *γ-hydroxy-γ-*n-*butyl-*n-Δ^{α}-*octenoic*, b.p. 114°/0·05 mm. (p-*phenylphenacyl* ester, m.p. 79°), and *γ-hydroxy-γ-ethyl-*n-Δ^{α}-*hexenoic acid*, b.p. 115°/0·6 mm. (p-*phenylphenacyl* ester, m.p. 77—78°), respectively, together with other products, which include *αζ-diphenyl-βε-dibenzyl-*$\Delta^{\alpha\gamma\epsilon}$-*hexatriene*, m.p. 184°, b.p. 215—220°/1·5 mm. (from $CH_2Ph{\cdot}MgCl$), (III) (from $MgBu^{\alpha}Br$), and (?) *γ*-ethylsorbic acid (p-*phenylphenacyl* ester, m.p. 138°) and *εζ-diethyl-*n-*octan-ζ-ol-γ-one*, b.p. 75°/1·5 mm. (from MgEtBr). *γ*-Butyrolactone and MgPhBr give *αα-diphenylbutane-αδ-diol*, m.p. 108°. The reaction mechanism is discussed. R. S. C.

Derivatives of β-*p*-anisyl-β-methylpyruvic [α-keto-β-*p*-anisylbutyric] acid. E. Cattelain (Compt. rend., 1938, **207**, 998—1000).—The $NaHSO_3$ compound of *α-p*-anisylpropaldehyde (I) with cold aq. KCN affords *α-hydroxy-*β-p-*anisylbutyronitrile*, decomp. ~50°/15 mm., converted by cold conc. HCl into *α-hydroxy-*β-p-*anisylbutyramide* (II), m.p. 123° (corresponding *acid*, m.p. 91—92°). (II) with $KMnO_4$–$COMe_2$ affords *α-keto-*β-p-*anisylbutyramide*, m.p. 119—120° (*semicarbazone*, m.p. 239°), hydrolysed (warm dil. NaOH) to *α-keto-*β-p-*anisylbutyric acid*, m.p. 30° [*semicarbazone*, m.p. 207·5°, converted by warm dil. NaOH into 3 : 5-*diketo-*6-α-p-*anisylethyl-*2 : 3 : 4 : 5-*tetrahydro-*1 : 2 : 4-*triazine*, m.p. 220·5° (4-*Me*, m.p. 159—160°, 2 : 4-Me_2, m.p. 142·5°, 4-*Et*, m.p. 132°, 4-*benzyl*, m.p. 206°, and 2 : 4-*dibenzyl*, m.p. 160·5—161·5°, derivatives)]. J. L. D.

Synthesis of αδ-di-3 : 4-dimethoxyphenylbutan-β-one (veratryl homoveratryl ketone). R. Carroll and P. E. Spoerri (J. Amer. Chem. Soc., 1938, **60**, 2656—2658).—
3 : 4-$(OMe)_2C_6H_3{\cdot}[CH_2]_2{\cdot}COCl$, b.p. 138—142°/0·5 mm., m.p. 40°, unstable, and CH_2N_2 in Et_2O give *α-chloro-*δ-3 : 4-*dimethoxyphenylbutan-*β-*one*, m.p. 53°, which, however, could not be caused to react with *o*-$C_6H_4(OMe)_2$. 3 : 4-$(OMe)_2C_6H_3{\cdot}CH_2{\cdot}CN$, 3 : 4-$(OMe)_2C_6H_3{\cdot}[CH_2]_2{\cdot}CO_2Et$, and NaOEt in EtOH give *α-cyano-αδ-di-*3 : 4-*dimethoxyphenylbutan-*β-*one* (I), m.p. 76°, which is difficult to hydrolyse but with conc. HCl–AcOH at 15—20° (4 days) gives *α-carbamyl-αδ-di-*3 : 4-*dimethoxyphenylbutan-*β-*one*, m.p. 123°, converted by hot, dil. HCl into *αδ-di-*3 : 4-*dimethoxyphenylbutan-*β-*one*, m.p. 76° [$(NO_2)_2$-derivative, m.p. 195°]. With hot, aq. H_2SO_4 (I) gives *α-cyano-*5 : 6 : 3′ : 4′-*tetramethoxy-*1-*benzylideneindane*, m.p. 209°. R. S. C.

Friedel–Crafts reaction. IV. Action of acetyl chloride and acetic anhydride on resorcinol and its derivatives. Evidence for γ-substitution in the resorcinol nucleus. R. D. Desai and M. Ekhlas (Proc. Indian Acad. Sci., 1938, **8**, **A**, 194—201).—Resorcinol, AcCl, and $AlCl_3$ in $PhNO_2$ at room temp. yield 4 : 1 : 3- but no 2 : 1 : 3-$C_6H_3Ac(OH)_2$. Similarly 4 : 1 : 3-$C_6H_3Et(OH)_2$ yields 6 : 4 : 1 : 3-$C_6H_2EtAc(OH)_2$. 2 : 6-*Dihydroxy-*3-*ethylacetophenone* (I) (not formed in the above reaction), m.p. 135° [*semicarbazone*, m.p. 252°; Ac_2 derivative, m.p. 76° (*semicarbazone*, m.p. 267°)], is synthesised as follows: 5 : 2 : 4 : 1-$C_6H_2Et(OH)_2{\cdot}CO_2Me$ with Ac_2O and $AlCl_3$ in $PhNO_2$ yields *Me* 2 : 4-*dihydroxy-*3-*acetyl-*5-*ethylbenzoate*, m.p. 76°, hydrolysed (10% NaOH) to (I). 1 : 2 : 4-$C_6H_3Et(OH)_2$, $CH_2Ac{\cdot}CO_2Et$, and 73% H_2SO_4 yield 7-hydroxy-4-methyl-6-ethylcoumarin [*Me ether*, m.p. 160°; *carbethoxy*-derivative (which failed to undergo the Fries transformation with $AlCl_3$ or $ZnCl_2$), m.p. 144°], the *Ac* derivative, m.p. 143°, of which with $AlCl_3$ at 140—150° yields 7-*hydroxy-*8-*acetylcoumarin*, m.p. 139° (*semicarbazone*, m.p. >290°). This is hydrolysed (2N-NaOH) to (I), with Ac_2O and NaOAc at 175—180° gives 3-*acetyl-*4 : 2′-*dimethyl-*6′-*ethylcoumarin-*7 : 8-*γ-pyrone*, m.p. 192°, and with Br in glacial AcOH in sunlight gives the 3-*Br*-compound, m.p. 180°, hydrolysed by Na_2CO_3 to 6-*hydroxy-*7-*acetyl-*3-*methyl-*5-*ethylcoumarone* (II), m.p. 66° (*semicarbazone*, m.p. >290°), together with the *coumarilic acid*, m.p. 204—206° (decomp.), decarboxylated to (II). 2 : 4 : 1-$C_6H_3(OH)_2{\cdot}CO_2Me$ does not condense with AcCl at room temp., but with Ac_2O and $AlCl_3$ in $PhNO_2$ yields 5 : 2 : 4 : 1- but no 3 : 2′ : 4 : 1-$C_6H_2Ac(OH)_2{\cdot}CO_2Me$. 4 : 1 : 3-$C_6H_3Ac(OH)_2$ under similar conditions yields both 2 : 4 : 1 : 3- and 4 : 6 : 1 : 3-$C_6H_2Ac_2(OH)_2$. Orcinol with AcCl and $AlCl_3$ in $PhNO_2$ yields orsacetophenone and a little 5-hydroxy-4 : 7-dimethylcoumarin [formed by way of 4 : 1 : 2 : 6-$C_6H_2MeAc(OH)_2$]. 2-Substitution in the *m*-$C_6H_4(OH)_2$ nucleus thus occurs in the last two cases only. A. Li.

Nuclear methylation of resacetophenone. 3-Methylresacetophenone and its derivatives. S. Rangaswami and T. R. Seshadri (Proc. Indian Acad. Sci., 1938, **8**, **A**, 214—219).—1 : 2 : 4-$C_6H_3Ac(OH)_2$ with MeI–MeOH–KOH at 0° yields 2-*hydroxy-*4-*methoxy-*3-*methyl-*, m.p. 82—83°, demethylated to 2 : 4-*dihydroxy-*3-*methyl-acetophenone*, m.p. 156—157°, also synthesised from 2 : 1 : 3-$C_6H_3Me(OH)_2$, MeCN, $ZnCl_2$, and HCl.
2 : 4 : 1-$C_6H_3(OH)_2{\cdot}CO{\cdot}CH_2{\cdot}OMe$ with MeI–MeOH–KOH yields 2-*hydroxy-*ω : 4-*dimethoxy-*3-*methylacetophenone*, m.p. 109°, which with NaOBz and Bz_2O at 200° gives 3 : 7-*dimethoxy-*8-*methylflavone* (I), m.p. 145—146°. ω-*Methoxy-*3-*methylresacetophenone* [from 2 : 1 : 3-$C_6H_3Me(OH)_2$, $OMe{\cdot}CH_2{\cdot}CN$, $ZnCl_2$, and HCl], m.p. 203—205°, with NaOBz and Bz_2O yields 7-*hydroxy-*3-*methoxy-*8-*methylflavone*, m.p. 252—253°, methylated (MeI–$COMe_2$–K_2CO_3) to (I). A. Li.

4-Acetyl-1-methylnaphthalene [and derivatives]. K. Dziewoński and (Mlle.) M. Marusińska (Bull. Acad. Polonaise, 1938, **A**, 316—323).—1-$C_{10}H_7Me$ in $PhNO_2$, AcCl, and $AlCl_3$ at −3° to −1°, then at room temp. for 24 hr., give 4 : 1-$C_{10}H_6AcMe$ (I), m.p. 41° (*semicarbazone*, m.p. 204—205°; *phenylhydrazone*, m.p. 141°) (cf. Haworth and Mavin, A., 1933, 57), the *oxime*, m.p. 125—126°, of which with dry HCl–Ac_2O–AcOH affords 1 : 4-$C_{10}H_6Me{\cdot}NHAc$, new m.p. 171°, hydrolysed by boiling 10% HCl for 2 hr. to the amine, m.p. 51—52° (cf. Lesser, A., 1914, i, 33). (I) and 3% NaOCl give 1 : 4-$C_{10}H_6Me{\cdot}CO_2H$, m.p. 175°. (I) and MgMeI–Et_2O yield 4-*methyl-*1-*naphthyldimethylcarbinol* (II), m.p. 85—86°, and 1-*methyl-*4-*isopropenylnaphthalene*, b.p. 140°/16 mm. (*picrate*, m.p. 89°). (I) and (II), with Zn–Hg–HCl–H_2O for 3 hr., give 1-*methyl-*4-*ethyl-*, b.p. 122°/40 mm. (*picrate*, m.p. 98—99°), and 1-*methyl-*4-*isopropylnaphthalene*, m.p. 196°, respectively. (I), NH_2Ph, and NH_2Ph,HCl at 170—175° for 2 hr. give 1 : 3 : 5-*tri*-(4′-*methyl-*1′-*naphthyl*)*benzene*, m.p. 185°; (I) and S

at 230—260° for 3 hr. afford 6 : 6′-*dimethyl*-4 : 5 : 4′ : 5′-*dibenzthioindigotin*, m.p. >410°. A. T. P.

Ketone derivatives of 2 : 6-dimethylnaphthalene. K. Dziewoński, K. Stec, and P. Zagała (Bull. Acad. Polonaise, 1938, **A**, 324—330; cf. preceding abstract).—2 : 6-$C_{10}H_6Me_2$ and AcCl–$PhNO_2$–$AlCl_3$ at −4° give 2 : 6 : 1-$C_{10}H_5Me_2Ac$ (I), m.p. 71° (*semicarbazone*, m.p. 193°) (cf. Clar *et al.*, A., 1929, 689), the *oxime*, m.p. 142—143°, of which with AcOH–Ac_2O–HCl affords 2 : 6 : 1-$C_{10}H_5Me_2$·NHAc, m.p. 205—206° (cf. A., 1922, i, 999), hydrolysed by 10% HCl (2 hr.) to 2 : 6 : 1-$C_{10}H_5Me_2$·NH_2 (II), m.p. 91°. (I) is oxidised (NaOCl) to 2 : 6 : 1-$C_{10}H_5Me_2$·CO_2H (III), m.p. 203—204°, and reduced (Clemmensen) to 2 : 6-*dimethyl*-1-*ethylnaphthalene*, b.p. 162°/23 mm. (*picrate*, m.p. 118°). EtCOCl similarly gives 1-*propionyl*-2 : 6-*dimethylnaphthalene*, m.p. 49°, b.p. 205—206°/23 mm. [*picrate*, m.p. 125°; *semicarbazone*, m.p. 188—189°; oxidised to (III)]; the *oxime*, m.p. 130°, affords 1-*propionamido*-2 : 6-*dimethylnaphthalene*, m.p. 199—200°, and thence (II). A. T. P.

Chalkones; synthesis of deoxybenzoins from chalkones. W. A. Hutchins, D. C. Motwani, K. D. Mudbhatkal, and T. S. Wheeler (J.C.S., 1938, 1882—1885).—The possibility of conversion (cf. Baker and Robinson, A., 1932, 859) of COAr·CH:CHR′ into COAr·CH_2R′ is not independent of the nature of the substituent groups. Ph *p*-methoxystyryl ketone and NHPh·NH_2–AcOH at 100° for 20 min. give 1 : 3-*diphenyl*-5-p-*anisyl*-4 : 5-*dihydropyrazole*, m.p. 125—126°. Ph, *p*-tolyl, 2 : 4 : 6-trimethoxyphenyl, and β-$C_{10}H_7$, m.p. 95—97°, *p*-methoxystyryl ketones, and 2 : 4-dimethoxyphenyl 3 : 4-methylenedioxystyryl ketone, with 30% H_2O_2–EtOH–$COMe_2$–4N-NaOH at 40° afford Ph (I), p-*tolyl* (II), m.p. 109—110°, 2 : 4 : 6-trimethoxyphenyl (III), m.p. 118—120°, and β-$C_{10}H_7$ (IV), m.p. 131°, αβ-epoxy-β-*p*-anisylethyl ketone, and 2 : 4-*dimethoxyphenyl* αβ-*epoxy*-β-3 : 4-*methylenedioxyphenylethyl ketone* (V), m.p. 143°, respectively. *m*-Nitrophenyl *p*-methoxystyryl ketone and H_2O_2 do not react, neither is an oxide obtained from *m*-NO_2·C_6H_4·CO·CH_2Br and *p*-OMe·C_6H_4·CHO by the method of Widman (A., 1916, i, 406). (I) and (III), refluxed with aq. NaOH–EtOH for 4 hr., give Ph [also from (X) (below)] and 2 : 4 : 6-*trimethoxyphenyl* p-*methoxybenzyl diketone*, m.p. 144—145°, respectively. (IV) does not react similarly; (II) and (V) give unstable diketones, that from (II) with *o*-$C_6H_4(NH_2)_2$–EtOH giving 2-p-*tolyl*-3-p-*methoxybenzylquinoxaline*, m.p. 113—115°. (I), (II), and (V), boiled with 30% aq. NaOH for 4 hr., give phenyl- (VI) and p-*tolyl*-p-*methoxybenzylglycollic acid* (VII), m.p. 153°, and 2 : 4-*dimethoxyphenyl*-3 : 4-*methylenedioxybenzylglycollic acid*, m.p. 181°, respectively. The latter heated at > m.p. or with AcOH for 4 hr. gives 3 : 4-*methylenedioxy*-α-2′ : 4′-*dimethoxyphenylcinnamic acid*, m.p. 176—177°. (VI) and (VII), with $K_2Cr_2O_7$ or K_2CrO_4 in aq. AcOH for 2 min., give Ph and p-*tolyl* *p-methoxybenzyl ketone*, m.p. 101—103°, respectively. (II) and (V), with N_2H_4,H_2O–EtOH for 5 min., give 4-*hydroxy*-5-p-*anisyl*-3-p-*tolyl*-4 : 5-*dihydropyrazole* (VIII), m.p. 168° (unstable NO-derivative), and 4-*hydroxy*-3-(2′ : 4′-*dimethoxyphenyl*)-5-(3′ : 4′-*methylenedioxyphenyl*)-4 : 5-*dihydropyrazole*, m.p. 151°, respectively. (III) does not react similarly and (IV) gives an unstable derivative (IX). (I) affords 4-hydroxy-3-phenyl-5-*p*-anisyl-4 : 5-dihydropyrazole (Freudenberg *et al.*, A., 1925, i, 70) [ON(1)-Ac_2 derivative, m.p. 125—126°]. (VIII) and (IX), boiled with NaOEt–EtOH for 1½ hr., give 5-p-*anisyl*-3-p-*tolyl*-, m.p. 170°, and -3-β-*naphthyl*-, m.p. 232°, -*pyrazoles*, respectively. (I) or (V) and MeOH–H_2SO_4 at 40° for 3 hr., diluted slightly, then at 0° for some days, afford *Ph* α-*hydroxy*-β-*methoxy*-β-p-*anisylethyl ketone* (X), m.p. 87—89°, and 2 : 4-*dimethoxyphenyl* α-*hydroxy*-β-*methoxy*-β-3 : 4-*methylenedioxyphenylethyl ketone*, m.p. 200° (β-*ethoxy*-analogue, m.p. 172°, from EtOH), respectively. (II) refluxed with AcOH for ½ hr. affords p-*tolyl* α-*hydroxy*-β-*acetoxy*-β-p-*anisylethyl ketone*, m.p. 103—105°, and (V) and HCO_2H give, similarly, 2 : 4-*dimethoxyphenyl* α-*hydroxy*-β-*formoxy*-β-3 : 4-*methylenedioxyphenylethyl ketone*, m.p. 212°. Ph *p*-methoxystyryl ketone, *p*-OMe·C_6H_4·CH_2·COPh, and EtOH–NaOEt give αε-*diketo*-αε-*diphenyl*-βγ-*di*-p-*anisylpentane*, m.p. 165—166°. Similarly prepared are αε-*diketo*-ε-*phenyl*-βγ-*di*-p-*anisyl*-α-, m.p. 146—147°, αε-*diketo*-αβ-*diphenyl*-γ-p-*anisyl*-ε-, m.p. 152—153°, αε-*diketo*-βγ-*di*-p-*anisyl*-αε-*di*-, m.p. 150—151°, and αε-*diketo*-γ-*phenyl*-ε-*o*-*hydroxyphenyl*-β-p-*anisyl*-α-, m.p. 167—168°, -p-*tolylpentane*. 1 : 2-$C_{10}H_6$Ac·OMe and PhCHO in aq. EtOH–alkali give 2-*methoxy*-1-*naphthyl styryl ketone*, m.p. 140—142°, which with *p*-tolyl *p*-methoxybenzyl ketone gives αε-*diketo*-γ-*phenyl*-β-p-*anisyl*-α-p-*tolyl*-ε-(2′-*methoxy*-1′-*naphthyl*)*pentane*, m.p. 156—157°. αε-Diketo-αβε-triphenyl-γ-*p*-anisylpentane and NH_2OH,HCl–EtOH at 140—145° for 5 hr. afford 2 : 3 : 6-*triphenyl*-4-p-*anisylpyridine*, m.p. 188—189°. *cyclo*Hexanone, *p*-OMe·C_6H_4·CH:CH·COPh, and 50% aq. NaOH–EtOH give 2-(β-*benzoyl*-α-p-*anisylethyl*)-cyclo*hexanone*, m.p. 140—141°. Similarly prepared from *p*-tolyl and β-$C_{10}H_7$ *p*-methoxystyryl ketone and β-$C_{10}H_7$ *styryl ketone* (XI), m.p. 105—107°, are 2-(β-p-*toluoyl*-α-p-*anisylethyl*)-, m.p. 133—134°, 2-(β-*naphthoyl*-α-p-*anisylethyl*)-, m.p. 128—130°, and 2-(β-*naphthoyl*-α-*phenylethyl*)-, m.p. 155—156°, -cyclo*hexanone*, respectively. (XI), β-$C_{10}H_7$ *p*-methoxystyryl and 1-hydroxy-2-naphthyl styryl ketones, respectively, refluxed with CH_2Ac·CO_2Et–NaOEt–EtOH for ½ hr., give *Et* 6-*phenyl*-4-β-*naphthyl*-, m.p. 174—175°, *Et* 6-p-*anisyl*-4-β-*naphthyl*-, m.p. 145—147°, and *Et* 6-*phenyl*-4-(1′-*hydroxy*-2′-*naphthyl*)-, m.p. 165—167°, -Δ^3-cyclo*hexen*-2-*one*-1-*carboxylate*. A. T. P.

Influence of α-halogen substitution on the enolisation of ketones. E. P. Kohler and H. M. Sonnichsen (J. Amer. Chem. Soc., 1938, **60**, 2650—2652).—The effect of α-halogen in increasing the enolisation of ketones is shown by (*a*) the solubility of α-bromo-ββ-diphenylpropionylmesitylene (I), m.p. 172—173°, in cold KOH–EtOH (it is only slightly sol. in EtOH) and (*b*) its conversion by KOH–MeOH–Me_2SO_4 into the *enol Me ether*, m.p. 115—116°, in 30% yield (traces are obtained by MeI). When kept in KOH–MeOH, (I) gives 2 : 4 : 6-$C_6H_2Me_3$·CO·CH:CPh_2 (II). 80—90% of (I) is obtained from 2 : 4 : 6-$C_6H_2Me_3$·CO·CH:CHPh by MgPhBr, followed by Br at <−5°. 2 : 4 : 6-$C_6H_2Me_3$·CO·CH_2·$CHPh_2$ or (I) with Br in aq. alkali

gives *αα-dibromo-ββ-diphenylpropionylmesitylene*, m.p. 135—136°, unstable when heated, converted slowly by aq. KOH or more rapidly by KOH–MeOH into (II). $CHPh_2$·CHBr·COPh is sol. in MeOH–KOH, although less so than (I), but is thereby converted into a substance, m.p. 230—240°. R. S. C.

Reaction of diazomethanes with Grignard reagents. G. H. Coleman, H. Gilman, C. E. Adams, and P. E. Pratt (J. Org. Chem., 1938, **3**, 99—107).—MgPhBr adds to the terminal N of CPh_2N_2 (modified prep.), giving, after hydrolysis, CPh_2:N·NHPh. If NPh_2·COCl is added before hydrolysis, the intermediate CPh_2:N·NPh·MgBr reacts therewith to give *benzophenone-ββδ-triphenylsemicarbazone*, CPh_2:N·NPh·CO·NPh_2, m.p. 160—161°, obtained also by treating CPh_2:N·NHPh first with MgPhBr or $NaNH_2$ and then with NPh_2·COCl, and hydrolysed by hot 20% HCl to $COPh_2$ and NH_2·NPh·CO·NPh_2. Similarly with CH_2Ph·MgCl, CPh_2N_2 gives CPh_2:N·NH·CH_2Ph or, if treated with NPh_2·COCl, *benzophenone-δδ-diphenyl-β-benzylsemicarbazone*, m.p. 137—139°, obtained also from CPh_2:N·NH·CO·NPh_2 by MgPhBr, followed by CH_2PhCl, and hydrolysed to $COPh_2$ and *δδ-diphenyl-β-benzylsemicarbazide*, NH_2·N(CH_2Ph)·CO·NPh_2, m.p. 109—110°. With MgMeI CPh_2N_2 gives CPh_2:N·NHMe, hydrolysed to NH_2·NHMe. With a slight excess of MgPhBr CH_2N_2 gives indefinite products, but with a large excess reacts thus: CH_2N_2 + MgPhBr → CH_2:N·NPh·MgBr → CH_2Ph·N(MgBr)·NPh·MgBr → CH_2Ph·NH·NHPh (I) (identified by oxidation by H_2O_2 to CHPh:N·NHPh). In the reaction of CH_2N_2 with CH_2Ph·MgCl or $MgBu^aBr$ reduction occurs, the products being α-benzyl-β-methylhydrazine (*hydrochloride*, m.p. 139—140°; reduced by Na–Hg to NH_2Me and NH_2·CH_2Ph) and α-methyl-β-*n*-butylhydrazine (*hydrochloride*, m.p. 114—115°), respectively. CH_2N_2 with MgEtI, MgMeI, and MgMeBr gives N_2 and indefinite products. R. S. C.

Degree of association of metal diaryl ketyls. L. Anschütz and A. Ungar (Annalen, 1938, **536**, 285—297).—The effect of the addition of K on the b.p. of solutions of Ph diphenylyl ketone (I) in Et_2O, C_6H_6, and dioxan (II), of $COPh_2$ in C_6H_6, and of *p*-OMe·C_6H_4·COPh in C_6H_6 and (II) has been studied. Solutions sufficiently conc. for the determination of mol. wt. are invariably supersaturated. In 36 successful experiments the results obtained agree satisfactorily with those required for the monomeric compound, the extreme deviations being −13% and +6%. Under the most favourable circumstances solutions of (I) in Et_2O and (II) give about 28% and 68%, respectively, of the theoretical amounts of metal ketyl. The metal diaryl ketyls have very little tendency towards association (cf. Doescher *et al.*, A., 1934, 1158). H. W.

Structure and absorption [spectra] of benzoylbenzoic acid and its derivatives. C. K. Lin (Compt. rend., 1938, **207**, 733—735; cf. A., 1917, i, 339; 1922, i, 833).—Comparison of the ultra-violet absorption spectra of *o*-benzoyl-*p*-methoxybenzoic acid (I), *o*-C_6H_4Bz·CO_2H (II), their Me esters, and Na salts with those of *p*-methoxyphenyl- and phenylphthalide, respectively, indicates that (I) and (II) exist in solution (Et_2O, EtOH) in the ketonic forms. J. L. D.

Catalytic properties of the phthalocyanines. III. A. H. Cook (J.C.S., 1938, 1774—1780; cf. A., 1939, I, 34).—The oxidation of tetra- and Δ^2-octa-(I) -hydronaphthalene, α-pinene, *cyclo*hexene, Δ^1-methyl*cyclo*hexene, CH_2Ph_2, and cholesteryl acetate by O_2 in presence of Fe phthalocyanine, yielding products containing CO and only rarely OH adjacent to the double linking, has been studied. Of 38 other metal phthalocyanines and related pigments, all were inactive except Cr and Co phthalocyanines, which were feebly active. Evidence for the formation of an intermediate peroxide of the compound being oxidised is discussed. The catalyst functions partly by promoting the formation of the peroxide and partly by accelerating its further rearrangement to a ketone. The product of oxidation of (I) is 1-*keto*-Δ^2-*octahydronaphthalene*, b.p. 114°/5 mm. (*semicarbazone*, m.p. 203—204°). 3-*Methyl*-Δ^2-cyclo*hexenone*-2 : 4-*dinitrophenylhydrazone* has m.p. 150°. E. S. H.

Condensation of acenaphthenequinone with xylenols and thymol. I. Matei and E. Bogdan (Ber., 1938, **71**, [*B*], 2292—2295; cf. A., 1935, 86).—Addition of a few drops of conc. H_2SO_4 to acenaphthenequinone and 3 : 4-$C_6H_3Me_2$·OH in boiling AcOH affords *anhydro*-8-*keto*-7 : 7-*di*-2′-*hydroxy*-4′ : 5′-*dimethylphenylacenaphthene* (+1AcOH), m.p. 301°. Under similar conditions 2 : 5-$C_6H_3Me_2$·OH yields 8-*keto*-7 : 7-*di*-4′-*hydroxy*-2′ : 5′-*dimethylphenylacenaphthene* (+1EtOH), m.p. 167—171° and, after re-solidification, m.p. 246—247° (also +1Et_2O); the *diacetate* (+1EtOH) has m.p. 198°. Thymol yields 8-*keto*-7 : 7-*di*-4′-*hydroxy*-2′-*methyl*-5′-*isopropylacenaphthene*, m.p. 197° (*dibenzoate*, m.p. 107°). 2 : 4-$C_6H_3Me_2$·OH gives *anhydro*-8-*keto*-7 : 7-*di*-2′-*hydroxy*-3′ : 5′-*dimethylphenylacenaphthene* (I) (+0·5$PhNO_2$), m.p. >350°, and *anhydro*-7 : 8-*di*-2′-*hydroxy*-3′ : 5′-*dimethylphenylacenaphthene*-7 : 8-*diol* (+$COMe_2$), m.p. 281—282°, transformed by conc. H_2SO_4 in AcOH into (I). H. W.

Hydroxy- and methoxy-phenylanthrones. I. II. F. F. Blicke and R. A. Patelski (J. Amer. Chem. Soc., 1938, **60**, 2638—2641, 2642—2644).—I. Addition of *o*-CH_2Ph·C_6H_4·CO_2Et or *o*-CH_2Ph·C_6H_4·CO·C_6H_4·OMe-*p* to *p*-OMe·C_6H_4·MgI in C_6H_6–Et_2O gives an oily carbinol, converted by HCl in AcOH or EtOH into 9 : 9-*di*-p-*anisyl*-9 : 10-*dihydroanthracene*, m.p. 166—167° (oxidised to the known anthrone). *p*-OMe·C_6H_4·CH_2·C_6H_4·CO_2Et-*o* (I) and *p*-OMe·C_6H_4·MgI give 4′ : 4″-*dimethoxy*-2-*p*-*methoxybenzyltriphenylcarbinol*, m.p. 147—148°, converted by HCl into 2-*methoxy*-9 : 9-*di*-p-*anisyl*-9 : 10-*dihydroanthracene*, m.p. 167—168°, oxidised to the known methoxy-anthrone, which with $AlCl_3$ in hot C_6H_6 gives 2-*hydroxy*-9 : 9-*di*-p-*hydroxyphenyl*-10-*anthrone*, m.p. 312—314° (decomp.) [(*m*-C_6H_4Br·*CO*)$_3$ derivative, m.p. 174—176°]. *Et* o-o′-*methoxybenzylbenzoate*, b.p. 268—270°/14 mm., gives similarly 4′ : 4″-*dimethoxy*-2-o-*methoxybenzyltriphenylcarbinol*, m.p. 139—140°, and thence, by way of the 9 : 10-H_2-compound, 4-*methoxy*-9 : 9-*di*-p-*anisyl*-10-*anthrone*,

m.p. 248—250°, and 4-*hydroxy*-9 : 9-*di*-p-*hydroxyphenyl*-10-*anthrone*, m.p. 254—256° (decomp.) [(m-$C_6H_4Br{\cdot}CO)_3$ derivative, m.p. 163—165°]. With *o*-OMe·C_6H_4·MgI (I) gives 2′ : 2″-*dimethoxy*-2-p-*methoxybenzyltriphenylcarbinol*, m.p. 129—130°, and thence 2-*methoxy*-9 : 9-*di*-o-*anisyl*-9 : 10-*dihydroanthracene*, m.p. 154—155°. 3-Methoxy-10-anthrone and Br–CS_2 at −5° give the 9 : 9-Br_2-derivative, m.p. 175—177°, which could not be condensed with PhOMe, but with Hg in C_6H_6 gives 2 : 2′- or 2 : 7′-*dimethoxydianthraquinone*, $\left[CO<\begin{matrix}C_6H_3(OMe)\\C_6H_4\end{matrix}>C:\right]_2$, m.p. 254—256° (decomp.).

II. *o*-$CO_2H{\cdot}C_6H_4{\cdot}CH(C_6H_4{\cdot}OR\text{-}p)_2$ (R = H or Ac) with $ZnCl_2$–Ac_2O at 100° gives 3 : 10-*diacetoxy*-9-p-*acetoxyphenylanthracene*, m.p. 188—189°, oxidised by $Na_2Cr_2O_7$ in hot AcOH to 9-*hydroxy*-3-*acetoxy*-9-p-*acetoxyphenyl*-10-*anthrone* (II), m.p. 186—187°, which, when rapidly hydrolysed, gives 3 : 9-*dihydroxy*-9-p-*hydroxyphenyl*-10-*anthrone* (III), m.p. 127—128° (3 : 4′-Me_2 *ether*, m.p. 155—156°). With mineral acids or when heated, (III) loses H_2O and gives a fuchsone. With HCl–AcCl–C_6H_6, (II) gives 9-*chloro*-3-*acetoxy*-9-p-*acetoxyphenyl*-10-*anthrone*, m.p. 128—129°, which with Ag gives the free radical (intense red) and thence the 9 : 9′-*peroxide*, m.p. 195—200° (decomp.). 2 : 5-Di-*p*-anisyl-3 : 4-benzfuran and Na–Hg in abs. EtOH give the 2 : 5-H_2-derivative, m.p. 115—116°, which with $Na_2Cr_2O_7$ gives *o*-$C_6H_4(CO{\cdot}C_6H_4{\cdot}OMe\text{-}p)_2$; with Na–Hg–EtOH this yields o-*di*-(α-*hydroxy*-p-*methoxybenzyl*)*benzene*, m.p. 139—140°, converted by $ZnCl_2$–Ac_2O–AcOH into 2-methoxy-9-*p*-anisylanthracene, m.p. 177—179° (lit., 175—176°), and thence 9-hydroxy-2-methoxy-9-*p*-anisyl-, m.p. 202—203° (lit., 199—201°), and 2-methoxy-9 : 9-di-*p*-anisyl-10-anthrone. R. S. C.

Deviations in the Claisen condensation. (Signa.) M. Freri (Gazzetta, 1938, **68**, 612—618).—The product of this condensation depends on the alkoxide used as condensing agent. Thus $COMe_2$ and $Et_2C_2O_4$, which in presence of NaOEt yield the Et ester of acetylpyruvic acid (A., 1912, i, 936), in presence of NaOMe form the *Me* ester, m.p. 63° (in each case the Na salt is first obtained, and is decomposed by dil. H_2SO_4 or by AcOH). Similarly COPhMe and either $Et_2C_2O_4$ or $Pr^a{}_2C_2O_4$ with NaOMe give *Me*, m.p. 60°, with NaOEt give Et, and with NaOPr^a give *Pr^a benzoylpyruvate*, m.p. 68°. $Me_2C_2O_4$ under similar conditions does not react. The mechanism of the reaction is discussed. E. W. W.

New derivatives of *meso*benzanthrone. W. H. D. Boyes, J. L. Grieve, and H. G. Rule (J.C.S., 1938, 1833—1841; cf. A., 1935, 859).—1 : 2-$C_{10}H_6Br{\cdot}CN$ (prep. from 1 : 2-$C_{10}H_6Br{\cdot}NH_2$) is hydrolysed (H_2SO_4–AcOH–H_2O) to 1 : 2-$C_{10}H_6Br{\cdot}CO_2H$, new m.p. 191°, the *Me* ester, m.p. 60°, of which with *o*-$C_6H_4I{\cdot}CO_2Me$ + Cu-bronze at 175—180° gives Me diphenate and (after heating with H_2SO_4) fluorenonecarboxylic acid (extracted with PhCl) and *benzanthr*-7-*one*-1-*carboxylic acid* (I), m.p. 285° (3% yield). (I) and *o*-$C_6H_4(CO)_2O$–P_2O_5 at 200° for 2 hr. give 1 : 11-ketobenzanthrone-7 (II); quinoline + Cu bronze afford *meso*benzanthrone, whilst oxidation (CrO_3, dil. H_2SO_4) gives anthraquinone-1-carboxylic acid. Br converts (I) in boiling dil. H_2SO_4 into the 3-*Br*-derivative, m.p. 319—320°, converted by *o*-$C_6H_4(CO)_2O$–P_2O_5 at 200° into 3-bromo-1 : 11-ketobenzanthrone. (I) and boiling conc. HNO_3 give a nitrated (?) *lactone*, m.p. 256—257°, of 11-hydroxybenzanthr-7-one-1-carboxylic acid. Benzanthrone-11-carboxylic acid (III) and Cl_2 in boiling dil. H_2SO_4 for 4 hr. give the 3-*Cl*-derivative, m.p. 317—318°, decarboxylated (quinoline + Cu) to 3-chlorobenzanthrone. Br similarly gives the 3-Br-derivative of (III) (cf. A., 1937, II, 424), but Br in boiling $PhNO_2$ for 3 hr. affords the lactone (IV) of 1-hydroxybenzanthrone-11-carboxylic acid. (III) and HNO_3 (*d* 1·42)–H_2SO_4 at 0° for 15 min. give the 3-NO_2-derivative (V), m.p. 310° (decomp.), whereas boiling HNO_3 affords the *lactone*, m.p. 317—318° (decomp.), of 3-nitro-1-hydroxybenzanthrone-11-carboxylic acid, also obtained similarly from (IV), or from (V) and CrO_3. (III) and excess of conc. HNO_3 in boiling AcOH yield only (IV). NaN_3 and (II) in H_2SO_4 + $CHCl_3$ at 45—50° give 11-*aminobenzanthrone*, m.p. 215—217° (*HCO*, m.p. 268—271°, and *Ac*, m.p. 278—279°, derivatives), converted by KOH at 220° for ½ hr. into (?) *diaminodibenzanthrone*. *Benzanthrone*-11-*carboxylamide* (VI), from the acid chloride and conc. aq. NH_3, sinters at 300—310°, softens at 320°, melts at 325—327°, and resolidifies at 327—330°; it is best hydrolysed [to (III) and ~25% of (IV)] by HNO_2. H_2SO_4–H_2O–CrO_3 and (VI) give (IV), but with $PhNO_2$–Br the *lactam*, m.p. >360°, of 1-aminobenzanthrone-11-carboxylic acid results. (II) and Cl_2 in AcOH (100°) for 10 min., or better in dil. H_2SO_4 at b.p. for 3 hr., give the 3-*Cl*-derivative, m.p. 335—336°, sinters at 245°, obtained also by cyclising 3-chlorobenzanthrone-11-carboxylic acid. Further chlorination in AcOH for 1 hr. gives a *mixture*, m.p. 334—339°, of isomeric Cl_2-derivatives. (II) and dil. H_2SO_4–Br (not in AcOH or $PhNO_2$) for 4 hr. give the 3-Br-derivative; with excess of Br at 50—60° for 2 hr. the 3 : 9-Br_2-compound results. (II)–H_2SO_4–HNO_3 (*d* 1·42) for ¼ hr. give the 3-NO_2-derivative, m.p. 284—285°, but excess of boiling HNO_3 gives an inseparable mixture. *Benzanthrone*-1 : 11-*ketoxime* (VII), m.p. 314°, is partly hydrolysed by boiling $PhNO_2$ to a 1 : 1 mol. *compound*, m.p. 322°, of (II) and $PhNO_2$, the latter being lost at 220° in 2 hr. (VII) and PhOMe–PCl_5 at 75° for 5 hr. afford the *lactam* (VIII), m.p. >360°, of 11-aminobenzanthrone-1-carboxylic acid (or the 1 : 11-compound), best prepared from (II) and NaN_3 in H_2SO_4. (VIII) fused with KOH at 280° for 1 hr. gives a crude *dilactam* of dibenzanthrone type (vat dye). 3 : 8 : 1-$NO_2{\cdot}C_{10}H_5Br{\cdot}CO_2Me$ and *o*-$C_6H_4I{\cdot}CO_2Me$ + Cu bronze at 160° for 1 hr., then 180° for 3 hr., give *Me* 3-*nitro*-8-(*o*-*carbomethoxyphenyl*)-1-*naphthoate*, m.p. 143°, converted by H_2SO_4 at 80° for ½ hr. or 100° for 1 hr. into 5-*nitrobenzanthrone*-11-*carboxylic acid* (IX), m.p. 309° (decomp.), or its anhydride, respectively. (IX) is converted by boiling quinoline and Cu-bronze into 5-*nitrobenzanthrone*, m.p. 287°, and by P_2O_5 in *o*-$C_6H_4(CO)_2O$ into 5-*nitro*-1 : 11-*ketobenzanthrone*, m.p. 319—320° (13% yield). A. T. P.

Derivatives of croconic acid. R. Malachowski and S. Prebendowski (Ber., 1938, **71**, [*B*], 2241—

2247).—Ag_2 croconate (I) and MeI in abs. Et_2O at room temp. yield *Me_2 croconate* (II) [3 : 4 : 5-*triketo*-1 : 2-*dimethoxy*-Δ^1-cyclo*pentene*], m.p. 114—115°, b.p. 250°/740 mm. (incipient decomp.), which is rapidly hydrolysed when exposed to air. *Et_2 croconate*, b.p. 174—175°/3 mm., m.p. 57·5—58·5°, is obtained similarly. *o*-$C_6H_4(NH_2)_2$ and (II) in MeOH give the *quinoxaline* derivative, $C_6H_4<\begin{matrix}N{:}C{\cdot}CO\\N{:}C{\cdot}C(OMe)\end{matrix}>C{\cdot}OMe$, m.p. 166°, transformed by an excess of KOH into the *salt*, $C_{12}H_7O_3N_2K$, whence the *acid*, $C_{12}H_8O_3N_2$, m.p. >340°. (I) is transformed by HCl–EtOH at room temp. into *croconic acid* β-*Et_2 acetal* [1 : 2-*dihydroxy*-3 : 5-*diketo*-4 : 4-*diethoxy*-Δ^1-cyclo*pentene*] (III), also obtained from croconic acid (IV). It has no definite m.p. When distilled with C_6H_6 it gives *Et H croconate*, decomp. >150°. With CH_2N_2–Et_2O (III) yields *Me_2 croconate* β-*Et_2 acetal*, b.p. 163—165°/11 mm., which does not condense with *o*-$C_6H_4(NH_2)_2$ and is hydrolysed slowly by cold but immediately by hot acids or alkalis to the free acid. It condenses with $(CH_2{\cdot}NH_2)_2$ to a mixture of the *compound*, $\left(\begin{matrix}CO{\cdot}CH(OMe)\\C(OEt)_2{-}CO\end{matrix}>C{:}N{\cdot}CH_2{\cdot}\right)_2$, m.p. 123° [which does not give a colour with $FeCl_3$ and is converted by warm dil. HCl into (IV)], and the *dihydropyrazine*, $\begin{matrix}CH_2{\cdot}N{:}C{\cdot}C(OEt)_2\\CH_2{\cdot}N{:}C{\cdot}CH(OMe)\end{matrix}>CO$, m.p. 124—125°, which is neutral, does not give a colour with $FeCl_3$, is unchanged by short warming with H_2O or dil. NaOH but readily transformed by dil. HCl into the *diketone*, $\begin{matrix}CH_2{\cdot}N{:}C{\cdot}CO\\CH_2{\cdot}N{:}C{\cdot}CH(OH)\end{matrix}>CO$, decomp. >300°, which with $CH_2{\cdot}(NH_2)_2$ gives the *bisdihydropyrazine*, $C_9H_{10}ON_4$, m.p. 208° (decomp.), also obtained from (II) and $(CH_2{\cdot}NH_2)_2$ in EtOH. H. W.

Unsaturated ketones of the androstane and pregnane series.—See B., 1938, 1502.

Ketones of the *cyclo*pentanopolyhydrophenanthrene series.—See B., 1938, 1502.

Relatively inert oxygen atom of digoxigenin, sarmentogenin, and the steroid compounds of the adrenal cortex. H. L. Mason and W. M. Hoehn (J. Amer. Chem. Soc., 1938, **60**, 2824).—The diketoætio-cholanic and -cholenic acid of the authors (A., 1938, II, 329, 497) and of Steiger and Reichstein (*ibid.*, 329) are shown by direct comparison to be identical, but the $(OH)_2$-acids are different (epimeric at $C_{(12)}$). The indifferent O of the steroids named is thus at $C_{(11)}$. R. S. C.

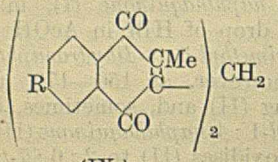
Syntheses in the hydroaromatic series. IV. (A) Condensation of 3-methyl-Δ^3-*cyclo*pentene-1 : 2-dione with 6-methoxy-1-vinyl-3 : 4-dihydronaphthalene. (B) Preparation and diene syntheses of 3-hydroxy-2 : 6-dimethyl-*p*-benzoquinone. E. Dane and J. Schmitt (Annalen, 1938, **536**, 196—203).—(A) 6-Methoxy-1-acetylenyl-3 : 4-dihydronaphthalene is hydrogenated (Pd–C in dioxan) to the 1-vinyl derivative (I), which is condensed with 3-methyl-Δ^3-*cyclo*pentene-1 : 2-dione at 120° to a *compound*, $C_{19}H_{20}O_3$, m.p. 170° (red) after softening.

(B) 3 : 5-Dimethyl-Δ^3-*cyclo*hexenone (II) is oxidised by SeO_2 in AcOH at 100° to 3-hydroxy-2 : 6-dimethyl-*p*-benzoquinone (III), m.p. 103°, and an additive *compound* (1 : 1), m.p. 41°, of 1 : 3 : 5-$C_6H_3Me_2{\cdot}OH$ and (II). Butadiene and (III) at 110° give almost quantitatively 3-*hydroxy*-2 : 9-*dimethyl*-5 : 8 : 9 : 10-*tetrahydro*-1 : 4-*naphthaquinone*, m.p. 120°, which gives a very marked reaction with $FeCl_3$ and is reduced (Pd–C in *cyclo*hexane) to a H_4-derivative, m.p. 117·5°. (I) and (III) yield the *chrysene* derivative, $C_{21}H_{22}O_4$, m.p. 167·5°. H. W.

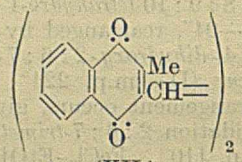
Syntheses and reactions of substituted α-naphthaquinones. E. Bergmann and F. Bergmann (J. Org. Chem., 1938, **3**, 125—136).—Toluquinone and $(CH_2{:}CMe)_2$ at 110° give 2 : 6 : 7-*trimethyl*-5 : 8 : 9 : 10-*tetrahydro*-1 : 4-*naphthaquinone* (I), m.p. 93—94°, rearranged by a drop of HBr in AcOH to 1 : 4-*dihydroxy*-2 : 6 : 7-*trimethyl*-5 : 8-*dihydronaphthalene* (II), m.p. 224°; however, at 150—170° rearrangement occurs, giving (II) and, sometimes, by oxidation, 2 : 6 : 7-*trimethyl*-1 : 4-*naphthaquinone* (III), m.p. 110°. $FeCl_3$–EtOH oxidises (II) to 2 : 6 : 7-*trimethyl*-5 : 8-*dihydro*-1 : 4-*naphthaquinone* (IV), m.p. 129°. Se converts (I) or (IV) into (III). Phenyl-*p*-benzoquinone (V) and $(CH_2{:}CMe)_2$ at 100° give 2-*phenyl*-6 : 7-*dimethyl*-5 : 8 : 9 : 10-*tetrahydro*-1 : 4-*naphthaquinone* (VI), m.p. 113—114°, rearranged by HBr–AcOH into 1 : 4-*dihydroxy*-2-*phenyl*-6 : 7-*dimethyl*-5 : 8-*dihydronaphthalene* (VII), m.p. 137°, which with $FeCl_3$–EtOH gives 2-*phenyl*-6 : 7-*dimethyl*-5 : 8-*dihydro*-1 : 4-*naphthaquinone* (VIII), m.p. 119°. With Se at 280—300° (VI) gives 1 : 4-*dihydroxy*-2-*phenyl*-6 : 7-*dimethylnaphthalene*, m.p. 197—198°, oxidised by $FeCl_3$ to 2-*phenyl*-6 : 7-*dimethyl*-1 : 4-*naphthaquinone*, m.p. 127° [which is obtained also from (VIII) by Se or in traces by the original diene reaction at 150—200°], and [as is (VI)] by air in KOH–EtOH to 3-*hydroxy*-2-*phenyl*-6 : 7-*dimethyl*-1 : 4-*naphthaquinone*, m.p. 158° (*Me ether*, m.p. 186°). *cyclo*Pentadiene and (V) in hot C_6H_6 give the normal *adduct*, $C_{17}H_{14}O_2$, m.p. 79—80°.

CH_2N_2 usually adds to 1 : 4-naphthaquinones in the 2 : 3-positions, giving the pyrazoline, which decomposes, when heated, into N_2 and a methylated quinone. 2-Bromo-1 : 4-naphthaquinone and CH_2N_2 give a product, m.p. 272—280° (decomp.), which with conc., aq. NH_3 loses HBr and yields 3 : 4-phthalylpyrazole, m.p. 345°. CH_2N_2 and (VI) give the pyrazole *derivative*, $C_{19}H_{20}O_2N_2$, b.p. 170°/0·3 mm. CH_2N_2 adds to (I), giving 3 : 4′ : 5′-*trimethyl*-3 : 4-$\Delta^{4'}$-*tetrahydrophthalyl*-$\Delta^{1:2}$-*pyrazoline*, $\begin{matrix}CMe{\cdot}CH_2{\cdot}CH{\cdot}CO{\cdot}CMe{-}N\\CMe{\cdot}CH_2{\cdot}CH{\cdot}CO{\cdot}CH{\cdot}CH_2\end{matrix}>N$, m.p. 146° (decomp.), decomposed in light petroleum at 130° into 2 : 3 : 6 : 7-tetramethyl-5 : 8 : 9 : 10-tetrahydro-1 : 4-naphthaquinone, a resin, which is isomerised by HBr–AcOH to 1 : 4-dihydroxy-2 : 3 : 6 : 7-tetramethyl-5 : 8-dihydronaphthalene, m.p. 232°, which with $FeCl_3$ yields 2 : 3 : 6 : 7-*tetramethyl*-5 : 8-*dihydro*-1 : 4-*naphthaquinone*, m.p. 155—156°. CH_2N_2 and (III) in MeOH give a crude product, m.p. 175°, which, when recrystallised, is oxidised to 2 : 3 : 6 : 7-*tetramethyl*-1 : 4-*naphthaquinone*, m.p. 167—168°. 2-Methylnaphthaquinone and CH_2N_2 in Et_2O at 0° give the normal *adduct*, $C_{12}H_{10}O_2N_2$, m.p. 114°, a *product* (IX) (R = H), m.p. 242°, and an oil, which, when distilled, gives 2 : 3-dimethylnaphthaquinone (X).

2 : 6-Dimethyl-1 : 4-naphthaquinone (XI) and CH_2N_2 at 0° give the *hydroquinone*, $C_{25}H_{22}O_4$, m.p. 293° [considered by Fieser *et al.* (A., 1935, 217) to be (IX) (R = Me) and given m.p. 300°; oxidised by $FeCl_3$ to the *diquinone* (IX) (R = Me), m.p. 249°], and an oil, which, when distilled, gives 2 : 3 : 6-*trimethyl*-1 : 4-*naphthaquinone*, m.p. 100°; sometimes a product, m.p. 228·5°, was also formed in small amount. With Zn dust and AcOH in EtOH (XI) gives 1 : 4-*dihydroxy*-2 : 6-*dimethylnaphthalene*, m.p. 187—188° (*Me_2 ether*, b.p. 129°/0·5 mm., m.p. 75—76°). When kept in dil. KOH–MeOH, (X) gives the *diquinone* (XII), m.p. 227—228°, oxidised by $FeCl_3$ to a *substance*, $C_{24}H_{16}O_5$, m.p. 184°. $CHPh_2Na$ in Et_2O causes enolisation of



(IX.)



(XII.)

(X) to 1-hydroxy-4-keto-2-methyl-3-methylene-3 : 4-dihydronaphthalene (XIII); some $CHPh_2Na$ adds to (XIII), giving 2-ββ-*diphenylethyl*-3-*methyl*-1 : 4-*naphthaquinone*, m.p. 167°; a second mol. of (X) also adds to (XIII) and, if air is passed through the mother-liquors, the *diquinone* [(XII) with ·CH_2— for ·CH=], m.p. 261—262°, or sometimes (XII) is obtained. R. S. C.

Condensation of phthalic anhydride with *p*-dichlorobenzene. I. M. Kogan and T. N. Ganina (Prom. Org. Chim., 1936, **1**, 87—91).—*o*-$C_6H_4(CO)_2O$, *p*-$C_6H_4Cl_2$ (5 mols.), and $AlCl_3$ (4 mols.) at 110°/6 hr. give *o*-2 : 5-dichlorobenzoylbenzoic acid (59·3%), converted by 5% oleum (7 parts) at 150°/4 hr. into 1 : 4-dichloroanthraquinone (83·5%). Ch. Abs. (*c*)

Intra-complex coloured compounds. Constants of alizarin and alizarates.—See A., 1939, I, 25.

Friedel–Crafts reaction. III. Condensation of acylarylamides and aromatic and heterocyclic amines with phthalic anhydride. P. Kränzlein (Ber., 1938, **71**, [*B*], 2328—2335; cf. A., 1937, II, 432, 460).—Replacement of $AlCl_3$ in $C_2H_2Cl_4$ by a molten mixture of NaCl and $AlCl_3$ frequently permits the conversion of amines directly into substituted anthraquinones without preliminary acylation or isolation of any intermediate. Successive additions of 1 : 3 : 4-NHAc·C_6H_3Me·OH and *o*-$C_6H_4(CO)_2O$ to $AlCl_3$–NaCl (3 : 1) at ≯115—120° give a 64% yield of *o*-2-acetamido-5-hydroxy-4-methylbenzoylbenzoic acid, m.p. 263°, converted by conc. H_2SO_4 at 100° into 1-*amino*-4-*hydroxy*-3-*methylanthraquinone*, m.p. 237°. Similay, *p*-C_6H_4Ph·NHAc and *o*-$C_6H_4(CO)_2O$ yield o-4-p′-*acetamidophenylbenzoylbenzoic acid*, m.p. 256°, converted by conc. H_2SO_4 at 110° into 2-*p*-aminophenylanthraquinone, m.p. 221°, also obtained directly (45% yield) from *p*-C_6H_4Ph·NH_2 and *o*-$C_6H_4(CO)_2O$ and $AlCl_3$–NaCl at 120° and subsequently at 150—155°. 3 : 1 : 4-C_6H_3MePh·NHAc and *o*-$C_6H_4(CO)_2O$ give (84% yield) o-p′-4″-*acetamido*-3″-*methylphenylbenzoylbenzoic acid*, m.p. 238°, transformed by conc. H_2SO_4 at 110° (yield 92%) into 2-4′-*amino*-3′-*methylphenylanthraquinone*, m.p. 199°, also obtained directly from 3 : 1 : 4-C_6H_3MePh·NH_2. 2-Aminocarbazole and *o*-$C_6H_4(CO)_2O$ with $AlCl_3$–NaCl at 110—115° and then at 150° afford 2-*aminophthalylcarbazole*, m.p. 355°, in 65—70% yield. The following compounds are prepared analogously: 3-*amino*-N-*ethylphthalylcarbazole*, m.p. 296°; 2-aminophthalyldiphenylene oxide, m.p. >300° (slow decomp.) after softening at 295° (*Bz* derivative, m.p. 338°); 3-aminophthalylphenanthrene, m.p. 291°; 2-*aminophthalylfluorene*, m.p. 293°; 2-*aminophthalylchrysene*, m.p. 325° after softening at 320°; 4-*aminophthalylfluoranthene*, m.p. >350°; 3-*aminophthalylpyrene*, m.p. >350°. H. W.

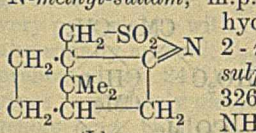
Dyes derived from chrysoquinone. K. M. P. Singh and S. Dutt (Proc. Indian Acad. Sci., 1938, **8**, **A**, 187—193).—Chrysoquinone (I) (*bisphenylhydrazone*, m.p. 228—229°) yields, with conc. HNO_3 in the cold, *nitro*-, m.p. 256—257°, and at 100°, *dinitro*-, m.p. 235°, and with fuming HNO_3 (*d* 1·5) at 100°, *tetranitro-chrysoquinone*, m.p. >300°. None of these could be reduced to the amine. (I) with Br at 110° yields in $PhNO_2$, a *Br_1*-compound, m.p. 246°, and in glacial AcOH, an *isomeride*, m.p. 218°, and with excess of Br in a sealed tube, *pentabromochrysoquinone*, m.p. >300°. These with NH_2Ph and Cu-bronze yield, respectively *anilino*-, m.p. 210—212° and 153—155°, and *bromotetra-anilino-chrysoquinone*, m.p. 291—293°. With *o*-$C_6H_4(NH_2)_2$, 1 : 2-$C_{10}H_6(NH_2)_2$, *o*-NH_2·C_6H_4·OH, and 2 : 3-diaminophenazine in glacial AcOH, (I) yields respectively *chryso-phenazine*, m.p. 207—208° ($PhNO_2$), 199° (AcOH), -1 : 2-*naphthazine*, m.p. 238°, -*phenoxazine*, m.p. 236°, and -2 : 3-*diaminophenazineazine*, m.p. >300°. The following were obtained from (I) and NH_2Ar (excess) in hot glacial AcOH: *chrysoquinonedi-phenyl*-, m.p. 228—229°, -o-, m.p. >300°, and -m-*tolyl*-, m.p. 163—165°, -o-*anisyl*-, m.p. 160—163°, -o-, m.p. 188—190°, and -p-*phenetyl*-, m.p. 205—207°, -α-, m.p. 198—200°, and -β-*naphthyl-imine*, m.p. 203°. The dyeing properties of these compounds are described. A. Li.

Action of hydroxylamine on camphor- and dithiocamphor-imide. A. Mannesier-Mameli (Congr. int. Quim. pura apl., **9**, IV, 588—593; Chem. Zentr., 1937, i, 3493; cf. A., 1933, 288).—Dithiocamphorimide, m.p. 135°, NH_2OH,HCl, and aq. Na_2CO_3 give *thiocamphorimideoxime* (I), m.p. 180° (decomp. 235°) (*Ac* derivative, m.p. 177°), and *camphorimidedioxime*, m.p. 250° (decomp. 265°). (I) is oxidised (alkaline $KMnO_4$) to camphorimide, which does not react with NH_2OH. H. B.

Stereoisomeric camphorylideneacetic acids. H. Rupe and O. Klemm (Helv. Chim. Acta, 1938, **21**, 1532—1538).—Condensation of camphorquinone with CH_2Br·CO_2Et in presence of well-amalgamated Mg (Zn is ineffective) gives *Et* β-*hydroxyisocamphorylacetate* (I), b.p. 172°/13 mm. (*Ac*, b.p. 182—184°/13 mm., and non-homogeneous Bz, b.p. 197—201°/13 mm., derivatives), with a neutral *by-product*, $C_{18}H_{29}O_4$, m.p. 178—179°, which contains 2 OH (Zerevitinov), gives a *compound*, $C_{32}H_{36}O_9N_2$, m.p. 147°, with *p*-NO_2·C_6H_4·COCl and C_5H_5N, and is oxidised by $KMnO_4$ to camphoric acid. (I) is hydrolysed to the

very stable *β-hydroxyisocamphorylacetic acid*, b.p. 212—225°/13 mm. (slight decomp.), which is best dehydrated by treatment with PBr_3 in C_6H_6 followed by heating the mixture alone and with KOH–MeOH to *trans-isocamphorylideneacetic acid* (II), b.p. 182—186°/13 mm. The chloride, *p*-toluidide, and Et ester obtained from (II) are identical with those derived from Claisen's *cis-iso*camphorylideneacetic acid (III). The consideration of (II) as the *trans*-form is based on the impossibility of hydrogenating it in presence of Ni or Pd under pressures up to 90 atm., whereas (III) is easily and completely hydrogenated (Ni at room pressure). (II) is oxidised ($KMnO_4$–Na_2CO_3) to camphorquinone. H. W.

Anomalous mutarotation of salts of Reychler's acid. VI. Synthesis and structure of the sultam of 2-*N*-methylamino-*d*-camphane-10-sulphonic acid. R. L. Shriner, J. A. Shotton, and H. Sutherland (J. Amer. Chem. Soc., 1938, **60**, 2794—2796; cf. A., 1938, II, 331).—The anhydroamide (I) (Armstrong and Lowry, J.C.S., 1902, **81**, 1448) with H_2–Raney Ni in warm 95% EtOH at 3 atm. gives the homogeneous *sultam*, m.p. 181—182°, $[\alpha]_D^{25}$ −33° in $CHCl_3$, of 2-*amino*-d-*camphane*-10-*sulphonic acid*, the Na derivative of which with MeI gives the *N-methyl-sultam*, m.p. 80°, $[\alpha]_D^{25}$ −59·6° in $CHCl_3$,



(I.)

hydrolysed by hot, conc. HCl to 2-*methylamino*-d-*camphane*-10-*sulphonic acid* (II), m.p. 325—326° (block), $[\alpha]_D^{25}$ −98° in EtOH. NH_2Me camphor-10-sulphonate in hot EtOH–$(CH_2{\cdot}OH)_2$ is converted into 2-methylimino-*d*-camphor-10-sulphonic acid, which with H_2–PtO_2 in EtOH gives the α-[= (II)] and β-, decomp. 338—343°, $[\alpha]_D^{25}$ +38·8° in EtOH, *forms* of (II). The structure of the sultams and of (I) is thus proved. R. S. C.

Triterpenes. XLI. Oxidation of betulin monoacetate by chromium trioxide to acidic products. L. Ruzicka, A. H. Lamberton, and E. W. Christie (Helv. Chim. Acta, 1938, **21**, 1706—1717).—Betulin monoacetate is oxidised by CrO_3 in AcOH at 20°, the products are dissolved in Et_2O, and the solution is shaken successively with aq. Na_2CO_3 and NaOH. Crystallisation from EtOAc of the mixture of acids obtained by acidifying the Na_2CO_3 extract leads to the isolation of "*acetyldicarboxylic acid* E," $C_{29-30}H_{48-50}O_5$, m.p. 339—340°, $[\alpha]_D$ +20·6° in $CHCl_3$ (*Me*$_2$ ester, m.p. 243—245°, $[\alpha]_D$ +19° in $CHCl_3$), which is indifferent towards Ac_2O and is hydrolysed (KOH–EtOH) to "*dicarboxylic acid* E" (I) (*Me* ester, m.p. 245—246°). The compounds do not give a colour with $C(NO_2)_4$. The EtOAc mother-liquor contains "*acetyldicarboxylic acid* A" (II), which is not readily isolated and is therefore hydrolysed to *dicarboxylic acid* A, $C_{29}H_{48}O_5$, m.p. 338—340°, $[\alpha]_D$ −53° in dioxan (*Me*$_2$ ester, m.p. 179—181°, $[\alpha]_D$ −57° in $CHCl_3$), which appears to yield an amorphous anhydride. Acidification of the NaOH extract liberates the monobasic *acetylbetulic acid* (III), $C_{32}H_{50}O_4$, m.p. 288—290°, $[\alpha]_D$ +20·1° in $CHCl_3$ (*Me* ester, m.p. 200—202°, $[\alpha]_D$ +17·1° in $CHCl_3$), hydrolysed and then esterified to *Me betulate*, m.p. 224—225°, $[\alpha]_D$ +5·0° in $CHCl_3$. Hydrogenation (PtO_2 in AcOH) of (III) gives acetyldihydrobetulic acid (*Me* ester, m.p. 238—239°), identical with the product obtained by the oxidation of dihydrobetulin monoacetate (work to be published later). Oxidation of (III) by CrO_3 in AcOH gives (I) and (II), each in about 10% yield; (III) is therefore an intermediate product in the formation of (I) and (II). All m.p. are corr. H. W.

Triterpenes. XLII. Keto-derivatives of oleanolic acid. L. Ruzicka, S. L. Cohen, M. Furter, and F. C. van der Sluys-Veer (Helv. Chim. Acta, 1938, **21**, 1735—1746).—Decarboxylation of acetylketo-oleanolic acid (I) (Kitasato, A., 1934, 412; Ruzicka and Cohen, A., 1937, II, 382) in boiling quinoline leads smoothly to a neutral *compound* (III), $C_{31}H_{46(or\ 48)}O_3$, m.p. 208—210°, which gives a marked yellow colour with $C(NO_2)_4$ in $CHCl_3$ and does not show the absorption spectrum typical of an αβ-unsaturated ketone. Comparison of the absorption curves of $\Delta^{1:4}$-cholestadien-3-one, phorone, $\Delta^{4:6}$-androstadiene-3 : 17-dione, santonin, dimethylquinol, and (II) does not decide whether it is possible to distinguish spectrographically between a ketone with double linkings at each side of CO and one containing two conjugated double linkings on one side. *iso*Acetylketo-oleanolic acid (II), m.p. 328—330°, $[\alpha]_D$ +61° in $CHCl_3$ (cf. Kitasato, A., 1935, 1126), best obtained from acetylketo-oleanololactone and HBr in boiling EtOH, appears from its absorption spectrum to contain the αβ-unsaturated CO group; this view is supported by the impossibility of detecting the double linking or CO in the usual manner. It is reduced (Clemmensen) to *isoacetyloleanolic acid*, m.p. 280—282°, $[\alpha]$ +75° in $CHCl_3$, which gives a yellow colour with $C(NO_2)_4$. (II) passes in boiling quinoline into a *substance*, $C_{32}H_{48}O_5$, m.p. 277—279°. (I), new m.p. 272—273° (Me ester, new m.p. 252—253°), is converted by KOH–MeOH into keto-oleanolic acid (III), m.p. 264—265° [Me ester (III), m.p. 196—197°]. The rates of hydrolysis of Me oleanonate, acetyloleanolate, acetylketodihydro-oleanolate, acetylketo-oleanolate, (III), and Me *iso*acetylketo-oleanolate have been compared. Theoretical discussion of the results leads to a preference for Haworth's modification of the C skeleton of triterpenes of the oleanolic acid type (Ann. Repts., 1937, **34**, 327 *seq.*). H. W.

Structure of some triterpenes. G. Giacomello (Atti R. Accad. Lincei, 1938, [vi], **27**, 574—578).—From a discussion of *X*-ray data for various triterpenes it is concluded that these have a structure analogous to that of the hydrocarbon $C_{24}H_{18}$ obtained by dehydrogenation of triterpenes. O. J. W.

Structure of lignin. A. B. Cramer, M. J. Hunter, and H. Hibbert (J. Amer. Chem. Soc., 1938, **60**, 2813).—The ketone, $C_{13}H_{18}O_4$ (2 : 4-*dinitrophenylhydrazone*, m.p. 134—136°) (A., 1938, II, 449), is identified as 4-*α-ethoxypropioveratrone* (I) by synthesis by the following steps: veratrole + EtCOCl → 4-propioveratrone → the α-Br-derivative → 1 : 2 : 4-$(OMe)_2C_6H_3{\cdot}CO{\cdot}CHMe{\cdot}OAc$ → (I) + the derived OH-compound. R. S. C.

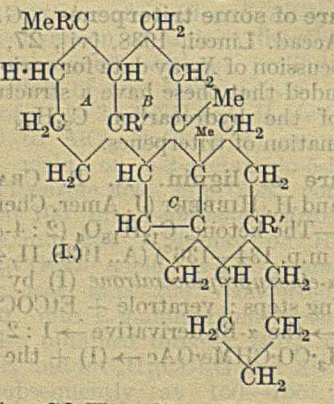
Structure of lignin. M. J. Hunter, A. B. Cramer, and H. Hibbert (J. Amer. Chem. Soc.,

1938, **60**, 2815—2816).—Solvent extraction of maple wood gives the known ketones, $C_{12}H_{16}O_4$ and $C_{13}H_{18}O_5$ (p-*nitrobenzoate*, m.p. 141—142·5°) (A., 1938, II, 449), in about equal amounts. R. S. C.

Dihydroabietic acids from so-called pyroabietic acids. E. E. Fleck and S. Palkin (J. Amer. Chem. Soc., 1938, **60**, 2621—2622).—A *dihydroabietic acid*, m.p. 174—176°, $[\alpha]_D^{20}$ +108° in EtOH, is isolated from α-pyroabietic acid. The "H_2-acid," $[\alpha]_D^{20}$ −3° (A., 1938, II, 239), is the lactone of Hasselstrom *et al.* (*ibid.*, 288). R. S. C.

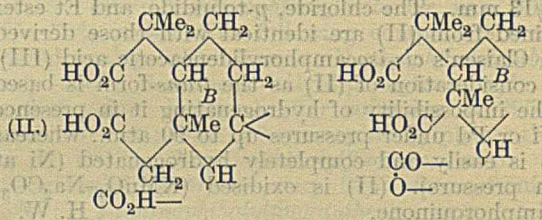
Substitution reactions of dehydroabietic acid. L. F. Fieser and W. P. Campbell (J. Amer. Chem. Soc., 1938, **60**, 2631—2636).—Sulphonation of pyroabietic acid (prepared by Pd) at −5° to sulphodehydroabietic acid (I), +0·5H_2O, m.p. variable, 247—248° (decomp.), $[\alpha]_D^{25}$ +72·4° [p-$C_6H_4Me{\cdot}NH_2$ salt, m.p. 271° (decomp.), $[\alpha]_D^{25}$ +57° in EtOH], and hydrolysis thereof by acid at 135° gives a 42—43% over-all yield of dehydroabietic acid (II). With NaOH at 280—300° (I) gives a mixture of acids, (III), m.p. 196·5—197·5°, and (IV), m.p. 167—169°. With Se (III) gives 68% of retene; (III) gives *anilides*, m.p. 255·5—257° and 114—114·5°, of acids, $C_{19-20}H_{24-28}O_3$ and $C_{19}H_{22}O_2$, respectively. (IV) gives *anilides*, m.p. 214—215° and 147·5—148°, the latter derived from an acid, $C_{19}H_{26}O_2$. The anilides resisted hydrolysis. The Me at $C_{(12)}$ is probably partly removed during the alkali fusion. No $(NO_2)_1$-derivative of (I) could be prepared; only the known (? 6 : 8-)dinitrodehydroabietic acid was formed. With AcCl and $AlCl_3$ in $PhNO_2$ at 0—5° the Me ester of (II) gives *Me 6-acetyldehydroabietate*, *forms*, m.p. 133·5—134° and 119·5—120°, $[\alpha]_D^{25}$ +56° in EtOH (*oxime*, m.p. 151·5—152°, $[\alpha]_D^{25}$ +83° in EtOH), converted by HNO_3 into 1 : 2 : 4 : 5-$C_6H_2(CO_2H)_4$, by I–KI into *Me 6-carboxydehydroabietate*, m.p. 190—191·5°, $[\alpha]_D^{25}$ +74° in EtOH, and by KOH–EtOH into 6-*acetyldehydroabietic acid*, m.p. 174·5—175°, $[\alpha]_D^{25}$ +74° in EtOH. M.p. are corr. R. S. C.

Constitution of acid sapogenins. XIV. Hederagenin and oleanolic acid. Z. Kitasato (Acta Phytochim., 1938, **10**, 239—258).—On the basis of the following and published work oleanolic acid (R = Me) and hederagenin (R = ·CH_2·OH) are considered



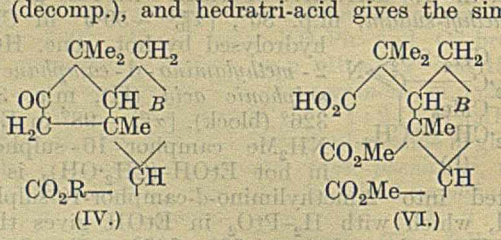
(I.)

to be (I) (R′ = CO_2H or Me; R″ = Me or CO_2H). Monobromo-oleanololactone and CrO_3–AcOH give oleanoltri-acid (II), $C_{30}H_{46}O_6$, +0·5EtOH, m.p. 294—296° (decomp.), and oleanintri-acid (III), $C_{29}H_{44}O_6$, +AcOH, m.p. 272—275° (decomp.) (cf. A., 1937, II, 462, which is also corr. in other respects below). (II) closely resembles hedratri-acid, whereas (III)



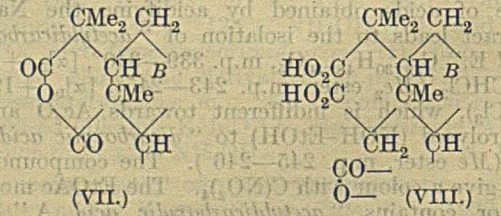
(II.) (III.)

usually reacts differently. The Me_3 ester, m.p. 167—168°, of (II), is converted by KOH–MeOH into the Me keto-ester (IV) (R = Me), new formula $C_{30}H_{46}O_3$, m.p. 183—185° (oxime, m.p. 215—216°), which with HBr–AcOH–$CHCl_3$ at room temp. (1 week) yields a *lactone* (V), $C_{29}H_{44}O_3$, m.p. >350°, the trimethylene ring having been converted into an ethylenic linking which lactonises with the CO_2H. However, the Me_3 ester, m.p. 183°, of (III) is hydrolysed by KOH–MeOH to the acid ester (VI), m.p. 222—224°. At about 340° (II) gives the *keto-acid* (IV) (R = H), $C_{23}H_{44}O_3$, m.p. 300° (decomp.), and hedratri-acid gives the similar



(IV.) (VI.)

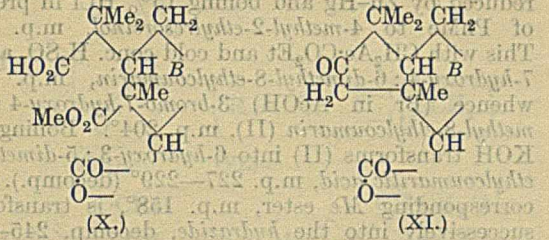
ketone, $C_{26}H_{40}O$, m.p. 205—207° (*oxime*, m.p. 199—200°); however, (III) gives the *anhydride* (VII), m.p. 222°, converted by hydrolysis and methylation into the *Me_2* ester, m.p. 145—147°, of the corresponding acid. With HBr–AcOH this ester gives a mixture, m.p. 155—164°, of a bromodicarboxylate and a lactonic ester, reduced by Zn dust–AcOH to a mixture, m.p. 165—175°, of a dicarboxylate and lactonic ester; a similar mixture, m.p. >300°, of the corresponding Br-free acids is also prepared. With HBr–AcOH (II) or its ester gives the *lactone* (VIII), $C_{32}H_{50}O_6$,



(VII.) (VIII.)

+0·5H_2O, m.p. 216°, and hedratri-acid gives a monolactone (IX) (Me_2 ester, m.p. 168—170°), but (III) or its ester gives the *monolactone-anhydride*, $C_{29}H_{42}O_5$ [as (VII), but containing a lactone group], m.p. 355—358° [*Me* (X), m.p. 265—267°, and *Et_2* ester, m.p. 222°]. At 340° (VIII) gives the *keto-lactone* (XI), $C_{29}H_{44}O_3$, m.p. >350°; a *product* (XII), m.p. 285° (*oxime*, m.p. 228—230°), is similarly obtained from (IX), but (X) regenerates the monolactone-anhydride. The Me_3 ester of keto-oleanintri-acid,

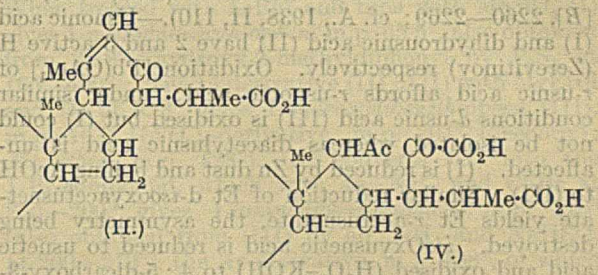
$C_{33}H_{52-54}O_7$, is now regarded as that of keto-oleanol-tri-acid, and the product obtained therefrom by



(X.) (XI.)

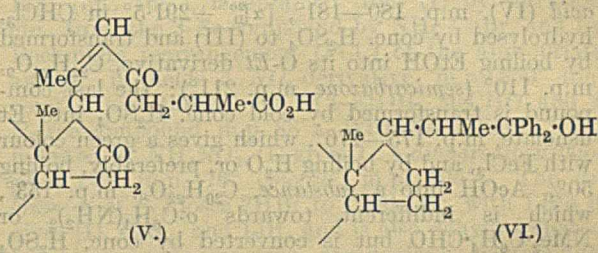
KOH–MeOH is a diketo-monoester, $C_{30}H_{46-48}O_4$, analogous to (IV). R. S. C.

Sarsasapogenin. II. Sarsasapogenoic acid. III. Deoxysarsasapogenin and the degradation of the C_{22}-hydroxylactone. L. F. FIESER and R. P. JACOBSEN (J. Amer. Chem. Soc., 1938, **60**, 2753—2761, 2761—2764; cf. A., 1938, II, 108).—II. Improved prep. of sarsasapogenoic acid (I) gives also small amounts of the OH-lactone acetate, $C_{22}H_{33}O_2{\cdot}OAc$, and (?) *hydroxysarsasapogenin acetate*, (?) $C_{29}H_{46}O_5$, m.p. 158—160°. With HCl–EtOH–C_6H_6, Na–Pr^{a}OH, semicarbazide, or NH_2OH–EtOH (I) gives gums; with NH_2OH at 130° its Me ester gives a *substance*, $C_{25}H_{40}O_5N_2$, m.p. 169—171°, in very poor yield; with NH_2OH–MeOH at 130° (I) gives abnormally an *acid*, $C_{27}H_{44}O_5N_2$, m.p. 247° (decomp.; preheated at 247°). With H_2–PtO_2 in AcOH (I) gives very slowly *anhydro-di-* or *-tetra-hydrosarsasapogenoic acid*, $C_{27}H_{42-44}O_4$, m.p. 174—178° [*Me* ester *acetate*, +0·5MeOH,0·5H_2O, m.p. 64—66° (decomp.), and *benzoate*, m.p. 138·5—140·5°]. Anhydrosarsasapogenoic acid (II) with H_2–PtO_2 in EtOH or Na–Pr^{a}OH gives the *H_4-acid* (III), m.p. between 179° and 188° [*Me* ester *diacetate*, m.p. 159·5—161°, also obtained by hydrogenating the oily Me ester of (II)]; absorption (max. at 2430 A.) proves that (I) is an αβ-unsaturated ketone, a system suggested by the Na–Pr^{a}OH reduction. One OH of (III) is at $C_{(3)}$, the other a new *sec.* OH obtained by reduction of the CO of (II). With boiling Ac_2O or BzCl–C_5H_5N at 55° (III) gives a *lactone acetate*, $C_{29}H_{44}O_4$, m.p. 200—203°, and *lactone benzoate*, m.p. 225—235°, respectively, proving that the new OH is γ or δ in respect to the CO_2H. (II) is thus a γ- or δ-keto-acid. The composition of (II) and the indifference of (III) to H_2-catalyst and $KMnO_4$ show that (II) contains a new ring. CrO_3 gives only oils from the Me ester acetate of (II), but with alkaline $KMnO_4$ (II) gives a dibasic *keto-acid* (IV), $C_{27}H_{40}O_7$, m.p. 206—207° (decomp.) [Me_2 ester, m.p. 164·5—165°; *anhydro-oxime*, $C_{27}H_{39}O_6N$, m.p. 268° (decomp.)], converted by NaOI into CHI_3 and a trace of a *substance*, $C_{25}H_{36-38}O_7$, m.p. 212—213° (decomp.). These oxidations prove that (II) contains ·CH:CMe·, converted into $CO_2H{\cdot}X{\cdot}COMe$. Thus, (II) contains ·CMe:CH·CO·C_2·CO_2H, the alternative ·CH:CMe·CO·C_2·CO_2H being incompatible with the cholesterol side-chain. It follows that (I) and thus sarsasapogenin (modified prep.) have the structures suggested by Tschesche and Hagedorn (A., 1935, 1126; 1936, 209). The annexed structures for (II) and (IV) follow. Those of (III) and its lactone are also certain, and structures (not proved) are suggested for other derivatives. With Zn–Hg–HCl–EtOH (II) gives a *lactone*, $C_{27}H_{42}O_3$, m.p. 226—229° (*acetate*, m.p. 214—216°).



(II.) (IV.)

III. Work of Simpson and Jacobs (A., 1935, 1248) is extended. Deoxysarsasapogenin (prep. improved to give a 43·5% yield) and CrO_3–80% AcOH at 60—65° give the deoxylactone (13%), $C_{22}H_{34}O_2$, m.p. 129·3—130·5°, a *diketo-acid*, $C_{27}H_{40}O_4$, $+H_2O$ (not lost on drying), m.p. 108—111° (*Me* ester, m.p. 78·5—79·5°; *oxime*, m.p. 189—191° (decomp. from about 178°) [probably (V), although the H_2O of crystallisation may be constitutional], and a trace of an *acid*, m.p. 218—220°. The diphenylcarbinol monoacetate (A., 1938, II, 108) with CrO_3–AcOH at 20—25° gives a *ketone acetate*, $C_{36}H_{46}O_4$, m.p. 157—159° [indifferent to CO-reagents; OAc at $C_{(3)}$; CO as in (V)], reduced by Zn–Hg–HCl–EtOH to a *deoxydiphenylcarbinol* (VI), $C_{34}H_{46}O_2$, m.p. 226—228°. M.p. are corr.



(V.) (VI.)

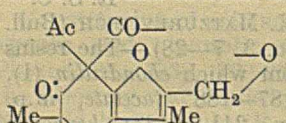
R. S. C.

Chondrilla resins. I. K. MATZUREVITSCH (Bull. Sci. Univ. Kiev, 1937, **3**, No. 3, 7—28).—The resins consist chiefly of esters, from which *chondrillin* (I), $C_{28}H_{47}OH$, + H_2O, m.p. 187—188° (*acetate*, m.p. 229—230°; *isobutyrate*, m.p. 241—242°; *benzoate*, m.p. 262—263°), is obtained by hydrolysis, together with other alcohols and HCO_2H, AcOH, and a no. of amorphous resinic acids of high mol. wt. (I) has one double linking, and forms a *dibromide*, m.p. 181—182° (*acetate*, m.p. 208—209°; *benzoate*, m.p. 186—189°). R. T.

Synthesis of 5-hydroxycoumarin. H. A. SHAH and R. C. SHAH (J.C.S., 1938, 1832—1833).—A detailed account of work already noted (A., 1938, II, 451). The following is new: Et 5-hydroxy-6-carbomethoxycoumarin-3-carboxylate is hydrolysed (NaOH) to *5-hydroxycoumarin*-3 : 6-*dicarboxylic acid*, m.p. 265—267° (efferv.), also obtained from 2 : 4-dihydroxy-3-formylbenzoic acid and $CN{\cdot}CH_2{\cdot}CO_2H$. *5-Hydroxycoumarin-3-carboxylic acid*, m.p. 272—274° (efferv.), is obtained from γ-resorcylaldehyde and $CN{\cdot}CH_2{\cdot}CO_2H$. The m.p. of 5-hydroxycoumarin (*Ac*

derivative, m.p. 88—89°) is now given as 222—225° (previously 221—223°). F. R. S.

Lichen substances. LXXXIX. Usnic acid. V. Y. ASAHINA and M. YANAGITA (Ber., 1938, **71**, [*B*], 2260—2269; cf. A., 1938, II, 110).—Usnonic acid (I) and dihydrousnic acid (II) have 2 and 3 active H (Zerevitinov) respectively. Oxidation [$Pb(OAc)_4$] of *r*-usnic acid affords *r*-usnonic acid; under similar conditions *d*-usnic acid (III) is oxidised but (I) could not be isolated whereas diacetylusnic acid is unaffected. (I) is reduced by Zn dust and boiling AcOH to (III). Similar reduction of Et d-*iso*oxyacetusnetate yields Et *r*-acetusnetate, the asymmetry being destroyed. *iso*Oxyusnetic acid is reduced to usnetic acid and oxidised (H_2O_2–KOH) to 4 : 5-dicarboxy-3-methylfuran-2-acetic acid, m.p. 251—252° (decomp.) after becoming discoloured at about 240°. Usnetic acid is hydrogenated (Pd-black in AcOH) to *dihydrousnetic acid*, m.p. 214° (*Me* ester, m.p. 161°). *Diacetyl*-d-*usnic acid*, m.p. 202°, $[\alpha]_D^{20}$ +200·2° in $CHCl_3$, obtained with a colourless *substance*, m.p. 132°, by means of Ac_2O containing a little conc. H_2SO_4 at 50°, is converted by 5% Na_2CO_3 into *monoacetyl*-d-*usnic acid* (IV), m.p. 180—181°, $[\alpha]_D^{20}$ +291·5° in $CHCl_3$, hydrolysed by conc. H_2SO_4 to (III) and transformed by boiling EtOH into its O-*Et* derivative, $C_{22}H_{24}O_9$, m.p. 110° (*semicarbazone*, m.p. 211°); the last compound is transformed by cold conc. H_2SO_4 into Et usnolate, m.p. 175—176°, which gives a green colour with $FeCl_3$, and by boiling H_2O or, preferably, boiling 50% AcOH into a *substance*, $C_{20}H_{22}O_8$, m.p. 153°, which is indifferent towards *o*-$C_6H_4(NH_2)_2$ or $NMe_2{\cdot}C_6H_4{\cdot}CHO$ but is converted by conc. H_2SO_4 into Et acetusnetate. (IV) is transformed by boiling 60% AcOH into *monoacetyldecarbousnic acid*, m.p. 128°, which gives a violet dye with *o*-$C_6H_4(NH_2)_2$. Diacetyldihydrousnic acid and 60% AcOH at 130° give *monoacetyldihydrousnic acid*, m.p. 132°, $[\alpha]_D^{20}$ −42·09° in $CHCl_3$, also obtained by means of aq. Na_2CO_3. Oxidation ($KMnO_4$–KOH) of *d*-dihydrousnic acid and thermal decomp. of the product affords



(*A*.)

2 : 6-dihydroxy-3-methylacetophenone (and a *by-product*, $C_{17}H_{18}O_5$, m.p. 217°), also obtained similarly from diacetyltetrahydrodeoxyusnic acid. Dry distillation of (II) gives 6-*hydroxy*-7-*acetyl*-3 : 5-*dimethylcoumaran*-2-*one* (V), m.p. 127° (*monoacetate*, m.p. 101—102°; p-*nitrophenylhydrazone*, m.p. 258°), transformed by alkali at 80° into α-2 : 4-*dihydroxy*-3-*acetyl*-5-*methylphenylpropionic acid*, m.p. 147° (vigorous decomp.). Reduction (Clemmensen) of (V) yields 6-hydroxy-3 : 5-dimethyl-7-ethylcoumaran-2-one, m.p. 113°. The coumarone skeleton of (III) is amended to (*A*). H. W.

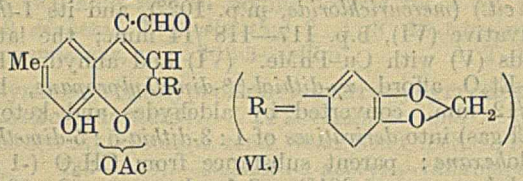
Synthesis of certain products of the decomposition of dihydrousnic acid. M. YANAGITA (Ber., 1938, **71**, [*B*], 2269—2273).—4 : 3 : 1-$C_6H_3Me(OH)_2$ (I) is rapidly transformed by $ZnCl_2$ in boiling AcOH into 5-*methylresacetophenone*, m.p. 170°. $CH_2Ac{\cdot}CO_2Et$, conc. H_2SO_4, and (I) at 0° yield 7-*hydroxy*-4 : 6-*dimethylcoumarin*, m.p. 254—255° (decomp.) after softening at about 210°. The corresponding *acetate*, m.p. 159°, is converted by $AlCl_3$ at 180° into 2 : 6-*dihydroxy*-3-*methylacetophenone*, m.p. 138°, reduced by Zn–Hg and boiling 15% HCl in presence of PhMe to 4-*methyl*-2-*ethylresorcinol*, m.p. 105°. This with $CH_2Ac{\cdot}CO_2Et$ and cold conc. H_2SO_4 affords 7-*hydroxy*-4 : 6-*dimethyl*-8-*ethylcoumarin*, m.p. 189°, whence (Br in AcOH) 3-*bromo*-7-*hydroxy*-4 : 6-*dimethyl*-8-*ethylcoumarin* (II), m.p. 204°. Boiling 10% KOH transforms (II) into 6-*hydroxy*-3 : 5-*dimethyl*-7-*ethylcoumarilic acid*, m.p. 227—229° (decomp.). The corresponding *Me* ester, m.p. 158°, is transformed successively into the *hydrazide*, decomp. 245—246° after becoming red at 235°, *azide*, decomp. about 135°, and 6-*hydroxy*-3 : 5-*dimethyl*-7-*ethylcoumarylurethane*, m.p. 140°; this is converted by boiling 10% KOH into NH_3 and α-2 : 4-*dihydroxy*-5-*methyl*-3-*ethylphenylpropionic acid*, which is anhydrised to 6-*hydroxy*-3 : 5-*dimethyl*-7-*ethylcoumaran*-2-*one*, m.p. 113°. H. W.

Stearoptens of orange-peel oil. I. H. BÖHME and G. PIETSCH (Arch. Pharm., 1938, **276**, 482—488).—The oil yields a fish-poison, *aurapten* (I), $C_{15}H_{16}O_4$, m.p. 91°, $[\alpha]_D^{20}$ −33·4° in 96% EtOH, which is a coumarin since it possesses lactonic properties and is hydrogenated (Pd–C) in AcOH or NaOEt–EtOH to *dihydroaurapten*, m.p. 116°, and *dihydroauraptenic acid*, $C_{15}H_{20}O_5$, m.p. 98·5° [oxidised by HNO_3 to $(CH_2{\cdot}CO_2H)_2$], respectively. Coumarin and (I) are stable to *o*-$CO_2H{\cdot}C_6H_4{\cdot}CO_3H$. R. S. C.

Egonol. III. Degradation of acetylegonol by ozone. S. KAWAI and F. YOSHIMURA. **IV. Oxidation of acetylegonol with hydrogen peroxide.** S. KAWAI and N. SUGIYAMA [with, in part, I. TSUBAKI] (Ber., 1938, **71**, [*B*], 2415—2420, 2421—2432; cf. A., 1938, II, 373, 501).—III. Ozonisation of acetylegonol (I) in EtOAc at 0° and treatment of the ozonide with steam gives CH_2O in amount insufficient to suggest the presence of a vinyl group and *acetylstyraxinaldehyde* (II), $C_{21}H_{20}O_8$, m.p. 97—98° [*phenylhydrazone*, m.p. 151° (slight decomp.)], which reduces cold Fehling's solution but does not give the Legal reaction; it is hydrolysed by 2N-NaOH at about 80° to piperonylic acid and the non-cryst. *styraxinolaldehyde* [*monophenylhydrazone*, $C_{17}H_{20}O_3N_2$, m.p. 153° (slight decomp.)]. Oxidation of (II) with AcO_2H gives *acetylstyraxic acid* (III), m.p. 168°. Styraxinolic acid with Me_2SO_4–KOH and CH_2N_2 followed by NaOBr gives *iso*hemipinic acid (IV), m.p. 248°. Allylvanillin is transformed by Me_2SO_4 and KOH into non-cryst. 3 : 4-*dimethoxy*-5-*allylbenzaldehyde*, b.p. 173—175°/24 mm., which does not give a colour with $FeCl_3$ and is converted by 1 : 3-dimethylbarbituric acid in 80% EtOH at 100° into 3 : 4-*dimethoxy*-5-*allylbenzylidenedimethylbarbituric acid*, m.p. 110°; it is oxidised (aq. $KMnO_4$–C_6H_6 at about 90°) to (IV).

IV. Investigation of *benzoylegonol*, m.p. 117·5—118°, p-*nitrobenzoylegonol*, m.p. 129—130°, and *egonolphenylurethane*, m.p. 132—132·5°, establishes the formula $C_{19}H_{18}O_5$ (not $C_{20}H_{18}O_5$) for egonol (V). (I), m.p. 108·5°, is oxidised by 30% H_2O_2 in AcOH to *noregonolonidine acetate* (VI), m.p. 179°, hydrogenated (Pt-black in dioxan) to *dihydronoregonolonidine acetate* (VII), m.p. 185—186°, which is relatively stable when dry but readily autoxidised when dissolved, particularly in AcOH. The mother-liquors from

(VII) contain piperonylic acid and (III), m.p. 168° (*Me* ester, m.p. 104°), which does not give colour



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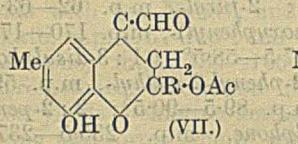

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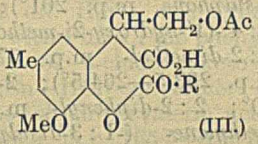

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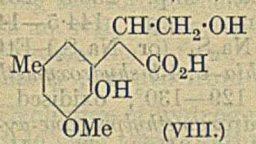

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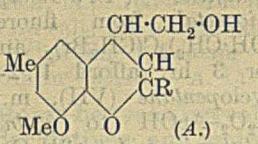


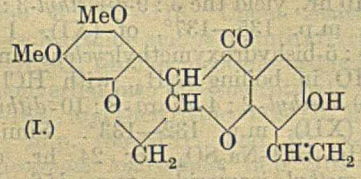
(*A*.)

reactions with $FeCl_3$ or $Cu(OAc)_2$ in EtOH but readily yields CHI_3. 2N-KOH transforms (III) into *styraxinolic acid* (VIII), m.p. 171°, which gives an unusually sensitive, dark blue colour with $FeCl_3$ and is converted by distillation at 200—230°/7 mm. into a substance, $C_{11}H_{12}O_4$ or $C_{10}H_{14}O_3$. p-*Bromophenacyl styraxinolate* has m.p. 137·5—138°. (III) is transformed by successive treatments with $SOCl_2$ and conc. NH_3 into *acetylstyraxamide*, m.p. 134—135°. (I) is probably *A*. H. W.

Benzylidenecoumaranones considered as chalkones. T. B. Panse and T. S. Wheeler (Current Sci., 1938, **7**, 181).—A preliminary note. R. S. C.

Synthesis of linear naphthaflavone. V. V. Virkar and T. S. Wheeler (Current Sci., 1938, **7**, 181—182).—A preliminary note. R. S. C.

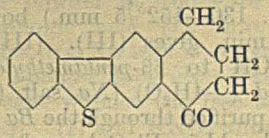
Buckley's substance, m.p. 183°, from *Derris* extract. J. J. Boam and R. S. Cahn (J.C.S., 1938, 1818—1820).—The substance, m.p. 183°, obtained by Buckley (B., 1936, 1117) appears to be homogeneous and analysis of the solvent-free crystals and the *solvate* (+0·5C_6H_6) agrees best with $C_{20}H_{16}O_6$, or less well with $C_{20}H_{18}O_6$. The structure (I) is suggested and the substance is held not to occur naturally as such but to be derived by degradation of deguelin by the alkali used in its isolation.



(I.)

F. R. S.

Dibenzthiophen : orientation and derivatives. H. Gilman and A. L. Jacoby (J. Org. Chem., 1938, **3**, 108—119).—Dibenzthiophen (I) (prep. in 65—70% yield from Ph_2, S, and $AlCl_3$ at 115—240°), m.p. 99°, gives (Friedel–Crafts) 3-*acetyldibenzthiophen*, m.p. 111° (*oxime*, m.p. 160—161°), oxidised by I–KI–NaOH to the 3-carboxylic acid (*Me* ester, m.p. 74—75°). When treated with $LiBu^a$, LiPh, $LiC_{10}H_7$-α, or LiC_6H_4·OMe-*p* and then with CO_2 (I) gives 55, 12, 7·6, and 0%, respectively, of *dibenzthiophen*-1-*carboxylic acid*, m.p. 252—253° (*Me* ester, m.p. 95°; decarboxylated by Cu in quinoline at 120—200°). When treated with $LiBu^a$ and then with Me_2SO_4 (I) gives 1-*methyldibenzthiophen*, m.p. 65·5°, also obtained from 2 : 2′-dihydroxy-3-methyldiphenyl by P_2S_5 at 165—400°. The Li derivative (II) of (I) with MgEtCl and O_2 at <3° gives 1-*hydroxydibenzthiophen* (III), m.p. 167° [$(NO_2)_2$-derivative, m.p. 204° (decomp.); *Me ether*, m.p. 123°]. Br converts (II) into the 1-Br-compound, which with aq. NH_3 and CuBr at 200—200° gives 1-*aminodibenzthiophen*, m.p. 110° [also obtained from (III) by aq. NH_3 and $NaHSO_3$ at 200—210°], the *Ac* derivative, m.p. 198°, of which gives 4-*bromo*-1-*acetamidodibenzthiophen*, m.p. 254°, and thence 4-*bromo*-1-*amino*-, m.p. 156°, and 4-*bromodibenzthiophen* (IV), m.p. 84° (1 : 1-*dioxide*, m.p. 170—171°). By the Grignard reagent (IV) gives *dibenzthiophen*-4-*carboxylic acid*, m.p. 176—177° (*Me* ester, m.p. 72—72·5°). Mercuration of (I) occurs at 140—150° (not in EtOH), but gives a mixture, m.p. 215° (decomp.). 3-Acetamidodibenzthiophen, m.p. 178° (lit., 168°), is obtained from (I) by nitration etc., from the 3-Br-compound by NH_3–CuBr, and by Beckmann rearrangement (PCl_5) of the appropriate amine; it yields a NO_2-derivative, m.p. 250° (decomp.), and thence, by HCl–EtOH, MeCHO and a N-free compound, m.p. 88°. With Na in liquid NH_3, followed by NH_4NO_3, (I) gives 1 : 4-*dihydrodibenzthiophen* (V), m.p. 76° (*picrate*, m.p. 105°). The *dibromide* of (V) loses 2HBr to yield (I); with LiPh it gives (I), C_6H_6, and LiH, and is also dehydrogenated by other very reactive organoalkali compounds. With $(CH_2{\cdot}CO)_2O$ and $AlCl_3$ in $C_2H_2Cl_4$–$PhNO_2$ (I) gives γ-*keto*-γ-3-*dibenzthiophenylbutyric acid*, m.p. 160·5—161°, reduced by Zn–Hg in aq. HCl–PhMe–AcOH to γ-3-*dibenzthiophenylbutyric acid*, m.p. 131°, which is cyclised by 88% H_2SO_4 to (?) 1-*keto*-1 : 2 : 3 : 4-*tetrahydro*-β-*thiobrazan* (VI), m.p. 178°.



(VI.)

With *o*-$C_6H_4(CO)_2O$ and $AlCl_3$ (I) gives 3-*o*-*carboxybenzoyldibenzthiophen*, m.p. 105—106°, converted by NaCl–$AlCl_3$ at 100—150° into *thionaphtheno*-1 : 2-2 : 3(or 1 : 2)-*anthraquinone*, m.p. 285—286°. R. S. C.

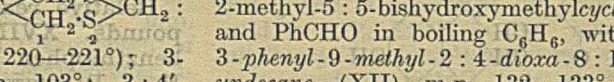
Relative reactivities of organometallic compounds. XVIII. Selective metalations of dibenzthiophen. H. Gilman, A. L. Jacoby, and H. A. Pacevitz (J. Org. Chem., 1938, **3**, 120—124; cf. A., 1937, II, 528).—In contrast to other organometallic compounds (preceding abstract) CaPhI attacks $C_{(2)}$ of dibenzthiophen. Treatment with CO_2 gives *dibenzthiophen*-2-*carboxylic acid*, decomp. 300—305° (*Me* ester, m.p. 129—130°), decarboxylated by Cu in quinoline at 200°. Dibenzthiophen *SS*-dioxide (modified prep.), m.p. 232°, with HNO_3 (*d* 1·5) in H_2SO_4–AcOH at 4° gives the 2-NO_2-derivative, m.p. 265—266° [further nitrated to the known 2 : 7-$(NO_2)_2$-compound], reduced (Sn–HCl) to the 2-NH_2-

dioxide, m.p. 259—260°, which yields 2-*bromodibenzthiophen* SS-*dioxide*, m.p. 224—225° (loses the Br when reduced). R. S. C.

Isosteric compounds. I. Acyl derivatives of dibenzthiophen. A. Burger, W. B. Wartman, jun., and R. E. Lutz (J. Amer. Chem. Soc., 1938, **60**, 2628—2630).—Since ·S· in rings is in many respects similar to ·CH:CH·, dibenzthiophen (I) and phenanthrene are said to be isosteric. With AcCl and $AlCl_3$ in CS_2 (I) gives 3-acetyl- (II), m.p. 111—112° [*semicarbazone*, m.p. 234—235° (decomp.)], and a little x-*acetyl*-, m.p. 129—130° [*semicarbazone*, m.p. 302—304° (decomp.)], and 3 : 6-*diacetyl-dibenzthiophen* (III), m.p. 208—209° [obtained similarly from (II) in 90% yield]. The structure of (II) is proved by conversion of its *oxime*, m.p. 161—164°, by HCl–AcOH–Ac_2O into the known 3-NHAc- and 3-NH_2-compounds, and that of (III) by similar conversion of its *dioxime*, m.p. 272—274° (decomp.), into the 3 : 6-$(NHAc)_2$- and -$(NH_2)_2$-compounds. (II) forms the main product at 0°, (III) at the b.p. R. S. C.

Some 1 : 3-dithiols and derived cyclic thioacetals. H. J. Backer and A. F. Tamsma (Rec. trav. chim., 1938, **57**, 1183—1210; cf. A., 1934, 900, 901; 1937, II, 267, 318).—1 : 1-Bisbromomethyl*cyclo*hexane (I) and K_2S–EtOH for 24 hr. (on bath) afford 2-*thia*-4-spiro*nonane* (II), b.p. 96°/18 mm. [*mercuri-chloride*, m.p. 161° (some decomp.) and *-bromide*, m.p. 157·5°; *-2-sulphone*, m.p. 72·5—73°; *-2-sulphoxide*, b.p. 148—151°/5 mm. (*mercuri-chloride*, m.p. 161·5°)], converted by MeI into *γ-iodo-ββ-pentamethylenepropyldimethylsulphonium iodide*, m.p. 92° (*picrate*, m.p. 117°), and by I–AcOH into 2-*thia*-4-spiro*nonane* 2 : 2-*dioxide*, m.p. 83—84°. (I) refluxed with Na_2S_2–EtOH for 3 hr. gives (II) and 2 : 3-*dithia*-5-spiro*decane* (III), b.p. 136°/11 mm., 147°/17 mm. (*mercurichloride*, m.p. 91°), and some (I). (I) and Na_2S_4–EtOH–H_2O afford (II), (III), and the 2 : 3 : 3-trisulphide, b.p. 152°/5 mm. (impure); the latter (b.p. 130—152°/5 mm.) boiled with Cu–PhMe for 20 min. gives (III). (III) is oxidised (H_2O_2) in AcOH to *ββ-pentamethylenepropane-αγ-disulphonic acid* (+$4H_2O$) [*Na* salt (+$4H_2O$); *Tl* salt (+$2H_2O$)], purified through the *Ba* salt (+$4H_2O$). (III) is reduced cold in Et_2O by anhyd. NH_3–Na to *αγ-dithiol-ββ-pentamethylenepropane* (IV), b.p. 136°/17 mm. (Hg salt, decomp. 140°). Its Na salt and I–EtOH yield (III). (IV) with aldehydes and ketones, and HCl, gives the following *derivatives* of 2 : 4-*dithia*-6-spiro*undecane*, $[CH_2]_5{:}C<^{CH_2\cdot S}_{CH_2\cdot S}>CH_2$: 3-methyl- (-2 : 4-*disulphone*, m.p. 220—221°); 3-*phenyl*-, m.p. 162°; 3-*furyl*-, m.p. 103°; 3 : 4′-1′-*hydroxy-2′-methoxyphenyl*-, m.p. 191—192°; 3 : 3-*dimethyl*-, m.p. 76—77° (*dimeride*, m.p. 215°) (-2 : 4-*disulphone*, m.p. 268·5—269·5°); 3-*methyl*-3-*ethyl*, m.p. 37—37·5; 3-*phenyl*-3-*methyl*- [*disulphone*, m.p. 293° (decomp.), colours from 265°]; 3 : 3-*diphenyl*-, m.p. 125°; 3 : 3-*tetra*-, m.p. 68—68·5°, and *-penta*-, m.p. 106—106·5°, *-methylene*-; *compounds* from (IV) and fluorenone, m.p. 172—173°, and from behenone, $CO(C_{21}H_{43})_2$, m.p. 63—64°.

$CMe_2(CH_2Br)_2$ and Na_2S_4 (Na_2S_2) in EtOH for 4 (10) hr. give 1 : 2-*dithia*-4 : 4-*dimethyl*cyclo*pentane* (V), b.p. 84—86°/17 mm. (cf. Backer and Evenhuis, *loc. cit.*) (*mercurichloride*, m.p. 102°), and its 1-*thio*-derivative (VI), b.p. 117—118°/14 mm.; the latter yields (V) with Cu–PhMe. (VI) and anhyd. NH_3–Na–Et_2O afford *αγ-dithiol-ββ-dimethylpropane*, b.p. 72°/12 mm., converted by aldehydes and ketones (HCl gas) into *derivatives* of 1 : 3-*dithia*-5 : 5-*dimethyl*-cyclo*hexane*: parent substance from CH_2O (-1 : 3-*disulphone*, m.p. 201°); 2-*furyl*-, m.p. 62—63·5°; 2 : 4′-(1′-*hydroxy-2′-methoxyphenyl*)-, m.p. 170—171°; 2 : 2-*dimethyl*-, m.p. 57·5—58·5° (-1 : 3-*disulphone*, m.p. 263·5—264·5°); 2-*phenyl*-2-*methyl*-, m.p. 59—60°; 2 : 2-*diphenyl*-, m.p. 89·5—90·5°; 2 : 2-*penta-methylene*- (-1 : 3-*disulphone*, m.p. 235·5—237°); *thioacetal* from fluorenone, m.p. 144·5—145°. $(OH\cdot CH_2)_2C(CH_2Br)_2$ and Na_2S_4 (or Na_2S_2)–EtOH for 3 hr. afford 1 : 2-*dithia*-4 : 4-*bishydroxymethyl*-cyclo*pentane* (VII), m.p. 129—130°, oxidised by H_2O_2–AcOH to *ββ-bishydroxymethylpropane-αγ-disulphonic acid* (+$3H_2O$) [*Ba* (+$3H_2O$), *Tl* (+H_2O), and *Na* (+$3H_2O$), salts] and a little 1 : 2-*disulphone*, m.p. 242—244° corresponding with (VII). (VII) and anhyd. NH_3–Na afford *ββ-bishydroxymethyl-αγ-bisthiolmethylmethane* (VIII), m.p. 97—98° (cryst. form examined), its Na salt and I–EtOH giving (VII). (VIII) and aldehydes and ketones, with HCl, yield *derivatives* of 1 : 3-*dithia*-5 : 5-*bishydroxymethyl*cyclo-*hexane*: 2-*methyl*-, m.p. 122—124° (-1 : 3-*disulphone*, m.p. 216—219°); 2-*phenyl*- (IX), m.p. 209—211° [*diacetate*, *i.e.*, 5 : 5-$(CH_2\cdot OAc)_2$, m.p. 134—136°]; 2 : 4′-(1′-*hydroxy-2′-methoxyphenyl*)-, m.p. 186·5—188°; 2 : 2-*dimethyl*-, m.p. 199·5—200·5°; 2-*phenyl*-2-*methyl*- (X), m.p. 164—165° (-1 : 3-*disulphone*, m.p. 290°); 2 : 2-*diphenyl*-, m.p. 169—170°; 2 : 2-*penta-methylene*-, m.p. 186·5—187·5°; 4-*methyl*-, m.p. 182°, and 4-*chloro*-, m.p. 194—196°, *-pentamethylene*-; *thioacetals* from (VIII) and camphor, m.p. 155—157° and from fluorenone, m.p. 244—245°. (VIII) and PhCHO–EtOH, refluxed for 3 hr., afford 3 : 9-*diphenyl*-2 : 4-*dioxa*-8 : 10-*dithia*-6-spiro*undecane* [(XI), R = H, R′ = Ph], m.p. 171·5—173·5°. (VIII) and excess of $COMe_2$–HCl gas give 30% of the 3 : 3 : 9 : 9-*tetramethyl* analogue, m.p. 127—128°, and 60% of



(XI.)

thioacetal (*loc. cit.*). (X) and COPhMe–HCl–C_6H_6, boiled for 10 hr., yield the 3 : 9-*dimethyl*-3 : 9-*diphenyl* derivative, m.p. 135—137°, of (XI). 1 : 3-Dithia-2-methyl-5 : 5-bishydroxymethyl*cyclo*hexane (*loc. cit.*) and PhCHO in boiling C_6H_6, with HCl gas, give 3-*phenyl*-9-*methyl*-2 : 4-*dioxa*-8 : 10-*dithia*-6-spiro-*undecane*, (XII), m.p. 132—133°. Similarly (IX) and MeCHO–HCl–Na_2SO_4 for 24 hr. afford the 9-*phenyl*-3-*methyl* isomeride, m.p. 156—158°. The thioacetal, m.p. 182° (*loc. cit.*) from 4-methyl*cyclo*-hexane, with PhCHO–HCl–C_6H_6 for 1 hr., yields 3-*phenyl*-9-(4-*methylpentamethylene*)-2 : 4-*dioxa*-8 : 10-*dithia*-6-spiro*undecane*, m.p. 126—143°, composed of two *isomerides*, m.p. 123—125° and 158—160°, possibly *cis*- and *trans*-. 2-Methyl-5 : 5-bishydroxy-methyl*cyclo*hexane-1 : 3-disulphone and PhCHO–HCl–C_6H_6 give 3-*phenyl*-9-*methyl*-2 : 4-*dioxa*-6-spiro-

undecane-8 : 10-*disulphone*, m.p. 229—231°, also obtained from (XII) and BzO_2H–$CHCl_3$. $C(CH_2{\cdot}OH)_4$ and COPhMe–HCl in boiling xylene for 4 hr. give 3 : 9-*diphenyl*-3 : 9-*dimethyl*-2 : 4 : 8 : 10-*tetraoxa*-6-spiro*undecane*, m.p. 146·5—147·5°. A. T. P.

Synthesis of oxyproline (γ-hydroxypyrrolidine-α-carboxylic acid). V. Feofilaktov and A. Onischtschenko (Compt. rend. Acad. Sci. U.R.S.S., 1938, **20**, 133—135).—δ-Chloro-α-acetyl-γ-valerolactone yields with aq. $NaNO_2$ and dil. H_2SO_4 the oxime acetate, m.p. 115—116°, and with PhN_2Cl the phenylhydrazone, m.p. 185—186°, of δ-chloro-α-keto-γ-valerolactone. Reduction (Sn+HCl) of either of these yields δ-chloro-α-amino-γ-hydroxyvaleric acid, having two forms, one of which, m.p. 165·5—166·5°, with aq. NH_3 yields (via the Cu salt) the *b*-form, and the other the *a*-form, of oxyproline. Leucine is similarly prepared from $CHAcBu^{\beta}{\cdot}CO_2Et$. A. Li.

Exchange of hydrogen atoms between pyrrole, indole, and their methyl derivatives, and water. V. Exchange of hydrogen atoms between *N*-methylindole and water. M. Koizumi, Y. Komaki, and T. Titani (Bull. Chem. Soc. Japan, 1938, **13**, 643—651).—Exchange of H between molten *N*-methylindole and aq. D_2O at 60° does not occur at $p_H > 2{\cdot}5$. At $p_H < 2{\cdot}5$ exchange proceeds rapidly, the β-H being substituted; there is no evidence of exchange with the α-H as is the case with indole (cf. A., 1938, I, 318). J. D. R.

Oxidation products of pyrrole amines. I. T. Ajello (Gazzetta, 1938, **68**, 602—608).—4-Amino-2 : 3 : 5-triphenylpyrrole (new prep., reducing the :N·OH compound by Al–EtOH) is oxidised by $FeCl_3$–AcOH to *triphenylpyrroleninylhydroxylamine*, $N\leqslant^{CPh{\cdot}CH{\cdot}NH{\cdot}OH}_{CPh:CPh}$ (I), m.p. 168° (cf. A., 1937, II, 30) (*Ac* derivative, m.p. 150°; *picrate*, m.p. 177°); by H_2O_2–AcOH to (I) and a substance, m.p. 210°; by CrO_3–AcOH to (I) and a substance, m.p. 290° (also obtained from oximinotriphenylpyrrole; cf. A., 1936, 997); by $K_3Fe(CN)_6$ to a compound (II), m.p. 170° (reduced to aminotriphenylpyrrole), and a compound, m.p. 256°; and by PbO_2 to (II). E. W. W.

Synthesis of compounds exciting parasympathetic nerves. Methyl *N*-methyl*iso*nicotinate and its tetra- and hexahydro-derivatives. J. V. Supniewski and M. Serafinówna (Arch. Chem. Farm., 1936, **3**, 109—118; Chem. Zentr., 1937, ii, 73—74).—*iso*Nicotinic acid is quantitatively esterified by MeOH–H_2SO_4 (unlike nicotinic or picolinic acids), the ester converted into Me *iso*nicotinate methiodide, m.p. 183—184°, and then reduced (Pt) to *Me N-methyltetrahydro-*, m.p. 130—131°, and *Me N-methylhexahydro-*isonicotinate *hydriodide*, m.p. 154—155°. *Me N-methyltetrahydro-* and *N-methylhexahydronicotinate*, b.p. 138°/32 mm., and their *methiodides*, m.p. 152—153°, 193—194°, respectively, were also prepared. The arecoline-like action of these esters which depends on the NMe group is described. A. H. C.

Ethyl acetonedicarboxylate. II. G. Jacini (Gazzetta, 1938, **68**, 592—595).—The *semioxamazone*, $(CH_2{\cdot}CO_2Et)_2C{:}N{\cdot}NH{\cdot}CO{\cdot}CO{\cdot}NH_2$, m.p. 116°, of Et acetonedicarboxylate (I) gives, with 20% aq. NH_3, 2-*hydroxy*-6-*ethoxy*-4-*pyridonesemioxamazone*, m.p. 274°. The *thiosemicarbazone*, m.p. 118°, of (I) and aq. NH_3 give, however, 2-*hydroxy*-6-*ethoxy*-1 : 4-*pyronethiosemicarbazone* (?), m.p. 133° (insol. *Cu*, *Ag*, *Pb* salts), also obtained by the action of conc. H_2SO_4; the corresponding *semicarbazone*, m.p. 128° is obtained similarly (also by heating; cf. A., 1938, II, 42). The structure of 2 : 4-dihydroxy-4-pyridonesemicarbazone (II) (*loc. cit.*) is confirmed by boiling (II) with conc. HCl, and converting the product into the known phenylhydrazone. E. W. W.

Action of sulphuryl chloride on pyridine oxide. R. Bobrański, L. Kochańska, and A. Kowalewska (Ber., 1938, **71**, [*B*], 2385—2388; cf. A., 1938, II, 201).—*o*-$CO_2H{\cdot}C_6H_4{\cdot}CO_3H$ and C_5H_5N in Et_2O give a ppt. of *pyridine oxide phthalate*, m.p. 122—123°, transformed by 10% HCl into *pyridine oxide hydrochloride*, m.p. 180° (overall yield 75%). This does not react with SO_2Cl_2 at room temp. or the b.p. but at 120° gives a mixture of 2- and 4-chloro- and pentachloro-pyridine. The Cl_1-compounds are separated from one another through their additive compounds with $HgCl_2$. H. W.

Nitration of halogen derivatives of pyridine. E. Płażek, A. Sorokowska, and D. Tołopka (Rocz. Chem., 1938, **18**, 210—216).—KNO_3 in conc. HNO_3, added to 3-halogenopyridines in 10% oleum at 270°, yields 3-*chloro-*, m.p. 88°, 3-*bromo-*, m.p. 110°, and 3-*iodo*-5-*nitropyridine*, m.p. 198°. The orientation of these compounds is determined by reduction to NH_2-compounds, of which 3-*iodo*-5-*aminopyridine*, m.p. 70° (*picrate*, m.p. 252°), is new. Under similar conditions of nitration NO_2-derivatives of 2- and 4-halogenopyridines are not obtained. R. T.

2-Aminopyridine-5-sulphonamide and its derivatives. C. Naegeli, W. Kündig, and H. Brandenburger (Helv. Chim. Acta, 1938, **21**, 1746—1756).—2-Aminopyridine is transformed by H_2SO_4,H_2O containing Al powder at 200—210° into 2-aminopyridine-5-sulphonic acid (I), m.p. 332—334°, in 60% yield. Its dry Na salt is converted by boiling Ac_2O into *Na* 2-*acetamidopyridine*-5-*sulphonate* [corresponding *Cu* salt, whence the free acid, m.p. 300—302° (decomp.)]. (I) and HNO_2 afford 2-pyridone-5-sulphonic acid (yield 92%), transformed by PCl_5 into 2-*chloropyridine*-5-*sulphonyl chloride* (II), m.p. 51°, also obtained from 1-methyl-2-pyridone-5-sulphonic acid and PCl_5 containing $POCl_3$ at 130—135°. Addition of (II) in $COMe_2$ to 20% NH_3 leads to 2-chloropyridine-5-sulphonamide (III), m.p. 158—159°, transformed by 20% NH_3 at 125—160° into 2-*aminopyridine*-5-*sulphonamide* (IV), m.p. 175—176·5° (*Bz*$_2$ derivative, m.p. 221—223°). (III) and 33% aq. NH_2Et at 100° or at 135—150° give 2-*ethylaminopyridine*-5-*sulphonamide*, m.p. 190—191° (yield 74%), or -5-*sulphonethylamide*, m.p. 139—141°, respectively. 2-*Diethylamino-*, m.p. 116—117°, 2-*butylamino-*, m.p. 121—122°, 2-*allylamino-*, m.p. 195—201°, 2-*benzylamino-*, m.p. 199—201°, and 2-*anilino-*, m.p. 181—183°, -*pyridine*-5-*sulphonamide* are described. NH_2Ph and (II) in C_6H_6 afford 2-*chloropyridine*-5-*sulphonanilide*, m.p. 149—151°, converted by aq. NH_3 at 100—130° into 2-*aminopyridine*-5-*sulphonanilide*, m.p.

176—178°. (II) and *p*-NH_2·C_6H_4·SO_2·NH_2 in C_5H_5N at >40° yield p-2′-*chloropyridine*-5′-*sulphonamidobenzenesulphonamide*, m.p. 200—202°, whence (25% NH_3 at 130—150°) p-2′-*aminopyridine*-5-*sulphonamidobenzenesulphonamide*, m.p. 200—202°. (II) and (IV) in anhyd. C_5H_5N at >35° afford 2-2′-*chloropyridine*-5′-*sulphonamidopyridine*-5-*sulphonamide*, m.p. 253—255°, decomp. 265°, whence aq. NH_3 (saturated at 0°) at 120—160° gives 2-2′-*aminopyridine*-5′-*sulphonamidopyridine*-5-*sulphonamide*, m.p. 260°. (III) and morpholine (V) at 120° give 2-N-*morpholylpyridine*-5-*sulphonamide*, m.p. 182—183°. Addition of H_2O to (II) and (V) in $COMe_2$ leads to 2-*chloropyridine*-5-*sulphonmorpholide*, m.p. 143—144°. 2-N-*Morpholylpyridine*-5-*sulphonmorpholide* has m.p. 189—191°. All the compounds are well tolerated. H. W.

Sesqui-sodium salt of iodohydroxyquinolinesulphonic acid. J. J. L. Zwikker and A. Kruysse (Pharm. Weekblad, 1938, **75**, 1310—1315).—The prep. of a red *Na* salt, $C_9H_4NI(ONa)$·SO_3Na,$C_9H_4NI(OH)$·SO_3Na,$10H_2O$, is described. S. C.

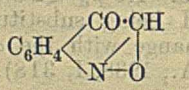
[**Synthesis of 1-alkyl*iso*quinolines and polymethylenedi-1 : 1′-*iso*quinolines.**] G. Hahn and H. F. Gudjons (Ber., 1938, **71**, [*B*], 2434).—An acknowledgement that the work of Child and Pyman (A., 1929, 1314) has been overlooked (cf. A., 1938, II, 513). H. W.

Nitrogen-terminated conjugated systems and maleic anhydride. F. Bergmann (J. Amer. Chem. Soc., 1938, **60**, 2811).—2-Styrylquinoline reacts with $(CH{\cdot}CO)_2O$ in xylene at 100°, but the product absorbs H_2O from the air, yielding 2-*styrylquinoline maleate*, m.p. 165—167°, identified by conversion by CH_2N_2 into Me_2 dimethylpyrazoline-4 : 5-dicarboxylate, m.p. 103—105°. CHPh:CH·CO·NHPh reacts similarly, but the maleate formed decomposes spontaneously into CHPh:CH·CHO and *cis*-CO_2H·CH:CH·CO·NHPh, m.p. 210° (lit., 198°). R. S. C.

3-Arylquinoline-4-carboxylic acids. B. Reichert and D. Ivanov (Arch. Pharm., 1938, **276**, 515—520).—With isatin in hot 40% KOH methoxyphenylacetaldoximes, prepared by reduction of the β-nitrostyrenes, give 3-(methoxyaryl)quinoline-4-carboxylic acids, two of which have no significant antipyretic activity or toxicity. 3-3′ : 4′-*Methylenedioxyphenyl*-, m.p. 268° (decomp.) (*Et* ester, m.p. 86°), 3-3′ : 4′-, m.p. 239·5° (decomp.) (*Et* ester, m.p. 118—119°), and 3-2′ : 4′-*dimethoxyphenyl*-, m.p. 266—267° (decomp.) (*Me* ester, m.p. 100°), 3-p-, m.p. 264° (decomp.), and 3-o-*anisyl*- (I), m.p. 253° (decomp.), -*quinoline*-4-*carboxylic acid* are prepared. By heating the acids above the m.p. are obtained 3-3′ : 4′-*methylenedioxyphenyl*-, m.p. 106°, and 3-p-*anisyl*-*quinoline*, m.p. 207°. With boiling HI (*d* 1·7) (I) gives *quinolino*-3 : 4-4′ : 3′-*coumarin*, m.p. 258—259°. R. S. C.

4-Arylamino-2-naphthylquinolines. K. Dziewoński, (Mlle.) M. Marusińka, and J. Moszew (Bull. Acad. Polonaise, 1938, **A**, 331—342).—1 : 4-$C_{10}H_6$MeAc (I) and $CS(NHPh)_2$ at 180°, then 220—280°, or $CS(NH{\cdot}C_6H_4Me$-*p*$)_2$ at 180—230° (270°), give 4-*anilino*-2-(4′-*methyl*-1′-*naphthyl*)*quinoline* (II), m.p. 214—215° [*hydrochloride*, m.p. 240—241° (decomp.); *picrate*, m.p. 285—286°; *methiodide*, m.p. 291—292°; 4-N-*NO*-derivative, m.p. 165° (decomp.); 4-N-*Ac* derivative, m.p. 181°; 4-N-*Me* derivative, m.p. 202°], and 4-p-*toluidino*-2-(4′-*methyl*-1′-*naphthyl*)-6-*methylquinoline* (III), m.p. 196° [*hydrochloride*, m.p. 316—317°; *picrate*, m.p. 271—273°; *methiodide*, m.p. 275—276°; 4-N-*NO*-, m.p. 233—235° (decomp.); 4-N-*Ac*, m.p. 165—166°; 4-N-*Me*, m.p. 232—233°, derivative] respectively. 2 : 6-$C_{10}H_6$MeAc and $CS(NHPh)_2$ at 180—210°, then 260°, give 4-*anilino*-2-(6′-*methyl*-2′-*naphthyl*)*quinoline* (IV), m.p. 172° (*picrate*, m.p. 278°; 4-N-*NO*-derivative, m.p. 216°; 4-N-*Ac* derivative, m.p. 197°), and β-$C_{10}H_7$·COEt affords 4-*anilino*-2-β-*naphthyl*-3-*methylquinoline* (V), m.p. 178—179° [*hydrochloride*, m.p. 253—254°; *picrate*, m.p. 261—262°; *methiodide*, m.p. 214—216°; 4-N-*NO* derivative, m.p. 153—154° (decomp.); 4-N-*Me* derivative, m.p. 131—132°]. (II), (III), (IV), and (V), and KOH–EtOH under pressure at 200°, 210°, 215°, 200° respectively, for 4 hr., yield 4-*hydroxy*-2-(4′-*methyl*-1′-*naphthyl*)-, m.p. 240°, -2-(4′-*methyl*-1′-*naphthyl*)-6-*methyl*-, m.p. 271—272°, -2-(6′-*methyl*-2′-*naphthyl*)-, m.p. 318—319°, and -2-β-*naphthyl*-3-*methyl*-, m.p. 323—324°, -*quinoline*. A. T. P.

Triangular structure for isatin. A. E. Klijnhout (Chem. Weekblad, 1938, **35**, 823—825).—The possiblity of isatin having the annexed structure is discussed.



S. C.

Tautomerism and mesomerism of the carbamyl group and their relation to light absorption; *o*- and *p*-hydroxy-azo-compounds. F. Arndt and B. Eistert (Ber., 1938, **71**, [*B*], 2040—2049).—In the tautomerism of compounds, R·CO·NHR′, it is clear that the relationships are more complicated than with keto–enol tautomerism, since any particular NH compound will have a structure intermediate between the mesomeric types R·CO·NHR′ (I) and R·CO^-:NHR'^+ (II). Usually (I) will predominate, but when the C:N bond can form part of a conjugated or aromatic system (II) will be favoured, and as this has the same electron arrangement as the tautomeride R·C(OH):NR′, optical measurements will not afford a distinction. In this way the results of Fromherz *et al.* (A., 1936, 1317; 1938, II, 381) and of Biltz (A., 1937, II, 78) with uric acid can be reconciled. The tautomerism of cyanuric acid, isatin, and of *o*- and *p*-hydroxy-azo compounds is discussed from the same aspect. F. J. G.

Synthesis of *r*-α-methylamino-β-3-indolylpropionic acid. E. J. Miller and W. Robson (J.C.S., 1938, 1910—1912).—1-Methylhydantoin, indole-3-aldehyde, and $C_5H_{11}N$ give 5-(3′-*indolal*)-1-*methylhydantoin*, m.p. 337—338°, which is reduced by H_2S in C_5H_5N to 5-(3′-indolylmethyl)-1-methylhydantoin, hydrolysed [$Ba(OH)_2$, 20 hr.] to *r*-α-methylamino-β-3-indolylpropionic acid, m.p. 245° (decomp.), in 90% yield. F. R. S.

Racemisation of amino-acids on acetylation with keten. R. W. Jackson and W. M. Cahill (J. Biol. Chem., 1938, **126**, 37—41).—*l*-Tryptophan, *l*-phenylalanine, and abrine with limited amounts of keten in dil. NaOH yield optically active Ac deriv-

atives, but with enough keten to make the solution acid, complete racemisation occurs. With proline there is no racemisation in either case. A. Li.

Acridine. XIX. Absorption spectra of *N*-hydroxyacridone and its sodium salt. K. Lehmstedt and F. Dostal (Ber., 1938, **71**, [*B*], 2432—2434).—Evidence is cited that the hydroxyacridone (I) obtained from *o*-$NO_2{\cdot}C_6H_4{\cdot}CHO$, C_6H_6, and conc. H_2SO_4 is an equilibrium mixture $C_6H_4\langle^{CO}_{N(OH)}\rangle C_6H_4 \rightleftharpoons C_6H_4\langle^{C(OH)}_{NO}\rangle C_6H_4$ in which usually the equilibrium is displaced strongly towards the left. The observation of Tanasescu *et al.* (A., 1936, 1266, 1520) that (I) and its Na salt have closely similar absorption spectra could not be confirmed. H. W.

Hydantoins. LII. Synthesis of *N*-3-phenyl-5-*p*-hydroxybenzylhydantoin-*N*-1-acetic acid from tyrosine-*N*-acetic acid. (Miss) E. Ware (J. Amer. Chem. Soc., 1938, **60**, 2653—2656; cf. A., 1933, 284).—Tyrosine-*N*-acetic acid (I) and PhNCO give 3-*phenyl*-5-p-*hydroxybenzylhydantoin*-1-*acetic acid* (II), m.p. 202—203°. The Me_2 ester, m.p. 84—85°, of (I), prepared by HCl–MeOH and liberated from its hydrochloride by the calc. amount of $NaHCO_3$, with 25% HCl gives (II) (also obtained from Cu phenylureidotyrosine-*N*-acetate by H_2S) and with PhNCO gives *Me*$_2$ *phenylureidotyrosine*-*N*-*acetate* (III), $+H_2O$ and anhyd., m.p. 124—125° (decomp.). The *Me* ester, m.p. 140—141°, of (II) is prepared from (II) by HCl–MeOH or from (III) by hot H_2O or, better, 25% HCl. The structure of (II) is proved as follows. 5-*p*-Anisylidene-3-phenylhydantoin and $CH_2Cl{\cdot}CO_2Et$ in NaOEt–EtOH give *Et* 5-p-*anisylidene*-3-*phenylhydantoin*-1-*acetate*, m.p. 89—91°, which with HI–red P yields (II) in one step. With conc. aq. $Ba(OH)_2$ at 100° (II) gives (I) and NH_2Ph. R. S. C.

Condensation of aminoantipyrine with aromatic amines in the presence of oxidising agents. E. Eisenstaedt (J. Org. Chem., 1938, **3**, 153—165).—Addition of 4 mols. of $FeCl_3$ to aminoantipyrine (I) (modified prep.) and the hydrochloride of an aromatic base having a *p*-H gives dyes of type $NMe{\cdot}CMe\rangle C{\cdot}N{:}C_6H_4{:}NR_2Cl$, which are reduced $(Na_2S_2O_4)$ to colourless leuco-compounds. Thus, *m*-$C_6H_4(NH_2)_2$ gives the *hydrochloride*, "*Antipyryl Red B*-3" (absorption max. at 4800±25 A.), reduced to 4-2′ : 4′-*diaminoanilinoantipyrine*, m.p. 264·9—267·9° (*hydrochloride*, m.p. 258·6—259·1°), the latter product being also obtained by condensing (I) with 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$ to 2′ : 4′-*dinitroanilinoantipyrine*, m.p. 213·1—213·9°, and reducing this with Sn–HCl. $NHPh_2$, (I), and $K_2Cr_2O_7$ in H_2SO_4–AcOH give an impure *dye*, "*Antipyryl Blue A*-93," reduced to 4-4″-*antipyryldiphenylamine*, m.p. 220·3—221·8°. R. S. C.

Method of Garelli and Racciu for the preparation of piperazine. A criticism. D. B. Rollins and H. N. Calderwood (J. Amer. Chem. Soc., 1938, **60**, 2751—2752).—Contrary to Garelli *et al.* (Atti accad. Sci. Torino, 1934, **69**, 162), $NH_2{\cdot}[CH_2]_2{\cdot}OH$ and H_2SO_4 or oleum give $NH_2{\cdot}[CH_2]_2{\cdot}HSO_4$. Piperazine gives a hexa- not a mono-hydrate. R. S. C.

Opening of the ring of the thiolactone of homocysteine. V. du Vigneaud, W. I. Patterson, and M. Hunt (J. Biol. Chem., 1938, **126**, 217—231; cf. A., 1936, 194).—*dl*-Homocysteine thiolactone hydrochloride (I) with aq. $NaHCO_3$ followed by aëration in presence of a trace of $FeCl_3$ yields an amorphous insol. *compound*, decomp. 260—270° (hydrolysed by conc. HCl to homocystine), but with $NaHCO_3$ in absence of air yields a mixture of dl- and meso-2 : 5-*diketobis*-β-*thiolethylpiperazine*, m.p. 208° and 237°, respectively. The former is also produced by mixing the d- and l-*compounds*, m.p. 212°, $[\alpha]_D^{25}$ ±54° in C_5H_5N [prepared from the *d*- and *l*-forms, m.p. 194°, $[\alpha]_D^{26}$ ±21·5° in H_2O, of (I)]. All four stereoisomerides are converted by CH_2PhCl and MgO in C_5H_5N into the corresponding S-*dibenzyl* derivatives: d- and l-, m.p. 183°, $[\alpha]_D^{25}$ ±61·0° in C_5H_5N, dl-, m.p. 165°, and meso-, m.p. 176°. The *d*-dibenzyl compound was also prepared by treating *S*-benzyl-*d*-homocysteine with MeOH–HCl, then Ag_2O, and heating the product at 70° for 18 hr. *l*-Diketobis-β-thiolethylpiperazine with H_2O_2 yields an amorphous product similar to the above. This and the amorphous product from the *d*-form of (I) with Na followed by CH_2PhCl, in liquid NH_3, yield the *l*- and *d*-dibenzyldiketopiperazines. dl-N-*Benzoylhomocysteine thiolactone*, m.p. 134—136°, prepared by reducing (Sn + HCl) dibenzoylhomocystine, reverts to the latter with dil. NaOH, no amorphous compound being formed. It is concluded that such compounds are polymerides containing ·S·S· linkings. All m.p. are corr. A. Li.

Structure of deoxyribonucleic acid. Diphosphoric esters of pyrimidine deoxyribosides. P. A. Levene (J. Biol. Chem., 1938, **126**, 63—66; cf. A., 1938, II, 295).—Analysis of freshly prepared Ba diphosphothyminedeoxyriboside (A., 1921, i, 821) has been repeated, with the same result. A. Li.

4 : 5-Dihydroglyoxalines.—See B., 1938, 1391.

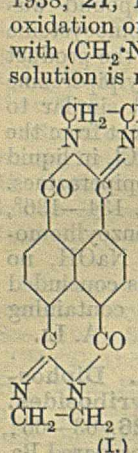
Catalytic hydrogenation of benziminazole derivatives. M. Hartmann and L. Panizzon (Helv. Chim. Acta, 1938, **21**, 1692—1694).—Benziminazole is not hydrogenated under high pressure in presence of Ni at 200° or of Pt at 100° in various media. Its 2-alkyl derivatives are readily reduced (PtO_2 in AcOH) to the H_4-compounds, 2-*methyl*- (I), m.p. 224°, 2-*ethyl*-, m.p. 202°, and 2-cyclo*hexyl*-, m.p. 267°, *-tetrahydrobenziminazole* being thus obtained. 2-cyclo-*Hexylbenziminazole*, m.p. 280°, is obtained by use of Ni at 180°. 1-Substituted benziminazoles cannot be hydrogenated in presence of Pt. The presence of a substituent in the C_6H_6 nucleus impedes hydrogenation even of the 2-substituted compounds as shown by the behaviour of 1-methyl-, 2 : 5-dimethyl-, and 1-ethyl-2 : 6-dimethyl-benziminazole. Hydrogenation of 5-ethoxy-2-methylbenziminazole causes loss of OEt and formation of (I). 1 : 2-*Dimethyltetrahydrobenziminazole*, b.p. 124°/4 mm., m.p. ~43° (*picrate*, m.p. 192°), is described. H. W.

Flavinduline derivatives. IX. K. Yamada and N. Hasebe (J. Soc. Chem. Ind. Japan, 1938, **41**, 290—292B; cf. A., 1938, II, 380).—The following halogen salts of flavinduline derivatives have been

prepared from *o*-$NH_2{\cdot}C_6H_4{\cdot}NHPr^{\alpha}$ and quinones: from phenanthraquinone: *chloride* (+0·5$ZnCl_2$), m.p. 195—197°, *bromide* (+0·5$ZnCl_2$), m.p. 204—206°, *iodide*, m.p. 159—161°; from 1 : 2-naphthoquinone: *chloride* (+0·5$ZnCl_2$), m.p. 190—192°, *bromide* (+0·5$ZnCl_2$), m.p. 199—201°, *iodide* (+0·5$ZnCl_2$), m.p. 163—165°; from *o*-benzoquinone: *chloride* (+0·5$ZnCl_2$), m.p. 217—219°, *bromide*, m.p. 229—231°, *iodide*, m.p. 140—142°. The colour reactions, solubility, dyeing properties, and fastness are described. A. Li.

Complex compounds of rhenium.—See A., 1939, I, 36.

Preparation of naphthoyleneiminazolines. H. E. Fierz-David and C. Rossi (Helv. Chim. Acta, 1938, **21**, 1466—1489).—The crude product of the oxidation of pyrene is suspended in H_2O, and treated with $(CH_2{\cdot}NH_2)_2$ followed by conc. HCl; the resulting solution is made feebly alkaline with 2N-Na_2CO_3 and heated for a week at 80—81°, thus giving *naphthoylenedi-iminazoline* (I) [*picrate*, softens, without melting, at 250° (corr.)], which does not give a vat with alkaline $Na_2S_2O_4$. It is transformed by Br in $C_6H_3Cl_3$ at 180—200° into the *compound*, $C_{18}H_5O_2N_4Br_3$ or $C_{18}H_4O_2N_4Br_4$, which gives yellow-brown to brown shades on cotton from an alkaline vat. The following observations are incidental. Naphthalene-1 : 4 : 5 : 8-tetracarboxylic anhydride (II) and $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}NH_2$ in boiling H_2O afford *naphthalene*-1 : 4 : 5 : 8-*tetracarboxydi*-β-*iminopropion-amide*, with which the Hofmann degradation could not be effected satisfactorily. Analogously (II) and $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Et$ yield *Et*$_2$ *naphthalene*-1 : 4 : 5 : 8-*tetracarboxydi*-β-*iminopropionate*. *Et*$_2$ *naphthalene*-1 : 4 : 5 : 8-*tetracarboxydi-iminoacetate* has m.p. 304—305° (corr.). *Naphthalene*-1 : 4 : 5 : 8-*tetracarboxydi-iminoacetic acid* (III) is obtained by oxidising naphthalene-1 : 4 : 5 : 8-tetracarboxydi-β-hydroxyethyldi-imide with $K_2Cr_2O_7$, AcOH, and 2N-H_2SO_4. With PCl_5 in $C_2H_2Cl_4$ followed by conc. aq. NH_3 (III) gives the corresponding *diamide*, also obtained directly from 1 : 4 : 5 : 8-$C_{10}H_4(CO_2H)_4$ and $NH_2{\cdot}CH_2{\cdot}CO{\cdot}NH_2$. Naphthalic anhydride (IV) and $NH_2{\cdot}[CH_2]_2{\cdot}OH$ in boiling H_2O afford *naphthal*-β-*hydroxyethylimide*, m.p. 175—176° (corr.), transformed by conc. HI at 170—175° into *naphthal*-β-*iodoethylimide*, m.p. 226—227° (corr.). This with *o*-$C_6H_4(CO)_2NK$ in boiling $PhNO_2$ yields *naphthal*-β-*phthalimidoethylimide*, m.p. 237—238° (corr.), hydrolysed by 46% HBr at 170—180° to *naphthal*-β-*amino-ethylimide*, m.p. 132° (Thiele), also obtained, with a *substance* $C_{26}H_{16}O_4N_2$, m.p. 372° (corr.), from (IV) and $(CH_2{\cdot}NH_2)_2$. This [*picrate*, m.p. 280—281° (corr.) after softening at 270°; *Ac* derivative, m.p. 201—202° (corr.)] passes at 100° into naphthoylene-2 : 3-iminazoline, m.p. 184—185° (corr.) [*ethiodide*, m.p. 286—287° (corr.; decomp.), converted by prolonged warming with H_2O into the *base*, $C_{16}H_{16}O_2N_2$, m.p. 92—93°; *picrate*, m.p. 294—295° (corr.; decomp.)].


(I.)

Naphthal-β-*chloroethylimide*, m.p. 206—207° (corr.), and -β-*bromoethylimide*, m.p. 222—223° (corr.), are described. *Naphthaliminoacetic acid*, m.p. 266—267° (corr.), obtained by oxidising the corresponding primary alcohol, gives a *Me* ester, m.p. 175—176° (corr.), and an *amide*, m.p. 323—324° (corr.; decomp.) after darkening at 306°, also obtained from (IV) and $NH_2{\cdot}CH_2{\cdot}CO{\cdot}NH_2$ in boiling H_2O. These methods cannot be completely extended to (II), which with $NH_2{\cdot}[CH_2]_2{\cdot}OH$ in boiling H_2O yields *naphthalene-tetracarboxydi*-β-*hydroxyethyldi-imide*, m.p. >360°. This is converted by conc. HBr at 170—180° into *naphthalene*-1 : 4 : 5 : 8-*tetracarboxydi*-β-*bromoethyldi-imide*, m.p. 250—251°, by conc. HCl at 170—180° into the corresponding *chloride*, m.p. 288—289° (corr.) [also obtained by chlorination with PCl_5 in $POCl_3$], and by boiling conc. HI into the corresponding *iodide*, m.p. 293—294° (corr.). $C_6H_4(CO)_2NK$ and $C_6H_4(CO)_2O$ at 210—250° convert the iodide into *naphthalene*-1 : 4 : 5 : 8-*di*-β-*phthaliminoethyldi-imide* [$(NO_2)_2$-derivative]; *p*-$C_6H_4Me{\cdot}SO_2{\cdot}NH_2$ and KOH in boiling $PhNO_2$ transform it into the red *compound*, $C_{32}H_{28}O_8N_4S_2$, m.p. 260° (corr.) after softening at 215°. H. W.

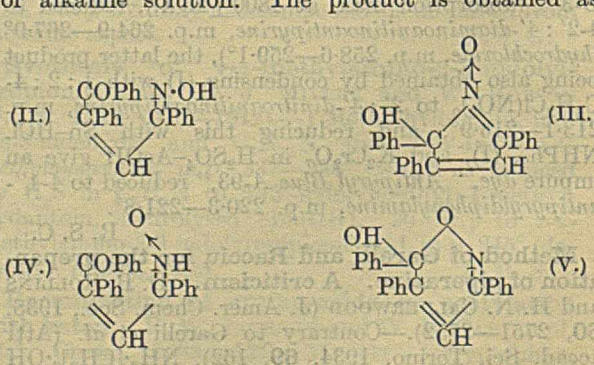
Phthalocyanines.—See B., 1938, 1394.

Catalytic properties of the phthalocyanines.—See A., 1939, I, 34.

Action of nitric acid on ethyl α-phenacyl-acetoacetate. S. Cusmano and (Signa.) G. Massara (Gazzetta, 1938, **68**, 566—570).—HNO_3 (*d* 1·40) converts $COPh{\cdot}CH_2{\cdot}CHAc{\cdot}CO_2Et$ into Et 5-phenyl-*iso*oxazole-3-carboxylate (I), converted by NH_2OH into 5-*phenyl*isooxazole-3-*carboxylhydroxamic acid*, m.p. 177°, which with boiling 25% H_2SO_4–EtOH yields the -3-*carboxylic acid*, m.p. 162° (decomp. to $COPh{\cdot}CH_2{\cdot}CN$), also obtained from (I) and aq. KOH–EtOH. E. W. W.

Action of nitric acid on diphenacyl. S. Cusmano and G. Sigillò (Gazzetta, 1938, **68**, 596—599).—$(CH_2{\cdot}COPh)_2$ and HNO_3 (*d* 1·40) give 3-benzoyl-5-phenyl*iso*oxazole (A., 1938, II, 71, 162). E. W. W.

Tautomerism of oximes. A. H. Blatt (J. Org. Chem., 1938, **3**, 91—98).—Only one CO of *cis*-$COPh{\cdot}CPh{:}CH{\cdot}COPh$ (I) reacts with NH_2OH in acid or alkaline solution. The product is obtained as


(II.) (III.) (IV.) (V.)

oxime or as derivatives in four forms (II)—(V) (cf. A., 1934, 355; 1936, 733). The tautomerides opposite

in configuration to (II) and (IV) do not exist and are those which by ring-closure without inversion give (V) and (III), respectively. Prep. of 6-*hydroxy*-3 : 5 : 6-*triphenyl*-$\Delta^{2:4}$-1 : 2-*oxazine* [-*orthazine*] (V), m.p. 159—160°, from (I) is detailed; it also sometimes gives some (?) β-*amino*-αγδ-*triphenylbutane*-αδ-*dione*, m.p. 191—192°. With HCl–MeOH (V) gives the 6-*OMe*-compound (VI), m.p. 108°, proving its glucosidic nature, but the reaction is reversible, for longer treatment gives PhCN and COPh·CHPh·CH(OMe)$_2$ (VII); (VII) is a secondary product, derived from COPh·CPh:CH·OH, which (with PhCN) is obtained from (V) or (VI) by warm AcOH. With Ac_2O (V) gives the 6-*acetate*, m.p. 117—118°, converted by HCl–MeOH into (VI) and hydrolysed to (V) and EtOAc by NaOH–EtOH. $PhSO_2Cl$ is without effect on (V), but PCl_5 causes mainly fission. (V) is insol. in aq., but sol. in alcoholic, alkali. MeI–NaOMe–MeOH with (V) gives a little (VI), but mainly the N-*Me* derivative, m.p. 167°, of (IV), hydrolysed by HCl to (I) and NHMe·OH. The production (Griffiths and Ingold, A., 1925, i, 1190) of 6-hydroxy-4 : 5-benz-$\Delta^{2:4}$-1 : 2-oxazine and *o*-$C_6H_4\langle^{CH=}_{CH(OH)}\rangle N\rightarrow O$ from *o*-$C_6H_4(CHO)_2$ indicates that stereoisomeric oximes are formed in the reaction with NH_2OH.

R. S. C.

Iminazoles. VII. Iminazole compounds of the heterocyclic series. R. Weidenhagen and U. Weeden (Ber., 1938, **71**, [*B*], 2347—2360).—The formation of glyoxalines by the interaction of *o*-diamines, aldehydes, and $Cu(OAc)_2$ depends on the initial production of a Schiff's base which is subsequently oxidised. The reaction with heterocyclic *o*-diamines appears to occur with increasing difficulty when the two NH_2-groups and the hetero-atom are present in the same ring. 2 : 3-Diaminodiphenylene oxide, CH_2O, and $Cu(OAc)_2$ in aq. MeOH at 100° give 5′ : 4′-*iminazolo*-2 : 3-*diphenylene oxide*, m.p. 217—218° [*Cu* salt; *hydrochloride*, decomp. 298°; *picrate*, m.p. 251° (decomp.)], converted by BzCl in anhyd. C_5H_5N into 1-*benzoyliminazolo*-5′ : 4′-2 : 3-*diphenylene oxide*, m.p. 186—187°. The following *iminazolo*-5′ : 4′-2 : 3-*diphenylene oxides* are obtained similarly by use of the requisite aldehyde: 2′-*methyl*-, m.p. 264·5° (*Cu* salt; *hydrochloride*, slow decomp. 278°; *picrate*, decomp. 279°); 2-*ethyl*-, m.p. 274° (*Cu* salt; *hydrochloride*, decomp. 318°; *picrate*, m.p. 258°); 2′-iso*propyl*-, m.p. 234—235·5° (*Cu* salt; *hydrochloride*, decomp. 276°; *picrate*, decomp. 271°); 2′-*hexyl*-, m.p. 99—104° and, after re-solidification, m.p. 144° (*Cu* salt; *hydrochloride*, decomp. 281°; *picrate*, m.p. 215—216°); 2′-*phenyl*-, m.p. 247—247·5° (*Cu* salt; *hydrochloride*, m.p. 335—336°); 2′-p-*nitrophenyl*-, m.p. 363° (*Cu* salt; *hydrochloride*). 5 : 6-Diaminoquinoline is transformed by boiling HCO_2H or by CH_2O and $Cu(OAc)_2$ in aq. EtOH at 100° into *iminazolo*-4′ : 5′-5 : 6-*quinoline* (+3H_2O), m.p. 216—217° (*hydrochloride*, decomp. 282—284°; 1′-*Bz* derivative, m.p. 166°). The following iminazolo-4′ : 5′-5 : 6-quinolines are obtained by analogous methods: 2′-*methyl*-, (+1·5H_2O), m.p. (anhyd.) about 142° after becoming glassy at > 100° [*Cu* salt; *hydrochloride*, m.p. 313°; *picrate*, m.p. 269°); 2′-*ethyl*-, (+2H_2O), m.p. 184° (*Cu* salt; *hydrochloride*, m.p. 284°); 2′-iso*propyl*-, (+1H_2O), softening when anhydrous at 100—105° [*Cu* salt; *hydrochloride*, m.p. 316°); 2′-*phenyl*-, m.p. 270° (also +1·5H_2O) (*Cu* salt; *nitrate*, decomp. 192°); 2′-p-*nitrophenyl*-, m.p. 356° (*hydrochloride*, m.p. 334·5°; *Cu* salt), obtained by oxidation of p-*nitrobenzylidenediaminoquinoline*, m.p. 222·5—223° (decomp.); 2′-*styryl*-, m.p. 258° [*Cu* salt; *hydrochloride*, m.p. 280° (decomp.)], from *mono*-*cinnamylidenediaminoquinoline*, m.p. 176—177°. 3 : 4-Diaminopyridine (I) is transformed by boiling HCO_2H into 4-*amino*-3(?)-*formamidopyridine*, m.p. 155·5—156°, and by boiling AcOH into 4-*amino*-3(?)-*acetamidopyridine*, m.p. 228—230°. CH_2O and $Cu(OAc)_2$ in boiling H_2O transform (I) into *iminazolo*-4′ : 5′-3 : 4-*pyridine*, (+0·5H_2O), m.p. 170—171° [*Cu* salt; *hydrochloride*, m.p. 221° (decomp.)]. The following iminazolo-4′ : 5′-3 : 4-pyridines are obtained similarly, heating in a sealed tube being sometimes necessary: 2′-*methyl*-, (+H_2O), m.p. 171° (*Cu* salt; *hydrochloride*, m.p. 271—273°); 2′-*ethyl*-, m.p. 191—192° [*Cu* salt; *hydrochloride*, m.p. 202° (decomp.)]; 2′-*phenyl*-, m.p. 224—225° (*Cu* salt; *hydrochloride*, m.p. 260°); 2′-p-*anisyl*-, m.p. 243° (*Cu* salt; *hydrochloride*, m.p. 254—255°); 2′-p-*aminophenyl*-, m.p. 324° (decomp.) (*hydrochloride*), by oxidation of *mono*-p-*nitrobenzylidenediaminopyridine*, decomp. 203°.

H. W.

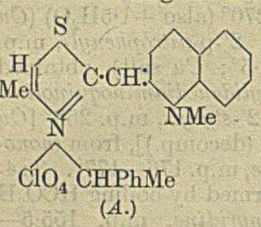
4 : 5-Dimethyl- and 4-methyl-5-β-chloroethylthiazole.—See B., 1938, 1391.

Properties of isosteric and structurally similar compounds. IX. Comparative investigations with 3-hydroxybenzthiazole. H. Erlenmeyer and H. Ueberwasser (Helv. Chim. Acta, 1938, **21**, 1695—1698; cf. A., 1938, II, 462).—Comparison of 3-hydroxybenzthiazole (I) with 8-hydroxyquinoline (II) shows that in the former the phenolic structure is more pronounced at the expense of the quinonoid form. (I) and (II) give mixed crystals. (I) is less useful than (II) in analytical chemistry. In the cases of $Zn^{\cdot\cdot}$, $Ni^{\cdot\cdot}$, and $Cu^{\cdot\cdot}$ the insolubility of the ppts. with (I) renders them suitable analytically whereas with the $Mg^{\cdot\cdot}$ and $Al^{\cdot\cdot\cdot}$ compounds this is not the case. The determination of (I) in these complexes is effected by bromination (KBr–$KBrO_3$–HCl) to 4 : 6-*dibromo*-3-*hydroxybenzthiazole* (III), m.p. 203°. (I), its Zn complex, and (III) fluoresce in ultra-violet light; among corresponding compounds only the Zn complex of (II) shows this behaviour. Qual. colour reactions with vanadates, molybdates, and tungstates are not given by (I). (III) in $COMe_2$ affords a very intense, green-black colour with $Fe^{\cdot\cdot\cdot}$.

H. W.

Optically active cyanine dyes. J. Götze (Ber., 1938, **73**, [*B*], 2289—2291).—CHPhMe·NH_2 is converted by boiling AcOH–Ac_2O into *acetphenylethylamide*, r-*form*, m.p. 79°, (+), m.p. 101—102°, $[\alpha]_D$ +150° in EtOH, and (—), m.p. 101—102°, $[\alpha]_D$ —170° in EtOH, *varieties*. Treatment of these with P_2S_5 followed by CH_2Cl·COMe and $HClO_4$ leads to 3-α-*phenylethyl*-2 : 4-*dimethylthiazolium perchlorate*, r-*form*, m.p. 172° (+), m.p. 162°, $[\alpha]_D$ +62° in EtOH, (—), m.p. 162°, $[\alpha]_D$ —68°, *varieties*; the corresponding *chloride* is transformed by KI into 3-α-*phenylethyl*-2 : 4-*dimethylthiazolium tri-iodide*, m.p. 92°. The requisite thiazolium perchlorate and 2-iodoquinoline meth-

iodide in boiling PrOH containing NEt_3 give 1′-*methyl*-2′-*quinoline*-4-*methyl*-3-α-*phenylethylthiazole*-2-*methinecyanine perchlorate* (*A*), r-*form*, m.p. 172°, (+)-*variety*, m.p. 166°, $[\alpha]_D$ + 1500° in EtOH, whilst with *p*-toluquinoline ethiodide and NaOH in boiling EtOH 6′-*methyl*-1′-*ethyl*-4′-*quinoline*-4-*methyl*-3-α-*phenylethyl*-2-*thiazolemethinecyanine perchlorate*, (−) *form*, m.p. 200°, $[\alpha]_D$ −1800° in EtOH, is produced. The high $[\alpha]_D$ depends on the immediate neighbourhood of the asymmetric C to the main conjugation system. H. W.



(*A*.)

Preparation of tetramethylglucothiodiazolines. M. H. Wuyts and F. Vandervelden (Bull. Soc. chim. Belg., 1938, **47**, 506—517; cf. A., 1933, 810; 1934, 537).—Tetramethylglucose and thiobenzoylphenylhydrazide in 5% EtOH–HCl yield *tetramethylglucothiodiazoline*, separated by EtOH into *dextro*- (I), $[\alpha]^{20}_{5461}$ +1154° in EtOH, and *lævo*- (II), $[\alpha]^{20}_{5461}$ −905° in EtOH, -isomerides. In EtOH at 78°, (I) and (II) show rapid mutarotation to approx. the same α of +100° to 150°, which is followed by a slow rise in α to about 200°. The second slow change of α cannot be attributed to oxidation as is the case with the galactothiodiazolines (cf. A., 1936, 1275). J. D. R.

Cyanine dyes; reaction of cyclic ammonium salts and indene. T. Ogata and S. Maruyama (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1938, **34**, 1197—1200; cf. A., 1934, 422; B., 1934, 314, 842).—2-(?-Phenylacetamido)vinyl-thiazoline- and -benzoxazole ethiodides, indene, and NEt_3 at 80° for 1 hr. afford 1 : 1′-*diethyl*-7 : 7′-*o*-*phenyleneheptamethinethiazolino*-, m.p. 265° (decomp.), and 1 : 1′-*diethyl*-9 : 9′-*o*-*phenyleneheptamethinebenzoxazolo*-, m.p. 288° (decomp.), -*cyanine iodides*, respectively. Vals. for sensitising max. of the dyes are recorded. A. T. P.

Hydrogenation of vitamin-B_1 and other quaternary thiazoles. F. Lipmann and (Miss) G. Perlmann (J. Amer. Chem. Soc., 1938, **60**, 2574—2578).—Reduction of vitamin-B_1 (I), 4-methyl-5-β-hydroxyethylthiazole methiodide (II), nicotinamide ethiodide, 5-ethoxy-4-methylthiazole methiodide, Et 4-methylthiazole-5-carboxylate methiodide (III), m.p. 140°, and 4-*methylthiazole*-5-*carboxylamide methiodide*, cryst., by $Na_2S_2O_4$ in $NaHCO_3$ leads to absorption of 2 H and evolution of 3 CO_2, but 4-amino-2-methyl-5-sulphomethylpyrimidine (IV) and 4-methyl-5-β-hydroxyethylthiazole (V) are unaffected. Reduction probably occurs at the 2 : 3-position of the quaternary thiazole ring. Benzthiazole methiodide (VI) is reduced by $Na_2S_2O_4$–$NaHCO_3$ only if the methiodide has not been long in contact with the $NaHCO_3$, which causes gradual decomp. to the non-reducible *o*-SNa·C_6H_4·NMe·CHO. The reduction products could not be purified or reoxidised, and that of (I) could not be oxidised to thiochrome and was biologically inactive. Since the Zn–HCl reduction product of (VI) is oxidised by I to (VI), it is probable that the initial $Na_2S_2O_4$-products are similar, but are later irreversibly rearranged. The codehydrogenase action of (I) depends on a similar 2 : 3-reduction, and in this case the primary reduction product is "fixed" as a compound with the protein. A colour appears temporarily during reduction, indicating the two-stage nature of the process. In presence of Pt-black (I) absorbs 2 H, (II) absorbs 4 H (1 mol. rapidly), (III) absorbs 2·4 H, (IV) absorbs 3·76 H (1 mol. rapidly) at p_H 8 (very little at p_H 10·5), (V) absorbs only a trace of H_2, and 4-methylthiazole methiodide absorbs 3·6 H. 4-*Methylthiazole*-5-*carboxylamide*, cryst., is prepared from the ester by NH_3–MeOH at 150°. R. S. C.

Constitution of the antineuritic vitamin. K. Makino (J. Biochem. Japan, 1938, **28**, 293—295).—Polemical on priority in the assignment of the Me group to its correct position in the pyrimidine nucleus (cf. Hörlein, A., 1938, II, 340). F. O. H.

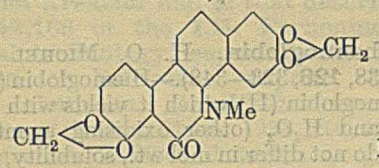
New general method for the conversion of amino-acids and polypeptides into alkaloids of the ephedrine and adrenaline types. P. P. T. Sah (Ber., 1938, **71**, [*B*], 2300—2301).—CH_2Ph·O·COCl and alanine (I) yield N-*carbobenzyloxy*-dl-*alanine*, transformed by PCl_5 into an acid chloride, which with MgPhBr in anhyd. Et_2O or with C_6H_6 and $AlCl_3$ affords *carbobenzyloxyaminopropiophenone*, CH_2Ph·O·CO·NH·CHMeBz. Catalytic reduction (Pd) of this affords PhMe, CO_2, and phenyl-α-aminoethylcarbinol, and a mixture of the optical isomerides of *dl*-norephedrine and *dl*-nor*iso*ephedrine. Cautious methylation transforms this into a mixture of *dl*-ephedrine and *dl*-ψ-ephedrine which is transformed into the hydrochlorides and extracted with $CHCl_3$, thereby giving homogeneous *dl*-ephedrine hydrochloride. The free base is resolved by the optically active mandelic acids. Further, by use of glycine in place of (I) and of veratrole and $AlCl_3$ or *p*-bromoveratrole and Mg it is possible to obtain arterenol Me_2 ether, whence adrenaline. Tyrosine, tryptophan, histidine, thyroxine, carnosine, or glutathione may be used for the prep. of the Bergmann acid chloride. H. W.

Proof of the synthesis and configurational relationships of abrine. W. M. Cahill and R. W. Jackson (J. Biol. Chem., 1938, **126**, 29—36; cf. A., 1935, 1015).—Racemised abrine [from abrine and $Ba(OH)_2$ in an autoclave] with NaOH and MeI–MeOH yields a *betaine Me ester iodide*, m.p. 194° (decomp.), and with keten in a solution kept alkaline to phenolphthalein yields an *Ac* derivative, m.p. 171°. These, and the picrate, are identical with the corresponding derivatives of synthetic α-methylamino-β-3-indolylpropionic acid. *Acetylabrine* has m.p. 175—176°, $[\alpha]^{25}_D$ −148·4° in 0·1N-NaOH. Betaines prepared from abrine and tryptophan have the same [α] as hypaphorine, showing that all three belong to the same configurational series. A. Li.

Reducing properties of a tautomeric form of geneserine; a chain reaction. M. Polonovski and P. Desgrez (Compt. rend., 1938, **207**, 685—687).—0·001N-Geneserine (I) in EtOH (1 c.c.) in vac. when insolated with a 300-watt lamp decolorises 0·6 c.c. of 0·001N-methylene-blue (II). In EtOH–AcOH at p_H 4·7, 0·48 c.c. of (II) is decolorised. The salts of (I) are less active than the base; the stronger is the acid the less is the activity. The nature of the solvent also changes the decolorising properties. The

N-oxido-grouping, which can exist in a tautomeric form, is the reactive one. Hydrasteine *N*-oxide and nornarceine *N*-oxide also give the reaction. (I) or dialkylhydroxylamines interfere with the determination of ascorbic acid with (II). (I) does not decolorise 2 : 6-dichlorophenol-indophenol in the light, but a trace of (II) will lead to decolorisation because the leuco-(II) serves to reduce the indophenol derivative. J. L. D.

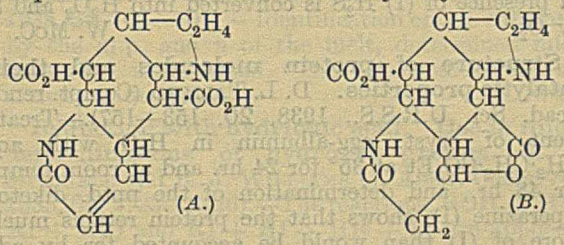
Alkaloids of *Sanguinaria canadensis*. F. SCHLEMMER and A. GEMPP (Arch. Pharm., 1938, **276**, 506—515).—Isolation of *oxysanguinarine*, $C_{20}H_{13}O_5N$, m.p. 360—361° (vac.) (photomicrograph), probably having the structure shown, is described.



R. S. C.

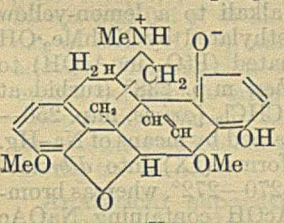
Action of strychnine on Bordeaux B. D. B. DOTT (Quart. J. Pharm., 1938, **11**, 363).—The *strychnine* salt of 1-naphthaleneazo-2-naphthol-3 : 6-disulphonic acid is described. P. G. M.

***Strychnos* alkaloids. CII. Isomeric substances $C_{13}H_{16}O_5N_2$ from brucinonic acid.** H. LEUCHS (Ber., 1938, **71**, [*B*], 2237—2238; cf. A., 1932, 953).—The NH_2-acid is *A*. It is reduced (PtO_2 in H_2O) to the *substance*, $C_{13}H_{18}O_5N_2$, $[\alpha]_D^{20}$ —115·3°/*d* in 0·1N-HCl. It is not possible to isolate the product of its oxidation but hydrolysis shows it



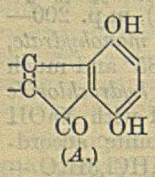
to be a derivative of $H_2C_2O_4$. The neutral reaction (CO_2H is neutralised by *b*-NH) and passive behaviour towards oxidation by MnO_4' or catalytic hydrogen indicate that the lactone is *B*. The product of its hydrolysis readily loses H_2O with production of an unsaturated, isomeric acid. H. W.

Thebaine-maleic anhydride, thebainequinone, thebainequinol, and the product, flavothebaone, of its isomerisation by acid. C. SCHÖPF, K. VON GOTTBERG, and W. PETRI (Annalen, 1938, **536**, 216—257).—Thebaine (I) and maleic anhydride in boiling abs. C_6H_6 yield thebaine-maleic anhydride (II), m.p. 270° (decomp.), which gives a colourless solution in conc. H_2SO_4. It is converted by KOH–MeOH into the K_2 salt (III) of the corresponding dicarboxylic acid (*K H* salt). Hydrogenation (Pd–$BaSO_4$ or Pd–$PdCl_2$) of (II) could not be accomplished; with PtO_2 in AcOH small amounts of substances sol. in alkali are obtained. Abs. EtOH and HCl slowly transform (II) at room temp. into *Et*$_2$ *thebainemaleate* (IV), m.p. 152°, also obtained from (III) and EtI in EtOH at 110° or by treatment of (II) with 20% HCl at 100° and subsequent esterification; the *hydrochloride* has m.p. 248°. (III) could not be hydrogenated (PtO_2 in EtOH) and (II) does not absorb H (Pd–$CaCO_3$ in H_2O). Attempted demethylation by conc. HBr leads to non-uniform products. Freshly sublimed *p*-benzoquinone and (I) in boiling C_6H_6 yield thebainequinone, m.p. 250° (*hydrochloride*, m.p. 280° after becoming colourless). It is converted by AcOH in boiling xylene or by KOH–EtOH into thebainequinol (V), m.p. 270° [*hydrochloride*, decomp. 280°; *p-toluenesulphonate* (VI), m.p. 283° (decomp.)], which shows an intense blue-violet fluorescence in ultra-violet light and gives an orange-red solution in conc. H_2SO_4. The presence of a double linking is established by its hydrogenation (PtO_2 in AcOH) to *dihydrothebainequinol*, m.p. 273°, which gives an almost colourless solution in conc. H_2SO_4 and is transformed by boiling HBr into the doubly demethylated *product*, $C_{23}H_{24}O_5NBr$, decomp. 295° (also *dihydrate*). (V) is converted by Ac_2O in C_5H_5N into a *monoacetate*, m.p. 259° (subsequent decomp.). With *p*-$C_6H_4Me{\cdot}SO_3Me$ at 120—130° (V) gives (VI) and *thebainequinol Me ether* (VII), m.p. 238° [*hydriodide*, m.p. 261° (decomp.); *Ac* derivative, m.p. 259°] [hence the betaine structure of (V)]. In boiling EtOH (VII) is transformed by NaOEt and $NPhMe_3Cl$ into *thebainequinol Me*$_2$ *ether* (+EtOH), m.p. 212°; (VI) could not be smoothly methylated by CH_2N_2 and is largely unchanged by *p*-$C_6H_4Me{\cdot}SO_3Me$ at 150°. (V) is readily converted by conc. HCl in AcOH at 100° into MeCl and *flavothebaone* (VIII), $C_{24}H_{23}O_5N$ (+1H_2O), m.p. 255—257°, or (+1MeOH), m.p. 200—206° (softens 195°), *normal hydrochloride monohydrate*, decomp. 330° after slight softening at 285° and much softening and darkening at 312°; the *H hydrochloride trihydrate*, decomp. 312°, can be titrated with NaOH without indicator, showing two end-points according to the scheme: $C_{24}H_{24}O_5NCl,HCl,3H_2O + NaOH \rightarrow C_{24}H_{24}O_5NCl + NaCl + 4H_2O$ and $C_{24}H_{24}O_5NCl + NaOH \rightarrow C_{24}H_{23}O_5N + NaCl + H_2O$. (VIII) is an unsaturated ketone since it yields an *oxime*, m.p. 222° (decomp.) after softening at 206° [*hydrochloride*, m.p. > 350° after darkening at 260°; (?) *Ac*$_3$ derivative, m.p. 231°], which is converted by $SOCl_2$ into a *base*, m.p. 275° (decomp.) after slow softening at 258° [*hydrochloride*, becomes brown at 280°, black at 315°; Ac_4 derivative (+1PhMe), m.p. 279° (decomp.)], and is reduced (H_2–Pd–$BaSO_4$ in H_2O or Na–Hg in EtOH) to *dihydroflavothebaone*, which is very readily autoxidised (*hydrochloride*, $C_{24}H_{26}O_5NCl,2H_2O$, m.p. 350° after softening at 340°, decomp. 365°, $[\alpha]_D^{14}$ +242° in abs. MeOH). The conjugation of the double linking with CO is established by the possibility of the use of Na–Hg and by production of the *compound*, $C_{24}H_{24}O_5N_2,NH_2OH,0{\cdot}5H_2O$, m.p. 282° (decomp.) (darkens at 265°), from (VIII) and NH_2OH in alkaline solution. The conversion of (VIII) by anhyd. NaOAc and boiling Ac_2O or by Ac_2O–C_5H_5N at room temp. into *triacetylflavothebaone*, m.p. 273° after softening at 270°, and by $NPhMe_3{\cdot}OH$ into *flavothebaone Me*$_3$



(V.)

ether (IX), m.p. 253°, which is insol. in alkali, shows the presence of 3 phenolic OH groups, two of which are due to the quinol residue whilst the third is due to fission of the O bridge by HCl. N remains *tert.* in (VIII) as in (V) since (IX) cannot be acetylated and is quantitatively converted by MeI into the *methiodide*, m.p. 251°, transformed by boiling H_2O into the de-*base* $C_{28}H_{31}O_5N$, m.p. 160—161°, more conveniently obtained from *flavothebaone* Me_3 *ether methosulphate*, m.p. 288° (decomp.) (softens 270°); de-N-*methylflavothebaone* Me_3 *ether methiodide* has m.p. 295° (decomp.) (sinters 280°). The Me_1 and Me_2 ethers of (V) are similarly converted by conc. acid into *flavothebaone* Me_1 *ether*, m.p. 276° (decomp.) (softens 270°) [*hydrochloride dihydrate*, m.p. 308° (decomp.)], and *flavothebaone* Me_2 *ether*, m.p. 257° (softens 254°); both of these dissolve in alkali to a lemon-yellow solution and are further methylated by $NPhMe_3 \cdot OH$ to (IX). (IX) is hydrogenated (PtO_2 in AcOH) to *dihydroflavothebaone* Me_3 *ether*, m.p. 238° (turbid at 219—220°), $[\alpha]_D^{16}$ +213° in $CHCl_3$ [*oxime*, m.p. 256—257° (softens 253°)], also obtained by means of Na–Hg. Br in AcOH at 80° transforms (IX) into *dibromoflavothebaone* Me_3 *ether*, m.p. 270—272°, whereas bromination in AcOH or dil. AcOH containing NaOAc gives amorphous products of higher m.p. Oxidation of (IX) with BzO_2H in $CHCl_3$ or 33% H_2O_2 at 100° yields *flavothebaone* Me_3 *ether* N-*oxide*, m.p. 200—202° (decomp.) [*hydrochloride*, m.p. 312° (decomp.) (darkens at 250°)]. (IX) gives an *oxime*, m.p. 258° [*hydrochloride* (+2·5H_2O), m.p. 271—272° (decomp.) (softens 265°), isomerised by $SOCl_2$ to the iso*oxime* (+0·5MeOH), m.p. 212—213° [*hydrobromide*, $C_{27}H_{31}O_5N_2Br$, m.p. 275—276° (decomp.)]; this appears unchanged by KOH–MeOH but is converted by MeOH–HCl followed by HI into the cryst. *hydriodide*, $C_{28}H_3O_5N_2I$, m.p. 275—276° (decomp.). With EtOH–HCl and then with HBr a *hydrobromide*, m.p. 252—254°, is produced. Oxidation of (VIII) or (IX) generally yields amorphous, non-characteristic products. It is suggested that the arrangement *A* is produced during the formation of (VII). H. W.


(*A*.)

Derivatives of dihydrothebainone.—See B., 1938, 1503.

Ergot alkaloids. XVI. Synthesis of substances related to lysergic acid. 6-Methylergoline and ergoline-7-carboxylic acid. W. A. Jacobs and R. G. Gould (J. Biol. Chem., 1938, **126**, 67—76; cf. A., 1937, II, 434).—3′-*Amino*-5 : 6-*benzoquinoline*-7-*carboxylic acid lactam methiodide* (from the lactam and MeI at 100° for 18 hr.), m.p. 291—292° (decomp.), is reduced (PtO_2) to 3′-*amino*-1-*methyl*-2 : 3 : 4-*trihydro*-5 : 6-*benzoquinoline*-7-*carboxylic acid lactam*, m.p. 220—221°, further reduced (Na–BuOH) to 6-*methylergoline*, m.p. 210—212° (*hydrochloride*). 3-Amino-1-naphthoic acid sulphate with paraldehyde and HCl yields 5 : 6-*benzoquinaldine*-7-*carboxylic acid*, m.p. 313—315° (decomp.) [*hydrochloride*, m.p. 314—316° (decomp.); *Me* ester, m.p. 114—116°; *Et* ester, m.p. 103—104°; *Et* ester *methiodide*, m.p. 201—203° (decomp.)], oxidised (SeO_2 in C_5H_5N) to 5 : 6-*benzoquinoline*-2 : 7-*dicarboxylic acid*, m.p. 258° (decomp.), which with HNO_3 (*d* 1·58) at 0° yields the 3′-NO_2-compound, reduced [$Fe(OH)_2$–aq. NH_3] to the 3′-NH_2-compound *lactam*, m.p. 270—271° (decomp.) [NH_4 salt, m.p. 273—276° (decomp.); *Me* ester, m.p. 305—307°; *Et* ester, m.p. 275—277°]. Partial hydrogenation (PtO_2) of this acid yields the 1 : 2 : 3 : 4-H_4-compound, m.p. 237—239° [*Me* ester (I), m.p. 234—236°; *Et* ester, m.p. 240—242°], whilst complete hydrogenation of its Et ester gives the 1 : 2 : 3 : 4 : 7 : 8 : 9 : 10-H_8-ester, m.p. 232—236°. Reduction (Na–BuOH) of (I), followed by careful decarboxylation, yields (?) *ergoline*-7-*carboxylic acid*. Ergoline purified by crystallisation of its hydrochloride has m.p. 201—203°. A. Li.

Sulph-hæmoglobin. H. O. Michel (J. Biol. Chem., 1938, **126**, 323—348).—Hæmoglobin (I) and the sulph-hæmoglobin (II) which it yields with sol. inorg. sulphide and H_2O_2 (other oxidising agents are ineffective) do not differ in mol wt., solubility, resistance to alkali, and cataphoretic mobility and the conversion is not accompanied by irreversible change in the hæm of the hæmoglobin. For the conversion 1 S is required for each Fe of (I). (II) contains 1 labile S not in form of free ·SH. The reduced from of (II) is very stable but the oxidised form is unstable. At p_H between 6 and 8 the amount of (II) produced decreases as p_H increases. (II) combines with CO, the compound probably containing 1 CO for each Fe in reduced (II). Myohæmoglobin yields a myosulph-hæmoglobin which combines with CO and is otherwise similar to (II). In presence of (I) H_2S is converted into H_2O_2 and S by O_2. W. McC.

Structure of protein molecules and their catalytic properties. D. L. Talmud (Compt. rend. Acad. Sci. U.R.S.S., 1938, **20**, 153—157).—Treatment of cryst. egg-albumin in H_2O with aq. $NH_2 \cdot CH_2 \cdot CO_2Et$ at 35° for 24 hr. and at room temp. for 48 hr., and determination of the pptd. diketopiperazine (I), shows that the protein retains much more of (I) than would be accounted for by adsorption. The results are quantitatively accounted for by the closed cyclol structure proposed by Wrinch, and indicate considerable "intraglobular" catalysis, the mechanism of which is discussed. A. Li.

Arrangement of peptide chains in the molecules of sphæroproteins. F. Haurowitz (Z. physiol. Chem., 1938, **256**, 28—32; cf. A., 1936, 1462; Wrinch, A., 1938, I, 311).—The yields of OMe-compound obtained by treating ovalbumin (I) and oxyhæmoglobin with Me_2SO_4 and that of acetate obtained by boiling (I) with Ac_2O are $\leqslant$ those required by the cyclol theory. W. McC.

Ultra-violet absorption spectrum of catalase. K. G. Stern and G. I. Lavin (Science, 1938, **88**, 263—264).—The ultra-violet absorption curve of horse-liver catalase shows a max. at ~2750 A., due to the protein carrier of the enzyme, and a max. at 4050 A., due primarily to the hæmin residue. In contrast with other hæmin-containing proteins such as hæmoglobin, and chlorocruorin, the extinction coeff. at 2750 A. is > that at 4050 A. Visual examination of the spectrum shows a structure typical of a

globulin, and bands due to tryptophan, tyrosine, and phenylalanine appear to be present. L. S. T.

Changes of nitrogen content brought about by denaturation of proteins.—See A., 1939, III, 96.

Use of Trautz's micro-Dumas method [for determining nitrogen] with the apparatus of Pregl.—See A., 1939, I, 38.

Fine adjustment device for use with micro-Dumas apparatus. S. RANGASWAMI (Proc. Indian Acad. Sci., 1938, **8**, A, 220—222).—A screw-regulated stopcock for controlling gas-flow is described. A. LI.

Possible analytical uses of the apparatus of Grote and Krekeler and of that described in the DRP 642,166 of the I.G. Farbenindustrie in chemical technology, especially for the determination of halogens, sulphur, and other volatile elements. B. WURZSCHMITT and W. ZIMMERMANN (Z. anal. Chem., 1938, **114**, 321—342).—The determination of S and halogens in org. substances is reviewed, and modifications of the Grote–Krekeler technique (B., 1934, 745) are described. A quick, explosive combustion, free from C-deposition, is obtained even with volatile org. compounds. The procedure is also applicable to the determination of Se and Hg, and of S in pyrites. L. S. T.

[Determination of selenium, mercury, halogen, and phosphorus.]—See A., 1939, I, 37.

Physical methods in the chemical laboratory. XXXVIII. Microscopic method of identifying organic substances. L. KOFLER (Angew. Chem., 1938, **51**, 703—707).—Identification of org. substances by the m.p. and n of the melt, determined microscopically, is described. The behaviour of 13 substances is described. R. S. C.

Reduction with hydriodic acid. Use in micro-determinations of hydroxyl groups. H. K. MITCHELL and R. J. WILLIAMS (J. Amer. Chem. Soc., 1938, **60**, 2723—2726).—The reactions, ROH + HI → RI + H_2O and RI + HI → HR + I_2, are applied at 100—134° on a micro-scale to determine alcohols. Only primary alcohols, polyalcohols, OH-acids, or negatively substituted compounds give useful results, reaction being incomplete or absent with other types. R. S. C.

Micro-chemical detection of *o*-diketo- and hydroxymethylene compounds. M. ISHIDATE (Mikrochim. Acta, 1938, **3**, 283—290).—A drop of the test solution is treated with a drop of NH_2OH solution (NH_2OH,HCl 1 g., NaOAc 1 g., H_2O 2 c.c.), a drop of the resulting solution being put on filter-paper with a drop of 5% aq. $Ni(OAc)_2$. A yellow or red colour is produced either immediately or after treatment with NH_3 vapour if an aliphatic ·CO·CO· group is present. AcOH solution is used to ensure formation of all three isomeric oximes. The method can also be applied to detection of a ·CO·CH_2· group if the CH_2 is first oxidised with SeO_2. An EtOH solution of the sample is treated with a few particles of SeO_2 for 20 min. at 170° in a closed capillary tube, and the product is tested with NH_2OH and $Ni^{··}$. In detection of aromatic *o*-diketones, which yield no dioximes, a drop of the test solution is treated with 2 drops of a solution of 2 : 5 : 1-NH_2·$C_6H_3(NMe_2)$·OH, when a blue colour is obtained immediately or on keeping. The reagent is freshly prepared by suspending 0·05 g. of 2 : 5 : 1-NO·$C_6H_3(NMe_2)$·OH in 5 c.c. of AcOH, shaking with Zn dust until decolorised, and then diluting to 10 c.c. with AcOH. J. W. S.

Micro-determination of formaldehyde. S. OHYAMA (Japan. J. Exp. Med., 1935, **13**, 327—330).—CH_2O forms a ppt. with trypaflavine in presence of HCl. The method is sp. and sensitive. CH. ABS. (*e*)

Micro-determination of lactic acid.—See A., 1939, III, 110.

Bromatometric determination of oxalate. L. SZEBELLÉDY and W. MADIS (Z. anal. Chem., 1938, **114**, 347—350).—The oxalate solution is diluted to 30 c.c. and 0·5 g. of $MnSO_4$,$5H_2O$, 0·5 g. of HgO, 20 c.c. of conc. H_2SO_4, and 5 c.c. of glacial H_3PO_4 are added. The solution is titrated with 0·1N-$KBrO_3$ until a permanent bright pink colour is obtained. A comparison solution can be used with advantage. An intense violet colour, due to a $Mn^{···}$ salt, is formed during the titration. L. S. T.

Analytical separation of various classes of sugars. C. D. HURD and S. M. CANTOR (J. Amer. Chem. Soc., 1938, **60**, 2677—2687).—Mixtures of (*a*) mono-, di-, and tri-saccharides or (*b*) hexoses and pentoses are analysed (±3%) by acetylation (Ac_2O–C_5H_5N) at 0°, followed by replacement of the acetal OAc by Cl using $TiCl_4$, replacement of Cl by OMe by MeOH–Ag_2CO_3, hydrolysis by NaOMe–MeOH, methylation by Me_2SO_4–NaOH, and fractional distillation. The procedures are not quant., but losses are about the same for each constituent (a correction is applied for mixtures of mono- and di-saccharides). Fructose is not amenable to this treatment. Other methods (*e.g.*, direct methylation) failed. The glucose mother-liquors from the hydrolysate of maize starch are shown to contain mono- 55·2, di- 38·4, and tri-saccharides 6·4%. R. S. C.

Determination of maltose.—See A., 1939, III, 110.

Determination of pentosans.—See A., 1939, III, 110.

Bromatometric determination of thiocarbamide. L. SZEBELLÉDY and W. MADIS (Z. anal. Chem., 1938, **114**, 253—256).—1 g. of KBr and 20 c.c. of conc. HCl are added to the neutral solution of $CS(NH_2)_2$ diluted to 35 c.c. After warming to 40—50°, 1 c.c. of 0·1% $AuCl_3$ is added, and the solution is titrated with 0·1N-$KBrO_3$ to the yellow colour obtained in a comparison solution of equal vol. containing 1 g. of KBr, 20 c.c. of conc. HCl, and 1 c.c. of 0·1% $AuCl_3$. The determination is also suitable for micro-titrations with 0·1N-$KBrO_3$ when the above vols. and wt. of KBr are reduced to one tenth. The reaction is $3CS(NH_2)_2+4HBrO_3+3H_2O=3CO(NH_2)_2 + 3H_2SO_4 + 4HBr$, and the KBr acts as a catalyst. L. S. T.

Ninhydrin reaction for determination of amino-acids. A. I. VIRTANEN and T. LAINE (Skand. Arch. Physiol., 1938, **80**, 392—397, and Nature, 1938, **142**, 754).—The reaction must be

carried out at p_H 2·0—2·2, since ninhydrin gives a distinct colour with $(NH_4)_2SO_4$ at p_H 2·5. The error is ±5% if the solution contains 2—12 mg. of NH_2-N per l. α-Alanine and leucine can thus be determined, giving MeCHO and $Bu^{\beta}CHO$ respectively. A. S.

Tyrosine determinations. C. Reiter (Science, 1938, **88**, 379).—Lugg's method (A., 1937, III, 447) is modified by making the 5 ml. of test solution N. with respect to H_2SO_4. The buffering action of the NH_2-acids present results in a p_H of ~ 1. The mean val. found for the tyrosine (I) content of ovalbumin by this method then becomes 3·81%. By diluting the test solution to 25 ml., it can be kept for ⩽ 24 hr. before the colorimetric comparison without a fall in the (I) val. L. S. T.

Determination of carnosine and anserine.—See A., 1939, III, 26.

Titration of coloured solutions of sulphonic acids. I. N. Kamenski-Schmidt (Zavod. Lab., 1938, **7**, 357—358).—Coloured solutions of sulphonation products cannot be titrated using the ordinary indicators. The solutions are decolorised by adding excess of $BaCl_2$, when the ppt. of $BaSO_4$ adsorbs coloured impurities, and the filtrate is titrated with 0·1N-NaOH (Me-orange), to give total acidity. A correction of 0·05 ml. should be added to the burette reading. R. T.

Determination of nitro-sulphonic acids, using zinc amalgam. M. M. Lobunetz (Bull. Sci. Univ. Kiev, 1937, **3**, No. 3, 71—78).—*m*-$NO_2 \cdot C_6H_4 \cdot SO_3H$ is determined by reduction with Zn–Hg in 4N-HCl or -H_2SO_4, followed by titration of the resulting NH_2-acid with standard $NaNO_2$ or $KBrO_3$–KBr. The reduction method is also applicable to 1 : 5-, 1 : 6-, 1 : 7-, and 1 : 8-$NO_2 \cdot C_{10}H_6 \cdot SO_3H$, but titration of the resulting NH_2-acids is rendered difficult by formation of intensely coloured solutions. R. T.

Microscopic identification of some important substituted naphthalenesulphonic acids. W. F. Whitmore and A. I. Gebhart (Ind. Eng. Chem. [Anal.], 1938, **10**, 654—661).—A method for the microscopic identification of several naphthylamine-, naphthol-, and aminonaphthol-sulphonic acids by means of their Bz derivatives is described. Characteristics and microscopic appearance of 15 acids and their derivatives are tabulated. F. N. W.

Determination of adrenalone in adrenalone hydrochloride. F. Reimers (Dansk. Tidsskr. Farm., 1938, **12**, 233—239).—Adrenalone hydrochloride (I) solutions may be titrated against 0·1N-NaOH (phenolphthalein) if the solution is conc. enough for the base to ppt. Vals. obtained are thus dependent on concn. (I) is best determined by pptg. the base from conc. aq. solution with $NaHCO_3$ at p_H 8; this is dissolved in 0·1N-HCl and back-titrated with 0·1N-NaOH to p_H 4·3 (bromophenol-blue). M. H. M. A.

Colorimetric determination of nicotinic acid and nicotinamide. H. Kringstad and T. Naess (Naturwiss., 1938, **26**, 709; cf. Strafford *et al.*, B., 1933, 764).—C_5H_5N, nicotinic acid, nicotinamide, and β-picoline are determined colorimetrically by means of CNBr and NH_2Ph in phosphate buffer at p_H 6·1. A. Li.

Determination of iodine in iodohydroxyquinolinesulphonic acid. J. J. L. Zwikker and A. Kruysse (Pharm. Weekblad, 1938, **75**, 1305—1310).—The official Dutch method gives variable results according to the amount of tartaric acid used for removing excess of $KMnO_4$. The following simplified method is satisfactory. 120 mg. of iodohydroxyquinolinesulphonic acid are boiled for 30 min. with 100 c.c. of H_2O, 10 g. of $Na_2B_4O_7$, and 1 g. of $KMnO_4$. The hot solution is treated with 2 c.c. of EtOH, boiled for 5 min., and filtered, the residue being washed with saturated aq. Na_2SO_4. The filtrate is treated with 10 c.c. of N-KI and 20 c.c. of 4N-H_2SO_4 and the liberated I titrated with 0·1N-$Na_2S_2O_3$. S. C.

Colour reactions of barbiturates. IV. Reaction of barbiturates with a polymethylene ring. M. Pesez (J. Pharm. Chim., 1938, [viii], **28**, 379—386).—*cyclo*Pentenylallylmalonylcarbamide (I) (1 mg.) with 5% vanillin–EtOH (5—6 drops) and H_2SO_4–H_2O (2 : 1; 2 c.c.) rapidly gives an intense emerald-green colour, changed at 100° into a blue-green and then an intense blue. The coloured material is pptd. by H_2O (Et_2O and $CHCl_3$ extracts are yellow). The reaction is sp.; vanillin gives better results than analogous aldehydes. *cyclo*Hexenylethylmalonylcarbamide (II) when similarly treated gives a yellowish colour changed after 4—5 min. at 100° to reddish-violet. On dilution an intense red-violet colour is obtained (the coloured product is pptd.) ($CHCl_3$ and Et_2O extracts are cherry-red and yellow, respectively). PhOH with (I) and H_2SO_4 gives a golden-yellow colour at room temp. and an intense orange at 100°. Aq. NH_3 decolorises the solution through violet and blue. (II) when similarly treated gives a colourless solution at room temp., changing at 100° to an intense raspberry-red; H_2O changes this to violet and NH_3 decolorises it. (I) with vanillin and conc. HCl at 100° gives a dark blue colour, changed to blue-green with H_2O. The reaction is characteristic of (I). Resorcinol, (I), and conc. HCl at 100° give an intense red, changed to orange with H_2O, which with NH_3 gives a reddish-violet solution with a green fluorescence. (I), resorcinol, and H_2SO_4 at 100° give an orange colour changed to red with H_2O. $CHCl_3$ extracts a reddish-violet colouring matter. J. L. D.

Determination of the tryptophan content of casein. M. X. Sullivan, H. S. Milone, and E. L. Everitt (J. Biol. Chem., 1938, **125**, 471—474).—To 99 c.c. of 17·5% HCl is added 1 c.c. of a 5% solution of *p*-$NMe_2 \cdot C_6H_4 \cdot CHO$ in 10% H_2SO_4. After the addition of casein (1 g.), the mixture is heated at 85° for 15 min. and 0·3 c.c. of 0·3% H_2O_2 added. The well-shaken mixture is cooled to 20—25°, the vol. adjusted to 100 c.c. with H_2O, and the blue colour compared with appropriate standards. Various casein samples by this method and by the longer procedure of May and Rose as modified by Holm and Greenbank (A., 1923, ii, 666) were found to have a tryptophan content of 2·4%. W. O. K.