BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

AUGUST, 1938.

Restricted internal rotation in hydrocarbons. K. S. PITZER and J. D. KEMP (J. Amer. Chem. Soc., 1938, **60**, 1515—1516).—The statement of Kistiakowsky and Wilson (cf. A., 1938, I, 178) that the authors' selection of potential barriers is arbitrary is refuted. The only assumption is that the restriction of rotation about a given C·C linking depends on the position and character of the attached groups. Uncertainties in the method depend on the accuracy of the experimental data. For C_3H_8 agreement is good. R. S. C.

Applications of infra-red absorption spectra [in organic chemistry]. J. LECOMTE and P. LAMBERT (Publ. sci. tech. Min. de l'Air, 1933, No. 34, 1—134; Chem. Zentr., 1936, ii, 454).—A comprehensive review of work on hydrocarbons. H. N. R.

Decomposition reactions of organic compounds in the gaseous state. C. N. HINSHELWOOD (Nature, 1938, **141**, 1010—1011).—Some of the conclusions of Travers *et al.* are criticised. L. S. T.

Induced liquid-phase decomposition of hydrocarbons. P. L. CRAMER (J. Amer. Chem. Soc., 1938, **60**, 1406—1410).—Et, prepared *in situ* by decomp. of $PbEt_4$ at 200—300°, has no effect on $C_{10}H_8$ or liquid C_6H_6. The amounts of H_2, C_2H_4, C_2H_6, C_4H_{10}, and olefines obtained similarly from *n*-C_7H_{16}, $Pr^{\beta}Bu^{\gamma}$, $Bu^{\beta}Bu^{\gamma}$, *n*-$C_{10}H_{22}$, *cyclo*hexane, Δ^{α}-hexene, $CH_2{:}CMePr^{\beta}$, Pr^{β}_2, $CH_2{:}CHBu^{\gamma}$, Δ^{α}-heptene, $CH_2{:}CMeBu^{\gamma}$, $(CH_2{:}CMe{\cdot}CH_2)_2$, *cyclo*hexene, tetra- and deca-hydronaphthalene are determined. CH_4 and products derived therefrom are not formed. Reaction is of two kinds: (*a*) $Et + RH \rightarrow R + C_2H_6$; (*b*) $Et + CHR{:}CH_2 \rightarrow CHEtR{\cdot}CH_2{\cdot}$. Unused Et reacts thus: $2Et \rightarrow H_2 + 2C_2H_4$; $2Et \rightarrow C_2H_4 + C_2H_6$; or $2Et \rightarrow C_4H_{10}$. Saturated compounds react only by (*a*). Both reactions occur with olefines, (*b*) being favoured by mobility of H and thus by presence of many $>CH_2$ and still more so by $\geqslant CH$; the nature and position of the ethylenic linking, as evidenced by its reactivity, have, however, also a great effect. The results are co-ordinated with the stability, ease of oxidation, and knocking characteristics of the hydrocarbons. R. S. C.

Probable structures of polymerides of lower olefines. A. WACHTER (Ind. Eng. Chem., 1938, **30**, 822—826).—Working rules are developed for predicting the polymerisation products of simple olefines based on the position of the double linking and the probability of rearrangements. Good agreement is found with experimental results given in the literature. E. G. H.

Addition of hydrochloric acid to unsaturated hydrocarbons at low temperature. J. J. LEENDERTSE (Rec. trav. chim., 1938, **57**, 795—797).—Olefines, $\cdot CH{:}C(C\leqslant)_2$, add HCl at −78° to give $\cdot CH_2{\cdot}CCl(C\leqslant)_2$, the Cl being readily lost at higher temp. Olefines, $\cdot CH{:}CH\cdot$, react with HCl at −78° only in presence of $AlCl_3$ and much polymerised chloride is formed. The polymeride is not formed by $AlCl_3$ or HCl alone. No experimental details are given. R. S. C.

Ethylenic isomerism. Δ^{γ}-Hexene. H. VAN RISSEGHEM (Bull. Soc. chim. Belg., 1938, **47**, 194—215, 221—240, 261—286).—Divinyl glycol, obtained by the action of Zn–Cu on acraldehyde, has b.p. 97·0—97·5°/13 mm., and appears to be a mixture of isomerides. It is hydrogenated (PtO_2 in Et_2O) to *hexane-γδ-diol*, form *A* (I), b.p. 102·6°/14·5 mm., m.p. 90·1—90·2°, and variety *B* (II), b.p. 108·65—108·75°/24 mm., m.p. 20·9°. By analogy with the m.p. of the erythritols (I) is regarded as the *meso*- and (II) as the *r*-form. This view is confirmed by the behaviour of *B. xylinum* or *Mycoderma aceti*, which convert (I) into a dextrorotatory ketol and (II) into a lævorotatory ketol with a residue of lævorotatory glycol. The polymorphism of (II) is established. By-products of the hydrogenation are hexan-γ-ol, b.p. 134—136°/750 mm., characterised by oxidation to $COEtPr^{\alpha}$ (semicarbazone, m.p. 111·8°), and *γ-hydroxy-δ-ketohexane*, b.p. 165—169°/750 mm. (*phenylosazone*, m.p. 159—159·5°; *semicarbazone*, m.p. 140·4—141·2°), oxidised by H_2O_2 in presence of $FeSO_4$ to $EtCO_2H$. Attempts to prepare the two diastereoisomeric hexane-γδ-diols from the corresponding divinyl glycols gave results less satisfactory than those just recorded. Hydrogenation (Pt-black in Et_2O) of $(\cdot COEt)_2$ slowly yields (I) without appreciable formation of (II) with unchanged initial material. The principal product of the action of depolymerised glyoxal on MgEtBr is (II) but (I) is formed in small amount.

The action of PBr_3 in $CHCl_3$ on (II) in the same solvent gives γδ-dibromohexane (III), b.p. 81·0—81·2°/15 mm., and γ-bromohexane, b.p. 49—49·2°/26 mm., converted by KOH–$CH_2Ph{\cdot}OH$ into a mixture of Δ^{β}- and Δ^{γ}-hexene, 67·75—68·25°/760 mm. The formation of HBr, H_3PO_3, PH_3, PH_4I, and P_4H_2 is observed. The changes involved are probably: $H_3PO_3 + 3PBr_3 = 3POBr_3 + PH_3$ and $2H_3PO_3 + 6PBr_3 = 6POBr_3 + P_2H_4 + H_2$. The action of PBr_3 on a mixture of (I) and (II) leads to a dibromohexane (IV), b.p. 79·2—83·2°/15·5 mm. Granulated Zn and (III) in boiling EtOH afford *Δ^{γ}-hexene*, b.p. 67·28—67·35°/760 mm., whereas the corresponding dibromide from (I) gives a hexene, b.p. 66·50—66·72°/760 mm.,

and (IV) gives mainly cis-Δ^{γ}-*hexene*, b.p. 66·58—66·93°/760 mm., possibly containing a little of the *trans* derivative. Addition of Br in $CHCl_3$ to the hexene from any source yields a $\gamma\delta$-dibromohexane b.p. 82·5°/16 mm., transformed by NaOPh in boiling EtOH into γ-bromo-Δ^{γ}-hexene, b.p. 34°/16 mm., which adds Br in $CHCl_3$ giving $\gamma\gamma\delta$-tribromohexane, b.p. 118·6—119·0°/18 mm. This is converted by NaOEt in EtOH into $\gamma\delta$-dibromo-Δ^{γ}-hexene, b.p. 72·2—74·2°/19 mm., which with Zn in boiling EtOH affords Δ^{γ}-*hexinene*, b.p. 81·65—81·98°/760 mm., which does not react with $AgNO_3$–EtOH or with CaCl–NH_3 but gives a white ppt. with HgCl in H_2O–EtOH; its Raman spectrum contains a line 2245 A. not observed previously in an analogous aliphatic hydrocarbon. Semi-hydrogenation (Raney Ni or Bourguel Pd) gives pure cis-Δ^{γ}-*hexene*, b.p. 66·85—67·15°/760 mm.

H. W.

Proof of the constitution of cetene. N. Schoorl (Rec. trav. chim., 1938, **57**, 719—726).—The difference in [*R*] due to the terminal ethylenic linking in the pairs, $(CH_2{:}CH{\cdot}CH_2)_2$–*n*-C_6H_{14}, Δ^{γ}-pentenoic–valeric acid, $CH_2{:}CH{\cdot}[CH_2]_8{\cdot}CO_2H$–undecoic acid (I), and Δ^{α}-octene–octane, is −0·50 to −0·57 (average −0·54). That for the non-terminal linking in the pairs, Δ^{β}-hexene–hexane, Δ^{β}-octene–octane, Δ^{β}- and Δ^{γ}-hexenoic–hexoic, elaidic–stearic acid, $CHMe{:}CH{\cdot}[CH_2]_7{\cdot}CO_2H$–(I), is −0·07 to −0·15 (average −0·10). The best val. for the difference for cetene and *n*-$C_{16}H_{34}$ is −0·52, conclusively proving that cetene is Δ^{α}-$C_{16}H_{32}$.

R. S. C.

Criterion for the mechanism of reaction between alkyl halides and hydroxylic solvents. Reactions of *tert.*-butyl chloride. L. C. Bateman, E. D. Hughes, and C. K. Ingold (J.C.S., 1938, 881—887; cf. A., 1935, 452).—A means is recorded of distinguishing between the two mechanisms of nucleophilic aliphatic substitution, one involving replacement in a single stage, the other, preliminary ionic fission. In bimol. substitution, the product is determined in a reaction the rate of which can be measured, whilst in unimol., it is formed, not in the rate-measured process, but in a subsequent fast reaction. Rate measurements of simultaneous hydrolysis and alcoholysis of $Bu^{\gamma}Cl$, and a determination of the amounts of $EtOBu^{\gamma}$ or $MeOBu^{\gamma}$, $Bu^{\gamma}OH$ (by difference), and *iso*butylene (by standard bromometric method), indicate that the reaction is unimol., confirming Hughes (*loc. cit.*). If the reaction were bimol. (cf. Olson and Halford, A., 1938, I, 86), the rate-derived consts. would allow calculation of the composition of the substitution product (alcohol + ether). There is no interconversion of products once formed. A summary is given of the four main methods (and their limitations) available for the diagnosis of reaction mechanism in those first-order substitutions in which the direct kinetic method is unavailable.

A. T. P.

Syntheses of polychloro-compounds by aluminium chloride. V. Condensation of hexachloropropylene with trichloroethylene. H. J. Prins (Rec. trav. chim., 1938, **57**, 659—666; cf. A., 1937, II, 438).—$CCl_3{\cdot}CCl{:}CCl_2$ (I), C_2HCl_3, and $AlCl_3$ in CH_2Cl_2 or $CHCl_3$ at 35—37° give $\alpha\alpha\beta\gamma\gamma\delta\varepsilon\varepsilon\varepsilon$-*nonachloro*-$\Delta^{\alpha}$-*pentene* (II), b.p. 128°/2—3 mm., and two $\alpha\alpha\beta\gamma\delta\varepsilon\varepsilon\varepsilon$-*octachloro*-$\gamma$-$\alpha'\beta'\beta'$-*tetrachloroethyl*-$\Delta^{\alpha}$-*pentenes*, m.p. 58—62° and 94—96°, respectively, the formation of the C_7 compounds being favoured by use of an excess of C_2HCl_3. The same products are isolated as by-products of the interaction of CCl_4 with C_2HCl_3, owing their formation to decomp. of the primary product, *s*-C_3HCl_7, to (I). At higher reaction temp. (II) loses HCl to give the known octachloropentadienes, which are at once isomerised by the $AlCl_3$ to the known octachloro*cyclo*pentene; these products are obtained from pure (II) by the successive action of KOH–EtOH and $AlCl_3$, and incidentally establish the structure of (II). ≮95—96% H_2SO_4 at 75—80° converts (II) into a difficultly separable mixture of *hexachloropentenoic acids*, *e.g.*, the $\alpha\beta\gamma\delta\delta\delta$-hexachloro-$\Delta^{\alpha}$-acid (*acids*, m.p. 132—134° and 75—81°, were isolated), which with KOH–EtOH give difficultly separable *pentachloropentadienoic acids* (*acids*, m.p. 61—66° and 120·5—122·5°, were isolated), converted by Cl_2 in light into (?) *heptachloropentenoic acid*.

R. S. C.

Synthesis and pharmacological action of some βββ-trialkylethanols. R. V. Rice, G. L. Jenkins, and W. C. Harden (J. Amer. Pharm. Assoc., 1938, **27**, 303—305).—The prep. (Grignard) of the (β) Me_3 b.p. 111—113°, m.p. 49°, Me_2Et, b.p. 134—135°, $MeEt_2$, b.p. 150—151°, and Et_3 derivative, b.p. 76—77°/11 mm., of EtOH is described. All possess anæsthetic properties but to a smaller extent than does $CBr_3{\cdot}CH_2{\cdot}OH$.

F. O. H.

Constants of ethylene glycol and propylene glycol. A. G. Pukirev (Sborn. Rabot Lab. Inst., 1937, **15**, 45—50).—$(CH_2{\cdot}OH)_2$ was synthesised from $(CH_2Br)_2$ and KOH and propylene glycol by the method of Wurtz (Ann. Chim. Phys., 1859, **55**, 438). The b.p., *n*, and *d* are recorded.

D. G.

Preparation of a *d*-mannitol dibromohydrin tetra-acetate. H. Vogel (Ber., 1938, **71**, [*B*], 1272).—Prolonged treatment of mannitol hexa-acetate with saturated HBr–AcOH at room temp. give a d-*mannitol dibromohydrin tetra-acetate*, m.p. 201° (corr.), $[\alpha]_D^{20}$ +10·26° in $CHCl_3$.

H. W.

Behaviour of glycerol mono- and di-triphenylmethyl ethers towards Criegee's reagent. P. E. Verkade (Rec. trav. Chim., 1938, **57**, 824—828).—The structures assigned to glycerol α- and β-CPh_3 ether are confirmed by the much faster reaction of the α- than of the β-ether with $Pb(OAc)_4$ in C_6H_6; in AcOH the difference is much less, probably owing to hydrolysis. In no case does reaction cease with use of 1 mol. of reagent. The difference in rate of reaction of the $\alpha\alpha'$- and $\alpha\beta$-$(CPh_3)_2$ ethers in AcOH–C_6H_6 is too small to be significant.

R. S. C.

Interaction of *l*-β-octyl nitrite and *dl*-β-butanol. J. Kenyon and D. P. Young (J.C.S., 1938, 965—966).—*l*-β-Octyl nitrite (1 mol.), b.p. 63—65°/15 mm., α_{5461} −5·28°, and *dl*-β-butanol (I) (2 mols.) afford *dl*-β-Bu nitrite, some *l*-β-octanol, and unchanged (I). The mechanism of interaction of a nitrous ester and an alcohol ("The Organic Chemistry of Nitrogen," Sidgwick, 1937) is not proved.

A. T. P.

Mercaptols. A. Sporzyński (Arch. Chemji Farm., 1936, **3**, 59—66; Chem. Zentr., 1936, ii, 1704).—

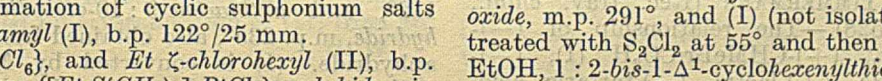
EtSH and HCl in $COMe_2$ afford Et mercaptol, b.p. 69—70°/11 mm.; decomp. of this at 125° and distillation at 140—200° yields EtSH and Et *iso*propenyl sulphide. Bu$^{\alpha}$ mercaptol, b.p. 112—112·5°/5·5 mm., (I) obtained similarly, yields BuSH and Bu *iso*propenyl sulphide (II) [in presence of $ZnCl_2$ (II) is further decomposed into BuSH and an unsaturated hydrocarbon] and oxidation with $KMnO_4$ yields dimethyldibutyl sulphone, m.p. 67·8—68°. An additive *compound* of (I) with $HgCl_2$, m.p. 172° (decomp.), is described. A. H. C.

Interaction of chlorine with different types of organic sulphur compounds. I. B. Douglass and T. B. Johnson (J. Amer. Chem. Soc., 1938, **60**, 1486—1489).—Passing Cl_2 into a suspension of EtSH or n-C_5H_{11}·SH in H_2O at 10° gives >70% of ethyl- and n-*amyl-sulphonyl chloride*, b.p. 77—78°/3 mm., respectively. PhSH gives successively Ph_2S_2, PhSCl (fairly stable to H_2O at 10°), and $PhSO_2Cl$ (55%). CH_2Ph·SH, CH_2Ph·SAc, or CH_2Ph·NaS_2O_3 gives $(CH_2Ph·S)_2$, $CH_2Ph·SO_2Cl$ (I), and $CH_2Ph·SO_2·S·CH_2Ph$, m.p. 108° [gives (I) when chlorinated, and is thus an intermediate product]. Bu$^{\alpha}{}_2S_2$ gives Bu$^{\alpha}SO_2Cl$, contaminated with some material substituted in the Bu; Bu$^{\alpha}$SCl is probably an intermediate. n-C_5H_{11}·SCl in CCl_4 is converted by Cl_2 mainly into a product containing 3 Cl. EtSAc gives 71% of $EtSO_2Cl$. $CH_2Ph·SBz$ gives BzCl, $CH_2Ph·SO_2Cl$, and a little BzOH. $NaMeS_2O_3$ and $NaEtS_2O_3$, prepared from R_2SO_4 and $Na_2S_2O_3$ in H_2O or aq. $COMe_2$ or from RI and $Na_2S_2O_3$ in aq. $COMe_2$, with H_2O–Cl_2 give about 55% of $MeSO_2Cl$ and $EtSO_2Cl$, respectively. *cyclo*Hexyl thiosulphate could not be prepared. $CH_2Cl·CO_2Et$ reacts with $Na_2S_2O_3$, but the product gives no sulphonyl chloride when chlorinated. OEt·CS_2Et gives $EtSO_2Cl$ and $ClCO_2Et$. S-*Benzyl ethylxanthate*, b.p. 143°/3 mm., gives $ClCO_2Et$, $CH_2Ph·SO_2Cl$, and (?) CH_2PhCl. OEt·CS_2K gives $ClCO_2Et$ (33%). NHBz·CS_2Et gives NBz:CCl_2 and $EtSO_2Cl$, identified by conversion by *p*-$C_6H_4Me·NH_2$ into *ethylsulphonyl*-p-*toluidide*, m.p. 81°, and *benzoyldi*-p-*tolylguanidine monohydrochloride*, m.p. 193—194°, respectively. R. S. C.

Rates of formation of six- and seven-membered ring compounds from ω-chloro-sulphides. G. M. Bennett and (Miss) E. G. Turner (J.C.S., 1938, 813—815).—Formation of cyclic sulphonium salts from *Et* ε-*chloroamyl* (I), b.p. 122°/25 mm. $\{[Et·S(CH_2)_5]_2PtCl_6\}$, and *Et* ζ-*chlorohexyl* (II), b.p. 128—131°/26 mm. $\{[Et·S(CH_2)_6]_2PtCl_6\}$, *sulphides*, in aq. $COMe_2$, is smooth and of the first order, and the 6-membered ring is formed 75 times as fast as the 7-membered (cf. ratio for 5- and 6-rings, A., 1930, 61). The reactions appear to proceed to completion, but the possibility that they are incomplete and reversible is not ignored. OH·$[CH_2]_6$·OH and HCl in petroleum (cf. A., 1931, 1032) give the *chlorohydrin*, b.p. 116—117°/19 mm., which with KSEt–EtOH gives OH·$[CH_2]_6$·SEt, b.p. 134—136°/17 mm., converted by SO_2Cl–CCl_4–$NPhEt_2$ into (II). ε-Chloroamyl acetate and aq. KSEt–EtOH afford OH·$[CH_2]_5$·SEt, b.p. 135°/20 mm., converted into (I). Cyclisation of Cl·$[CH_2]_6$·SPh is not effected in boiling 70% aq. $COMe_2$, 10% aq. AcOH, or $(CH_2·OH)_2$. A. T. P.

Lignin. X. Reaction of sulphuric acid with unsaturated compounds. H. Friese (Ber., 1938, **71**, [*B*], 1303—1306).—Conc. H_2SO_4 is added gradually to a solution of allyl alcohol in Ac_2O–AcOH at 0° and the mixture is heated at 60—70°, whereby αβ-dihydroxypropane-γ-sulphonic acid, isolated as the *Ba* salt, is obtained; it is remarkably stable towards dil. H_2SO_4 and $Ba(OH)_2$. Similarly CHMe:CMe_2 affords (?) β-hydroxy-β-methylbutane-γ-sulphonic acid (*Ba* salt) in excellent yield. Glucal triacetate yields a tetrahydroxysulphonic acid [*salt* $(C_6H_{11}O_8S)_2Ba$], which exists as a syrup freely sol. in H_2O but very readily resinified and then insol. This property and its powerful reducing action towards Fehling's solution indicate that SO_3H has become added at $C_{(2)}$ and the original arrangement of the glucose configuration has been restored at $C_{(2)}$. The results considered from the viewpoint of lignin do not indicate an aromatic nature of the latter. H. W.

Reaction between sulphur dioxide and olefines. VII. Co-polymerides from mixtures of olefines, acetylenes, and olefine derivatives with sulphur dioxide. C. S. Marvel, S. J. Davis, and F. J. Glavis (J. Amer. Chem. Soc., 1938, **60**, 1450—1455; cf. A., 1937, II, 315).—SO_2 and mixed olefines, *e.g.*, CH_2:CMe_2 and *cyclo*hexene (I), CH_2:$CHPr^{\alpha}$ (II) and CH_2:CH·$[CH_2]_8$·CO_2Me (III), CH_2:CH·$[CH_2]_8$·CH$_2$·OH, or CPh:CH, are polymerised by ascaridole and EtOH at room temp. The analyses, solubilities, and m.p. indicate that the *products* are not mixtures, but contain each olefine, even if one of them was used in preponderatingly large amount. That from 1 : 1 mol. mixtures of (II) and (III) is mainly $[·CH(·[CH_2]_8·CO_2Me)·SO_2·CH_2·CHPr^{\alpha}·SO_2·]_x$, since liquid NH_3 gives >75% of 2-n-*propyl*-6-θ-*carboxy*-n-*octyl*-1 : 4-*dithian* 1 : 4-*bisdioxide* (IV), m.p. 198°, as sole product. 5 : 1 mol. mixtures of (II) and (III) give a mixed product of the type $[·CHR·CH_2·SO_2·CH_2·CHR'·SO_2·]_x$, since liquid NH_3 gives both (IV) and 2 : 6-di-*n*-propyl-1 : 4-dithian 1 : 4-bisdioxide. *cyclo*Hexenepolysulphone and liquid NH_3 give anomalously the *product* (V), m.p. 145—145·5°, converted by hot AcOH into the expected



(V.)

2 : 3 : 5 : 6-*bistetramethylene*-1 : 4-*dithian* 1 : 4-*bisdioxide*, m.p. 291°, and (I) (not isolated). When (I) is treated with S_2Cl_2 at 55° and then with Na_2S in dry EtOH, 1 : 2-*bis*-1-Δ^1-cyclo*hexenylthiol*cyclo*hexane*, b.p. 175—180°/16 mm., is anomalously obtained; with H_2O_2 this yields (V). The structure of the mixed product from (I) and CH_2:CMe_2 was not determined; the product is reconverted into (I) and CH_2:CMe_2 by alkali, and with liquid NH_3 gives a substance containing 2 SO_2 and 3 (I) units. R. S. C.

Action of sulphuric acid on aliphatic carboxylic acids of high mol. wt. and their glycerides. J. Hetzer (Seifens.-Ztg., 1936, **63**, 242—243; Chem. Zentr., 1936, ii, 557).—A review. H. N. R.

Preparation of volatile acid chlorides. H. C. Brown (J. Amer. Chem. Soc., 1938, **60**, 1325—1328).—Twelve aliphatic acid chlorides are best prepared, usually in >75% yield, by distilling a mixture of the

acid and 1·5—2 mols. of BzCl. The reaction mechanism is discussed. R. S. C.

Allylic transposition. IX. A. KIRRMANN (Bull. Soc. chim., 1938, [v], **5**, 915—919; cf. A., 1937, II, 175; 1938, II, 215).—The structures CH_2:CH·CHCl·OAc (I) and CH_2Cl·CH:CH·OAc (II) ascribed to compounds described previously are supported by their Raman spectra, which are analogous to those of CH_2:CH·CH$(OAc)_2$ and CH_2:CH·$CHCl_2$ and to that of CHMe:CH·OAc, respectively. The frequency at 1417 cm.$^{-1}$, characteristic of the vinyl group, is shown by (I) but not by (II). The CO frequency is higher in these compounds than in EtOAc. The Raman spectrum of CHMe:CH·CH$(OAc)_2$ (III) contains the vinyl and C:C frequencies at 1430 and 1679 cm.$^{-1}$, respectively. The product (b.p. 64°/13 mm.) obtained by the action of HCl on (III) is CHMeCl·CH:CH·OAc, by analogy with (II), since the mol. refraction is abnormally high, and the C–Cl frequency is at 635 cm.$^{-1}$ The structure is confirmed by the action of Br followed by oxidation. The allylic rearrangement of CHMe:CH·CHCl·OAc to yield (III) is much more rapid than that of (I) to form (II). J. W. S.

Electrolysis of mixtures of *iso*butyrates with nitrates. F. FICHTER and P. SUTTER (Helv. Chim. Acta, 1938, **21**, 891—900; cf. A., 1937, II, 45; 1938, II, 40).—Electrolysis of solutions 4N in $Pr^{\beta}CO_2Na$ and 2N in $NaNO_3$, and containing 10% of Na_2CO_3, at Pt electrodes, yields $Pr^{\beta}OH$, $COMe_2$, $Pr^{\beta}O{\cdot}NO$, $Pr^{\beta}NO_3$, $Pr^{\beta}CO_2Pr^{\beta}$, $\alpha\beta$-$C_3H_6(NO_3)_2$, CHMePr^{β}·CH_2·OH, CHMeBu^{β}·OH, $COMeBu^{\beta}$, and $\beta\gamma$-$C_6H_{12}(OH)_2$. The theory of the reactions involved is discussed. J. W. S.

Transformations of esters of unsaturated fatty acids with hydrogenation catalysts in the absence of hydrogen. H. I. WATERMAN and C. VAN VLODROP (Rec. trav. chim., 1938, **57**, 629—636).—Et oleate is shown by change in the van der Steur I equilibrium const. (Diss., Delft, 1928) to be converted into Et elaidate by heating with 10% of Ni–kieselguhr in N_2 at 290°. This change also occurs, but much more slowly, when the oil is heated alone or with 10% of kieselguhr. R. S. C.

Configuration of optical antipodes of various substances. J. TIMMERMANS (Rec. trav. chim., 1938, **57**, 525—528).—The relationship of (−)-OH·CHMe·CO·NH_2, (+)-CHMeBr·CO_2H (I), (−)-malic, (+)-aspartic, (+)-lactic, (−)-tartaric acid, (−)-(CHCl·$CO_2H)_2$, and (+)-asparagine, deduced by the author's method, agrees with that of Kuhn and Freudenberg, except for (I). R. S. C.

Optical rotation of *d*-lactic acid and its derivatives. I. Anhydride formation of muscle-lactic acid at ordinary temperatures. II. Benzoylation of *d*-lactic acid. S. FUKUDA (J. Biochem. Japan, 1938, **27**, 241—246, 247—249).—I. Tabulated data are given for [α] of H_2O–*d*-lactic acid (I)–lactic anhydride (II) mixtures of [α] +2·40° [H_2O 10·65, (I) 89·35, (II) 0%] to [α] −64·21° [H_2O approx. 2·35, (I) 2·76, (II) 99·59%]. (I) is considered to be partly in the hydrated form in the more dil. solutions. II. (I) with BzCl at 110° yields *α-benzoyloxypropionic acid* (III), m.p. 84°, $[\alpha]_D^{20}$ +15·91° in EtOH, +44·31° in C_6H_6. Vals. for [α] of the oily mixture of (III) and its anhydride are compared with those of Strecker (1854) and Wislicenus (1865). F. O. H.

α-Hydroxyacetoacetic acid. I. Preparation, properties and estimation. H. WEIL-MALHERBE (Biochem. J., 1938, **32**, 1033—1044).—Solutions of α-hydroxyacetoacetic acid (I) (containing AcOH) are obtained by hydrolysis of Et α-acetoxyacetoacetate in presence of NaOH under anaërobic conditions at 25°. (I) loses CO_2 relatively slowly at p_H 7·4, but much more rapidly at low p_H vals. and especially in presence of NH_2Ph; this reaction carried out at p_H 4·6 may be conveniently applied for manometric determination. The acid is oxidised by mol. O_2 in 0·1M-$NaHCO_3$, 1 mol. of O_2 being absorbed and 1 mol. each of CO_2, AcOH, and $EtHC_2O_4$ formed, and also in 0·1N-NaOH with the formation of 1 mol. each of CO_2, HCO_2H, and AcOH, the last apparently in a polymerised form. W. O. K.

Action of hydrobromic acid on βζ-epoxyheptane-γ-carboxylic [2 : 6-dimethyltetrahydropyran-3-carboxylic] acid. Δ$^{\zeta}$-Hepten-β-ol. M. DELÉPINE (Rec. trav. chim., 1938, **57**, 520—524).—2 : 6-Dimethyltetrahydropyran-3-carboxylic acid, m.p. 91°, and 40% HBr–AcOH at 100° give impure βζ-dibromoheptane-γ-carboxylic acid, an oil, which with Na_2CO_3 gives *ζ-bromo-Δ$^{\beta}$-heptene* (I), b.p. 114—116°/164 mm (by way of O<CMe/CO>CH·$[CH_2]_2$·CHMeBr), and the *lactone*, b.p. 141—143°/23 mm., of *ζ-hydroxy-Δ$^{\beta}$-heptene-γ-carboxylic acid* (by way of CHMe<$[CH_2]_2$/O·CO>CH·CHMeBr). With AgOAc–AcOH (I) gives *ζ-acetoxy-Δ$^{\beta}$-heptene*, b.p. 127—129/170 mm., hydrolysed by KOH–EtOH to *Δ$^{\beta}$-hepten-ζ-ol*, b.p. 160—161° (*diphenylurethane*, m.p. 96°). R. S. C.

Diene syntheses. XXX. Acetylenedicarboxyl chloride. O. DIELS and W. E. THIELE (Ber., 1938, **71**, [*B*], 1173—1178).—(:C·$CO_2H)_2$ is converted by PCl_5 in AcCl into *chlorofumaryl chloride*, b.p. 66—68°/13 mm. Treatment of anthracene-9 : 10-*endo*-acetylenedicarboxylic anhydride with PCl_5 at 115° in a sealed tube gives unchanged anhydride, *anthracene*-9 : 10-endo*acetylenedicarboxyl chloride* (I), m.p 112°, and *anthracene*-9 : 10-endo*dichloromaleic anhydride*, m.p. 235°, also obtained from dichloromaleic anhydride. (I) is converted by MeOH into Me_2 anthracene-9 : 10-*endo*acetylenedicarboxylate, m.p. 161°, and by NH_3–H_2O in Et_2O into *anthracene*-9 : 10-endo*acetylenedicarboxylamide*, m.p. 285°, whence (P_2O_5 in boiling MeCN) the corresponding *dinitrile*, m.p. 263°. The temp. of decomp. of (I) is so high that the reaction products are anthracene, CO, CO_2, and $COCl_2$; at lower temp. (I) distils almost entirely unchanged. When heated at 185—195° with maleic anhydride (I) yields *acetylenedicarboxyl chloride* (II), m.p. 115°, and Me_2 fumarate whilst (II) and (?) *chloropropiolyl chloride*, b.p. 77·5°/9 mm., are isolated from the product obtained at 205—210°. (II) is very sensitive to moisture. It is characterised by conversion into the corresponding Me_2 ester and thence into Me_2 pyrazole-4 : 5-dicarboxylate, m.p. 141°. H. W.

Oxidation of sorbic acid and, particularly, of its methyl ester with molecular and peroxidic oxygen. P. HEINÄNEN (Ann. Acad. Sci. Fennicæ, 1938, [*A*], **49**, 7—112; cf. A., 1935, 731).—Autoxidation of Me sorbate (I) yields Me H fumarate (II), Me fumaraldehydate, AcOH, MeCHO, and a polymerised peroxide, $(C_7H_{10}O_4)_4$. Autoxidation of (I) is examined under varying conditions of concn., solvent, acidity, light (Hg quartz lamp), and in presence of catalysts, *e.g.*, Os, $PdCl_2$, $FeCl_3$. (I) and H_2O_2–MeOH give a peroxide, $(C_7H_{10}O_4)_5$. (I) and BzO_2H in $CHCl_3$ give *Me γδ-oxido-*Δ^{α}*-hexenoate* (III), b.p. 89°/10 mm. [*hexenoic acid*, m.p. 84—86° (*Ag* salt)], which with $KMnO_4$–NaOH affords αβ-oxidobutyric acid and with H_2O_2 gives (II). (III) and NaOH form *γδ-dihydroxy-*Δ^{α}*-hexenoic acid*, m.p. 68—77° (*Ag* salt). Ozonisation of (I) in $CHCl_3$ forms a mixture of mono- and di-ozonides.

A. T. P.

Isomeric *r*-β-methylmalic [α-hydroxy-β-methylsuccinic] acids. E. B. ABBOT and A. MCKENZIE (Ber., 1938, **71**, [*B*], 1214—1217).—$COEt{\cdot}CO{\cdot}CHMe{\cdot}CO_2Et$ is reduced by Al–Hg in Et_2O better than by Na–Hg to Et_2 α-hydroxy-β-methylsuccinate (I), b.p. 116°/11·5 mm., hydrolysis of which gives α-hydroxy-β-methylsuccinic acid *A*, m.p. 122—123°, also obtained in modest yield by condensation of $CHMe(CO_2Et)_2$ with $CCl_3{\cdot}CHO$ in presence of C_5H_5N; it is partly resolved into its optical antipodes by quinine in H_2O. With well-cooled NH_3–MeOH (I) yields a mixture of r-α-*hydroxy-β-methylsuccindiamide A* (II), m.p. 159—160° (decomp.), and *B* (III), m.p. 203° (decomp.). Alkaline hydrolysis of (II) appears to give a mixture of acids whereas that of (III) leads to r-α-*hydroxy-β-methylsuccinic acid B*, m.p. 124—125°; this can be partly resolved by brucine. H. W.

Optical activation of racemic acid by (+)-citramalic acid. E. B. ABBOT, E. A. KIDNEY, and A. MCKENZIE (Ber., 1938, **71**, [*B*], 1210—1213).—(+)-Citramalic [α-hydroxy-α-methylsuccinic] acid (I), m.p. 108—109°, $[\alpha]_D^{14}$ +23·2°, $[\alpha]_{5461}^{14}$ +27·7° in H_2O, is obtained by resolution of the *r*-acid by brucine in H_2O. Addition of 1 mol. of (I) to an aq. solution of *r*-tartaric acid neutralised with KOH causes the separation of a feebly dextrorotatory mixture of K H *r*-tartrate (II) and K H (+)-tartrate. A similar mixture is obtained by crystallisation of (II) from an aq. solution of (I). H. W.

Oxidation of *l*-ascorbic acid in presence of ammonia or primary amines. J. PARROD (Bull. Soc. chim., 1938, [v], **5**, 938—941).—*l*-Ascorbic acid and aq. NH_3, NH_2Me, or N_2H_4 afford $(CO{\cdot}NH_2)_2$, $(CO{\cdot}NHMe)_2$, and $(CO{\cdot}NH{\cdot}NH_2)_2$, respectively. NH_2Et, NH_2Bu^{α}, NH_2Bu^{a}, $NH_2{\cdot}[CH_2]_2{\cdot}CHMe_2$, and $NH_2{\cdot}C_6H_{11}$ similarly give the corresponding di-substituted *NN*-oxamides (cf. A., 1936, 968).

A. T. P.

Biochemistry of carbohydrates. XXX. Iodometric determination of glycuronic acid. Y. TANABE (J. Biochem. Japan, 1938, **27**, 251—256).—The sample [equiv. to 2—8 mg. of glycuronic acid (I)] is hydrolysed with conc. HCl and the hydrolysate is neutralised and steam-distilled, the solution being maintained just saturated with NaCl. The distillate is treated with 0·01N-$NaHSO_3$ followed by 0·01N-I, excess of which is titrated with 0·01N-$Na_2S_2O_3$ [1 c.c. ≡ 0·48 mg. of furfuraldehyde (II) or 3·36 mg. of (I)]. Chondrosin ester gives < theoretical yields of (II). F. O. H.

Glycuronic acid as intermediate in biochemical formation of citric acid from sugar.—See A., 1938, III, 696.

Essential oil of *Achasma Wolang*, Val. P. VAN ROMBURGH (Rec. trav. chim., 1938, **57**, 494—499).—The oil from the leaves (0·25%), stems (0·21%), and roots (0·15%) of this plant contains *n*-Δ^{α}-decenaldehyde (I), b.p. 229—231°/760 mm., 104°/13 mm. [*semicarbazone*, m.p. 162°; no colour with $C(NO_2)_4$], with smaller amounts of n-Δ^{α}-*octenaldehyde*, b.p. 83°/14 mm. [*semicarbazone*, m.p. 163°; oxidised by O_2 to n-Δ^{α}-*octenoic acid*, b.p. 245° (*Ag* salt), and by $KMnO_4$ to *n*-hexoic acid], a terpene, b.p. 165°, [α] −22°, and Δ^{α}-dodecenaldehyde (oxidised by O_2 to Δ^{α}-dodecenoic acid and by $KMnO_4$ to αβ-dihydroxylauric acid). With O_2 (I) gives *n*-Δ^{α}-decenoic acid (II), b.p. 165°/15 mm., m.p. 8° (*Ag* salt; *chloride*, b.p. 120—122°/14 mm.; *amide*, m.p. 121°), with $KMnO_4$ gives n-$C_7H_{15}{\cdot}CO_2H$, with H_2–Pt-black gives *n*-decanol, and with H_2–PtO_2 gives n-$C_9H_{19}{\cdot}CHO$ or, by oxidation, *n*-decoic acid. The root oil contained 30% of (II), probably formed during storage.

R. S. C.

Preparation of *dl-erythro*-αβ-dihydroxybutaldehyde. J. W. E. GLATTFELD and W. G. STRAITIFF (J. Amer. Chem. Soc., 1938, **60**, 1384—1387).—$OH{\cdot}CHMe{\cdot}CH(OH){\cdot}CO_2H$ (OH are *cis*), now termed *dl-erythro*-αβ-dihydroxybutyric acid (prep. from *trans*-$CHMe{:}CH{\cdot}CO_2H$ and BzO_2H modified to give an 80% yield), m.p. 81·5° (open tube), 82·5° (closed tube) [$NHPh{\cdot}NH_2$ salt, m.p. 105·5° (decomp.); *phenylhydrazide*, m.p. 123·5°; *Me*, b.p. 109°/10 mm., *Et*, b.p. 113°/10 mm., *Pr*^{a}, b.p. 117°/10 mm., *Bu*^{a}, b.p. 127°/10 mm., and n-*amyl* ester, b.p. 139°/10 mm.], with Ac_2O–HCl gives the *diacetate*, $+2H_2O$, m.p. 50°, and anhyd., an oil, b.p. about 127° (decomp.)/4 mm., converted by $SOCl_2$ into the acid *chloride diacetate*, b.p. 79°/3 mm., which is hydrogenated (Pd–$BaSO_4$) in xylene at 150° to dl-erythro-αβ-*diacetoxybutaldehyde*, b.p. 87°/4 mm., in 87·3% yield. 0·1N-HCl yields the $(OH)_2$-*aldehyde*, an oil, the osazone, m.p. 173°, from which was obtained by Wohl and Frank (A., 1902, i, 532) from "methylglyceraldehyde." R. S. C.

Ketones from higher fatty acids. VII—IX. K. KINO (J. Soc. Chem. Ind. Japan, 1938, **41**, 91—94B; cf. A., 1937, II, 483).—Ketone formation from fatty acids and MnO, $MnCO_3$, and $MgCO_3$ at ~330° for 0·5, 1, and 1·5 hr. is studied. Intermediate soap formation must be as rapid as possible to prevent frothing. MnO and $MnCO_3$ cause frothing, also induced by $MgCO_3$ unless in excess, but MgO and certain proportions of Mg–MgO, Mg–$MgCO_3$, and $MgCO_3$–MgO give no frothing. A. T. P.

Transformation of dihydroxyacetone derivatives into pyruvaldehyde derivatives. C. L. BERNIER and W. L. EVANS (J. Amer. Chem. Soc.,

1938, **60**, 1381—1384).—*Dihydroxyacetone monoacetate semicarbazone*, m.p. 137·5—138°, and m-*nitrobenzoylhydrazone*, decomp. 253—260°, are converted, when recrystallised or heated with 16% H_3PO_4, into *pyruvaldehyde-disemicarbazone*, m.p. 265—267° (decomp.), and -m-*nitrobenzoylosazone*, m.p. 278—282° (decomp.) (both also obtained from $AcCO_2H$), respectively, with liberation of $CO(CH_2{\cdot}OH)_2$ and AcOH. R. S. C.

Preparation of di*iso*propylidene-sugars. H. VAN GRUNENBERG, C. BREDT, and W. FREUDENBERG (J. Amer. Chem. Soc., 1938, **60**, 1507).—By adding fused $ZnCl_2$ (120) and P_2O_5–85% H_3PO_4 (20 : 40) successively to the sugar (100 g.) in $COMe_2$ (2 l.) and stirring at room temp. for 2 hr., pure di*iso*propylidene derivatives are obtained in the yields stated from the following sugars: *l*-sorbose 85, *d*-arabinose 90, *d*-galactose 78, *d*-mannose 92, and *d*-glucose 75%. The products are those normally obtained by use of H_2SO_4. R. S. C.

Application of cyclic acetals. G. SLOOFF (Rec. trav. chim., 1938, **57**, 673—676).—The use of cyclic acetals for purifying sugar alcohols, determining orientation of diols, and protecting CO etc. during reactions is stressed o-$C_6H_4{:}O_2CMe_2$ and HNO_3 (*d* 1·2—1·4) give (quant.) 4-nitro- and 4 : 5-*dinitropyrocatechol*, and thence readily the 4-NH_2- (I) and 4 : 5-$(NH_2)_2$-compounds. The *iso*propylidene derivative of (I), but not (I) itself, is readily diazotised and gives the usual diazo-reactions. R. S. C.

Inter-conversion of simple sugars. (SIR) J. C. IRVINE and G. J. ROBERTSON (Rec. trav. chim., 1938, **57**, 575—581).—Recorded reactions and conversion of galactose into an idose derivative (unpublished) indicate that conversion of a simple sugar into another is effected artificially only by way of derivatives containing an ethylene oxide ring. R. S. C.

Carbonate derivatives of the sugars. W. N. HAWORTH, C. R. PORTER, and A. C. WAINE (Rec. trav. chim., 1938, **57**, 541—547).—Passing $COCl_2$ into galactose in $COMe_2$ gives *di*isopropylidenegalactose 6-*chloroformate* (I), m.p. 53°, $[\alpha]^{21}_{5461}$ —56° in 33% aq. $COMe_2$; also obtained from di*iso*propylidenegalactose by $COCl_2$ in PhMe and hydrolysed thereinto by $Ba(OH)_2$ in aq. EtOH. With NH_2Ph in Et_2O (I) gives *di*isopropylidenegalactose-6-*phenylcarbimide*, m.p. 84—85°, $[\alpha]^{22}_{5461}$ —49° in EtOH, with MeOH at room temp. gives 6-*carbomethoxydi*isopropylidenegalactose, m.p. 94°, $[\alpha]^{16}_{5461}$ —49° in EtOH (decomposed by hot H_2O), and with 12N-HCl–MeOH gives 6-*carbomethoxy*-α-*methylgalactopyranoside*, decomp. 141°, $[\alpha]^{16}_{D}$ +150° in H_2O, converted by $Ba(OH)_2$ into α-methylgalactoside and $BaCO_3$. Xylose and $COCl_2$ in $COMe_2$ give 1 : 2-iso*propylidenexylose* 3 : 5-*carbonate*, m.p. 138°, $[\alpha]^{22}_{D}$ +7·5° in $CHCl_3$, +19·5° in $COMe_2$, +9° in MeOH (hydrolyses, when kept), converted in MeOH or MeOH–HCl into 5-*carbomethoxy*-1 : 2-iso*propylidenexylose* (II), m.p. 135—136°, $[\alpha]_D$ —13° in MeOH, also obtained from *iso*propylidenexylose (III) and $ClCO_2Me$ in NaOH–aq. MeOH. (II) gives the 3-p-*toluenesulphonate*, m.p. 106°, $[\alpha]^{22}_{D}$ —14° in MeOH, hydrolysed by $Ba(OH)_2$ to 1 : 2-iso*propylidenexylose* 3-p-*toluenesulphonate*, m.p. 64—66°, $[\alpha]^{19}_{D}$ —15° in MeOH; the 5-*p*-toluenesulphonate, m.p. 138—139°, is obtained from (III). Mannose dicarbonate (IV) and $SOCl_2$ in dioxan give α-*chloromannose dicarbonate*, m.p. 192° (sinters at 186°), $[\alpha]^{18}_{D}$ +67° in $COMe_2$, converted by MeOH–Ag_2CO_3–dioxan into β-*methylmannofuranoside dicarbonate*, m.p. 219—220°, $[\alpha]^{15}_{D}$ —89° in $COMe_2$. β-*Ethylmannofuranoside dicarbonate*, m.p. 153—156°, $[\alpha]^{19}_{D}$ —74° in $COMe_2$, is similarly prepared. Aq. Br–$BaCO_3$ converts (IV) into the acid, which yields *Me mannonate dicarbonate*, m.p. 200—202° (decomp.). R. S. C.

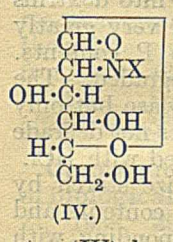
2 : 6-Dimethylglucose. D. J. BELL and R. L. M. SYNGE (J.C.S., 1938, 833—836; cf. A., 1937, II, 484).—4 : 6-Ethylidene-β-methylglucoside 2 : 3-dinitrate and NaI in $COMe_2$ at 100° afford the 3-*nitrate* (I), m.p. 146—148°, $[\alpha]^{18}_{D}$ —30·8° in $CHCl_3$. The 2-*Me* derivative of (I), m.p. 104·5—105·5° after softening at 101°, $[\alpha]^{16}_{D}$ —28·7° in $CHCl_3$, and Na_2S–EtOH give 4 : 6-*ethylidene*-2-*methyl*-β-*methylglucoside*, m.p. 122—123°, also obtained from 2-methyl-β-methylglucoside and paraldehyde (H_2SO_4) at 0°. (I) and Ac_2O–H_2SO_4 give 2 : 6-*diacetyl*-4-α-*acetoxyethyl*-β-*methylglucoside* 3-*nitrate*, m.p. 125—126° after softening at 124°, $[\alpha]^{20}_{D}$ +13·4° in $CHCl_3$, converted by HNO_3 (*d* 1·5) in $CHCl_3$ into 2 : 6-*diacetyl*-β-*methylglucoside* 3 : 4-*dinitrate*, m.p. 90—91°, $[\alpha]^{20}_{D}$ —27·3° in $CHCl_3$, which with NaOMe–$CHCl_3$ at room temp. forms β-*methylglucoside* 3 : 4-*dinitrate*, m.p. 116—118°, $[\alpha]^{16}_{D}$ +13·9° in MeOH. 2 : 6-*Dimethyl*-β-*methylglucoside* 3 : 4-*dinitrate*, m.p. 74—76°, $[\alpha]^{20}_{D}$ —13·7° in $CHCl_3$, and NaOH–EtOH–H_2S at 100° give 2 : 6-*dimethyl*-β-*methylglucoside*, m.p. 50—52°, $[\alpha]^{20}_{D}$ —43·5° in $CHCl_3$ (3 : 4-di-*p*-toluenesulphonate, m.p. 156—158°, $[\alpha]^{18}_{D}$ —8·2° in $CHCl_3$) (cf. A., 1932, 500), converted by dil. HCl at 100° into 2 : 6-*dimethylglucose* (not cryst.), $[\alpha]^{17}_{D}$ +58·3° in H_2O (2 : 6-*dimethylgluconophenylhydrazide*, m.p. 127—129°, $[\alpha]^{17}_{D}$ +48·6° in EtOH). A. T. P.

β-Methylglucoside 2 : 3 : 6-trinitrate. D. J. BELL and R. L. M. SYNGE (J.C.S., 1938, 836—838; cf. preceding abstract).—β-Methylglucoside 2 : 3-dinitrate and CPh_3Cl–C_5H_5N at 37° afford the 6-CPh_3 *ether*, which with Ac_2O–C_5H_5N at room temp. gives 4-*acetyl*-6-*triphenylmethyl*-β-*methylglucoside* 2 : 3-*dinitrate*, m.p. 153—155°, $[\alpha]^{18}_{D}$ +31·8° (rotations in $CHCl_3$), converted by HNO_3 (*d* 1·5) in $CHCl_3$ at 0° into 4-*acetyl*-β-*methylglucoside* 2 : 3 : 6-*trinitrate*, m.p. 94—95°, $[\alpha]^{19}_{D}$ +0·4°. NaOMe–$CHCl_3$ then gives β-*methylglucoside* 2 : 3 : 6-*trinitrate* (not cryst.). Its constitution is proved by methylation (Ag_2O–MeI) to the 4-*Me* derivative, removal of nitrate (AcOH–Zn–Fe) followed by acetylation (Ac_2O) yielding 4-methyl-β-methylglucoside 2 : 3 : 6-triacetate, m.p. 105—106°, $[\alpha]^{20}_{D}$ —34·9°. A. T. P.

New ethylidene compounds of α- and β-methylglucosides. H. APPEL and W. N. HAWORTH [with, in part, E. G. COX and F. J. LLEWELLYN] (J.C.S., 1938, 793—797).—α- and β-Methylglucoside and paraldehyde (H_2SO_4) form 2 : 3-*oxidodiethylidene*-4 : 6-*ethylidene*-α- (I), m.p. 182·5—183·5°, $[\alpha]^{20}_{D}$ +83·5° in $CHCl_3$, and -β- (II), m.p. 208—209°, $[\alpha]^{21}_{D}$ —57·8° in $CHCl_3$, -*methylglucosides*, confirmed by MeCHO and mol. wt. determinations. The structure of 4 : 6-ethylidene-α-methylglucoside (III), $[\alpha]^{20}_{D}$ +109·1° in H_2O, is confirmed (cf. Hibbert and Hill, A., 1924, i,

133); (III) and MeI–Ag_2O in $COMe_2$, followed by PhCHO–$ZnCl_2$, yield 4 : 6-benzylidene-2 : 3-dimethyl-α-methylglucoside, $[\alpha]_D^{25}$ +96·2° in $CHCl_3$. (I) or (II) and Et_2O–Br yield (III) and the β-glucoside, new m.p. 189—190°, $[\alpha]_D^{19}$ −76·9° in H_2O, respectively, suggesting that 2 mols. of MeCHO are involved in linking between $C_{(2)}$ and $C_{(3)}$ of the glucose chain. 4 : 6-Benzylidene-α-methylglucoside affords a 2 : 3-*oxidodiethylidene* derivative, m.p. 192—193°, $[\alpha]_D^{20\cdot5}$ +66·4° in $CHCl_3$, similar in configuration and structure to (I). *X*-Ray data are recorded and the bearing of the results on configuration is discussed. A. T. P.

Halogenoalkyl glucosides. III. Quaternary salts. Glucosamine quaternary derivative. H. W. Coles and F. H. Bergeim (J. Amer. Chem. Soc., 1938, **60**, 1376—1379; cf. A., 1938, II, 261).—The prep. of tetra-acetyl-β-*d*-glucosido-1-trimethylammonium bromide (I), m.p. 192°, $[\alpha]_D^{18}$ +10·2° in H_2O, is improved; it yields the Ac-free salt (II), m.p. 161—162°, $[\alpha]_D^{16}$ +5°. β-*d*-β-Bromoethylglucoside tetra-acetate and NEt_3 in C_6H_6 give *tetra-acetyl*-β-d-*glucosidoethyltriethylammonium bromide*, m.p. 67°, $[\alpha]_D^{20}$ −33° in H_2O. β-d-*Glucosidocholine chloride* (III) (prep. in aq. EtOH), a syrup, and Ac_2O at 100° give the *tetra-acetate*, m.p. 217—218°, $[\alpha]_D^{20}$ −25° in H_2O, also obtained from β-*d*-β-chloroethylglucoside tetra-acetate and NEt_3 in C_6H_6 at 100°. β-*d*-γ-Chloropropylglucoside tetra-acetate gives γ-*tetra-acetyl*-β-d-*glucosidohomocholine chloride*, m.p. 165—167·5°. Glucosamine hydrochloride and MeI in hot KOH–MeOH give the *substance* (IV) (X = Me_2I,2MeI), m.p. >280°, which gives no picrate and reacts with Fehling's solution only in presence of acid. (I), (II), and (III) have no effect on the blood-pressure of rabbits in doses of 5 mg. per kg. body-wt. (IV) has an action similar to that of choline; 1 mg. per kg. produces slight spasms and marked vagal stimulation, followed by 180% increase in blood-pressure (returning to normal in 2 min.) if stimulation is abolished by atropine. M.p. are corr. R. S. C.



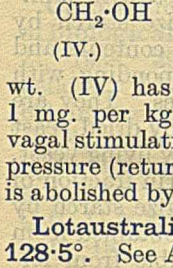
(IV.)

Lotaustralin and its Ac derivative, m.p. 127—128·5°. See A., 1938, III, 633.

Amino-alcohols. I. Preparation and dehydration of certain aliphatic tertiary amino-alcohols. B. K. Campbell and K. N. Campbell (J. Amer. Chem. Soc., 1938, **60**, 1372—1376).—In accordance with expectation from the inductive effect, the ease of dehydration of *tert.* alcohols is greatly decreased and that of esterification increased by the proximity of a basic group to the OH, the influence being dependent on the distance separating these groups. Addition of $CH_2Cl{\cdot}CO_2Me$ to MgMeI gives $CH_2Cl{\cdot}CMe_2{\cdot}OH$, converted by $NHMe_2$ in C_6H_6 at 135—140° into *dimethylaminotert.-butyl alcohol* (I), b.p. 130—130·3°/743 mm. (*hydrochloride*, m.p. 114·5—115·5°; *aurichloride*, m.p. 126—128°), which readily gives a *benzoate hydrochloride*, m.p. 200°, resists heating with anhyd. $CuSO_4$ or KOH, and is only partly converted by I into a *substance*, m.p. 113° (contains ionisable I). With MgEtBr (I) gives a complex, decomposed at 280° into α-*dimethylamino*-Δ^{α}-iso*butene* (II), the structure of which follows from the hydrolysis of its unstable *hydrochloride*, m.p. 142—150°, by dil. HCl to $Pr^{\beta}CHO$ and $NHMe_2$. With conc. H_2SO_4 at 100° (I) gives $NHMe_2$, $Pr^{\beta}CHO$ [probably by way of (II)], and γ-*dimethylamino*-Δ^{α}-iso*butene* (*hydrochloride*, m.p. 142—144°; *aurichloride*, m.p. 116—118°; with O_3 gives CH_2O).

$CH_2Br{\cdot}CH_2{\cdot}CO_2Me$ and MgMeCl give the bromohydrin, converted by $NHMe_2$–C_6H_6 at 140—150° into γ-*dimethylaminotert.-amyl alcohol*, b.p. 160·1—160·5°/743 mm. (*hydrochloride*, m.p. 141—141·5°), which readily gives a *benzoate hydrochloride*, m.p. 165—166°, and is largely unchanged by I or KOH, but is dehydrated by $CuSO_4$; pyrolysis of the complex obtained with MgEtBr gives a tar. $Cl{\cdot}[CH_2]_3{\cdot}CO_2Me$ (prep. in 80% yield from $Cl{\cdot}[CH_2]_3{\cdot}CN$) gives similarly ε-*dimethylamino*-β-*methylpentan*-β-*ol*, b.p. 99°/30 mm. (hygroscopic *hydrochloride*, m.p. 153—154°), which gives less vigorously a *benzoate hydrochloride*, m.p. 114°, and is unchanged by I or KOH, but is dehydrated by $CuSO_4$. $Br{\cdot}[CH_2]_4{\cdot}CO_2Me$ gives ζ-*dimethylamino*-β-*methylhexan*-β-*ol*, b.p. 118—118·5°/30 mm. (hygroscopic *hydrochloride*, m.p. 100—101°), which gives no benzoate and is dehydrated by I. R. S. C.

Osazones. III. Dehydro-osazones. O. Diels, E. Cluss, H. J. Stephan, and R. König (Ber., 1938, **71**, [*B*], 1189—1196).—Osazones of mono- and di-saccharides are readily dehydrogenated by atm. O_2 in alkaline solution to compounds very similar to the osazones but containing 2 H less. The assumption of a simple transition of osazone into the corresponding osotetrazine is negatived by the impossibility of the reverse change and can scarcely be reconciled with colour and m.p. The formation of a ·N:NPh residue is also improbable. It appears most likely that dehydro-osotetrazines are first produced and become isomerised to the much more stable osotriazoles (cf. *A*). Thus *d*-glucosazone affords d-*dehydroglucosazone*, $C_{18}H_{20}O_4N_4$, m.p. 203° (*triacetate*, m.p. 173°). Galactosazone gives *dehydrogalactosazone*, m.p. 208° (decomp.), which retains 1EtOH with unusual firmness and is converted by Ac_2O in dioxan into an isomeric *dehydrogalactosazone*, m.p. 180°, which does not unite with EtOH, and by N_2H_4,H_2O or CH_2N_2 into a further *isomeride*, m.p. 212° (decomp.), which is indifferent towards EtOH. *Dehydrogalactosazone diacetate* has m.p. 188° (decomp.). *Dehydromaltosazone*, $C_{24}H_{30}O_9N_4,H_2O$, m.p. 246° (decomp.), yields a *penta-acetate*, m.p. 220° (decomp.); *maltosazone penta-acetate* has m.p. 159° (decomp.). *Dehydrolactosazone* (+$1H_2O$), m.p. 238° (decomp.), and its *hexa-acetate*, m.p. 139°, are described. H. W.



(*A*.)

Mannans. IV. Configuration of nut- and salep-mannan and the extent of the validity of Hudson's rules of superposition among derivatives of mannose. F. Klages and R. Maurenbrecher (Annalen, 1938, **535**, 175—204).—Malt extract has almost equally pronounced actions towards salep- and nut- (I) -mannan, thus giving new evidence of the similar structure of these compounds, but fission of the enzyme into a di- and a poly-saccharase is not observed. With aged samples of enzyme the hydro-

lysis is frequently incomplete but cautious evaporation of the solution restores the enzymic activity almost to its original val. (I) is subjected to acetolysis until fission has reached 65%, the product is hydrolysed, and mannose is removed from the conc. solution as completely as possible as phenylhydrazone; the remaining solution yields *mannobiosazone* (II), $C_{24}H_{32}O_9N_6$, m.p. 136—138° (corr.) with slight previous softening, decomp. about 190° (corr.), $[\alpha]_D$ —42° in MeOH, —22° in C_5H_5N–EtOH (4 : 6). The corresponding carbohydrate could be obtained only in a syrupy although nearly homogeneous form whilst the corresponding acetate could not be caused to crystallise. The suitability of osazones for determinations of configuration is established by observations of the compounds from glucose, maltose, cellobiose, and lactose. Determinations of $[\alpha]_D$ particularly in MeOH and to a somewhat smaller extent in C_5H_5N–EtOH show satisfactory fulfilment of the rules of superposition and an unequivocal assignment of disaccharides to the α- or β-series is secured. The slight displacement (about 10°) of the observed vals. with respect to the calc. vals. is a general phenomenon with 1 : 4-disaccharides and is caused by adopting glucosazone instead of a 4-substituted derivative as standard. The positive displacement of (II) is particularly marked but the MeOH val. and the corr. C_5H_5N–EtOH val. prove conclusively the β-configuration. There is no polarimetric evidence for the presence of α-mannosidic linkings in the syrupy by-products of the prep. of (II) so that a solely β-mannosidic structure must be assigned to the various mannans. Various modes of comparison of $[\alpha]_D$ of glucosides and the corresponding polysaccharides in connexion with the application of Hudson's rules are discussed. The calculations for all glucose derivatives are considerably more accurate than those of the corresponding mannose derivatives; this is due partly to the small contribution of the $C_{(1)}$ atom of mannose derivatives towards $[\alpha]_D$ whereby the relative discrepancy for a similar abs. error is larger. A much more pronounced dependence of $[\alpha]_D$ of all investigated derivatives accompanies these discrepancies of the mannose compounds. Thus the methylated derivatives between H_2O, C_6H_6, and $CHCl_3$ and the methylmannosides between H_2O, MeOH, and C_5H_5N–EtOH show differences of about the same order of magnitude as are caused by the replacement of non-glucosidic Me by Ac or H and the variations of $[\alpha]_D$ of methylmannan in various solvents exceed the changes by all substitutive processes. It is remarkable that by compounds so similar chemically as methylmannan and β-pentamethylmannose (or to a smaller extent as methylcellulose and β-pentamethylglucose) the transition from C_6H_6 to $CHCl_3$ causes reversed and extraordinarily pronounced displacements of rotation. It therefore appears reasonable to consider $[\alpha]_D$ as influenced by two partial causes: (*a*) a constitutive cause brought about by the mutual action of the atoms through the chain and corresponding approx. with $[\alpha]_D$ of the gaseous product and (*b*) an association or solvent cause. Since, in spite of great constitutive similarities, the solvate sheaths, *e.g.*, around the Me groups of the glucosides and around the sugar residues of the polysaccharides, are of widely differing natures the solvent influence on $[\alpha]_D$ of the two compounds can differ in magnitude and even in sign and thus explain the discrepancy from Hudson's rules. H. W.

Polysaccharide produced from sucrose by *Leuconostoc dextranicum*. S. Peat, M. Stacey, and E. Schlüchterer (Nature, 1938, **141**, 876).—The purest dextran isolated is a non-reducing, H_2O-sol., white powder, $[\alpha]_D^{20}$ +180° in H_2O; hydrolysis (boiling N-H_2SO_4) gives a 92% yield of glucose. Methylation proceeds normally, yielding a homogeneous product, $[\alpha]_D$ 210—214° in $CHCl_3$ (OMe 44·5%), which is more stable towards hydrolysing agents than is methylated starch. Complete hydrolysis (50% aq. AcOH + 4% of conc. HCl) gave 2 : 3 : 4-trimethylglucopyranose as the principal product, establishing the nature of the link between the glucose units of dextran as being 1 : 6-glucosidic. The isolation of a small proportion of tetramethylglucoside by vac. distillation of the glucosides indicates a terminated chain. L. S. T.

Dextrins and starch. I. K. Myrbäck. **II. Takadiastase and maize starch.** K. Ahlborg and K. Myrbäck. **III. Trisaccharides as degradation products of starch.** K. Myrbäck (Biochem. Z., 1938, **297**, 160—171, 172—178, 179—183).—I. β-Amylase (I) converts starch into dextrins having very low reducing power, high, very greatly varying mol. wts., and very variable P contents. Approx. 40% of the starch is thus degraded. The dextrins are further degraded by α-amylase but only slowly or not at all by (I) which also does not degrade the dextrins after they have been treated with HCl.

II. The dextrins produced from maize starch by takadiastase (II) have very variable P contents and reducing powers and mol. wts. corresponding with mols. composed of 3—6 glucose residues. They are fermented as rapidly as is starch itself by dried yeast and by yeast maceration juice but not by living yeast.

III. (Cf. A., 1938, II, 128.) The dextrin fraction of mol. wt. approx. 495 obtained from maize starch by the action of (II) and similar fractions obtained from beer wort, when freed as far as possible from fermentable carbohydrates and non-carbohydrates, yield tri- and tetra-saccharides or very similar substances. W. McC.

Analysis of diastatic split-products of starch. M. Somogyi (J. Biol. Chem., 1938, **124**, 179—187).—Glucose is produced directly from starch or glycogen by diastase at an early stage, and is not merely a hydrolysis product of maltose produced by the action of other enzymes. The non-fermentable reducing fraction behaves as a trisaccharide, but is not homogeneous. The separate determination of glucose, maltose, and non-fermentable fraction is described. P. G. M.

Preparation of alkoxyurethanes. J. Miliotis (Praktika, 1935, **10**, 445—447; Chem. Zentr., 1936, ii, 1708).—Treatment of halogenated acid amides with Br and Na alkoxides yields urethanes of the corresponding alcohols. Et (cf. A., 1926, 943) and *Me methoxymethylcarbamates*, b.p. 89—91°/16 mm., are described. A. H. C.

Reaction of amino-acids, peptides, and related substances with sugars. II. N. Shiga (J. Biochem. Japan, 1938, **27**, 307—334; cf. A., 1938, II, 6).—Data for the reaction between glycylalanine anhydride or ovalbumin and glucose (I) at p_H 7—9 are given and discussed. In their reactions with (I), glycine and glycylglycine behave like dipeptide and tripeptide, respectively, when H_2O is replaced by 28·6% aq. dioxan as solvent. The displacement of p_H accompanying the reactions is not indicative of the acid produced, being dependent on the buffering power of the solution. No optimum p_H for combination of NH_2-acid with glucose appears to exist (cf. Frankel and Katchalsky, A., 1937, II, 402). F. O. H.

Formation of amino-acids from α-diketo-compounds. Glycine derivatives from glyoxal. K. Maurer and E. H. Woltersdorf (Z. physiol. Chem., 1938, **254**, 18—24).—Glyoxal–$NaHSO_3$ with $NHEt_2$ in EtOH gives diethylaminoacetdiethylamide (I) [*ethiodide*, m.p. 155°; *reineckate*; picrate, m.p. 122° (cf. Hahn and Loos, A., 1919, i, 18)]. Similarly, from appropriate bases, were prepared diethylaminoacetamide, ethylaminoacetethylamide, and sarcosinemethylamide (II) (Abderhalden *et al.*, A., 1933, 265) (*picrate*, m.p. 175°). Polymerised glyoxal with $NHEt_2$ in EtOH yields (I), Et diethylaminoacetate (*ethiodide*, m.p. 123—125°), and triethylbetaine; the reaction in presence of AcOH yields the ester but not the amide whilst the yield of ester+amide is increased from 40 to 65% by passing CO_2 through the reacting mixture. Polymerised glyoxal and NH_2Me in EtOH afford sarcosine Et ester and (II). F. O. H.

Compounds of mercuric chloride with betaines of biological importance. R. Krimberg (Biochem. Z., 1938, **297**, 261—269).—Alcoholic solutions of betaine, β-homobetaine, γ-butyrobetaine, crotonobetaine, and *r*-carnitine with alcoholic solution of $HgCl_2$ yield, respectively, the following *compounds*: $C_5H_{11}O_2N,2HgCl_2$, m.p. 183°; $C_6H_{13}O_2N,3HgCl_2$, m.p. 150°; $C_7H_{15}O_2N,2HgCl_2$, m.p. 185°; $C_7H_{13}O_2N,2HgCl_2$, m.p. 174°; and $C_7H_{15}O_3N,2HgCl_2$, m.p. 191°. Free choline does not combine with $HgCl_2$ but choline chloride gives the *compound*, $C_5H_{14}ONCl,6HgCl_2$, m.p. 248°. W. McC.

Preparation of esters of carnitine and of crotonic acid betaine. E. Strack and K. Försterling (Ber., 1938, **71**, [*B*], 1143—1150).—The hydrochlorides of the bases are esterified with MeOH (EtOH)–HCl and the esters are converted into their reineckates either directly or through the aurichloride or platinichloride. The reineckates are converted by Ag_2SO_4 into the corresponding sulphates from which the hydrochlorides or hydriodides are obtained by $BaCl_2$ or BaI_2. Thus carnitine Me_2 ester gives a *hydrochloride*, m.p. 178°, *aurichloride*, m.p. 108°, *platinichloride*, m.p. 197—198° (decomp.), reineckate, m.p. 136°, *rhodanilate*, m.p. 154—156°, and *mercurichloride*, m.p. 110°. Carnitine Et ester yields a hydrochloride, m.p. 146°, aurichloride, m.p. 105°, platinichloride, m.p. 211—212° (decomp.), reineckate, m.p. 135—136°, *rhodanilate*, m.p. 94°, and *mercurichloride*. The *hydriodide*, m.p. 140°, *sulphate*, m.p. 121·5°, *aurichloride*, m.p. 95·5°, *platinichloride*, decomp. 186° after softening at 184°, *reineckate* ($+1H_2O$), m.p. (anhyd.), 149°, and *rhodanilate*, m.p. 170°, of acetylcarnitine Me ester are described. Acetylcarnitine Et ester gives a *hydriodide*, m.p. 113·5°, *sulphate*, m.p. 128—129°, non-cryst. *aurichloride*, *platinichloride*, m.p. 187° after softening at 185°, *reineckate*, m.p. 150°, *rhodanilate*, m.p. 166° after softening at 163°, and *mercurichloride*, $C_{11}H_{22}O_4NCl,6HgCl_2$, m.p. (indef.), 150—155°. Crotonobetaine Me ester affords a *hydrochloride*, m.p. 173—174°, *aurichloride*, m.p. 163°, *platinichloride*, decomp. 212—213° after softening at 210°, *reineckate*, m.p. 163°, *rhodanilate*, m.p. 171°, and *mercurichloride*, m.p. 131°. A *hydrochloride*, m.p. 150° after softening at 148°, *aurichloride*, m.p. 105°, platinichloride, decomp. 208°, *reineckate*, m.p. 164—166°, *rhodanilate* ($+1COMe_2$), m.p. 132°, and *mercurichloride*, $C_9H_{18}O_2NCl,HgCl_2$, m.p. 112°, are derived from crotonobetaine Et ester. *Carnitine rhodanilate* ($+1H_2O$), m.p. 110° after softening at 108°, *acetylcarnitine hydriodide*, m.p. 169°, and *rhodanilate* ($+1H_2O$), m.p. 107° after softening at 204°, *crotonobetaine reineckate*, m.p. 159°, and *rhodanilate*, m.p. 135°, are described. The solubilities at 20° and 0° of the phosphotungstates of carnitine and its Me and Et ester, acetylcarnitine and its Me and Et esters, and crotonobetaine and its Me and Et esters are recorded. H. W.

Preparation of pure *d*-arginine. S. W. Fox (Science, 1938, **87**, 418—419).—Essential precautions for obtaining pure *d*-arginine (I) from the hydrochloride appear to be the choice of a satisfactory protein source, *e.g.*, salmin and gelatin of good grades, but not casein, hog's blood, or defatted canned sardine spermatic tissue, and the removal of the (I)–Ag complex from the solution of the free base. Details for a 96% recovery of pure (I) from its hydrochloride are given. (I) absorbs CO_2 from the air, but this can be removed by boiling the solution for recrystallisation. L. S. T.

Synthesis of *dl*-threonine. H. Adkins and E. W. Reeve (J. Amer. Chem. Soc., 1938, **60**, 1328—1331).—OH·N:CAc·CO_2Et (I) (modified prep.) is converted by H_2–Raney Ni at 90—100°/120 atm. into $CO_2Et{\cdot}C\langle^{CMe{\cdot}N}_{N:CMe}\rangle C{\cdot}CO_2Et$, but at 300 atm. gives 37% of mixed esters, OH·CHMe·$CH_2(NH_2)$·CO_2Et, whence 50% of *dl*-threonine (II) is obtained. Et_2SO_4 and NaOH in dioxan at 75—90° convert (I) into *Et ethyloximinoacetoacetate*, b.p. 97—98°/8 mm., hydrogenation of which gives 75% of esters, giving a 50% over-all yield of (II). R. S. C.

Electrometric titration of aminoalkylsulphonic acids. P. Rumpf (Bull. Soc. chim., 1938, [v], **5**, 871—887).—$NH_3^+{\cdot}[CH_2]_n{\cdot}SO_3^-$ [$n = 0$—4, m.p. 263°; 5, m.p. 310—312°; 10, m.p. 340° (decomp.)], $NH_2^+Ph{\cdot}[CH_2]_n{\cdot}SO_3^-$ ($n = 1$—3, m.p. 265°), $NMe_3^+{\cdot}[CH_2]_2{\cdot}SO_3^-$ (cf. Cortese, A., 1936, 459), $(NH_3^+){\cdot}CHMe{\cdot}CH_2{\cdot}SO_3^-$, $C^+Ph[C_6H_4{\cdot}NH{\cdot}(CH_2)_2{\cdot}SO_3^-]_2H^+$, are prepared, by improved methods in many cases. Electrometric titration shows that basicities increase

with the no. of CH_2 separating the two ionic groups, rapidly at first and then approaching a limit. A. T. P.

Bridged derivatives of trimethylarsine with palladous halides.—See A., 1938, I, 388.

Hydrides of boron. IX. Preparation of some methyltriborinetriamines. H. I. Schlesinger, D. M. Ritter, and A. B. Burg (J. Amer. Chem. Soc., 1938, **60**, 1296—1300; cf. A., 1938, I, 207).—The cyclic structure of $(\cdot BH\cdot NH\cdot)_3$ (I) is confirmed by prep. of the theoretical no. of Me derivatives. (I) is best (41·5% yield) prepared from B_2H_6 and NH_3 at 200°/100 atm. during 15 min. With NH_3 and NH_2Me B_2H_6 gives mixtures of (I), its N-*Me* (II), b.p. 84°, NN′-Me_2, b.p. 108°, and NN′N″-Me_3 derivative (III), b.p. 134°. In absence of NH_3 only (III) and the liquid *compound*, B_2H_6,2NH_2Me, are obtained. $BMe_2\cdot NH_2$ with (I) gives rather small amounts of B-*Me*, BB′-Me_2, and BB′B″-Me_3 derivatives, H_2, solid by-products, and, occasionally, CH_4. BMe_3 and (I) or (II) give the NB-Me_2, b.p. 124°, NBB′-Me_3, b.p. 139°, and NBB′B″-Me_4 derivative, b.p. 158°. The compounds, particularly (I), are associated in the vapour phase. Homogeneity of the products is proved by agreement of the determined v.p. with those deduced from the Clapeyron–Clausius equation. R. S. C.

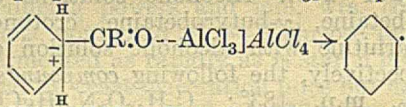
Reducing action of Grignard reagents on acyl chlorides. F. C. Whitmore (Rec. trav. chim., 1938, **57**, 562—568).—Adding RCOCl (1 mol.) to $MgBu^{\gamma}Cl$ (4 mols.) gives $CH_2R\cdot OH$, $CHBu^{\gamma}R\cdot OH$, and *iso*-C_4H_8 (2 mols. for each $CH_2R\cdot OH$ and 1 mol. for each $CHBu^{\gamma}R\cdot OH$); the reaction involves (*a*) reduction of RCOCl successively to RCHO and $CH_2R\cdot OH$, with addition of $MgBu^{\gamma}Cl$ to RCHO, or (*b*) reduction of RCOCl to $CH_2R\cdot OH$, formation of the ketone from RCOCl, and reduction of the ketone. Thus, $Pr^{\alpha}COCl$, $Pr^{\beta}COCl$, and $Bu^{\gamma}COCl$ give 9, 20, and 94% of $CH_2R\cdot OH$ and 71, 63, and 1·5%, respectively, of $CHBu^{\gamma}R\cdot OH$. Adding $Bu^{\gamma}COCl$ (0·22 mol.) to $MgBu^{\gamma}Cl$ (0·1 mol.) gives *iso*-C_4H_8 (0·27 mol.) and 45% each of $CH_2Bu^{\gamma}\cdot OH$ and $Bu^{\gamma}CO_2\cdot CH_2Bu^{\gamma}$. Adding $MgBu^{\gamma}Cl$ (1·5 mols.) to $Bu^{\gamma}COCl$ (8 mols.) and keeping at —10° gives only $Bu^{\gamma}CO_2\cdot CH_2Bu^{\gamma}$ (8%), *iso*-C_4H_8 (17%), and $COBu^{\gamma}_2$ (32%), 6·2 mols. of $Bu^{\gamma}CO_2H$ being recovered. Adding $MgBu^{\gamma}Cl$ (2·5 mols.) to AcCl (3·2 mols.) gives *iso*-C_4H_8 (8%), EtOAc (9·5%), pinacolone (17%), and pinacolyl acetate (6·6%). Heating AcCl and anhyd. $MgCl_2$ in dry Et_2O for 4 days gives only 10% of EtOAc and (?) EtCl. Reduction is not confined to $MgBu^{\gamma}Cl$; thus, adding AcCl (2 mols.) to $MgBu^{\alpha}Br$ (5 mols.) gives C_4H_8, EtOH (8%), and β-hexanol (13%). Adding $Bu^{\gamma}COCl$ (1 mol.) to $MgBu^{\alpha}Br$ (4 mols.) gives $CH_2Bu^{\gamma}\cdot OH$ (27%), $CHBu^{\alpha}Bu^{\gamma}\cdot OH$ (69%), and C_4H_8, but no $CH_2Bu^{\alpha}\cdot OH$. Adding MeCHO (2 mols.) to $MgBu^{\alpha}Br$ (5 mols.) gives EtOH (20—25%), β-hexanol (34%), and some C_4H_8; $MgBu^{\gamma}Cl$ similarly gives EtOH (22%) and pinacolyl acetate (56%), so that branching in the Bu is seen to have little effect. Adding $Bu^{\gamma}CO_2Et$ (1 mol.) to $MgBu^{\alpha}Br$ (4 mols.) gives C_4H_8 and $CHBu^{\alpha}Bu^{\gamma}\cdot OH$ (40—45%), but no $CH_2Bu^{\gamma}\cdot OH$. R. S. C.

Organocalcium iodides. C. Glacet (Bull. Soc. Chim., 1938, [v], **5**, 895—900).—EtI and Ca in Et_2O yield a 1 : 1 mixture of $(Et_2O)_2CaI_2$ and Et_3OCaI. MeI, $Pr^{\alpha}I$, BuI, $CH_2{:}CH\cdot CH_2I$, $CH_2Bu^{\beta}I$, *n*-$C_8H_{17}I$, PhI, and *m*-C_6H_4MeI react easily with Ca. $Pr^{\beta}I$ and *sec.*-BuI react with difficulty and $Bu^{\gamma}I$ and CMe_2EtI not at all. The organo-Ca derivatives react normally with aldehydes, ketones, nitriles, and acid esters, but not with acid chlorides; *e.g.*, PhCHO and the respective Ca derivative yields $CHPhR\cdot OH$ (R=Me, Et; Pr; CH_2Bu^{β}; Ph); COMeEt and BuI–Ca give $CMeEtBu^{\alpha}\cdot OH$ and $COPh_2$–PhI–Ca yield $CPh_3\cdot OH$; MeCN and PhCN, and EtI–Ca, afford COMeEt and COEtPh, respectively; HCO_2Et (EtOAc) and EtI–Ca afford $CHEt_2\cdot OH$ ($CMeEt_2\cdot OH$), and EtOBz–PhI–Ca give $CPh_3\cdot OH$ and some $CHPh_3$ (cf. A., 1926, 1130). A. T. P.

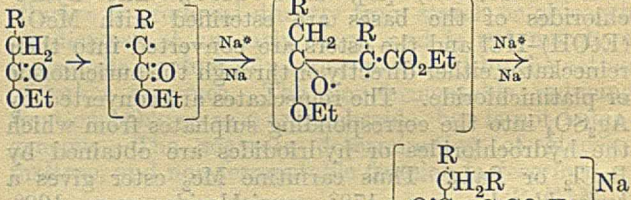
Reactivity of substituents in benzene derivatives. I, II. A. Mangini (Ric. sci. Progr. tecn., 1935, **6**, II, 344, 439—440; Chem. Zentr., 1936, ii, 601—602).—Reactivity is correlated with dipole moment with special reference to compounds containing ⩽3 substituents. H. N. R.

Advances in the Friedel–Crafts reaction and its technical application. P. Kranzlein (Angew. Chem., 1938, **51**, 373—381).—A lecture dealing with the use of $AlCl_3$ in the synthesis of hydrocarbons and its applications in the oil and artificial resin industries, in the synthesis of aldehydes and, most extensively, of ketones. H. W.

Positive hydrogen atoms. IX. Friedel–Crafts and ethyl acetoacetate syntheses. A parallel and a proposed reaction mechanism. W. Dilthey (Ber., 1938, **71**, [*B*], 1350—1353).—For the Friedel–Crafts reaction the following mechanism is proposed: $R\cdot C{:}O\text{--}AlCl_3]AlCl_4 + C_6H_6 \rightarrow$



$HCl + AlCl_3$. It is thus obvious that $AlCl_3$ attached to O of COCl remains attached in the final product and hence cannot act as a catalyst whereas the italicised mol. $AlCl_3$ behaves as a catalyst since it is continuously re-formed from the very unstable $AlCl_3$–HCl. It is thus obvious why >1 mol. of $AlCl_3$ must be used and why often only a very slight excess suffices. The acetoacetic synthesis is formulated:



+ Na*OEt. The ionoid adduct immediately decomposes with elimination of NaOEt, which can then form a new salt with EtOAc. The Na* functions as catalyst. H. W.

Halogenation of aromatic and aliphatic compounds. R. Oda, K. Tamura, and K. Imai (Sci.

Papers Inst. Phys. Chem. Res. Tokyo, 1938, **34**, 596—618).—2-Me increases, but 9-Br, 9-NO_2, 2-Cl, and 2-CO_2H decrease, the rate of addition of Br to anthracene in AcOH. 7-Cl decreases slightly the very rapid reaction of Na anthracene-2-sulphonate with Br in H_2O. 2-Hydroxy- and -amino-anthracene absorb Br rapidly, but not instantaneously. *o*- and *p*-OH·C_6H_4·CHO react with Br in AcOH at the same rate, but more slowly than does *m*-OH·C_6H_4·CHO; this and the ability of the *m*-compound to undergo the Cannizzaro reaction may be connected with ability of the *o*- and *p*-compounds to exist in the keto-form. The following relative rates of reaction with Br in AcOH are established: saligenin > CH_2:CH·CH_2·OH > CHPh:CH·CH_2·OH; CH_2Ph·OH does not react in AcOH. Dipentene, linoleic acid, geraniol, and linalool react with 1 mol. of Br_2 in AcOH instantaneously, but relatively slowly with the second mol. The relation between rate of absorption of Br and structure is discussed, with particular reference to the purity of oleic acid and the ease of coupling.

β-$C_{10}H_7$·OH reacts rapidly with $(SCN)_2$; oleic acid, *cyclo*hexene, and anthracene react more slowly; PhOH and NH_2Ph barely react. $(SCN)_2$ is a less potent cationoid reagent than is Br. Results obtained by Brunner's method, but using 2 mols. of KI, are very similar to those obtained using 1 mol. 9-Nitroanthracene reacts more rapidly with NaO·C_5H_{11} than with NaOEt, and still more slowly with NaOMe.

R. S. C.

Condensations by sodium. XIII. Wurtz–Fittig synthesis of amylbenzene and reactions of sodium benzyl. A. A. Morton and F. Fallwell, jun. (J. Amer. Chem. Soc., 1938, **60**, 1429—1431).—C_5H_{11}Na and PhCl give little C_5H_{11}Ph, even if the C_5H_{11}Cl and PhCl are added together to Na; the main product is a *polymeride*, b.p. 155—165°/4 mm., containing 1 C_5H_{11} and 3 Ph, and probably formed by disproportionation to C_5H_{12} and $C_6H_4<$. Further, NaPh reacts very incompletely with C_5H_{11}Cl or PhCl. When NaPh is prepared from C_5H_{11}Cl and Na in C_6H_6, converted by PhMe into CH_2PhNa, and caused to react with BuCl or C_5H_{11}Cl at 75°, 70% of C_5H_{11}Ph or 61% of C_6H_{13}Ph, respectively, is formed. CH_2Cl_2 similarly gives 18% of $CH_2(CH_2Ph)_2$, and MeI or EtBr gives PhEt or PhPr, respectively. The greater reactivity of CH_2PhNa is, however, not general, for NaPh reacts quantitatively with I, PhMe, or CO_2; with $(CH_2O)_3$, C_5H_{11}Na, NaPh, and CH_2PhNa give 28% of C_6H_{13}·OH, 19% of CH_2Ph·OH, and 17% of CH_2Ph·CH_2·OH, respectively.

R. S. C.

Condensation of aliphatic alcohols with aromatic hydrocarbons. I. Preparation of mesitylene and *s*-triethylbenzene. J. F. Norris and J. N. Ingraham (J. Amer. Chem. Soc., 1938, **60**, 1421—1423).—Alcohols and $AlCl_3$ react to give $AlCl_2$·OR, which decomposes, when heated, into RCl and AlOCl. The mixture is thus effective for alkylation of aromatic hydrocarbons. When alkyl halides are used, <1 mol. of $AlCl_3$ per mol. of C_6H_6 gives a complex mixture, but 2 mols. of $AlCl_3$, 3 of RCl, and 1 of C_6H_6 give mainly *s*-$C_6H_3R_3$. Similarly, addition of MeOH (1·33 mols.) and PhMe (0·33 mol.) to PhMe (0·33 mol.) and $AlCl_3$ (2·66 mols.) at 10—15° and subsequent heating at 110° give a good yield of *s*-$C_6H_3Me_3$, obtained in better yield from *m*-xylene, MeOH, and $AlCl_3$ in the mol. proportions 1 : 1 : 3. EtOH and C_6H_6 similarly give *s*-$C_6H_3Et_3$, b.p. 214·8°/755·1 mm. (corr.), the identity of which is proved by prep. of the Br_3-, m.p. 104·6—104·8°, and $(NO_2)_3$-derivative, m.p. 112·4—112·6°, and by oxidation to *s*-$C_6H_3(CO_2H)_3$.

R. S. C.

Influence of directing groups on nuclear reactivity in oriented aromatic substitution. IV. Nitration of the halogenobenzenes. M. L. Bird and C. K. Ingold (J.C.S., 1938, 918—929; cf. A., 1931, 1405).—Rates of nitration are determined in terms of the rate of nitration in C_6H_6; *e.g.*, in $AcNO_3$–Ac_2O at 18° (C_6H_6 = 1): PhF, 0·15; PhCl, 0·033; PhBr, 0·030; PhI, ~0·18. The difference in the rates of nuclear and side-chain substitution is attributed to the greater relative importance of polarisability effects, particularly the electromeric, in the former case; it is deduced that these effects collectively are electron-releasing in the order I > Br > Cl > F. Nitrations of PhCl and PhBr (+ C_6H_6) by $AcNO_3$ in excess of Ac_2O, MeCN, or $MeNO_2$ at 0°, 25°, and 35° are examined in detail. Solvent effect on the relative reaction rates is small and irregular, but the temp. effect is large and regular. It shows that the orienting substituents alter reaction rates at the several nuclear positions mainly by changing the energies of activation.

A. T. P.

Action of alcoholic alkali on polychloro- and polybromo-benzenes in methyl ethyl ketone. T. van der Linden (Rec. trav. chim., 1938, **57**, 781—788).—NaOMe in COMeEt converts C_6Br_6 into C_6HBr_5 and C_6HBr_5 into $C_6H_2Br_4$ (80% of which is the 1 : 2 : 4 : 5-compound), but has little effect on less brominated benzenes. Reaction in $COMe_2$ is similar, but in EtOH and, more so, in C_5H_{11}·OH or C_6H_6 is slower. In COMeEt C_6Cl_6 and NaOMe give C_6Cl_5·OMe, less chlorinated benzenes being substantially unaffected.

R. S. C.

Reduction reactions of *p*-dinitrobenzene. I. Antener (Helv. Chim. Acta, 1938, **21**, 812—816).—*p*-$C_6H_4(NO_2)_2$ is converted by boiling NaOMe–MeOH into 4 : 4′-dimethoxyazobenzene, m.p. 116°, and *p*-nitroanisole, m.p. 53°. In alkaline solution *p*-$C_6H_4(NO_2)_2$ is reduced by glucose to 4 : 4′-dinitroazoxybenzene, m.p. 200°, and 4 : 4′-dinitroazobenzene, m.p. 220°.

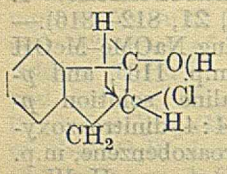
H. W.

Nitration of benzenesulphonyl chloride and fluoride. G. M. Bennett and P. V. Youle (J.C.S., 1938, 887—893).—$PhSO_2Cl$ and abs. HNO_3–H_2SO_4 at 30° afford a nitration product, converted (96%) by NH_2Ph into mixed nitrobenzenesulphanilides (80% *m*-NO_2-derivative from C_6H_6), analysed by thermal means, using the thaw-point device (A., 1936, 1241), or by extraction with amyl valerate at 20° and examination of vals. of *n*. Anomalous results by the latter method are due to the presence of 2 : 4 : 6-trinitro-3-hydroxydiphenylamine (I) [2-*chloro*-3 : 4 : 6-*trinitrodiphenylamine* has m.p. 147—148° (3-*piperidino*-derivative, m.p. 161—162°)]. The analyses show *m*- (*Na* salt, anhyd. and $+2H_2O$), 91·3±0·5; *o*- (*Na* salt, anhyd. and $+2H_2O$), 5·2±1; and *p*-, 1·8±1%, -NO_2·C_6H_4·SO_2·NHPh (cryst. forms examined), with

1·7±1% of (I). $PhSO_2F$ gives 95·6% of *m*-NO_2-derivative (thermal method); *p*-, m.p. 79°, and *o*-, m.p. 59°, -NO_2·C_6H_4·SO_2F, are described. Fuming HNO_3 and *pp'*-(NO_2·C_6H_4·S·)$_2$, new m.p. 181° (sulphoxide, m.p. 177—179°; sulphone, m.p. 251—254°), give the sulphonic acid, converted through the chloride into p-*nitrobenzenesulphonanilide*, m.p. 171° (anhyd. *Na* salt). A. T. P.

Preparation of disaccharine. (Derivatives of *mm'*-ditolyl.) M. Dominikiewicz and M. Kijewska (Arch. Chem. Farm., 1936, **3**, 27—33; Chem. Zentr., 1936, ii, 1719).—Tetrazotised *mm'*-dimethylbenzidine is converted by SO_2 in presence of Cu powder into 3 : 3'-*ditolyl*-4 : 4'-*disulphinic acid*, decomp. 150°, and thence by oxidation ($KMnO_4$–K_2CO_3) into 3 : 3'-*ditolyl*-4 : 4'-*disulphonic acid* (*K* salt, m.p. >300°), which with PCl_5 affords the *disulphonyl chloride*, m.p. 164—166°, and this with $(NH_4)_2CO_3$ at 150° the *diamide* (I), resinifies at 230—240°. Oxidation of (I) to the dibasic acid was not achieved. A. H. C.

Reactions of indene dichloride and the *cis*- and *trans*-chlorohydrins. Mechanism of ketone formation. C. M. Suter and G. A. Lutz (J. Amer. Chem. Soc., 1938, **60**, 1360—1365).—Indene and Cl_2 in CCl_4 give a homogeneous dichloride (I), b.p. 83—85°/2 mm., obtained also by PCl_5 from the *trans*-chlorohydrin (II) and by $SOCl_2$ from (II) or its *cis*-isomeride (III). Hydrolysis of (I) gives mostly (II) with some (III). Pyrolysis of (I) at 225—235° gives HCl and 37% of 2-chloroindene (IV), a trace being formed also by distillation in vac. $HgCl_2$ in $MeNO_2$ probably does not affect (I). Pt-hydrogenation of (IV) gives indane; conc. H_2SO_4 resinifies it slowly. P_2O_5 in CCl_4 converts (II) and (III) into (IV), but under certain conditions (II) gives an *ether*, $C_{18}H_{16}OCl_2$, b.p. 153—155°/3 mm., which with Br gives HBr and a compound, decomposed at the b.p./760 mm. into (IV). (III) yields indan-1-one in H_2O at <80°, the rate of reaction being unaffected by acid, but greatly accelerated by alkali or $Ag^{\cdot}$ (removes HCl); the reaction mechanism is thus that illustrated in the annexed formula. $Ag^{\cdot}$ is without effect on (II), which in slightly alkaline solution at 100° gives mostly indan-2-one, reaction occurring by way of the ether. (II) and, more readily, (III) give indan-1-one in dil. H_2SO_4. With aq. NaOAc (III) gives a mixture, containing mostly the *trans*-glycol, but no ketone. R. S. C.



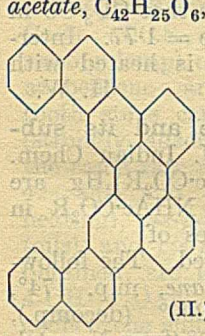
Constitution of monobromodialene [bromodihydronaphthalene]. H. A. Weidlich (Ber., 1938, **71**, [*B*], 1201—1202).—The product obtained by loss of HBr from 1 : 2-dibromo-1 : 2 : 3 : 4-tetrahydronaphthalene is 2-*bromo*-3 : 4-*dihydronaphthalene* (I) since it is converted by Mg in Et_2O followed by CO_2 into 3 : 4-dihydro-2-naphthoic acid, β-$C_{10}H_7$·CO_2H, $C_{10}H_8$, and 2 : 2'-di-3 : 4-3' : 4'-dihydrodinaphthyl (II). Further the Mg derivative of (I) and 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene yield (II) and 2 : 1'-*di*-3 : 4-3' : 4'-*dihydrodinaphthyl*, m.p. 87°, dehydrogenated (Pd–C at 300°) to 2 : 1'-dinaphthyl. H. W.

Halogenation. XX. Halogenation of fluorene. P. S. Varma and V. S. Rao (J. Indian Chem. Soc., 1938, **15**, 72—76; cf. A., 1937, II, 331).—2-*Chloro*-7-*bromofluorene*, m.p. 157°, is obtained by brominating 2-chlorofluorene (I) (prep. by Cl_2 and a little I in C_6H_6 at 80—90°) in presence of a little Fe in $CHCl_3$, by chlorinating 2-bromofluorene (II) with a little I in $CHCl_3$ in light, and by diazo-reactions from 2-chloro- (III) or 2-bromo-7-aminofluorene (IV). Addition of HNO_3–oleum to (I) and I in AcOH and heating at 100° gives 2-*chloro*-7-*iodofluorene*, m.p. 122°, also obtained from (III) and by a diazo-reaction, applied to the reduction product (not isolated) of 2-iodo-7-nitrofluorene. 2-*Bromo*-7-*iodofluorene*, m.p. 162°, is prepared by HNO_3–oleum from I and (II) or (IV) and by a diazo-reaction from 2-iodo-7-aminofluorene (V). Iodination, as above, of 2 : 7-dibromofluorene gives 2 : 7-*dibromo*-x-*iodofluorene*, m.p. 146·5°. The Cl_2-compound gives 2 : 7-*dichloro*-x-*bromofluorene*, m.p. 143°. 2 : 7-*Di-iodofluorene*, m.p. 155·5°, is prepared from 2 : 7-diaminofluorene, from (V), and by iodination, as above, of fluorene in boiling AcOH. R. S. C.

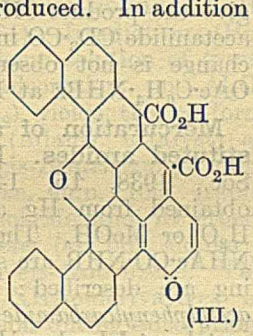
Synthesis of condensed ring systems. I. H. A. Weidlich (Ber., 1938, **71**, [*B*], 1203—1209).—Dodecahydrophenanthrene-9 : 10-dicarboxylic anhydride, readily obtained from octahydrodiphenyl and maleic anhydride (I), is converted by Br in $CHCl_3$ into *octahydrophenanthrene*-9 : 10-*dicarboxylic anhydride*, m.p. 310°, dehydrogenated (Pd–C at 300°) to *phenanthrene*-9 : 10-*dicarboxylic anhydride*, m.p. 321°. 1 : 1'-Di-3 : 4-3 : 4'-dihydrodinaphthyl and (I) in boiling $PhNO_2$ give *octahydro*-3 : 4-5 : 6-*dibenzphenanthrene*-9 : 10-*dicarboxylic anhydride*, m.p. 254° [corresponding *acid*, m.p. 125° (decomp.), and its *Me*$_2$ ester, m.p. 172°], which with Br in $CHCl_3$ gives *tetrahydro*-3 : 4-5 : 6-*dibenzphenanthrene*-9 : 10-*dicarboxylic anhydride* (II), m.p. 282° (corresponding, very unstable *acid* and its *Me*$_2$ ester, m.p. 243°); this is decarboxylated by Cu powder in boiling quinoline to *tetrahydro*-3 : 4-5 : 6-*dibenzphenanthrene*, b.p. 180°/0·1 mm., m.p. 142°. Dehydrogenation (Pd–C at 300°) of (II) affords 3 : 4-5 : 6-*dibenzphenanthrene*-9 : 10-*dicarboxylic anhydride*, m.p. >360°. 3 : 4-5 : 6-*Dibenzphenanthrene*, m.p. 177°, is best obtained by heating (II) with Cu powder, anhyd. $Ba(OH)_2$, and $SnCl_2$ at ~400° in N_2, distillation, and treatment of the distillate with S at 250—300°; in the absence of $SnCl_2$ and presence of air, the main product is 1 : 12-benzperylene, m.p. 372°. 2 : 2'-Di-3 : 4-3' : 4'-dihydrodinaphthyl and (I) in boiling xylene give *octahydropicene*-9 : 10-*dicarboxylic anhydride*, m.p. 217—218°, whence (Br in $CHCl_3$–AcOH) *tetrahydropicene*-9 : 10-*dicarboxylic anhydride*, m.p. 309°, converted by Cu powder and anhyd. $Ba(OH)_2$ at 400° followed by Pd–C at 300° into picene. 1 : 2'-Di-3 : 4-3' : 4'-dihydrodinaphthyl and (I) in boiling xylene yield *octahydro*-1 : 2-5 : 6-*dibenzphenanthrenedicarboxylic anhydride*, flat prisms, m.p. 208°, or yellow needles, m.p. 236°, whence *tetrahydro*-1 : 2 : 5 : 6-*dibenzphenanthrenedicarboxylic anhydride*, m.p. 228—229°, and 1 : 2-5 : 6-*dibenzphenanthrene*, m.p. 122°. H. W.

Dinaphthoperylene. Chemistry of chrysene. B. Schiedt (Ber., 1938, **71**, [*B*], 1248—1253).—

Gradual addition of $AlCl_3$ to chrysene (I) suspended in C_6H_6 at 60° gives dinaphthoperylene (II), m.p. 240°, which is oxidised by $Na_2Cr_2O_7$ in AcOH to 2 : 3-10 : 11-*dinaphtho*-1 : 12-*furanoperylene*-3 : 9-*quinone* (or its H_2-derivative), m.p. 288°; this does not react with *o*-$C_6H_4(NH_2)_2$ and hence is not an *o*-quinone and is reduced by N_2H_4,H_2O. The furan O is identified by reductive acetylation, whereby a *triacetate*, $C_{42}H_{25}O_6$, m.p. 287°, is produced. In addition



(II.)



(III.)

to the quinone a *ketodicarboxylic acid* (III), m.p. 268° (decomp.), is produced which is readily reduced (Zn dust in AcOH–C_5H_5N or $NHPh{\cdot}NH_2$ in AcOH–C_5H_5N) to a *substance*, $C_{35}H_{18}O_6$, m.p. 330° (*Ac* derivative, m.p. 291°). (III) is transformed by molten alkali into phenanthrene-1-carboxylic acid, m.p. 232°, and a *phenanthrenedicarboxylic acid*, m.p. 318°, from which an anhydride could not be derived. Finely divided (I) is converted by BzCl and $AlCl_3$ in CS_2 into *tribenzoyldinaphthoperylene*, m.p. 227°, by SO_2Cl_2 in C_6H_6 into *trichlorodinaphthoperylene*, m.p. 266°, and by conc. HNO_3 in AcOH at 100° into *trinitrodinaphthoperylene*, m.p. 262°. (I) and SO_2Cl_2 in $PhNO_2$ at room temp. and then at 100° afford dichlorochrysene, m.p. 270°, oxidised by $Na_2Cr_2O_7$ in AcOH to 8-*chlorochrysene*-1 : 2-*quinone*, m.p. 248°, which with *o*-$C_6H_4(NH_2)_2$ in boiling AcOH gives the *azine*, $C_{24}H_{12}N_2Cl$, m.p. 243°. H. W.

Hydrophenanthrenes. J. R. Durland and H. Adkins (J. Amer. Chem. Soc., 1938, **60**, 1501—1505).—Hydrogenation of phenanthrene in EtOH in presence of Raney Ni gives 91% of the 9 : 10-H_2- (I), b.p. 162°/10 mm., and 4% of the 1 : 2 : 3 : 4-H_4-derivative (II), b.p. 170—171°/10 mm., m.p. 34—35° (picrate, m.p. 110—111°). If, however, a mixture of 2 mols. of H_2 and sufficient N_2 to give 100 atm. is used, hydrogenation at 110° gives 33—40% of (II), 43% of (I), and a little H_8-compound. The 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-H_8-derivative (III), b.p. 161°/10 mm., is obtained at 100°, but the 1 : 2 : 3 : 4 : 9 : 10 : 13 : 14-H_8-compound (IV), b.p. 145°/10 mm., is formed at 130° in methyl*cyclo*hexane in 25—29% yield with twice its wt. of (III). 60—70% of the $\Delta^{11:12}$-H_{12}-derivative (V), b.p. 134°/10 mm., is obtained at 200° with 26% of H_8-compounds and 5—10% of H_{14}-compound (VI), b.p. 131°/10 mm. Hydrogenation of (I) to (III) involves migration of H. Accordingly, (I) is disproportionated by Raney Ni in N_2, giving good yields of (II); the reaction proceeds with increasing velocity as the temp. is raised from 150° to 250°. (III) and (IV) are similarly isomerised at 130°, (III) being the more stable. H-migration occurs in two ways in the case of (V): a slow disproportionation to (VI) and H_8-compounds, and a shift in the position of the ethylenic linking take place during distillation. Cu–Cr_2O_3 causes most of the above-mentioned reactions, but, except for the prep. of (I), gives poorer yields and requires a 50—100° higher temp. In particular, in the H_2–N_2 prep. of (II) the temp. necessary depends on the pressure with Cu–Cr_2O_3, but not with Raney Ni, and with the former catalyst reaction is never complete. The structure of (V) is uncertain, depending on absorption of 1 mol. of H_2 (Raney Ni; 240°) to give (VI), analysis, and correspondence of *n* and *d* with recorded data; presence of 5—10% of (III), (IV), or (VI) is not excluded and rigid purification is impossible owing to migration of H. O_3 in CCl_4 at 0° gives (?) αβ-*di*-2-*keto*cyclo*hexylethane* [*bis*-2 : 4-*dinitrophenylhydrazone* (VII), m.p. 242—243° (decomp.); a *dinitrophenylhydrazone*, m.p. 112—114°, and a small amount of acid were also formed]. With Raney Ni–H_2 at 150°/100—125 atm. (VII) absorbs 16 H_2, giving $C_6H_3(NH_2)_3$ and 2 : 3 : 5 : 6-*ditetramethylenehexahydroazepine*, b.p. 107—110°/2 mm. (*hydrochloride*, m.p. 256—257°; *α-naphthyl-*, m.p. 153—154°, and *phenylcarbamide*, m.p. 165—167°), also obtained by H_2–Raney Ni in dioxan at 220°/200—250 atm. from *oo'*-diaminodibenzyl, m.p. 73—75° [picrate, m.p. 226—230°; benzoate, m.p. 255—257°; prep. from the *oo'*-$(NO_2)_2$-compound by H_2–Raney Ni at 100°/100 atm.]. This necessitates presence of the $\Delta^{12:13}$-H_{12}-compound in (V); the yield of (VII) is, however, only 12%, but is increased by previously heating (V) for a long time, thus proving the isomerisation of (V) and the origin of (VII) in the product formed. Separation of the H-derivatives by distillation is sometimes difficult (b.p. are given for 6, 10, 13, and 26 mm., with details of technique); phenanthrene and (II) are best separated by crystallisation, (I) and (II) by way of the picrate, and (III) and (IV) by distilling at 10—13 mm. (II) and (V) cannot be completely separated. Any desired H-derivative can be prepared in quantity by choice of method. R. S. C.

$\Delta^{2:4}$-Cholestadiene : its photochemical transformation. A. Butenandt and H. Kudssus (Z. physiol. Chem., 1938, **253**, 224; cf. A., 1938, II, 270).—The formula given for cholesterylene is to be replaced by that of a $\Delta^{3:5}$-cholestadiene. W. McC.

Preparation of β-*p*-hydroxyphenyl*iso*propylmethylamine.—See B., 1938, 764.

Derivatives of *cyclo*hexylamine.—See B., 1938, 764.

Walden rearrangement. II. Reaction of *cis*- and *trans*-2-aminodi*cyclo*pentyl with nitrous acid. W. Hückel, A. Gross, and W. Doll (Rec. trav. chim., 1938, **57**, 555—561; cf. A., 1938, II, 50).—In this series, the reaction with HNO_2 is anomalous. Na–EtOH reduces the oxime, m.p. 82° (Bz derivative, m.p. 70°), of 2-ketodi*cyclo*pentyl, b.p. 232°/740 mm., 97°/10 mm., m.p. —30° (semicarbazone, m.p. 208—210°), to trans-2-*amino*di*cyclopentyl* (I), b.p. 96—97°/10 mm. (*Bz*, *forms*, m.p. 148° and 152°, and *Ac* derivative, m.p. 116°), whereas H_2–Pt-black or, better, H_2–PtO_2 in AcOH gives about 20% of (I) and 80% of the cis-*isomeride*, b.p. 108—

111°/20 mm. (*Bz*, m.p. 128°, and *Ac* derivative). HNO_2 causes complete inversion, the *trans*- and *cis*-bases giving only the *cis*- and *trans*-alcohols, respectively, with about 50% of 1-*cyclo*pentyl-Δ^1-*cyclo*pentene. The following revised data are given: *cis*-, m.p. 55° (H phthalate, m.p. 126°; phenylurethane, m.p. 110°; p-*nitro*-, m.p. 83°, p-*benzamido*-, m.p. 141—142°, and p-*amino-benzoate*, m.p. 50°), and *trans*-2-hydroxydi*cyclo*pentyl, m.p. 8·5° (phenylurethane, m.p. 93—94°; p-*nitro*-, m.p. 78—79°, p-*amino*-, m.p. 72°, and p-*benzamido-benzoate*, m.p. 145—146°), best characterised by, and separated by way of, the 3 : 5-*dinitrobenzoates*, m.p. 144—145° and 76—78°, respectively. R. S. C.

Identification of alkylbenzenes. II. Identification of the eight amylbenzenes and *cyclo*pentylbenzene by means of their mono- and di-acetamido- and monobenzamido-derivatives. V. N. Ipatiev and L. Schmerling (J. Amer. Chem. Soc., 1938, **60**, 1476—1479).—The amylbenzenes and *cyclo*pentylbenzene (0·5—1 c.c.) are readily identified by their *p*-NHAc-, *p*-NHBz-, and $(NHAc)_2$-derivatives (method: A., 1937, II, 331). Mixed m.p. depressions are satisfactory. Some *o*-nitration also occurs if the substituent is CHRR′ (R and R′ are not H), but the *o*-NHAc-derivatives are readily removed, being much more sol. The separation of *o*- and *p*-NHBz-derivatives is sometimes difficult. The $(NHBz)_2$-derivatives have undesirably high m.p. The following are described: *p*-, m.p. 101—102°, and o-*acetamido*-, m.p. 79—80°, *p*-, m.p. 128—129°, and o-*benzamido*-, m.p. 99° (relationship established by interconversion), and 2 : 4-*diacetamido*-n-*amylbenzene*, m.p. 202°; *p*-acetamido-, m.p. 114°, *p*-benzamido-, m.p. 151° [obtained from *p*-*iso*-$C_5H_{11}\cdot C_6H_4\cdot NH_2$ (I); from *iso*-$C_5H_{11}Ph$ only a mixture, m.p. 132—136°, of *o*- and *p*-derivatives was obtained], and 2 : 4-*diacetamido*-iso*amylbenzene*, m.p. 215—216°; p-*acetamido*-, m.p. 115—116°, *p*-benzamido-, new m.p. 126°, and 2 : 4-*diacetamido*-β-*methyl*-n-*butylbenzene*, m.p. 193—194°; p-*acetamido*-, m.p. 107°, p-*benzamido*-, m.p. 127—128°, and 2 : 4-*diacetamido*-sec.-*amylbenzene*, m.p. 181—182°; p-*acetamido*-, m.p. 147—148°, p-*benzamido*-, m.p. 141—142°, and 2 : 4-*diacetamido*-sec.-iso*amylbenzene*, m.p. (anhyd.) 193° and $(+x H_2O)$ 189°; p-*acetamido*-, m.p. 145—146°, p-*benzamido*-, m.p. 154°, and 2 : 4-*diacetamido*-α-*ethyl*-n-*propylbenzene*, m.p. 199—200°; p-*acetamido*-, m.p. 164°, p-*benzamido*-, m.p. 164—165°, and 2 : 4-*diacetamido*-ββ-*dimethyl*-n-*propylbenzene*, m.p. 240—241°; p-*acetamido*-, m.p. 141—142°, *p*-benzamido-, m.p. 112—113° (lit. 158°), and 2 : 4-*diacetamido*-tert.-*amylbenzene*, anhyd., m.p. 180—181°, and $+0{\cdot}5H_2O$, *forms*, m.p. 169—170° and 179—180°; p-*acetamido*-, m.p. 134°, p-*benzamido*-, m.p. 154°, and 2 : 4-*diacetamido*-cyclo*pentylbenzene*, m.p. 228°. H_2SO_4–HNO_3 converts (I) at 0° into 3-*nitro*-4-iso*amylaniline*, m.p. 90°. R. S. C.

Karrer's theory of coupling. W. J. Hickinbottom and E. W. Lambert (Nature, 1938, **141**, 1056).—Di-*n*- (I) and di-*iso*-butylaniline (II) and di-*iso*amylaniline (III) couple normally with diazosulphanilic acid without loss of alkyl. Karrer's observations (A., 1915, i, 1073) are thus untrustworthy, and there is no experimental basis for his theory of coupling. Contrary to Karrer (*loc. cit.*), (I), (II), and (III) react with aq. HNO_2 to form *p*-NO-derivatives. L. S. T.

Exchange experiments with trideuteroacetyl compounds. H. Erlenmeyer and H. Schenkel (Helv. Chim. Acta, 1938, **21**, 706—708).—Trideuteroacetanilide (I) (90·3% pure) and AcCl (1 : 2) at 140° give the product $CH_{2\cdot56}D_{0\cdot44}\cdot COCl$ so that $CD_3\cdot CO$ in acetanilide/$CD_3\cdot CO$ in acetyl chloride = 1·77. Interchange is not observed when (I) is heated with $OAc\cdot C_6H_4\cdot NHBz$ at 148°. H. W.

Mercuration of acetylurethane and its substituted amides. L. D. Shah (J. Indian Chem. Soc., 1938, **15**, 149—151).—$(NAc\cdot CO_2R)_2Hg$ are obtained from Hg acetamide and $NHAc\cdot CO_2R$ in H_2O or MeOH. The Hg derivatives of $NHAc\cdot CO\cdot NHR$ are similarly prepared. The following are described: *Hg acetylurethane*, m.p. 174°, *acetylphenylcarbamide*, m.p. 205—206° (decomp.), *acetyl*-m-*tolylcarbamide*, m.p. 196—197° (from N-*acetyl*-N′-m-*tolylcarbamide*, m.p. 128°), *acetyl*-o-*tolylcarbamide*, m.p. 209—210°, *acetyl*-p-*tolylcarbamide*, m.p. 227—228° (decomp.), *acetyl*-α-*naphthylcarbamide*, m.p. 225—228° (decomp.), *acetyl*-β-*naphthylcarbamide*, m.p. 215—216° (decomp.), *acetyl*-m-4-*xylylcarbamide*, m.p. 231—232° (decomp.), *acetyl*-p-*anisylcarbamide*, m.p. 222° (decomp.) (from N-*acetyl*-N′-p-*anisylcarbamide*, m.p. 172—173°), and *phenylurethane*, m.p. 203°. The Hg derivatives with KI give K_2HgI_4 and the original ester (or carbamide); with N_2H_4 or $NHPh\cdot NH_2$ Hg is liberated. A. L.

4-*p*-Aminobenzenesulphonamidobenzenesulphonamides.—See B., 1938, 847.

Aromatic polysulphonamido-compounds.—See B., 1938, 764.

Electronic effect of the second nucleus on the behaviour of homonuclear naphthalene derivatives. H. H. Hodgson and R. L. Elliott (J. Soc. Dyers and Col., 1938, **54**, 264—268).—The reactions of substituents in one ring of $C_{10}H_8$ are influenced by the negative inductive effect of the other ring which *inter alia* reduces the basicity of NH_2 at 1 as compared with 2. Evidence for the existence of this effect, its electronic mechanism, and for the Erlenmeyer static formula for $C_{10}H_8$ is adduced from sundry experimental results, including (i) the preferential acetylation of β- as compared with α-$C_{10}H_7\cdot NH_2$, (ii) the formation of a hydrochloride by 3 : 1- but a stannichloride by 1 : 3-$C_{10}H_6Cl\cdot NH_2$ when the corresponding NO_2-compounds are reduced by $SnCl_2$; similarly hydrochlorides are formed by 1 : 2- and 1 : 4- but stannichlorides by 1 : 5- and 1 : 8-$C_{10}H_6(NH_2)_2$, as also by 2 : 4 : 1-$NH_2\cdot C_{10}H_5Cl\cdot NHAc$; (iii) monohydrochlorides are formed at 4 and 2, respectively, by 2 : 1 : 4- (I) and 4 : 1 : 2-$C_{10}H_5Cl(NH_2)_2$ (II) whilst (I) forms a di- but (II) a (2-)mono-acetyl derivative; (iv) HNO_2 interacts with 2 : 1 : 4-$C_{10}H_5Cl(NH_2)_2$ (III) tetrazotising 1 mol. which forthwith couples with (III) (2 mols.) eliminating Cl and yielding 2-chloro-1 : 4-bis-(1′ : 4′-diamino-2′-naphthaleneazo)naphthalene; (v) a solid Na salt is formed by 4 : 2 : 1-$NO_2\cdot C_{10}H_5Cl\cdot OH$ but with Br

or I at 2 no solid Na or K salts are formed, whereas 4-halogeno-2-nitro-α-naphthols form stable co-ordination compounds with Na, K, or Ag. The hydrolysis of 2 : 1- and 4 : 1-NO_2·$C_{10}H_6$·NHAc by boiling aq. NaOH, the formation of dinaphthyls by Ullmann's reaction, and the coupling of 1 : 5-$C_{10}H_6(OH)_2$ with diazo-compounds are similarly explained.

K. H. S.

Preparation of some *cis*-azo-compounds. A. H. Cook (J.C.S., 1938, 876—881).—Irradiation (Hg-vapour lamp) of a light petroleum solution of *trans*-azobenzene and selective adsorption on Al_2O_3 (both steps carried out in N_2) yields the *cis*-form (strongly adsorbed), reduced (Adams' catalyst) at the same rate as the *trans*-. cis-*Benzeneazo*-p-, m.p. 42—45°, and cis-pp′-*azo-toluene*, m.p. 105° (rapid heating), *cis-p*-benzeneazophenol Me and *Et* ethers (oils), and *cis-p*-chloroazobenzene (an oil), similarly obtained, are less stable than *cis*-azobenzene. The 4-OH-, -OAc-, -NH_2-, and -NHAc-derivatives of azobenzene show some separation during adsorption, but no *cis*-forms could be isolated. Benzeneazo-α-, αα′-azo-, and ββ′-azo-naphthalene, *p*-cyanoazobenzene, and *oo′*- and *mm′*-azotoluene show no evidence of *cis*-forms. The last when irradiated in air gives a *compound*, $C_{14}H_{14}ON_2$, m.p. 59°, differing from any known azoxytoluene.

A. Li.

Action of *p*-toluenesulphonyl chloride on phenols containing azo-groups. A. B. Sen (Proc. Nat. Acad. Sci. India, 1937, **7**, 218—221).—The *p-toluenesulphonates* (m.p. in parentheses) of the following are obtained when the hydroxyazobenzene is heated with *p*-C_6H_4Me·SO_2Cl and $NPhEt_2$; in no case was the phenolic OH replaced by Cl: 3-nitro-4-hydroxy- (112°), 5-bromo-3-nitro-4-hydroxy- (150°), 2′- (132°) and 4′-nitro-4-hydroxy- (167°), 2′ : 4′-dinitro-4-hydroxy- (125°), 4′-nitro-4-hydroxy-3-methyl- (180°), 3-chloro- (178°) and 3-bromo-4′-nitro-4-hydroxy- (178°), 3-benzeneazo-4-hydroxy- (152°), 3 : 4′-dinitro-4-hydroxy- (157°), 3 : 5-dibromo-4′-nitro-4-hydroxy- (171°), 3 : 2′- (154°) and 3 : 3′-dinitro-4-hydroxy- (148°), 3-nitro-4-hydroxy-4′- (135°), -3′- (124°), and -2′-methyl- (134°), 2′ : 4′ : 6′-tribromo-3-nitro-4-hydroxy- (163°) -azobenzene. *s*-Trisbenzeneazophenol does not form an ester. Of the foregoing esters only the last eight (*i.e.*, those containing NO_2 *ortho* to OH and also NO_2 or Me in the second ring) react with NH_2Ph in boiling EtOH–anhyd. NaOAc, the *p*-C_6H_4Me·SO_2·O· being replaced by NHPh. In this way the following were obtained: 3 : 4′-, m.p. 205°, 3 : 3′-, m.p. 180°, and 3 : 2′-, m.p. 166°, *-dinitro-*, 3 : 5-dibromo-4′-nitro- (?), m.p. 196°, 3-*nitro*-4′-, m.p. 138°, -3′-, m.p. 120°, and -2′-, m.p. 146°, *-methyl-*, and 2′ : 4′ : 6′-*tribromo*-3-*nitro-* (?), m.p. 154°, -4-*anilinoazobenzene*.

H. G. M.

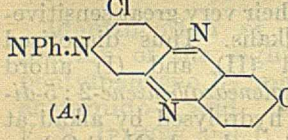
Congo-red synthesis. E. R. Kline (J. Chem. Educ., 1938, **15**, 244).—A correction (cf. A., 1938, II, 229).

L. S. T.

1-Amino-2-naphthyl ethyl ether and its homologues as middle components in secondary bisazo-dyes. H. E. Fierz-David and H. Ischer (Helv. Chim. Acta, 1938, **21**, 664—706).—Dyes in which the group *o*-X·R·N:N·R·Y-*o* (R and R′ are substituted aromatic residues: X = OH, OMe, OEt, SO_3H, O·CH_2·CO_2H, NH_2, Cl and Y = OH, NH_2) is present at least once can be converted by treatment with Cr or Cu salts into complex compounds of the corresponding 2 : 2′-dihydroxyazo-dyes. 1-*o*-Methoxybenzeneazo-β-naphthol-6-sulphonic acid is thus converted by $CuSO_4$ and C_5H_5N into the complex Cu compound of the 1-*o*-hydroxybenzeneazo-derivative, which is treated with Na_2S and then reduced ($Na_2S_2O_4$) to *o*-OH·C_6H_4·NH_2 and 1 : 2 : 6-NH_2·$C_{10}H_5(OH)$·SO_3H, showing thus that complex formation is accompanied by replacement of OMe by OH. Bisazo-dyes with 1 : 2-NH_2·$C_{10}H_6$·OEt (I) as intermediate component are unsuitable for analogous complex formation owing to their very great sensitiveness towards acids and alkalis. Thus diazotised aniline-2 : 5-disulphonic acid (II) and (I) afford 1-(4-*amino*-3-*ethoxy*-1-*naphthaleneazo*)*benzene*-2 : 5-*disulphonic acid* (III), rapidly hydrolysed by alkali at 100° to NH_3 and a product, reduced ($Na_2S_2O_4$) to (II) and 4-*amino*-2-*ethoxy*-α-*naphthol* [*hydrochloride*, m.p. 235° (decomp.); *Bz*$_2$ derivative, m.p. 186°]; in acid or neutral solution, also, NH_2 is replaced by OH. To determine the influence of SO_3H, *dyes* are prepared from (I) and sulphanilic and metanilic acid or NH_2Ph and it is shown that the effect is considerable but not of a fundamental nature. Examination of the *dyes* derived from (II) and α-$C_{10}H_7$·NH_2 (IV), 1 : 2-NH_2·$C_{10}H_6$·OMe, 2 : 1-$C_{10}H_6Me$·NH_2, and 3 : 1 : 4-NH_2·C_6H_3Me·OMe and from 1 : 2-NH_2·$C_{10}H_6$·SO_3H + *p*-NH_2·C_6H_4·SO_3H shows that the dye from (IV) is stable towards hot acid or alkali. OMe has much the same action as OEt. Me causes marked loosening of NH_2, the effect being somewhat less pronounced than that of OAlk. SO_3H appears to ensure complete stability. The 1-position in the $C_{10}H_8$ nucleus appears to have unique properties and not to be comparable with the corresponding C_6H_6 derivative. 1 : 2-NO·$C_{10}H_6$·OH is oxidised by HNO_3 to 1 : 2-NO_2·$C_{10}H_6$·OH, which is methylated (Me_2SO_4 on the Na salt in PhMe) and then reduced (Fe paste) to 1 : 2-NH_2·$C_{10}H_6$·OMe, m.p. 54°, b.p. 110°/0·05 mm. Diazotisation of (III) requires unusual care and is best effected in solutions containing about 10% of NaCl; the products couple with β-$C_{10}H_7$·OH (*dye* described), Schäffer salt, *R*-salt, or resorcinol in presence of C_5H_5N, NH_3 + EtOH, or Na_2CO_3 but not of NaOH. The bisazo-compounds are decomposed in acid or alkaline solution at 75°. In both cases the mol. is divided at the *sec.* N_2 group. Primary N_2 and OEt are largely unaffected. Degradation occurs with loss of N and re-formation of the terminal components through the stage of the mono-azo-dye of the two first components whereby OH replaces 1-NH_2. Marked decomp. does not take place below 60°; at >75° this occurs also in presence of AcOH, NH_3, and org. bases, *e.g.*, C_5H_5N. A scheme of degradation is advanced. Decomp. is introduced by a hydrolysis and in its course resembles the conversion of ketonecarbazones into hydrocarbons (Wolff–Kishner). The bisazo-dye of this configuration behaves therefore like a readily hydrolysed carbazone. The prep. of 2 : 4-OH·$C_{10}H_6$·SO_3H from 1 : 2 : 4-NH_2·$C_{10}H_5(OH)$·SO_3H is described.

H. W.

Azo-dyes and their intermediates. XX. Polyazobenzenes. P. Ruggli and C. Petitjean (Helv. Chim. Acta, 1938, **21**, 711—732).—*p*-(Benzeneazo)azobenzene (I), m.p. 167°, obtained in 87% yield from PhNO and NPh:N·C_6H_4·NH_2-*p* in AcOH, when hydrogenated (Raney Ni in dioxan at 70°) and then acetylated affords p-α- or -β-*acetyl*-β-*phenylhydrazinoazobenzene*, m.p. 185°, which when further hydrogenated gives *p*-NH_2·C_6H_4·NHAc, NH_2Ph, *p*-$C_6H_4(NH_2)_2$, and NHPhAc. When boiled with acids in contact with air it is not hydrolysed but converted into (I), whereas boiling NaOH–EtOH in N_2 transforms it into *p*-phenylhydrazinoazobenzene, which is converted by HCl into a *substance*, m.p. 263—264° (probably *A*), the filtrate from which gives a *Bz* derivative, $C_{25}H_{20}ON_4$, m.p. 208°.



(*A*.)

4 : 4′-Di(benzeneazo)azobenzene, m.p. 232—233°, is readily obtained from (*p*-NH_2·C_6H_4·N:)$_2$ and PhNO in AcOH. NH_2Ph and *p*-$C_6H_4(NO)_2$ in warm EtOH containing a little AcOH yield p-(*benzeneazo*)*azoxybenzene*, NPh:N·C_6H_4·NO:NPh, m.p. 134°, which when completely hydrogenated and acetylated gives NHPhAc and *p*-$C_6H_4(NHAc)_2$ and when partly hydrogenated yields (I), also obtained by use of Zn dust and alkali. *p*-$C_6H_4(NO)_2$ and *p*-C_6H_4Br·NH_2 yield 4-*bromo*-4′-(p-*bromobenzeneazo*)*azoxybenzene*, m.p. 246°, reduced (Raney Ni in C_5H_5N) to 4-*bromo*-4′-(p-*bromobenzeneazo*)*benzene*, m.p. 274°. Analogously *p*-$C_6H_4(NO)_2$ and *p*-NH_2·C_6H_4·CO·NHAc afford 4-*acetamido*-4′-(p-*acetamidobenzeneazo*)*azoxybenzene* (II), NHAc·C_6H_4·N_2·C_6H_4·NO:N·C_6H_4·NHAc, m.p. 317°, hydrolysed by N-KOH–EtOH to the corresponding *diamine* (III), m.p. 246—247° [Bz_2 derivative, m.p. 328°; (:CHPh)$_2$ *compound*, m.p. 209°]. (III) and PhNO or *p*-$C_6H_4(NO)_2$ and *p*-NH_2·C_6H_4·N_2Ph yield 4-*benzeneazo*-4′-(p-*benzeneazobenzeneazo*)-*azoxybenzene* NPh:N·C_6H_4·N:N·C_6H_4·NO:N·C_6H_4·N:NPh, m.p. 257°, contaminated with the -*azobenzene*, C_6H_4(N:N·C_6H_4·N:NPh)$_2$ (IV). Hydrogenation (Raney Ni in C_5H_5N at room temp.) of (III) and treatment of the product with boiling Ac_2O under N_2 gives 4-*acetamido*-4′-(p-*acetamidobenzeneazo*)*azobenzene*, m.p. 325° (corresponding Bz_2 derivative, m.p. 336°), hydrolysed (1·4N-NaOH) to 4-*amino*-4′-(p-*aminobenzeneazo*)*azobenzene*, m.p. 256—257°. This base with an excess of PhNO in boiling AcOH yields (IV), m.p. 275°. *p*-NHAc·C_6H_4·N:N·C_6H_4·NH_2-*p* (V) and *p*-$C_6H_4(NO)_2$ afford the *substance*, *p*-C_6H_4(N:N·C_6H_4·N:N·C_6H_4·NHAc)$_2$, amorphous, decomp. 290—300°, hydrolysed by alkali to the corresponding *diamine*, m.p. 292°, which with PhNO yields a *substance*, $C_{42}H_{30}N_{12}$. *p*-C_6H_4(N_2·C_6H_4·NH_2-*p*)$_2$ and Ac_2O in cold C_5H_5N yield 4-*amino*-4′-(p-*acctamidobenzeneazo*)*azobenzene*, m.p. 271—272°, which does not appear to condense with *p*-$C_6H_4(NO)_2$. (V) and 30% H_2O_2 in AcOH yield a mixture (VI), m.p. 333—335° (decomp.), of (:N·C_6H_4·N_2·C_6H_4·NHAc)$_2$ and (II), hydrolysed to a mixture of the *bases*, m.p. 263°. Catalytic hydrogenation of (VI) yields homogeneous 4 : 4′-*di*-(p-*acetamidobenzeneazo*)*azobenzene*, m.p. 345—348° (decomp.), hydrolysed to the *diamine*, m.p. (indef.) 280—283°. H. W.

Diazo-chemistry. Tetrazotisation of *o*-phenylenediamine. H. A. J. Schoutissen (Rec. trav. chim., 1938, **57**, 710—718).—The tetrazotisation of phenylenediamines is reviewed. The following is new. *o*-$C_6H_4(NH_2)_2$ is tetrazotised by NO·HSO_4 in H_3PO_4 or AcOH, freed from excess of HNO_2, and coupled with 1 mol. of PhOH (in AcOH), thus giving a cryst. *product* (I), which explodes when heated, and is reduced by abs. EtOH at 100° to *p*-OH·C_6H_4·N_2Ph. Coupling with PhOMe or PhOEt results in loss of Me or Et and gives (I); β-$C_{10}H_7$·OH (1 mol.) gives a product, reduced by EtOH to 2 : 1-OH·$C_{10}H_6$·N_2Ph. $SnCl_2$-reduction of tetrazotised *o*-$C_6H_4(NH_2)_2$ gives only *o*-$C_6H_4(NH_2)_2$. The above mono-couplings show the existence of *o*-N_2X·C_6H_4·N:NX in strong acid. In dil. acid the second N_2X couples. R. S. C.

Adsorption of diazo-compounds on cadmium and magnesium hydroxides. III. Purification of nitrodiazoamino-compounds. F. P. Dwyer (J. Proc. Austral. Chem. Inst., 1938, **5**, 67—77).—Nitro- and dinitro-diazoamino-compounds are obtained pure by dissolving in aq. MeOH and adsorption of the impurities (diazoaminoazo-compounds) on $Cd(OH)_2$. Compounds having NO_2 at 2 and/or 4 afford intense colours when dissolved in alcoholic alkali; with NO_2 at 3 the colour is weak. The m.p. of 17 purified compounds are recorded: 2-, m.p. 105—106°, 3-, m.p. 132°, and 4-, m.p. 151°, -nitro-; 2 : 2′-, m.p. 199°, 2 : 3′-, m.p. 173—174°, 2 : 4′-, m.p. 193—194°, 3 : 3′-, m.p. 197—198°, 3 : 4′-, m.p. 226°, and 4 : 4′-, m.p. 227°, -dinitro-; 2-nitro-3′-, m.p. 120°, and -4′-, m.p. 113—114°, 3-nitro-2′-, m.p. 114°, -3′-, m.p. 115°, and -4′-, m.p. 108°, and 4-nitro-2′-, m.p. 146—147°, -3′-, m.p. 149°, and -4′-, m.p. 160°, -methyl-benzenediazoaminobenzene. K. H. S.

Iodometric determination of phenol. B. G. Šimek and S. Polátšik (Mitt. Kohlenforschungsinst. Prag, 1937, **3**, 204—217).—Reaction between PhOH and I in the presence of borax leads to the formation of complex mixtures having no definite stoicheiometric composition; it cannot be used as the basis of a method of determining PhOH. A. B. M.

Crystalline products of the initial reaction in the formation of phenol plastics. H. Stäger and J. Biert (Helv. Chim. Acta, 1938, **21**, 641—650).—Trihydric phenolic alcohols are not formed during the production of phenol plastics in alkaline solution. Oily or resinous condensation products are obtained from PhOH, CH_2O, and NaOH or $Ca(OH)_2$ in the mol. ratio 1 : 3 : 1. From PhOH, CH_2O, and NH_3 (1 : 3 : 0·8) cryst. hexamethylenetriphenol is isolated. Molar mixtures of PhOH and alkali with a slight excess of CH_2O afford *o*- and *p*-OH·C_6H_4·CH_2·OH. *m*- or *p*-Cresol, CH_2O, and NaOH (1 : 1 : 1) do not give cryst. products but merely resinous mixtures; if the ratio is 1 : 2 : 1 the corresponding hydroxytoluyl alcohols are obtained cryst. Acid (HCl) condensation of PhOH and CH_2O (1 : 1 or 2 : 1) gives derivatives of dihydroxydiphenylmethane. PhOH, CH_2O, and NaOH (1 : 1·4 : 1·2) give *o*- and *p*-OH·C_6H_4·CH_2·OH, whereas $CH_2(C_6H_4$·OH-*p*$)_2$ results when the ratio is 1 : 1 : 0·2. It is therefore possible under suitable conditions for

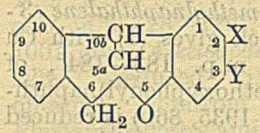
the same primary cryst. products to result in acid and in alkaline solution. The following courses of action are probable: $R{\cdot}OH+CH_2O\rightarrow OH{\cdot}R'{\cdot}CH_2{\cdot}OH$ (I); $R{\cdot}OH+xCH_2O\rightarrow OH{\cdot}R^x(CH_2{\cdot}OH)_x$; (I) $+R{\cdot}OH\rightarrow H_2O+OH{\cdot}R'{\cdot}CH_2{\cdot}R'{\cdot}OH$ (II); (II) $+CH_2O\rightarrow OH{\cdot}R'{\cdot}CH_2{\cdot}R''(OH){\cdot}CH_2{\cdot}OH$ (III); (III) $+R{\cdot}OH\rightarrow OH{\cdot}R'{\cdot}CH_2{\cdot}R''(OH){\cdot}CH_2{\cdot}R'{\cdot}OH$ or, in general, $xR{\cdot}OH+(x-1)CH_2O\rightarrow OH{\cdot}R'{\cdot}CH_2{\cdot}R''(OH{\cdot}CH_2)_{x-2}{\cdot}R'{\cdot}OH+(x-1)H_2O$. The second stage is doubtful. H. W.

Properties and uses of pentachlorophenol. T. S. Carswell and H. K. Nason (Ind. Eng. Chem., 1938, **30**, 622—626).—$C_6Cl_5{\cdot}OH$, m.p. 190·2°, in dil. aq. EtOH can be titrated with standard NaOH to thymol-blue; 1, 5, and 25% aq. solutions of the Na salt have p_H approx. 8·0, 9·6, and 10·5, respectively. The phenol is stable to heat and boiling H_2O or dil. acids. It yields coloured Cu, Ag, and Hg salts. Data for solubility and v.p. are given. The min. lethal dose (Na salt) intravenously in rabbits and guinea-pigs is approx. 36 mg., and subcutaneously 60 mg., per kg.; the toxæmia produced is accompanied by fever, hyperglycæmia, glycosuria, and circulatory failure. Comparative data for its fungicidal properties are tabulated and its use for preserving timber etc. is discussed. F. O. H.

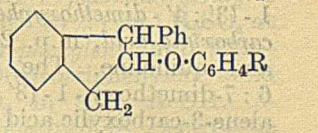
Ozonisation of anethole, estragole, and *ψ*-estragole. Properties of ozonides. E. Briner and S. de Nemitz (Helv. Chim. Acta, 1938, **21**, 748—671).—Ozonisation of p-$OMe{\cdot}C_6H_4{\cdot}CH{:}CHMe$ (I) occurs more regularly and with less production of resinous products that does that of p-$OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH{:}CH_2$ or p-$OMe{\cdot}C_6H_4{\cdot}CMe{:}CH_2$. Spontaneous scission of the ozonide of (I) gives p-$OMe{\cdot}C_6H_4{\cdot}CO_2H$ and MeCHO, whereas in the presence of H_2O the products are $OMe{\cdot}C_6H_4{\cdot}CHO$ and AcOH and reductive fission affords the two aldehydes. The action of reducing agents (KI, $NaHSO_3$) proves that the ozonide exercise a peroxidising action equal to that of the absorbed O_3. The constitution of ozonides is discussed. H. W.

Preparation of *N*-monomethylated derivatives of aminophenols. M. Morren (Congr. Chim. ind. Bruxelles, 1935, **15**, I, 383—386; Chem. Zentr., 1936, ii, 1909).—p-$NH_2{\cdot}C_6H_4{\cdot}OH$ (I) is N-methylated (yield 70%) by first converting into p-$OH{\cdot}C_6H_4{\cdot}NH{\cdot}CN$ [from (I) and CNCl in aq. NaOAc at 20°], methylating this (Me_2SO_4; 10% NaOH), and hydrolysing the p-$OH{\cdot}C_6H_4{\cdot}NMe{\cdot}CN$ with boiling 20% H_2SO_4. p-$OH{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}NH_2$ is methylated (Me_2SO_4) to p-$OMe{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}NH_2$. A. H. C.

Reaction of indene dichloride with phenols. C. M. Suter and G. A. Lutz (J. Amer. Chem. Soc., 1938, **60**, 1365—1368).—Indene dichloride and p-$C_6H_4Cl{\cdot}OH$ at 150—170° give 2 HCl, 2-*chloro*-5a : 10b-*dihydro* 6-*benz*(b)*indeno*[-1 : 2-d]-*furan* [(I); X=Cl; Y=H], m.p. 114—115°, b.p. 185—195°/4 mm. (unaffected by HI or $KMnO_4$), 3-5′-*chloro*-2′-*hydroxyphenylindene*, b.p. 180—190°/4 mm. (*benzoate*, m.p. 139—140°), and 1 : 1-*di*-(5′-*chloro*-2′-*hydroxyphenyl*)-*indane*, b.p. 257—262°/4 mm. *m*-Cresol gives the *ether* [(I); X=H; Y=Me], b.p. 170—175°/4 mm., m.p. 131·5—132·5° (with Br gives HBr and a *substance*, $C_{16}H_{12}OBr_2$, m.p. 234·5—235°), impure *hydroxy-m-tolylindene*, b.p. 175—185°/4 mm., and 1 : 1-*dihydroxy*-m-*tolylindane*, b.p. 250—255°/4 mm. *p*-Cresol gives the *ether* [(I); X=Me; Y=H], b.p.



(I.)



(II.)

189—195°/4 mm., m.p. 85—86°, *hydroxy*-p-*tolylindene*, and 1 : 1-*dihydroxy*-p-*tolylindane*, b.p. 250—255°/4 mm. PhOH gives the *ether* [(I); X=Y=H], m.p. 78·5—79°, b.p. 165—175°/4 mm. [Br_2-derivative, m.p. 195—196° (decomp.)], *dihydroxydiphenylindanes* (?), m.p. 224—225° (*Me ether*, m.p. 208—210°; also obtained in boiling PhBr in 8% yield), and (mostly) b.p. 250—255°/4 mm. [derived *di*(*aryloxyacetic acid*) (Ag_2 salt); the Me_2 *ether*, b.p. 200—210°/3 mm., with C_6H_6 and $AlCl_3$ gives PhOMe and (?) 3-phenylindene]. Ethers (I) with C_6H_6 and $AlCl_3$ give 3-phenylindene and the appropriate phenol, probably by way of (II); *e.g.*, (I) (X=Me; Y=H) gives *p*-cresol. M.p. are corr. R. S. C.

Cyclic acetals from diacetyl and pyrocatechol. J. J. van der Spek (Rec. trav. chim., 1938, **57**, 677—680).—The cryst. product obtained from Ac_2 and o-$C_6H_4(OH)_2$ (van der Spek, Diss., Delft, 1938) is o-$C_6H_4{<}\begin{matrix}CO{\cdot}CR{\cdot}O\\CO{\cdot}CR{\cdot}O\end{matrix}{>}C_6H_4$-$o$ (I) (R=Me) and not, as previously supposed, the *substance*, $[o$-$C_6H_4{<}\begin{matrix}O\\O\end{matrix}{>}CMe{\cdot}]_2$, which is obtained (m.p. 127—128°) by condensing o-$C_6H_4(OH)_2$ with $COMe{\cdot}CHMe{\cdot}OAc$ to give o-$C_6H_4{<}\begin{matrix}O\\O\end{matrix}{>}CMe{\cdot}CHMe{\cdot}OAc$, which is then hydrolysed, oxidised, and finally condensed further with o-$C_6H_4(OH)_2$. Similarly, the product, m.p. 159°, obtained from o-$C_6H_4(OH)_2$ and $(CHO)_2$ is (I) (R=H). Both compounds (I) have the same dipole moment (1·26), and hence a *cis*-structure. R. S. C.

Constituents of natural phenolic resins. XI. Synthesis of 6 : 7-dimethoxy-1-(3′ : 4′-dimethoxyphenyl)-2- and -3-methylnaphthalenes. R. D. Haworth and D. Woodcock (J.C.S., 1938, 809—813).—The lactone of 6 : 7-dimethoxy-1-(3′ : 4′-dimethoxyphenyl) - 2 - hydroxymethylnaphthalene - 3 - carboxylic acid (A., 1935, 860; 1936, 80) is reduced (Na–Hg in boiling KOH) to *one*, m.p. 180°, of the four possible racemates of conidendrin Me_2 ether (*loc. cit.*), since it is oxidised by NaOBr to a mixture of a lactone, $C_{22}H_{24}O_7$, m.p. 205—206°, 2-veratroylveratric acid, and (?) 6 : 7-dimethoxy-1-(3′ : 4′-dimethoxyphenyl) - 1 : 2 : 3 : 4 - tetrahydronaphthalene - 2 : 3 - dicarboxylic acid (Me_2 ester, m.p. 148—149°), and (abnormally) by $Pb(OAc)_4$ in AcOH to 6 : 7-*dimethoxy*-1-(3′ : 4′-*dimethoxyphenyl*)-2-*methylnaphthalene* (I), m.p. 141°, also synthesised as follows: 3 : 4-$(OMe)_2C_6H_3{\cdot}COEt$ (from veratrole, EtCOCl, and $AlCl_3$ in $PhNO_2$) with Br in $CHCl_3$ yields *α-bromo-α-veratroylethane*, m.p. 83—84°, which when treated with $CHNa(CO_2Et)_2$ in C_6H_6 and the product hydrolysed and heated to 180° affords *β-veratroyl-n-butyric acid*, m.p. 129°. The Na salt of this with veratraldehyde and Ac_2O yields the *lactone* m.p.

183°, of β-veratroyl-α-veratrylidene-*n*-butyric acid. The crude acid with CH_2N_2 followed by MeOH–HCl affords the *Me* ester, m.p. 178°, of 6 : 7-*dimethoxy*-1 - (3′ : 4′ - *dimethoxyphenyl*) - 2 - *methylnaphthalene* - 3 - *carboxylic acid*, m.p. 232°, which gives (I) with Cu and quinoline. The *chloride*, m.p. 183—184°, of 6 : 7-dimethoxy - 1 - (3′ : 4′ - dimethoxyphenyl)naphthalene-3-carboxylic acid (II) (A., 1935, 860) is reduced (Pd–$BaSO_4$ in xylene) to the 3-*aldehyde*, m.p. 163—164° (*oxime*, m.p. 185°), the *hydrazone*, m.p. 175—176°, resolidifying with m.p. 305—306°, or *semicarbazone*, m.p. 223—224°, resolidifying with m.p. 308—309°, of which on reduction (NaOEt) and remethylation (CH_2N_2) gives 6 : 7-dimethoxy-1-(3′ : 4′-dimethoxyphenyl)-3-methylnaphthalene (cf. A., 1937, II, 498) (*picrate*, m.p. 133°).

6 : 7 - *Dimethoxy* - 1 - (3′ : 4′ - *dimethoxyphenyl*) - 3 - *methyl*-1 : 2 : 3 : 4 - *tetrahydronaphthalene* - 2 - *carboxylic acid*, m.p. 220—222°, is synthesised from OH·CH:C(CO_2Et)·CHMe·CO_2Et and veratrole, by treating with conc. H_2SO_4–AcOH, followed by boiling AcCl, then $AlCl_3$ in $PhNO_2$ at 0°, and reducing the product with Zn–Hg and HCl. Reduction (Na–Hg in boiling KOH) of (II) yields 1 : 2 : 3 : 4-*tetrahydronaphthalene*-3-*carboxylic acid*, m.p. 170° (*monohydrate*, m.p. 133°; *Me* ester, m.p. 143—144°).

A. Li.

Aromatic hydroxy-sulphones. M. E. Heppenstall and S. Smiles (J.C.S., 1938, 899—905).—Na salts of *o*-OH-sulphones may be obtained in the covalent state, a fact consistent with the rearrangement of OH-sulphones to ether sulphinic acids (A., 1934, 647). They are decomposed by *o*-OH·C_6H_4·CHO, are readily methylated in cold aq. solution, and react normally with 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$. The following sulphones have been prepared: substituted diphenylsulphones: 2-hydroxy-, m.p. 97° [*monohydrate*, m.p. 82°; *Me ether*, m.p. 143°; *Ac*, m.p. 84°, and *Na* derivative, m.p. 290—293° (more sol. in cold $CHCl_3$ than in hot)]; 3-*hydroxy*-, m.p. 163° (from 3-nitro- via 3-*amino*-, m.p. 117°) (*Me ether*, m.p. 90·5°); 4-hydroxy- (from 4-nitro-) (*monohydrate*); 2-*methoxy*-5-*methyl*-, m.p. 140° (from 2 : 5-OMe·C_6H_3Me·SO_2Cl, C_6H_6, and $AlCl_3$), hydrolysed (HBr) to the *phenol*, m.p. 139° (*monohydrate*; *Na* derivative, m.p. 260°, sol. in warm $CHCl_3$); 5-*chloro*-2-*methoxy*-, m.p. 144° (from 2 : 5-OMe·C_6H_3Cl·SO_2Cl, C_6H_6, and $AlCl_3$), hydrolysed to the *phenol*, m.p. 139° {*Ac*, m.p. 134°, and *Na* derivative, m.p. 247°; 2 : 4-*dinitrophenyl ether*, m.p. 187° [from the latter and 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$ in hot EtOH]; *Li* derivative (*dihydrate*, m.p. 198°)}; 2 : 2′-dihydroxy-5 : 5′-dimethyl- (*Ac*$_2$, m.p. 211°, and *Na* derivative, m.p. 190°); and 2-*hydroxy*-2′-*methoxy*-5 : 5′-*dimethyl*-, m.p. 153° (from 1 : 4 : 2-CO_2Et·O·C_6H_3Me·SO_2Cl, *p*-C_6H_4Me·OMe, and $AlCl_3$, and hydrolysis of the product with EtOH–NaOH) [*Na*, m.p. 219° (sol. in $CHCl_3$), and *Li* derivative]; phenylmethylsulphones: 2-*methoxy*-, m.p. 95° (by methylating *o*-OMe·C_6H_4·SO_2H), hydrolysed (HBr) to 2-*hydroxy*-, m.p. (almost anhyd.) 67° (*monohydrate*, m.p. 87·5°); 3-amino-, m. p. 58° (from 3-NO_2-compound, Sn, and HCl); 3-*hydroxy*-, m.p. 82° (from 3-NH_2-compound) (*Me ether*, m.p. 47°, also obtained from *m*-OMe·C_6H_4·SO_2H); 4-*methoxy*-, m.p. 121° (from *p*-OMe·C_6H_4·SO_2H), hydrolysed to 4-*hydroxy*-, m.p. 94° (*monohydrate*, m.p. 49°); 2-*hydroxy*-5-*methyl*-, m.p. 89° (from the Me ether and HBr) (*monohydrate*, m.p. 78°); and 5-*chloro*-2-*hydroxy*-, m.p. 140° (from the Me ether). Reduction (Na_2SO_3) of 1 : 2 : 4-OMe·$C_6H_3(SO_2Cl)_2$ and treatment of the K salt of the product with MeI affords 2 : 4-*bismethylsulphonylanisole*, m.p. 197°, hydrolysed to the *phenol* (poor yield), m.p. 220°, better prepared as follows: *p*-C_6H_4Cl·SO_2Me with $ClSO_3H$ at 170° yields 1-chloro-2-chlorosulphonyl-4-methylsulphonylbenzene, m.p. 144° (*anilide*, m.p. 161°); this, either by treatment with CHNa(CO_2Et)$_2$ and then MeI, or by reduction (HI in AcOH) to *di*-2-*chloro*-5-*methylsulphonylphenyl disulphide*, m.p. 253°, further reduction (glucose) and methylation (Me_2SO_4) to 1-*chloro*-4-*methylsulphonyl*-2-*methylthiolbenzene*, m.p. 107°, and oxidation (H_2O_2) of this, yields 1-*chloro*-2 : 4-*bismethylsulphonylbenzene*, m.p. 187°. This is readily hydrolysed to the phenol, reacts with NaOEt in boiling EtOH at about the same rate as 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$, giving the *Et ether*, m.p. 201°, and yields with NH_2Ph, 2 : 4-*bismethylsulphonyldiphenylamine*, m.p. 218°, with piperidine, N-2′ : 4′-*bismethylsulphonylphenylpiperidine*, m.p. 156°, with NaSPh in boiling EtOH, 2 : 4-*bismethylsulphonyldiphenyl sulphide*, m.p. 232°, and with $PhSO_2Na$ in boiling (CH_2·OH)$_2$, the *sulphone*, m.p. 270—271°, also obtained by oxidising the sulphide with H_2O_2 in AcOH.

A. Li.

Preparation of benzyloxyalkyl *p*-toluenesulphonates. C. L. Butler, (Misses) A. G. Renfrew, and M. Clapp (J. Amer. Chem. Soc., 1938, **60**, 1472—1473).—The glycol (5 mols.), CH_2PhCl (2 mols.), and 85% KOH (2 mols.) at 90—130° give 66—72% yields of ethylene, b.p. 131°/13 mm., *propylene*, b.p. 128°/12 mm., and *trimethylene glycol* CH_2Ph *ether*, b.p. 142°/10 mm., which with *p*-C_6H_4Me·SO_2Cl and C_5H_5N afford β-*benzyloxyethyl*, m.p. 45°, β-*benzyloxy*iso-, m.p. 49°, and γ-*benzyloxy*-n-*propyl* p-*toluenesulphonate*, m.p. 37°, respectively. *Glycerol* αγ-(CH_2Ph)$_2$ *ether* β-p-*toluenesulphonate*, amorphous, is also prepared.

R. S. C.

Stereoisomerism of *cyclo*hexanediols. II. Preparation and properties of the 1 : 4-*cyclo*hexanediols. J. Coops, J. W. Dienske, and W. M. Smit (Rec. trav. chim., 1938, **57**, 637—642; cf. A., 1938, II, 184).—Passage of dry HCl into *cis-cyclo*hexane-1 : 4-diol (CPh_3)$_2$ ether in C_6H_6 gives a syrupy compound of the free diol, 1HCl, and $x$$C_6H_6$, soon passing into a cryst. compound, 4diol,2HCl,C_6H_6 which in a vac. gives the free diol. The *trans*-ether gives similarly a very unstable, solid compound, 5 diol + 4HCl, passing rapidly into the free diol. Both diols have the properties previously reported (*loc. cit.*). The *cis*-diol is shown to give liquid crystals at 101·4° and a normal liquid at 113°, the first change requiring 4 times as much heat as does the second.

R. S. C.

Stereo-chemistry of seven-membered carbon rings. P. H. Hermans and C. J. Maan (Rec. trav. chim., 1938, **57**, 643—652).—According to Stuart models, *trans-cyclo*heptane-1 : 2-diol in a form suitable for ring-formation with H_3BO_3 occurs in the statistically preferred configurations of the "chair" form. This is, however, not the case for the *cis*-diol

in either the " boat " or the " chair " form. Yet both diols form rings with H_3BO_3. Connexion of potential energy of the mol. with considerations of the probability of forms and of chemical reactions thus appears invalid. R. S. C.

Phenanthrene series. XVI. Amino-alcohols and miscellaneous derivatives of phenanthrene. J. VAN DE KAMP, A. BURGER, and E. MOSETTIG (J. Amer. Chem. Soc., 1938, **60**, 1321—1325; cf. A., 1937, II, 423).—The following are prepared: 3-, m.p. 120·5—121°, and 9-*phenanthrodimethylamide*, m.p. 182·5—183°. β-*Dimethylaminoethyl* 3-, m.p. 202—202·5°, and 9-*phenanthroate hydrochloride* (from the acid chloride and $NMe_2{\cdot}[CH_2]_2{\cdot}OH$ in $CHCl_3$), m.p. 171—171·5° (corresponding *picrates*, m.p. 177·5—178° and 144—145°, respectively). 9-*Aminomethylphenanthrene* [by hydrogenation (slow; PtO_2) of the 9-CN-derivative in AcOH], m.p. 108—108·5° [*hydrochloride*, m.p. 292—294° (decomp.)]. 3-*Oximinoacetylphenanthrene* (by $BuNO_2$; 40—45% yield), m.p. 272—273°, which with $SnCl_2$–HCl–EtOH gives 3-*glycylphenanthrene hydrochloride*, m.p. 260—320° (decomp.) [corresponding *picrate*, m.p. 193° (decomp.)], hydrogenated (PtO_2) in EtOH to 3-β-*amino*-α-*hydroxyethylphenanthrene*, m.p. 139—139·5° [*hydrochloride*, m.p. 235—236° (decomp.); *picrate*, m.p. 218·5—219·5°]. 2-*Oximinoacetylphenanthrene* (by $C_5H_{11}{\cdot}NO_2$; 30% yield), m.p. 175—176° (decomp.). 2-*Glycyl*-[*hydrochloride*, m.p. 280—310° (decomp.); *picrate*, m.p. 185—189° (decomp.)], and 2-β-*amino*-α-*hydroxyethyl-phenanthrene*, m.p. 143—144° [*hydrochloride*, m.p. 251—254° (decomp.); *picrate*, m.p. 205—206° (decomp.)]. 3-β-*Diethylamino*-α-*acetoxyethylphenanthrene hydrochloride*, m.p. 221—221·5°. 3-1′:2′:3′:4′-*Tetrahydroisoquinolino*-4-*hydroxy*-1:2:3:4-*tetrahydrophenanthrene*, m.p. 125—126° {*acetate*, m.p. 118—122°; *Ac* derivative, m.p. 123—125° [*hydrochloride*, m.p. 200—201° (decomp.)]}. 3-*Hydroxy*-6-β-*diethylamino*-α-*hydroxyethylphenanthrene* (prep. from 6-β-diethylaminoacetyl-3-acetoxyphenanthrene perchlorate by H_2–PtO_2 in MeOH and subsequent hydrolysis), m.p. 124·5—125·5°, with Ac_2O–C_5H_5N at room temp. gives the 6-β-*diethylamino*-α-*acetoxyethyl* derivative (I) (20—30% yield) (*hydrochloride*, m.p. 199—201°), and with hot Ac_2O–NaOAc gives the 3-*Ac* derivative of (I) (*hydrochloride*, m.p. 201—202°). 3-1′:2′:3′:4-*Tetrahydroisoquinolinoacetylphenanthrene hydrochloride* (from 3-bromoacetylphenanthrene and tetrahydro*iso*quinoline at room temp.), m.p. 246—248° (decomp.), converted by H_2–PtO_2 in 80% MeOH into 3-β-1′:2′:3′:4′-*tetrahydroisoquinolino*-α-*hydroxyethylphenanthrene hydrochloride*, m.p. 198—199° (decomp.) (corresponding *picrate*, m.p. 180—181·5°). 3-*Acetoxy*-(? 7 or 8-)*acetylphenanthrene* (obtained in 1% yield as a by-product from 3-acetoxyphenanthrene, AcCl, and $AlCl_3$), m.p. 124—125°, and thence the 3-*OH*-, m.p. 237—238°, and 3-*OMe*-derivative, m.p. 93—94°, 3-*methoxy*-, m.p. 220—223° (decomp.) (*Me* ester, m.p. 127·5—128°), and 3-*hydroxy-phenanthrene*-(? 7- or 8-)*carboxylic acid*, m.p. 281—284° (decomp.). β-2-, m.p. 164—165°, and β-3-*Phenanthrylpropionhydrazide*, m.p. 189—190°, and β-3-*phenanthrylpropionamide*, m.p. 161·5—162° (all prepared from the esters). β-1:2:3:4:5:6:7:8-*Octahydro*-9-*phenanthroylpropionic acid* [from octahydrophenanthrene, $(CH_2{\cdot}CO)_2O$, and $AlCl_3$ in CS_2], m.p. 143—144°, reduced (Clemmensen) to γ-1:2:3:4:5:6:7:8-*octahydro*-9-*phenanthrylbutyric acid*, m.p. 128—129°, which with 75% (vol.) H_2SO_4 at 100° gives 4-*ketododecahydrotriphenylene*, m.p 222—222·5°, reduced to dodecahydrotriphenylene and obtained therefrom by CrO_3 in 80% AcOH. β-Phenanthrylethylamines are obtained by electrolytic reduction of β-nitro-α-phenanthrylethylenes. Conversion of phenanthraldehydes into the acrylic and propionic acids and subsequent Curtius degradation give good yields, except of the urethanes. R. S. C.

Structure and absorption [spectra] of basic triphenylmethane dyes. (MME.) RAMART-LUCAS (Compt. rend., 1938, **206**, 1656—1659; cf. A., 1938, II, 110).—The change in absorption when the salts are changed to free base is small and the degree of ionisation has little effect on the colour. The bases and some of their derivatives exist in solution in two forms in equilibrium; the colourless form probably has the same structure as the leuco-base (cf. A., 1928, 627) whereas the coloured form has Nietzki and Armstrong's quinonoid structure. Spectroscopic measurements show that the proportions of the colourless and coloured forms present depend on the nature of the dye, the solvent, p_H, and the λ of light. In EtOH, fuchsin and crystal-violet bases are almost entirely quinonoid, but alkali changes them to the colourless forms. J. L. D.

Cholesterol. XIV. *iso*Cholesterol, m.p. 141—143°, and *epi*cholesterol. R. DE FAZI (Ann. Chim. Farm., 1938, **1**, 38—42).—The *epi*cholesterol, m.p. 141°, of Marker *et al.* (A., 1936, 604) is considered identical with the author's *iso*cholesterol, m.p. 141—143° (A., 1933, 710). Structures of the two chlorodihydrocholesterols, m.p. 126—127°, and 136—138°, are discussed. E. W. W.

Oxidation of the trianhydrolactone of ouabain, and of *epi*neoergosterol. P. N. CHAKRAVORTY and E. S. WALLIS (J. Amer. Chem. Soc., 1938, **60**, 1379—1381).—Fieser and Newman's formula (A., 1936, 1116) for the trianhydrolactone from ouabain is untenable, since the acetate with CrO_3 gives no ketone and with HNO_3 gives no aromatic acid. *epi*Neoergosterol has m.p. 175—176°; its acetate, m.p. 98°, with CrO_3–AcOH at 60—65° gives a *ketone*, $C_{18}H_{20}O$, m.p. 114—115° [*semicarbazone*, m.p. 255° (decomp.)], the absorption of which resembles that of neoergopentaene (cf. Marker *et al.*, A., 1936, 1256; Windaus *et al.*, A., 1937, II, 99). R. S. C.

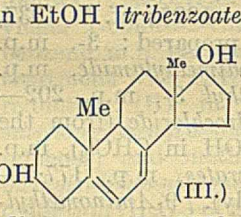
Sterol group. XXXVII. Structure of lumisterol and its stereoisomerides. I. M. HEILBRON, T. KENNEDY, F. S. SPRING, and G. SWAIN (J.C.S., 1938, 869—876).—Reduction [$Al(OPr^\beta)_3$ + $Pr^\beta OH$] of ergostatrienone yields a complex, m.p. 196°, spectroscopically identical with ergosterol, which after keeping has m.p. 155° and a much decreased light absorption. Resolution before or after with digitonin gives ergosterol and a trienol, m.p. 152° (cf. Marker *et al.*, A., 1937, II, 496) [formed by isomerisation of the unstable, intermediate *epi*ergosterol (cf. Windaus and Buchholz, A., 1938, II, 186)], which with Ac_2O and

NaOAc gives *ergostatetraene*, m.p. 104°, $[\alpha]_D^{20}$ −40·5° in $CHCl_3$. Oxidation [$Al(OBu^{\gamma})_3$ in $COMe_2$] of lumisterol gives *lumistatrienone*, m.p. 139—140°, $[\alpha]_D^{20}$ +48·7° in $CHCl_3$ [*semicarbazone*, m.p. 247° (decomp.); *enol-acetate*, m.p. 98°, $[\alpha]_D^{20}$ +293·7° in $CHCl_3$], reduced to a complex, m.p. 159·5°, of lumisterol with epi*lumisterol*, m.p. 109—110°, $[\alpha]_D^{20}$ +224·6° in $CHCl_3$ (*acetate*, m.p. 114—115°, $[\alpha]_D^{20}$ +175° in $CHCl_3$). Oxidation of dehydroergosterol yields *ergostatetraenone*, m.p. 140—142°, $[\alpha]_D^{20}$ +190° in $CHCl_3$ [*semicarbazone*, m.p. 224° (decomp.); *enol-acetate*, m.p. 161°, $[\alpha]_D^{20}$ −232·5° in $CHCl_3$], reduced to a complex of dehydro- and (unstable) *epi*dehydroergosterol. That *epi*ergo- differs from lumi-sterol and pyrocalciferol, and *epi*lumi- from ergo-sterol and *iso*pyrocalciferol substantiates the structures assumed by Windaus and Dimroth (A., 1937, II, 147). *Ergostatrienone enol-acetate* (Ac_2O–C_5H_5N), m.p. 146°, $[\alpha]_D^{20}$ −143·5° in $CHCl_3$, is hydrolysed (MeOH–KOH) to *iso*ergostatrienone (A., 1937, II, 417) (*enol-acetate*, m.p. 137°, $[\alpha]_D^{20}$ −84·6° in $CHCl_3$). A. LI.

Chemical investigation of the roots of *Hemidesmus indicus*. I. A. T. DUTTA, S. GHOSH, and R. N. CHOPRA (Arch. Pharm., 1938, **276**, 333—340).—The roots contain 0·225% (on dry wt.) of an essential oil [80% of which is 2 : 4 : 1-$OH{\cdot}C_6H_3(OMe){\cdot}CHO$ (*oxime*, m.p. 141°; *semicarbazone*, m.p. 224°), responsible for the typical odour], two sterols, *hemidosterol*, $C_{34}H_{60}O$, m.p. 182·4°, $[\alpha]_D^{30}$ +83° in $CHCl_3$ (*Ac*, m.p. 198°, and *Bz* derivative, m.p. 188·5°), and *hemidesmol*, $C_{33}H_{58}O$, m.p. 161°, $[\alpha]_D^{30}$ +57° in $CHCl_3$ (*Ac*, m.p. 188°, and *Bz* derivative, m.p. 222·5°), sugars, resins, tannins, and a small amount of a glucoside, m.p. 133—136° (decomp.). R. S. C.

Preparation and reactions of mono- and di-hydroxycholestanes. I. M. HEILBRON, W. SHAW, and F. S. SPRING (Rec. trav. chim., 1938, **57**, 529—534).—BzO_2H and Δ^4-cholestene in $CHCl_3$ give a homogeneous *oxide* (I), m.p. 100—101°, $[\alpha]_D^{19}$ +81·7°, which with a little H_2SO_4 in AcOH gives 5-*hydroxy*-4-*acetoxycholestane* (II), m.p. 175°, $[\alpha]_D^{20}$ +184°, hydrolysed by 10% KOH–EtOH to the $(OH)_2$-compound, m.p. 169—170°. (II) is resinified by dehydrating agents and converted into (I) by K–CS_2–MeI in C_6H_6; (IV) (below) is similarly converted into α-Δ^5-cholestene oxide (III). 5 : 6-Dihydroxycholestane with Ac_2O gives the 6-*acetate* (IV), m.p. 108—109°. Hydrogenation (colloidal Pd) of (I) and (III) gives cholestane. EtOH–conc. HCl dehydrates (I), (II), (III), and (IV) to the cholestadiene, m.p. 80—81°, $[\alpha]_D^{21\cdot5}$ −68·5° (absorption max. at 2350 and 2450 A. in EtOH). Cholesteryl chloride gives similarly an *oxide*, m.p. 97·5°, $[\alpha]_D^{23}$ −34·95°, and 3-*chloro*-5-*hydroxy*-6-*acetoxycholestane*, m.p. 147—147·5°, $[\alpha]_D^{19}$ −17·5°. Hydrogenation (PtO_2) of 7-keto-$\Delta^{3:5}$-cholestadiene in EtOAc gives 7-keto- (V) and 7-*hydroxy-cholestane*, m.p. 119—120°, $[\alpha]_D^{19\cdot5}$ +50·6° [better obtained from (V) by Na–$C_5H_{11}{\cdot}OH$; oxidised to (V) by CrO_3; *H phthalate*, m.p. 165—167°]. R. S. C.

$\Delta^{5:7}$-Androstadiene-3 : 17-diol. A. BUTENANDT, E. HAUSMANN, and J. PALAND [with, in part, D. VON DRESLER and U. MEINERTS] (Ber., 1938, **71**, [*B*], 1316—1322).—Δ^5-Androstenediol diacetate is oxidised by CrO_3 in AcOH at 55° to 7-*keto*-Δ^5-*androstene*-3 : 17-*diol diacetate* (I), m.p. 218—219°, $[\alpha]_D^{20}$ −135° in $CHCl_3$, hydrolysed (NaOMe) to 7-*keto*-Δ^5-*androstene*-3 : 17-*diol* ($+1H_2O$), m.p. 201°, $[\alpha]_D^{20}$ −133° in EtOH. Boiling MeOH–HCl converts (I) into $\Delta^{3:5}$-*androstadien*-17-*ol*-7-*one*, m.p. 171—172°, $[\alpha]_D^{20}$ −375° in EtOH (*acetate*, m.p. 222°, $[\alpha]_D^{20}$ −400° in $CHCl_3$). With $Al(OPr^{\beta})_3$ in $Pr^{\beta}OH$ (I) yields Δ^5-*androstene*-3 : 7 : 17-*triol*, m.p. 236°, $[\alpha]_D^{23}$ +26° in EtOH [*tribenzoate* (II), m.p. 250°, $[\alpha]_D^{23}$ +87° in $CHCl_3$]. Slow distillation of (II) in a high vac. or, better, treatment of it with boiling $NPhMe_2$ affords $\Delta^{5:7}$-*androstadiene*-3 : 17-*diol dibenzoate*, m.p. 217—218°, hydrolysed to $\Delta^{5:7}$-*androstadiene*-3 : 17-*diol* (III), m.p. 212° (*diacetate*, m.p. 132°, $[\alpha]_D^{23}$ +41° in EtOH). The absorption spectrum of (III) is almost identical with that of ergosterol and 7-dehydrocholesterol, thus supporting the assigned constitution. The physiological properties of the compounds are detailed. H. W.



(III.)

Sterols. XXXIV. Isolation of hexahydro-œstradiols from human non-pregnancy urine. R. E. MARKER, E. ROHRMANN, E. L. WITTLE, and E. J. LAWSON (J. Amer. Chem. Soc., 1938, **60**, 1512—1513; cf. A., 1938, II, 329).—Female non-pregnancy urine contains *hexahydro-œstradiols*, (I), m.p. 242° (*di-acetate*, m.p. 160°), and (II), m.p. 204° (*diacetate*, m.p. 160°), both indifferent to Br and digitonin and converted by Pt-black into equilenin. (II) is identical with a diol obtained from œstrone by Dirscherl (A., 1936, 472) and gives a *diketone*, $C_{18}H_{26}O_2$, m.p. 148°; (I) gives an isomeric *diketone*, m.p. 124°. (I) and (II) differ in configuration at $C_{(5)}$ or $C_{(10)}$. They are not present in pregnancy urine. R. S. C.

Biological formation of *epi*ætiocholanediol.—See A., 1938, III, 660.

Preparation of polyhydroxypregnane compounds. A. SERINI and W. LOGEMANN (Ber., 1938, **71**, [*B*], 1362—1366).—17-Ethinyl*iso*androstanediol is hydrogenated (Ni–MeOH) to 17-*vinyl-iso*androstanediol (I), m.p. 207°, which is converted by permonophthalic acid in $CHCl_3$ into the corresponding *oxide*, m.p. 180—182°, and by OsO_4 followed by Na_2SO_3 in boiling EtOH–H_2O into 3 : 17 : 20 : 21-*tetrahydroxy*-allo*pregnane*, m.p. 230—232°. Addition of Br in CCl_4 to (I) in Et_2O–CCl_4 containing a little C_5H_5N affords 5 : 6-*dibromo*-17-*vinylandrostanediol*, m.p. 116—118° (decomp.), transformed by OsO_4 followed by Na_2SO_3 and then by Zn dust into 3 : 17 : 20 : 21-*tetrahydroxy*-$\Delta^{5:6}$-*pregnene*, m.p. 229—231°, $[\alpha]_D^{20}$ −73·3° in dioxan, whence (Ac_2O in anhyd. C_5H_5N at room temp.) the 3 : 20 : 21-*triacetate*, m.p. 166—167°, $[\alpha]_D^{20}$ −88·5° in dioxan. 17 : 20 : 21-*Trihydroxy*-$\Delta^{4:5}$-*pregnen*-3-*one*, m.p. 233—235°, $[\alpha]_D^{20}$ +65·6° in dioxan [*semicarbazone*, m.p. 216—218° (decomp.)], is obtained by the successive action of OsO_4 and Na_2SO_3 on pregnadien-17-ol-3-one, and is converted by Ac_2O–C_5H_5N at room temp. into the 20 : 21-Ac_2 derivative, m.p. 178—179°, $[\alpha]_D^{20}$ +43·6° in dioxan. H. W.

Alkyl and alkamine esters of *p*-aminomandelic acid and related compounds. L. S. FOSDICK

and G. D. Wessinger (J. Amer. Chem. Soc., 1938, **60**, 1465—1466).—*p*-$NO_2 \cdot C_6H_4 \cdot CH(OH) \cdot CN$ with the appropriate alcohol and HCl in Et_2O at 0° gives the imino-ether hydrochloride, hydrolysed by H_2O to Me, m.p. 87°, Et, m.p. 76—77°, *Pr*$^{\alpha}$, m.p. 84—84·5°, *Bu*$^{\alpha}$, m.p. 44—45°, and β-*chloroethyl* p-*nitromandelate*, m.p. 79·5—80°, hydrogenated (PtO_2) in EtOH to *Me*, m.p. 162°, *Et*, m.p. 119—119·5°, *Pr*$^{\alpha}$, m.p. 84—84·5°, *Bu*$^{\alpha}$, m.p. 104—105°, and β-*chloroethyl* (I) p-*aminomandelate*, m.p. 95—96°. With NHR_2 at 100° (I) gives β-*di-ethyl-* (II) [*hydrochloride*, m.p. 129—133° (decomp.)], *-propyl-* [*hydrochloride*, m.p. 135—140° (decomp.)], and *-butyl-aminoethyl* p-*aminomandelate* [*hydrochloride*, m.p. 150—155° (decomp.)]. (II) is a rather weak local anæsthetic. M.p. are corr.

R. S. C.

Hydrogenation of compounds containing halogen using platinum-black. G. Vavon and R. Mathieu (Compt. rend., 1938, **206**, 1387—1389).—Many Cl- and Br-compounds in EtOH are easily reduced by H_2–Pt-black. The latter react the more readily, particularly if halogen is linked to a C adjacent to Ph or CO_2H. αβ-Dibromo-β-phenylpropionic acid, its Et ester and amide, αβ-dibromo-β-phenylethyl Me ketone, αβ-dibromo-α-phenylpropane, and $CHMeBr \cdot CHBr \cdot CO_2H$ first absorb 2 H to give 2 HBr and the corresponding ethylenes, which are then further reduced. Similar Cl_2-compounds react more slowly; intermediates could not be isolated.

J. L. D.

Constituents of natural phenolic resins. X. Structure of *l*-matairesinol dimethyl ether: condensation of reactive methylene groups with *O*-methyleugenol oxide. R. D. Haworth and J. R. Atkinson (J.C.S., 1938, 797—808; cf. A., 1936, 985).—*l*-Matairesinol Me_2 ether (I) with dil. NaOH at 180°, boiling 50% KOH, or EtOH–NaOEt followed by boiling dil. HCl yields a mixture, $[\alpha]_D^{17}$ about +18° in $CHCl_3$, of (I) with d-iso*matairesinol* Me_2 *ether*, m.p. 111—112°, $[\alpha]_D^{19}$ +78° in $CHCl_3$ [Br_2-, m.p. 144°, $[\alpha]_D^{20}$ +18·8° in $CHCl_3$, and $(NO_2)_2$-derivative, m.p. 161—162°, $[\alpha]_D^{20}$ +105·5° in $CHCl_3$]. Cold MeOH–KOH converts this into (I), and hot NaOH into the equilibrium mixture, $[\alpha]_D$ +18°. It is hydrolysed [MeOH–$Ba(OH)_2$] at the same rate as (I), and with $Pb(OAc)_4$ gives the *cyclo*dehydrolactones also obtained (*loc. cit.*) from (I). The Na salt from (I) and MeOH–NaOMe with dil. AcOH gives the *OH-acid*, m.p. 90—95° (loss of H_2O), resolidifying with m.p. 127°, $[\alpha]_D^{18}$ −32° in EtOH. When the mixed acids from (I) and NaOH at 180°, pptd. by AcOH, are boiled with EtOH, the *l*-acid is preferentially lactonised, leaving (after extraction with $CHCl_3$) the d-iso*hydroxy-acid*, m.p. 160°, $[\alpha]_D^{18}$ −23° in EtOH. It is concluded that the *l*- and *d-iso*lactones are *trans*- and *cis*-, respectively. The synthetic isomeride (II) (*loc. cit.*) with $Pb(OAc)_4$ gives a mixture of two *diacetates*, $C_{26}H_{30}O_9$, m.p. 150—151°, and $C_{26}H_{30}O_{10}$, m.p. 158—159°, hydrolysed to *compounds*, $C_{22}H_{26}O_8$, m.p. 101—103°, and $C_{22}H_{24}O_7$, m.p. 147—148°, respectively, both oxidised ($KMnO_4$) to veratric acid. β-Veratroyl-*n*-butyric acid when reduced (Na + EtOH) and lactonised (dil. acid) yields γ-(3 : 4-*dimethoxyphenyl*)-β-*methyl*-γ-*butyrolactone*, m.p. 112—113°, differing from (II). $CH_2Ph \cdot CN$, Et succinate, and NaOEt yield 2-*cyano*-2-*phenyl*cyclo*pentane*-1 : 3-*dione*, m.p. 149°, hydrolysis of which presented difficulties. 3 : 4-$(OMe)_2C_6H_3 \cdot CH_2 \cdot COCl$ with CH_2N_2 followed by Et_2O–HCl affords *veratryl* CH_2Cl *ketone*, m.p. 52°, which could not be condensed with $CH_2(CO_2Et)_2$, whilst 3 : 4-$CH_2O_2 \cdot C_6H_3 \cdot CH_2 \cdot COCl$ treated similarly gives 2-*chloropiperonyl* CH_2Cl *ketone* (?), m.p. 107—108°, one Cl of which is hydrolysed by MeOH–KOH.

3 : 4-$(OMe)_2C_6H_3 \cdot CH_2 \cdot COCl$ with Et sodioacetosuccinate, followed by hydrolysis, yields γ-*keto*-γ-*veratrylbutyric acid* (an oil), reduced (Na + EtOH) and lactonised to γ-*veratryl*-γ-*butyrolactone*, m.p. 83—84° (*NO*$_2$-derivative, m.p. 115—116°), also prepared from *O*-methyleugenol oxide and $CHNa(CO_2Et)_2$, or by hydrolysing its α-Ac derivative (*loc. cit.*). It differs from (II), is oxidised ($KMnO_4$) to veratric acid, and is not cyclised by MeOH–HCl, AcOH–HCl, or 80% H_2SO_4. Piperonyl chloride and Et sodioacetoglutarate yield an acid which when reduced and lactonised gives γ-(3 : 4-methylenedioxybenzyl)-γ-butyrolactone, b.p. 170—180°/0·1 mm. (*NO*$_2$-derivative, m.p. 98—99°). Na α-acetyl-γ-(3 : 4-methylenedioxybenzyl)-γ-butyrolactone and 3 : 4-methylenedioxybenzyl chloride yield an α-*Ac*-derivative, b.p. 270—280°/1 mm., hydrolysed to αγ-bis-(3 : 4-methylenedioxybenzyl)butyrolactone, identical with that obtained (*loc. cit.*) from safrole oxide. From the above it appears that active CH_2 groups react with the γ-C of *O*-methyleugenol and safrole oxides, and that (II) is αγ-diveratryl-γ-butyrolactone. On this basis a list of corr. formulæ is given. (II) is hydrolysed [as for (I)] to γ-*hydroxy*-αγ-*bis*-(3 : 4-*dimethoxybenzyl*)*butyric acid*, an oil. α-Acetyl-γ-veratryl-γ-butyrolactone is hydrolysed to the *hydroxyketone*, b.p. 185—188°/0·3 mm.; with conc. HCl–AcOH this gives 6 : 7-*dimethoxy*-3 : 1-endo*methyleneoxy*-1-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 96°, whilst the lactone itself gives the -2-*carboxylic acid*, m.p. 182—183° (*Me* ester, m.p. 142°). Either product with Se at 280° yields 6 : 7-*dimethoxy*-1 : 3-*dimethylnaphthalene*, m.p. 97—98° (*picrate*, m.p. 119—120°), also synthesised by reducing (Clemmensen) β-veratroyl-*n*-butyric acid, heating the product with 80% H_2SO_4, and treating the resulting 1-*keto*-6 : 7-*dimethoxy*-3-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 132—133°, with MgMeI, followed by Se. Similarly Me γ-hydroxy-γ-piperonylpropyl ketone and α-acetyl-γ-(3 : 4-methylenedioxybenzyl)-γ-butyrolactone yield 6 : 7-*methylenedioxy*-3 : 1-endo*methyleneoxy*-1-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 85—86°, and the -2-*carboxylic acid*, m.p. 219—220° (*Me* ester, m.p. 156—157°), respectively. It is suggested that a pinacolinic transformation occurs in the formation of these naphthalene derivatives.

O-Benzylvanillin with $CN \cdot CHNa \cdot CO_2Na$ in EtOH–NaOH, followed by HCl, yields α-*cyano*-β-(*O-benzylvanillyl*)*acrylic acid*, m.p. 202°, reduced (Na–Hg) and esterified (MeOH–HCl) to *Me* α-*cyano*-β-(*O-benzylvanillyl*)*propionate*, m.p. 72°.

$CH_2Ph \cdot CO \cdot CH_2 \cdot OPh$ is reduced [$Al(OPr^{\beta})_3$ + $Pr^{\beta}OH$] to β-*hydroxy*-γ-*phenoxy*-α-*phenylpropane*, m.p. 92°. 3 : 4-$(OMe)_2C_6H_3 \cdot CH_2 \cdot CN$, $OPh \cdot CH_2 \cdot CO_2Me$, and NaOEt yield α-*cyano*-β-*keto*-γ-*phenoxy*-α-(3 : 4-*dimethoxyphenyl*)*propane*, m.p. 111—112°, hydrolysed by fuming HCl–AcOH in the cold to β-*keto*-γ-*phenoxy*-

α-(3 : 4-*dimethoxyphenyl*)*butyramide*, m.p. 173°, which when boiled with 8% HCl gives *γ-phenoxy*-α-(3 : 4-*dimethoxyphenyl*)*acetone*, m.p. 63—64°, reduced [$Al(OPr^{\beta})_3$] to the sec.-*alcohol*, m.p. 100°. Veratrole and glutaric anhydride with $AlCl_3$ in $PhNO_2$ yield *γ-veratroyl*-, m.p. 140—142°, reduced (Clemmensen) to *γ-veratryl*-n-*butyric acid*, m.p. 78°. A. Li.

Two stereoisomeric 2-methyl*cyclo*hexanol-1-carboxylic acids. M. Godchot and (Mlle.) G. Cauquil (Compt. rend., 1938, **206**, 1523—1525; cf. A., 1937, II, 63, 149).—The $NaHSO_3$ compound of 2-methyl*cyclo*hexanone (I) with KCN affords a cyanohydrin which with conc. HCl affords about 20% of a mixture of 2-methyl*cyclo*hexanol-1-carboxylic acids [separated by fractional crystallisation into a form, m.p. 109° (II) (*Me* ester, b.p. 99°/15 mm.; *anilide*, m.p. 129°; NH_4 salt), and a little of an *isomeride*, m.p. 70—71° (*Me* ester, b.p. 89—90°/15 mm.; *anilide*, m.p. 84°; NH_4 salt)], and neutral substances which with boiling 30% KOH afford (I) and (II). J. L. D.

Resolution of 3 : 3′-dibromo- and 3 : 3′-disulpho-*cyclo*butane*spirocyclo*butane-3 : 3′-dicarboxylic acids. H. J. Backer and H. G. Kemper (Rec. trav. chim., 1938, **57**, 761—769).—Addition of Br to $CO_2H{\cdot}CH<\begin{matrix}CH_2\\CH_2\end{matrix}>C<\begin{matrix}CH_2\\CH_2\end{matrix}>CH{\cdot}CO_2H$ and red P and then heating first at 100° and finally at 130—140°, gives 79% of 3 : 3′-*dibromo*cyclo*butane*spirocyclo*butane*-3 : 3′-*dicarboxylic acid* (I), m.p. 182—183° (decomp. at about 230°) (*dichloride*, b.p. 163—164°/5 mm., m.p. 37·5—38·5°; Me_2, b.p. 153—154°/2·5 mm., Et_2, b.p. 160°/2·5 mm., Bu^{γ}_2, m.p. 80—81°, and Ph_2 ester, m.p. 90·5—91·5°; *diamide*, m.p. 175·5—176°; *dianilide*, m.p. 187·5—188·5°), resolved by brucine to the *d*-acid, $[M]_D$ +5·4° in EtOH (Na_2 salt, $[M]_D$ +14·4° in H_2O). (I) is hydrolysed by shaking in H_2O with Ag_2CO_3 to the 3 : 3′-$(OH)_2$-*acid* (*Ba*, $+H_2O$, and *diquinine* salt, $+2H_2O$), and converted (as NH_4 salt) by $(NH_4)_2SO_3$ at 75° into the 3 : 3′-disulpho-3 : 3′-dicarboxylic acid [*tetraquinine*, $+9H_2O$, *tetrastrychnine*, $+9H_2O$, Ba_2, $+5H_2O$ ($3H_2O$ lost at 150°/vac.), and Tl_4 salt], which is resolved by way of the polybrucine salt to the *d*-acid (Na_4 salt, $[M]_D$ +26·6°). R. S. C.

Influence of directing groups on nuclear reactivity in oriented aromatic substitutions. III. Nitration of ethyl benzoate. C. K. Ingold and M. S. Smith (J.C.S., 1938, 905—917; cf. A., 1928, 164; 1931, 1405).—Nitration of an equimol. mixture (large excess) of C_6H_6 and EtOBz with $AcNO_3$ in Ac_2O at 18° for 6 hr. shows that C_6H_6 is nitrated 272 ±6 times as rapidly as EtOBz. The products are extracted with Et_2O, treated with Na_2SO_3 and $NaHCO_3$ to remove $C(NO_2)_4$, and hydrolysed, the $PhNO_2$ separated from the mixed NO_2-acids by Et_2O extraction in NaOH solution, and both determined by reduction with excess of $TiCl_3$. Nitration of EtOBz under the same conditions produces the *o*-, *m*-, and *p*-NO_2-isomerides in the ratio 24 : 72 : 4. The acids obtained by alkaline hydrolysis are extracted with Et_2O, BzOH removed by steam distillation, and each acid is determined by extracting the solid mixture with H_2O saturated with the other two, and measuring the increased acidity, correction being made for alterations in solubility, and for traces of BzOH. These results indicate partial rate factors: *o*-, 0·0026, *m*-, 0·0079, and *p*-, 0·0009. A. Li.

β-Monoalkylaminoethyl *p*-aminobenzoates.—See B., 1938, 847.

Isomorphism of organic compounds. IV. H. Lettré and H. Barnbeck (Ber., 1938, **71**, [*B*], 1225—1228; cf. A., 1938, II, 139).—Examination of a series of substituted benz-*p*-nitroanilides shows that here as in the case of substituted benzoic acids H is not isomorphously replaceable by Cl, Br, or Me. The mixed crystal formation of Bz derivatives substituted in the same position by Cl, Br, or Me corresponds with that of the benzoic acids themselves. Structural isomerides are incapable of forming mixed crystals. The following *-benz*-p-*nitroanilides* appear new: o-, m-, and p-*chloro*-, m.p. 187, 197°, and 221°, respectively; o-, m-, and p-*bromo*-, m.p. 199°, 194°, and 247°, respectively; o-, m-, and p-*methyl*-, m.p. 177·5°, 151°, and 206·5°, respectively. H. W.

Stereochemistry of diphenyls. XLIII. Effect of substituents in the 4-position of 2-nitro-2′-methoxydiphenyl-6-carboxylic acid. R. Adams and H. R. Snyder. **XLIV. *Meso*- and racemic *iso*phthalamides of 3-nitro-3′-aminodimesityl.** R. Adams and R. M. Joyce, jun. (J. Amer. Chem. Soc., 1938, **60**, 1411—1415, 1489—1491; cf. A., 1936, 723).—XLIII. The rate of racemisation of 2-nitro-2′-methoxydiphenyl-6-carboxylic acid is very little affected by NO_2, Cl, Br, or Me in position 4, in contrast to the great effect of these substituents in position 3′, 4′, or 5′. The effect of a substituent thus depends on the nature of the other groups in the ring substituted. 5-*Bromoisatoic anhydride*, m.p. 286—288° (decomp.), prepared from 5-bromoisatin and CrO_3–AcOH at 10—15°, is converted by $NaNO_3$–H_2SO_4 at 5—10° into 5-*bromo*-7-*nitroisatoic anhydride* (I), m.p. 94°, and 5-*bromo*-3-*nitro*-2-*aminobenzoic acid* (II), m.p. 245—247° [obtained from (I) by hot HCl–AcOH]. With $K_2S_2O_5$–fuming HNO_3, followed by I–KI, (II) yields 5-*bromo*-2-*iodo*-3-*nitrobenzoic acid*, m.p. 213—214·5°, the *Me* ester, m.p. 63°, of which with *o*-$C_6H_4I{\cdot}OMe$ and activated Cu-bronze at 210—230° gives a product, hydrolysed to dl-4-*bromo*-2-*nitro*-2′-*methoxydiphenyl*-6-*carboxylic acid*, m.p. 181°, resolved by strychnine into the l-*acid*, [α] −46° in EtOH (all rotations are at 28° for the *D* line) [*strychnine* salt, m.p. 139° (decomp.), [α] −166° in $CHCl_3$]. Similarly are prepared 5-*chloro*-, m.p. 267° (decomp.), and 5-*chloro*-7-*nitro-isatoic anhydride*, m.p. 85°, 5-*chloro*-3-*nitro*-2-*amino*-, m.p. 240°, and 5-*chloro*-2-*iodo*-3-*nitro-benzoic acid*, m.p. 204° (*Me* ester, m.p. 66—67°), dl-, m.p. 171°, and l-4-*chloro*-2-*nitro*-2′-*methoxydiphenyl*-6-*carboxylic acid*, [α] −24·5° in EtOH [*strychnine* salt, m.p. 137° (decomp.), [α] −120° in $CHCl_3$]. 7-Nitro-5-methylisatoic anhydride (modified prep.), new m.p. 177°, and boiling dil. HCl yield 5-*nitro*-4-*amino*-m-*toluic acid*, m.p. 256—257° (decomp.); the position of the NO_2 in these compounds is proved by conversion by diazotisation (Cu-bronze) into 5 : 1 : 3-$NO_2{\cdot}C_6H_3Me{\cdot}CO_2H$, new m.p. 175·5—176·5°. 4-*Iodo*-5-*nitro*-m-*toluic acid*, m.p. 207—209° (*Me* ester, m.p. 43—44°), dl-, m.p. 179°, and l-2-*nitro*-2′-*methoxy*-4-*methyldiphenyl*-6-*carboxylic acid*, m.p. 175—178°,

[α] −30° in EtOH [*strychnine* salt, m.p. 143° (decomp.), [α] about −110° in $CHCl_3$], are prepared. 3 : 2 : 1-$NO_2{\cdot}C_6H_3Br{\cdot}CO_2H$ and fuming HNO_3–H_2SO_4 give 3 : 5 : 2 : 1-$(NO_2)_2C_6H_2Br{\cdot}CO_2H$, new m.p. 215—216°, and thence by way of the *Me* ester thereof, m.p. 106—108°, dl-, m.p. 185°, and 1-2 : 4-*dinitro*-2′-*methoxydiphenyl*-6-*carboxylic acid*, m.p. 182—185°, [α] −12° in EtOH [*strychnine* salt, m.p. 136° (decomp.), [α] about −185° in $CHCl_3$].

XLIV. 3 : 3′-Dinitrodimesityl (modified prep.), m.p. 162—163° (corr.), and anhyd. $SnCl_2$–HCl–AcOH give 3-*nitro*-3′-*aminodimesityl* (III), m.p. 145—146° [*hydrochloride*, m.p. 244—247° (decomp.) (sinters at 236°)], which with *m*-$C_6H_4(COCl)_2$ and C_5H_5N in C_6H_6 give *isophthaldi*-3-3′-*nitromesitylmesitylamide*, (?) meso-, m.p. 302°, and (?) dl-*form*, m.p. 247° (corr.). $COCl{\cdot}[CH_2]_4{\cdot}COCl$ and (III) give only one form of *adipdi*-3-3′-*nitromesitylmesitylamide*, m.p. 230—231° (corr.). $(COCl)_2$, however, gives *fractions*, m.p. 304—307° (corr.) and 273—283° (corr.), which could not be obtained pure. CS_2 and (III) in KOH–EtOH give 3-*nitrodimesityl*-3′-*thiocarbimide*, m.p. 119—120°.

R. S. C.

Synthesis of 5-chloro-10-methyl-1 : 2-benzanthracene and related compounds. M. S. Newman (J. Amer. Chem. Soc., 1938, **60**, 1368—1370).—The Grignard reagent from *o*-C_6H_4ClBr with 1 : 2-$C_{10}H_6(CO)_2O$ in Et_2O–C_6H_6 gives 43% of 2-*o*-*chlorobenzoyl*-1-*naphthoic acid*, m.p. 202—202·8°, the structure of which is proved by decarboxylation to β-$C_{10}H_7{\cdot}CO{\cdot}C_6H_4Cl$-*o*, identified as 2 : 4-*dinitrophenylhydrazone*, m.p. 265·2—266·2°. With MgMeBr the acid gives 79% of the *lactone*, m.p. 122—122·6°, of 2-α-*hydroxy*-α-*o*-*chlorophenylethyl*-1-*naphthoic acid*, reduced (Zn dust, aq. NaOH) to 2-α-*o*-*chlorophenylethyl*-1-*naphthoic acid*, m.p. 168—168·8°. With H_2SO_4 this gives 5-*chloro*-10-*methyl*-1 : 2-*benzanthracene*, m.p. 133—133·4° (purified by way of the *picrate*, m.p. 141·8—142·4°; oxidation gives only a trace of a *substance*, m.p. 175—176°; a *by-product*, m.p. 133—133·4°, is also formed), converted by CuCN in C_5H_5N at 260° into 5-*cyano*-10-*methyl*-1 : 2-*benzanthracene*, m.p. 182·8—183·2°, and thence by 65% H_2SO_4 in AcOH into 10-*methyl*-1 : 2-*benzanthracene*-5-*carboxylamide*, m.p. 308—310° (uncorr.). M.p. are corr.

R. S. C.

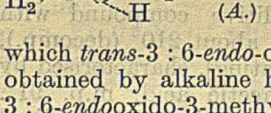
Condensations by sodium. XII. Mechanism of formation of phenylmalonic acid and the syntheses of butyl- and phenyl-malonic acids from monocarboxylic acids. A. A. Morton, F. Fallwell, jun., and L. Palmer (J. Amer. Chem. Soc., 1938, **60**, 1426—1429; cf. A., 1937, II, 101).—When $CHPh(CO_2Na)_2$ is prepared from $C_5H_{11}Cl$, Na, and C_6H_6 by successive addition of PhMe and CO_2, reaction proceeds by way of NaPh, $NaCH_2Ph$, $CH_2Ph{\cdot}CO_2Na$, and $CHPhNa{\cdot}CO_2Na$. The presence of NaPh is proved by adding CO_2 before the PhMe and thus forming BzOH. That of $NaCH_2Ph$ is proved by adding MeI or BuCl instead of CO_2, thus forming PhEt or PhC_5H_{11}, respectively. That of $CHPhNa{\cdot}CO_2Na$ is proved by the fact that more $CH_2Ph{\cdot}CO_2Na$ is formed at the expense of $CHPh(CO_2Na)_2$ if the CO_2 is added more rapidly, and by the prep. of $CHPh(CO_2Na)_2$ from isolated $CH_2Ph{\cdot}CO_2Na$ by NaPh–CO_2. Na hexoate and NaPh in boiling C_6H_6 lead to $CHBu^{\alpha}(CO_2Na)_2$; with NaC_5H_{11} in light petroleum at 45° no reaction occurs. Addition of MeI to NaPh and PhMe at room temp. gives PhEt, indicating presence of $NaCH_2Ph$ in the mixture, but CO_2 gives only BzOH; when NaPh and PhMe are heated at 60° for 2 hr., CO_2 then leads to much $CH_2Ph{\cdot}CO_2H$, but formation of $NaCH_2Ph$ is complete (as judged by the acids formed) only at 75°. Only traces of $C_6H_4(CO_2Na)_2$ are formed.

R. S. C.

Electrolysis of aromatic acids. VII. [Potassium] alkyl phthalates. V. M. Rodionov and V. C. Zvorikina (Bull. Soc. chim., 1938, [v], **5**, 840—847; cf. A., 1937, II, 291).—Electrolysis (Pt anode, Hg cathode) of K Et phthalate (I) yields 50—55% of *Et H* $\Delta^{2:6}$-*dihydrophthalate* (II), m.p. 121—122°, hydrolysed to *trans*-$\Delta^{2:6}$-dihydrophthalic acid, m.p. 222—223° (cf. von Baeyer, A., 1892, 1211) [the anhydride (III), m.p. 84—85°, is convertible by EtOH into (II)], phthalide (29%), and small amounts of EtOBz and hydrodiphthalyls. K Me phthalate similarly yields phthalide, PhCHO, and Me H $\Delta^{2:6}$-dihydrophthalate, m.p. 125—126°, also obtained from (III) and MeOH. Electrolysis of (I) with a diaphragm gives phthalide, phthalic and dihydrophthalic acids, but no (II). Electrolysis (Pt electrodes) of (I) yields only a little EtOBz, suggesting that K–Hg is the reagent which forms (II). Electrolysis (Hg cathode) of α- and β-Et K hemipinates affords mainly unchanged material, with a little ψ-meconine and meconine, respectively.

A. T. P.

Steric course of additive and substitutive reactions. IX. Steric course of the catalytic hydrogenation of double linkings in dicyclic systems. *endo*- and *exo*-Isomerism. K. Alder and K. H. Backendorf (Annalen, 1938, **535**, 113—122).—Reduction of the double linking in the 3 : 6-*endo*-oxido-system follows the reverse course to that in the di*cyclo*-[1 : 2 : 2]-heptene system. Whereas in the latter the H addition proceeds from the CH_2 bridge, in the former under the same conditions the same addendum does not proceed from the O bridge but from the *endo*-position of the double linking. 3 : 6-*endo*-Oxido-Δ^1-tetrahydrophthalic acid is hydrogenated (PtO_2 in AcOH) to exocis-3 : 6-endo*oxidohexahydrophthalic acid* (cf. *A*), m.p. 169—170°, converted by boiling AcCl into the corresponding *anhydride*, m.p. 158—159°; it is converted by CH_2N_2 into the Me_2 ester, from which *trans*-3 : 6-*endo*-oxidohexahydrophthalic acid is obtained by alkaline hydrolysis. Hydrogenation of 3 : 6-*endo*oxido-3-methyl-Δ^1-tetrahydrophthalic acid leads to exocis-3 : 6-endo*oxido*-3-*methylhexahydrophthalic acid*, m.p. 160—161° (*anhydride*, m.p. 87—89°). Similarly, 3 : 6-*endo*oxido-3 : 6-dimethyl-Δ^1-tetrahydrophthalic acid yields exocis-3 : 6-endo*oxido*-3 : 6-*dimethylhexahydrophthalic acid*, m.p. 202—203° (*anhydride*, m.p. 175—177°), the Me_2 ester, m.p. 41—42°, of which is hydrolysed by alkali to the corresponding *trans*-acid.



(*A*.)

H. W.

New cholesterol derivatives. A. Dansi (Gazzetta, 1938, **68**, 273—276).—$CH_2Ph{\cdot}CH_2{\cdot}MgCl$ and β-cholestanone (I) in Et_2O yield, after distillation and

dehydration by $KHSO_4$, 3-β-*phenyl-ethylcholestene* (or *-ethylidenecholestane*), m.p. 94—95°, $[\alpha]_D^{20}$ +61° in CCl_4. Similarly, cholestenone (II) gives 3-β-*phenyl-ethylcholestadiene* (or *-ethylidenecholestene*), m.p. 94—95°, $[\alpha]_D^{20}$ −131° in CCl_4. With Zn and $CH_2Br{\cdot}CO_2Et$ in C_6H_6, (I) yields, after hydrolysis, 3-*carboxymethyl-cholestene* (or 3-*carboxymethylenecholestane*), m.p. 161°, $[\alpha]_D^{20}$ +60° in CCl_4, and (II) gives 3-*carboxymethyl-cholestadiene* (or 3-*carboxymethylenecholestene*), m.p. 221—223°, $[\alpha]_D^{20}$ +199°. E. W. W.

Bile acids. LIV. M. Schenck (Z. physiol. Chem., 1938, **253**, 244—252; cf. A., 1938, II, 99).—The β-acid $C_{24}H_{34}O_{10}N_2$ (I) boiled for 20 min. with 10% HCl gives the *NH_2-acid* B, $C_{24}H_{36}O_{11}N_2$ (II), decomp. 155—160°, also obtained (with decomp. ~167°) from the isomeric NH_2-acid *A* (III) (from the α-acid by cleavage of the lactam ring) and 90% H_2SO_4 at 100° for 15 min. With alkaline $KMnO_4$ (I) loses approx. 33% of its N in gaseous form; similarly (II) [but not (III)] also yields a gas (probably N_2). Formulæ taking account of these results are proposed for the acids. W. McC.

Attempted syntheses of the antirachitic vitamin. I. Syntheses of β-unsaturated alcohols and aldehydes with hemicyclic double linking. K. Dimroth [in part with Jonsson] (Ber., 1938, **71**, [*B*], 1333—1345).—Attempts are described to obtain simple systems containing three hemicyclic double linkings arranged as in vitamin-D_2. *cyclo*-Hexylideneacetic acid is converted through the chloride into cyclo*hexylideneacet-o-toluidide*, m.p. 105—106°; under mild conditions this reacts with PCl_5 in C_6H_6 at 0° or with $SOCl_2$ alone or in CCl_4 or C_6H_6 giving cyclo*hexenylacet-o-toluidide*, m.p. 126°, identical with the synthetic material. 1-Ethinyl*cyclo*hexanol is hydrogenated (Pd sponge) to 1-vinyl*cyclo*hexanol (I), which is slowly converted by Ac_2O at 100° into *cyclo*hexylidene-ethyl alcohol (II), b.p. 95—96°/13·5 mm. (*dinitrobenzoate*, m.p. 90—91°), accompanied by much vinyl*cyclo*hexene. (II) is preferably obtained by the use of $CCl_3{\cdot}CO_2H$–Ac_2O–AcOH at 55°; at >55° or if reaction is prolonged, the yellow, condensed hydrocarbons are obtained. PBr_3 and C_5H_5N transform (I) into *cyclo*hexylidene-ethyl bromide, b.p. 80—81°/12 mm., transformed by KOAc followed by hydrolysis into (II). Addition of CrO_3–AcOH to (II)–C_6H_6–AcOH affords *cyclo*hexylideneacetaldehyde, b.p. (indef.) 86—92°/13·5 mm. [additive compound with $NaHSO_3$; *semicarbazone*, m.p. about 210° (decomp.), according to the manner of heating], characterised by oxidation to *cyclo*hexylideneacetic acid, m.p. 91°. For comparison *cyclo*hexenylethyl alcohol is oxidised to *cyclo*hexenylacetaldehyde (*semicarbazone*, m.p. 177°). *trans*-2-Ketodecahydronaphthalene, C_2H_2, and K amyloxide yield trans-*ethinyldecahydro-β-naphthol*, b.p. 122—128°/13 mm., m.p. 91·5°, reduced (Pd in MeOH) to trans-*vinyldecahydro-β-naphthol*, m.p. 72°, which is isomerised to *trans*-2-decahydronaphthylidenylethyl alcohol (p-*nitrobenzoate*, m.p. 99°), oxidised to *trans*-2-decahydronaphthylidenylacetaldehyde [additive *compound* with $NaHSO_3$; *semicarbazone*, m.p. 229—230° (decomp.)]. trans-*Ethinyldecahydro-α-naphthol*, b.p. 120—121°/12 mm. (p-*nitrobenzoate*, m.p. 111°), is reduced to *trans*-vinyldecahydro-α-naphthol, b.p. 116—121°/11 mm. This is isomerised to 1-decahydronaphthylidenylethyl alcohol, b.p. 151—152°/12mm. (*dinitrobenzoate*, m.p. 99°, with apparently an isomorphous form which softens at 75°), whence 1-decahydronaphthylidenylacetaldehyde [*semicarbazone*, m.p. 235° (decomp.)], oxidised to 1-*decahydronaphthylidenylacetic acid*, m.p. 155—156°. H. W.

Induced oxidation of iodobenzene during the oxidation of benzaldehyde.—See A., 1938, I, 406.

Velocity of the Cannizzaro reaction.—See A., 1938, I, 404.

Thioketonic esters. VI. S. K. Mitra (J. Indian Chem. Soc., 1938, **15**, 129—132).—The reaction between RCHO and β-thioketonic esters to give β-trithioaldehydes (I) probably occurs by hydrolysis of an intermediate, additive hydroxysulphide to OH·CHR·SH, which loses H_2O to give (I). Et methylthioacetoacetate with PhCHO, anisaldehyde, vanillin, and CH_2O in EtOH–HCl gives respectively β-trithiobenzaldehyde, β-trithioanisaldehyde, β-trithiovanillin, and β-trithioformaldehyde (II), m.p. 218°. Et sodiothioacetoacetate in C_6H_6 with $CH_2Cl{\cdot}OMe$ affords *Et* β-*methoxymethylthiol-α-methylcrotonate*, b.p. 120°/12 mm., which with aq. HBr gives (II). A. L.

Reaction of magnesium phenyl bromide with β-methoxy-β-mesitylacrylonitriles. R. C. Fuson, G. E. Ullyot, R. F. Stedman, and P. O. Tawney (J. Amer. Chem. Soc., 1938, **60**, 1447—1450).—Either form of 2 : 4 : 6-$C_6H_2Me_3{\cdot}C(OMe){:}CH{\cdot}CN$ (I) or the 1 : 1 mol. compound of the two reacts with MgPhBr (usually 5 mols.) to give amounts, which vary according to the conditions used, of *α-imino-γ-methoxy-α-phenyl-γ-mesityl-Δ^β-propene hydrobromide* (II), m.p. varies between 110° and 130°, β-*imino-β-phenylpropiomesitylene* (III), m.p. 145·5—146·5°, *γ-methoxy-α-phenyl-γ-mesityl-Δ^β-propen-α-one* (IV), m.p. 111·5—112·5°, and $C_6H_2Me_3{\cdot}CO{\cdot}CH_2{\cdot}COPh$ (V); some of the lower-melting form of (I) is always recovered, isomerisation taking place under the conditions of reaction. Melting of (II) is accompanied by decomp. to (III) and MeBr. $NaNH_2$ and Me_2SO_4 convert (V) into (IV). NH_3–MeOH converts (V) into (III), but yields NH_2Bz and COPhMe or COPhEt, respectively, from CH_2Bz_2 or $CHMeBz_2$. Hydrolysis of (II), (III), or (IV) by aq. EtOH–HCl gives (V). 2 : 4 : 6-$C_6H_2Me_3{\cdot}C(OMe){:}CMe{\cdot}CN$ and MgPhBr give similarly *α-imino-γ-methoxy-α-phenyl-γ-mesityl-β-methyl-Δ^β-propene hydrobromide* (VI), m.p. 110—130° (decomp.), and *α-phenyl-γ-mesityl-β-methylpropane-αγ-dione* (VII), an oil (*Cu* derivative) [obtained also by hydrolysis of (VI)]. At the m.p. (VI) gives MeBr and an oil, which is probably *α-imino-α-phenyl-γ-mesityl-β-methylpropan-γ-one*, since hydrolysis gives (VII). (VII) has been synthesised from $C_6H_2Me_3{\cdot}COEt$. Methylquinolinium bromide has m.p. 96—97° (lit. 70°). R. S. C.

Double reductions. Z. C. Glacet and J. Wiemann (Compt. rend., 1938, **206**, 1736—1737).—Reduction (Zn dust) of a mixture of PhCHO and Ac_2 under the conditions described by Wiemann (cf. A., 1936, 589) affords β-acetyl-α-phenylpropylene glycol (unstable), isolated as its *$:CMe_2$ ether*, b.p. 70°/about

10 mm. CH_2:CH·CHO and Ac_2 similarly afford γδ-dihydroxy-δ-acetyl-Δ^{α}-pentene (:*CMe*$_2$ *ether*, b.p. 81—82°/14 mm.). J. L. D.

Reactivity of nitrosyl chloride. R. Perrot (Compt. rend., 1938, **206**, 1575—1577; cf. A., 1934, 1216).—Deoxybenzoin with NOCl at 80° rapidly (slowly at room temp.) affords COPh·CHPhCl. Benzilmonoxime is formed at room temp. in the absence of light. MeCN with NOCl at 200° affords a little AcCl. $CHCl_2$·CN behaves similarly but also gives CCl_3·CN, which at >220° affords C_2Cl_6 and $(CN)_2$. HCN at 200° similarly affords CNCl which is somewhat polymerised. At 350°, CO and NOCl afford $COCl_2$. CPh:CPh with NOCl at 150—200° affords BzCl. J. L. D.

Attempted synthesis of the antirachitic vitamin. II. Condensation of *cyclo*hexylideneacetaldehyde with *cyclo*hexanone. K. Dimroth (Ber., 1938, **71**, [*B*], 1346—1350).—*cyclo*Hexanone is condensed with *cyclo*hexylideneacetaldehyde by 1% aq. NaOH under N_2 at room temp. to α-cyclo*hexylidene*-β-2-*keto*cyclo*hexylidene-ethane* (I), m.p. 67°. This when treated with MgMeI and then distilled in a vac. gives an oil which is very sensitive to air. (I) is treated with Zn and CH_2Br·CO_2Et in C_6H_6 and the product is hydrolysed and distilled, thus yielding α-cyclo*hexylidene*-β-2-*methylene*cyclo*hexylidene*-*ethane*, the absorption spectrum of which resembles that of tachysterol much more closely than that of vitamin-D_2. H. W.

Diphenylketazine oxide. K. von Auwers (Ber., 1938, **71**, [*B*], 1260).—The spectrochemical behaviour of the compound obtained by oxidising CPh_2:N·OH with $K_3Fe(CN)_6$ harmonises with the formula CPh_2:NO·N:CPh_2 and not $CPh_2<^{N:N}_{O}>CPh_2$ proposed by Schönberg *et al.* (A., 1938, II, 298). H. W.

Diaryl ketone peroxides. C. S. Marvel and V. E. Nichols (J. Amer. Chem. Soc., 1938, **60**, 1455—1457).—Passing O_3 into CPh_2:CHR (R = H, Me, or Et), but not CPh_2:C:CHBu$^{\gamma}$, in CCl_4 under varied conditions gives some BzOH and 3—7% of dimeric *benzophenone peroxide* (I), m.p. 206·5—207·5° to 214·5—215·5° (decomp.). The *dimerides*, m.p. 210·5—211·5° (decomp.), 183—184° (decomp.), and 186·5—187·5° (decomp.), of *di*-p- and -m-*tolyl* and *Ph* p-*tolyl ketone peroxide*, respectively, were similarly obtained in 3—7% yield with some of the acids formed by cleavage of the ketone. CH_2:C$(C_6H_4Ph)_2$ gives no ketone peroxide, but yields p-*carboxyphenyl diphenylyl ketone*, m.p. 287—288°. The dimerides sublime slightly at the m.p., and decompose partly when recrystallised, but are unusually inert to reagents. Zn–AcOH reduces (I) to COPh·CPh_3; Al–Hg gives $CHPh_2$·OH; at 214—215° (I) gives $COPh_2$. (I) is obtained in 3% yield by keeping CPh_2Cl_2 in 30% H_2O_2 for 2 weeks, but not from $COPh_2$ by H_2O_2, H_2O_2–H_2SO_4, $H_2S_2O_8$, or O_3. as-*Di*-m-*tolylethylene*, b.p. 134—139°/5 mm., is prepared by adding EtOAc to *m*-C_6H_4Me·MgBr and heating the carbinol at 210—215°. *Di*-m-*tolyl ketone* has m.p. 51°. R. S. C.

Deformations of valency angles according to absorption spectra; structures of benzocyclanones, their oximes, and benzocyclenes. (Mme.) P. Ramart and J. Hoch (Bull. Soc. chim., 1938, [v], **5**, 848—871).—Partly a more detailed account of work previously reviewed (A., 1936, 471). Much of the following appears new (cf. A., 1935, 621). The absorption spectra of $C_6H_4<^{[CH_2]_n}_{CR}>CH$ (R = H and Me, *n* = 1, 2) and $C_6H_4<^{[CH_2]_n}_{C(:CHMe)}>CMe_2$ (*n* = 1, 2) are compared; the latter are also compared with the oximes of $C_6H_4<^{[CH_2]_n}_{CO}>CR_2$ (R = H and Me). COPhPr^{β} (+ $NaNH_2$) and Ph·$[CH_2]_2$·Br give *Ph γ-phenyl-αα-dimethylpropyl ketone*, b.p. 206—208°/15 mm., converted by $NaNH_2$ in PhMe into the *amide*, m.p. 108°, of *γ-phenyl-αα-dimethylbutyric acid*, m.p. 98°, b.p. 176—180°/13 mm., the *chloride*, b.p. 137—139°/18 mm., of which with $AlCl_3$ in light petroleum below 30° for 24 hr. yields 1-*keto*-2 : 2-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. 147°/25 mm. (*oxime*, m.p. 131°). Similarly *Ph δ-phenyl-αα-dimethylbutyl ketone*, b.p. 219—220°/20 mm., yields the *amide*, m.p. 91°, of *δ-phenyl-αα-dimethylvaleric acid*, m.p. 35°, b.p. 180—181°/10 mm., the chloride of which is cyclised to (probably) 2-phenyl-5 : 5-dimethyl*cyclo*pentanone. 2 : 2-*Dimethylbenzsuberone*, $C_6H_4<^{[CH_2]_3}_{CO}>CMe_2$, b.p. 140°/16 mm. (*oxime*, m.p. 139°), is prepared from benzsuberone (2-*oximino*-derivative, m.p. 136°) and MeI–$NaNH_2$ (cf. Haller and Bauer, A., 1910, i, 490). 2 : 2-*Dimethyl*-1-*ethylidene-indane*, b.p. 112—114°/13 mm., and -1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. 122—123°/14 mm., are prepared by dehydration (AcCl–Ac_2O) of $C_6H_4<^{[CH_2]_n}_{CEt(OH)}>CMe_2$ (from the ketone and MgEtBr). *o*-C_6H_4Me·CMe_2·OH could not be dehydrated. *o*-C_6H_4Me·COEt and MeCHO–HCl (saturated) give o-*tolyl* α-*methyl*-Δ^{α}-*propenyl ketone*, b.p. 127°/10 mm.; 1-*keto*-2-*ethylidene*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 45—46°, b.p. 158—160°/10 mm., is similarly prepared. A. T. P.

Keto–enol tautomerism of acenaphthenone. (Signa.) E. Ghigi (Gazzetta, 1938, **68**, 184—192).—Acenaphthenone (I) in aq. EtOH–KOH with PhN_2Cl or *o*-OMe·C_6H_4·N_2Cl gives the mono-phenyl- or -*o*-anisyl-hydrazone (cf. A., 1916, i, 212) of acenaphthenequinone (II), by isomerisation of the corresponding azo-derivative of enolic (I). Similarly (I) in aq. EtOH–KOH with $NaNO_2$, rapidly acidified by HCl, yields the monoxime of (II). Attempts to isolate the enol of (I) by Hieber's method (A., 1921, ii, 466) were unsuccessful. $K_3Fe(CN)_6$ and (I) in EtOH–KOH give 7 : 7′-diacenaphthyliden-8-one (III) (A., 1896, i, 444), whilst $FeCl_3$ gives 7 : 7′-diacenaphthenonyl (A., 1938, II, 20). With boiling Ac_2O, (I) yields 8-*acetoxy*-7-*acetylacenaphthylene* (?) (IV), m.p. 133—134°, hydrolysed (H_2SO_4) to a *substance* (V), m.p. 117°, or (NaOH) to (III) with traces of (V). It is suggested that (IV) is formed by way of acetoxyacenaphthylene and acetylacenaphthenone, by repeated enolisation. E. W. W.

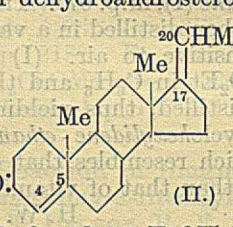
Syntheses in the naphthindene series. G. Wojack, S. Glupe, and H. Jatzkewitz (Ber., 1938,

71, [*B*], 1372—1381).—Et α-1-naphthoylpropionate is converted by the successive action of PCl_5 in CCl_4 and AcCl containing a little conc. H_2SO_4 into 3-*chloro*-2-*methyl*-4 : 5-*benzoindone* (I), m.p. 133°, transformed by warm conc. H_2SO_4 or by NaOH–EtOH into 2-methyl-4 : 5-benzoindane-1 : 3-dione, m.p. 110°. Et α-2-naphthoylpropionate (II) is converted by PCl_5 first in boiling CCl_4 and subsequently at 140° into 2 : 3 : 3-*trichloro*-2-*methyl*-6 : 7-*benzoindan*-1-*one* (III), m.p. 95°, whence (conc. H_2SO_4 at 70—80°) 2-chloro-2-methyl-4 : 5-benzoindanedione, m.p. 132°. Partial dehalogenation of (III) by Cu powder in abs. EtOH at about 90° gives 3-*chloro*-2-*methyl*-6 : 7-*benzoindone*, m.p. 97°, also obtained from (II) and PCl_5 (1 : 1) in CCl_4 and then accompanied by β-*chloro*-β-2-*naphthyl*-α-*methylacrylic acid*, m.p. 145°. Successive additions of SO_2Cl_2 and PCl_5 to Et 2-naphthoylacetate (IV) in CCl_4 and final heating of the mixture at 150° leads to 2 : 2 : 3 : 3-*tetrachloro*-6 : 7-*benzoindan*-1-*one* (V), m.p. 135°, transformed by 96% H_2SO_4 at 110—120° into 2 : 2-*dichloro*-6 : 7-*benzoindane*-1 : 3-*dione*, m.p. 182°, which is converted by HI (*d* 1·7) and red P into 6 : 7-benzoindane-1 : 3-dione, m.p. 177—178° (decomp.). Cu powder in boiling EtOH transforms (V) into 2 : 3-*dichloro*-6 : 7-*benzoindone*, m.p. 136°. (IV) and PCl_5 (3·5 mols.) in CCl_4 give mainly β-*chloro*-, m.p. 214° (decomp.), and α-β-*dichloro*-β-2-*naphthylacrylic acids*, m.p. 172°. 1-Naphthylacrylic acid is converted into the dibromide, m.p. 189° (decomp.), transformed by anhyd. KOH in boiling EtOH into 1-*naphthylpropiolic acid*, m.p. 137°. This is transformed by boiling AcOH–Ac_2O into 8-α-*naphthylphenanthrene*-6 : 7-*dicarboxylic anhydride*, m.p. 206°, and by the successive action of Br in Et_2O and P_2O_5 at 85° into 2 : 3-*dibromo*-4 : 5-*benzoindone*, m.p. 168° [oxidised by HNO_3 at 140° to 1 : 2 : 3 : 4-$C_6H_2(CO_2H)_4$]. H. W.

Attempted preparation of ninhydrin from 2-nitroindane-1 : 3-dione. G. Wanag and A. Lode (Ber., 1938, 71, [*B*], 1267—1272).—The decomp. of 2-nitroindane-1 : 3-dione (I) by heat gives indication of the formation of ninhydrin (II) (bisphenylhydrazone, new m.p. 180°) which could not thus be obtained cryst. Decomp. in a vac. is sometimes accompanied by violent explosion. In boiling AcOH (I) yields hydrindantin, m.p. 236° (red at 200°) (also + $2H_2O$) (cf., Ruhemann, J.C.S., 1911, 99, 792), and an amorphous yellow *compound*, m.p. about 135° (decomp.). Oxidation of (I) gives *o*-$C_6H_4(CO_2H)_2$ as the only isolable product. 2-Bromo-2-nitroindane-1 : 3-dione does not give appreciable amounts of (I) when heated by itself, whereas in boiling $PhNO_2$ (II) is obtained in about 40% yield accompanied by 2 : 2-dibromoindanedione, m.p. 178°. Rapid passage of Cl_2 through a solution of (I) in H_2O gives 2-*chloro*-2-*nitroindane*-1 : 3-*dione* (III), m.p. 124°, decomp. about 150°, in 89·1% yield; the yield diminishes if the passage of Cl_2 is prolonged on account of the oxidation to *o*-$C_6H_4(CO_2H)_2$. In boiling $PhNO_2$ (III) affords (II) (yield 22·5—45%) and dichloroindanedione, m.p. 124°. H. W.

Steroids and sex hormones. XLIV. Elimination of hydrogen bromide from 2-bromocholestanone and 2-bromoandrostanedione. L. Ruzicka, P. A. Plattner, and R. Aeschbacher (Helv. Chim. Acta, 1938, 21, 866—872).—2-Bromocholestanone is converted by boiling C_5H_5N into 3-*keto*-2-*cholestanylpyridinium bromide*, m.p. 310° (decomp.) when placed in a preheated bath, which in EtOH gives an immediate ppt. of AgBr when treated with $AgNO_3$. It passes when distilled at 250—300°/10 mm. into Δ^4-cholestenone, m.p. 80—80·5°, $[\alpha]_D$ +87° in EtOH. Analogously, 3 : 17-*diketo*-2-*androstanylpyridinium bromide* (+H_2O), m.p. about 315° (decomp.), affords Δ^4-androstene-3 : 17-dione, m.p. 172—173°, $[\alpha]_D$ +193° in $CHCl_3$. That Br is at $C_{(2)}$ is proved by conversion of 2-bromocholestan-3-one by NaOAc in boiling AcOH into 2-*acetoxycholestan*-3-*one*, m.p. 146°, which is hydrolysed to 2-*hydroxycholestan*-3-*one*, m.p. 126°; this is oxidised to the dicarboxylic acid, $C_{27}H_{46}O_4$, m.p. 196°, identical with that derived directly from cholestanol. H. W.

Transformation products of 17-ethyltestosterone. A. Butenandt, J. Schmidt-Thomé, and H. Paul (Ber., 1938, 71, [*B*], 1313—1316; cf. A., 1936, 727).—An improved method for the conversion of dehydroandrosterone into 17-ethyltestosterone (I) is described. Dehydration of (I) is best effected by distillation with anhyd. $CuSO_4$ in a high vac. and the product is identified as $\Delta^{4:5\text{-}17:20}$-*pregnadien*-3-*one* (II), m.p. 135°, since it is converted by successive treatment with OsO_4 in Et_2O and aq. EtOH–Na_2SO_3 into Δ^4-*pregnene*-17 : 20-*diol*-3-*one*, m.p. 199°, which is oxidised by $Pb(OAc)_4$ to MeCHO and the known Δ^4-androstene-3 : 17-dione.



(II.)

H. W.

Colouring matter of the lobster (*Astacus gammarus*, L.). R. Kuhn and N. A. Sörensen (Angew. Chem., 1938, 51, 465—466; cf., A., 1933, 509).—"Ovoverdin" from fresh lobster eggs is purified by repeated adsorption on $Al(OH)_3$, extraction with 40% $(NH_4)_2SO_4$, and pptn. with 65% $(NH_4)_2SO_4$. Fission of "ovoverdin" (dil. acids, EtOH, $COMe_2$, or heat) yields *astaxanthin* (I), $C_{40}H_{52}O_4$, a di-α-ketol [and not an ester (cf. *loc. cit.*)], which is autoxidised by alkali to astacin, and gives blue salts with alkali in absence of O_2. (I) is formulated as a diketodihydroxy-β-carotene, and the blue colour of the "ovoverdin" is ascribed to salt formation between (I) and proteins. J. D. R.

Formation of isomeric phenylhydrazones in the Japp–Klingemann reaction. A. Sempronj (Gazzetta, 1938, 68, 263—271).—2-$C_{10}H_7$·CH_2Cl with NaOEt and CH_2Ac·CO_2Et gives *Et* α-*acetyl*-β-2-*naphthylpropionate*, b.p. 180°/1·2 mm., which in EtOH with aq. NaOH and PhN_2Cl yields, after hydrolysis, 2-*naphthylpyruvic acid phenylhydrazone* (I), m.p. 187—188°, with β-2-*naphthylpropionic acid*, m.p. 134—135°. With EtOH–HCl, (I) forms 3-β-*naphthylindole*-2-*carboxylic acid*, m.p. 223—224° (decomp. to 3-β-*naphthylindole*, m.p. 141—142°). 2-$C_{10}H_7$·CH_2·CN and $Et_2C_2O_4$ with NaOEt furnish the *Na* derivative of *Et* β-*cyano*-β-2-*naphthylpyruvate*, m.p. 143—144°, hydrolysed to β-$C_{10}H_7$·CH_2·CO·CO_2H, giving the normal phenylhydrazone. 1 : 2-$C_{10}H_6Br$·CH_2Br with NaOEt and CH_2Ac·CO_2Et gives

Et α-acetyl-β-1-bromo-2-naphthylpropionate, which in EtOH with NaOH and PhN_2Cl gives, after hydrolysis, two stereoisomeric *1-bromo-2-naphthylpyruvic acid phenylhydrazones*, m.p. 178° and 187—188°; both of these give, after hydrolysis, 3-(*1'-bromo-2'-naphthyl*)*indole-2-carboxylic acid*, m.p. 240° (decomp.). 1 : 2-$C_{10}H_6Br{\cdot}CH_2{\cdot}CN$ with $Et_2C_2O_4$ and NaOEt yields the *Na* derivative of *Et* β-*cyano*-β-1-*bromo*-2-*naphthylpyruvate*, m.p. 194—195°, hydrolysed (H_2SO_4) to 1-*bromo*-2-*naphthylpyruvic acid*, m.p. 190—191°, which gives the phenylhydrazone of m.p. 187—188° (see above). E. W. W.

Degradation of deoxycholic acid to ætiodeoxycholic acid through ætiodeoxycholyl methyl ketone. W. M. Hoehn and H. L. Mason (J. Amer. Chem. Soc., 1938, **60**, 1493—1497).—Deoxycholic acid is degraded by the Barbier–Wieland process (cf. A., 1927, 247) to *ætiodeoxycholic acid* (I), m.p. 283—286°, $[\alpha]_{5461}^{25}$ +102±1·5°. Oxidation of the diphenyl-carbinols or -ethylenes by CrO_3 in hot AcOH gives about 50% yields, but at <15° gives 70% yields. In the last stage direct oxidation of αα-*diphenyl*-β-3 : 12-*diacetoxyternorcholanylethylene*, m.p. 215—217°, $[\alpha]_{5461}^{25}$ +537° in EtOH, gives only 16% of (I), but ozonolysis (excess of O_3 to be avoided) in $CHCl_3$ to 3 : 12-*diacetoxyætiocholanyl Me ketone* (II), m.p. 121—122·5°, $[\alpha]_{5461}^{25}$ +190·4±2·5° in EtOH, condensation with PhCHO by NaOEt (which partly hydrolyses the OAc), reacetylation by Ac_2O, ozonisation of the crude product to the glyoxal (not purified), oxidation thereof by HIO_4 in aq. EtOH, and finally hydrolysis by hot 2N-NaOH give an over-all yield of about 40% of (I). The following intermediates are described. αα-*Diphenyl*-β-3 : 12-*diacetoxynorcholanylethylene*, m.p. 160°, $[\alpha]_{5461}^{25}$ +118±2° in EtOH; *nordeoxycholic acid*, +$COMe_2$, double m.p. 140—145° and 206—210°, $[\alpha]_{5461}^{25}$ +62±2·5° in EtOH; αα-*diphenyl*-β-3 : 12-*diacetoxybisnorcholanylethylene*, m.p. 158—160°, $[\alpha]_{5461}^{25}$ +183±2° in EtOH; *bisnordeoxycholic acid*, +H_2O, double m.p. 195—202° and 236—238°, $[\alpha]_{5461}^{25}$ +35·8±5° in EtOH. 2N-KOH hydrolyses (II) to 3 : 12-*dihydroxyætiocholanyl Me ketone*, m.p. 165—166°, $[\alpha]_{5461}^{25}$ +165±5° in EtOH, converted by CrO_3 into 3 : 12 : 17-*triketoætiocholane*, m.p. 189—191°, $[\alpha]_{5461}^{25}$ +235±2·5° in EtOH. *Dehydro-nor-*, m.p. 230—232°, $[\alpha]_{5461}^{25}$ +114±2° in EtOH, *-bisnor-*, m.p. 275—276° (sinters at 265°), $[\alpha]_{5461}^{25}$ +98±5° in EtOH, and *-ætio-deoxycholic acid*, m.p. 177—178·5°, $[\alpha]_{5461}^{25}$ +166±4° in EtOH, are prepared. M.p. are corr. R. S. C.

Sterols. XXXIII. 3 : 11-Dihydroxy-12-ketocholanic acid and derivatives [thereof]. R. E. Marker and E. J. Lawson (J. Amer. Chem. Soc., 1938, **60**, 1334—1337; cf. A., 1938, II, 276).—Partial hydrogenation of dehydrodeoxycholic acid gives a mixture (not a mol. compound) of 3-(α-) (I) and 3-(β-)hydroxy-12-ketocholanic acid (cf. Kyogoku, A., 1937, II, 150). When deoxycholic acid is heated with slightly >0·5 mol. of Ac_2O in AcOH at 135° and then oxidised with CrO_3 in 50% AcOH at 20—30°, the product after hydrolysis may be separated into deoxycholic acid and (I), anhyd., m.p. 161—162°, and +xC_6H_6, double m.p. 110° and 161—162° (Ac derivative, m.p. 195°). Ruzicka and Goldberg's prep. (A., 1935, 749) of lithocholic acid, m.p. 184°, from (I) is improved. The semicarbazone of (I) has m.p. 241°. With $3Br_2$ at 60—80° the Ac derivative of (I) gives a Br_2-derivative, but when treated with Br–HBr in Ac_2O–AcOH at 70° and then hydrolysed by KOH–aq. MeOH, gives 3(α-) : 11-*dihydroxy*-12-*ketocholanic acid*, m.p. 196° (3-*Ac* derivative, m.p. 268°; *semicarbazone*, m.p. 238°); this resists Clemmensen reduction owing to steric protection of the CO by the OH; the 11-OH is readily removed by dehydration. R. S. C.

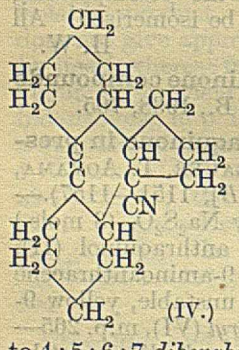
New degradation of digoxigenin. M. Steiger and T. Reichstein (Helv. Chim. Acta, 1938, **21**, 828—844).—Identical products, as expected from the present constitutional formulæ of digoxigenin (I) and corticosterone (II), are not obtained by the oxidation of these substances. It is therefore probable that OH placed at present at $C_{(11)}$ in (I) and (II) has actually a different position. Digoxigenin diacetate is oxidised by $KMnO_4$ in $COMe_2$ at room temp. to 14-*hydroxy*-3 : (?)11-*diacetoxyætiocholanic acid*, m.p. 229—230°, hydrolysed (KOH–MeOH) to 3 : (?)11 : 14-*trihydroxyætiocholanic acid* (III), different samples m.p. 246—247° (decomp.), 214—215° (decomp.), and 188—190° (probably minute amounts of impurities have a very pronounced effect on the m.p.) (*Me* ester, m.p. 90—95° and 208—212° after re-solidification at about 125°). This is oxidised by CrO_3 in AcOH at room temp. to 14-*hydroxy*-3 : (?)11-*diketoætiocholanic acid*, m.p. 236—237° (*Me* ester, m.p. 174—178°). 5% H_2SO_4 converts (III) in dioxan at 100° into a mixture of acids including cryst. 3 : (?)11-*dihydroxyætiocholenic acid* (IV), m.p. 282—286° (decomp.) (hygroscopic *Me* ester, m.p. 170—172°); this is hydrogenated with extreme difficulty and is oxidised (CrO_3 in AcOH at room temp.) to a substance, m.p. 220—235°. The amorphous material obtained from the mother-liquors of (IV) is esterified (CH_2N_2), hydrogenated (PtO_2), and hydrolysed to 3 : (?)11-*dihydroxyætiocholanic acid*, m.p. 280—286° (slight decomp.), the *Me* ester, m.p. 180—183°, of which is oxidised to *Me* 3 : (?)11-*diketoætiocholanate* (V), m.p. 171—172°, $[\alpha]_D^{20}$ +138·3°±2° in MeOH. 3 : (?)11-Diketoætiocholanic acid is reduced (Zn–Hg and conc. HCl) to ætiocholanic acid. (V) is transformed by the successive action of Br–HBr–AcOH and boiling C_5H_5N into *Me* Δ^4-3 : (?)11-*diketoætiocholenate*, m.p. 236—237°, $[\alpha]_D^{19}$ + 185°±2° in MeOH, to which the corresponding ester derived from (II) could not be isomerised. All m.p. are corr. H. W.

Conversion of leuco-anthraquinone compounds into their oxidised forms.—See B., 1938, 765.

Action of ammonia on anthraquinone in presence of reducing agents. K. Lauer, T. Aoyama, and H. Shingu (Ber, 1938, **71**, [*B*], 1151—1157).—Anthraquinone (I) is converted by $Na_2S_2O_4$ (3 mols.) and NH_3 (*d* 0·88) at 150° into anthraquinol (II), anthranol (III), dianthranol (IV), 9-aminoanthracene (V) (main product), and the very unstable, yellow 9-*imino*-9'-*keto*-10 : 10'-*dihydrodianthryl* (VI), m.p. 265—266° (decomp.). This is sol. in warm alkali, cannot be methylated or acetylated, does not give a vat, and does not couple. The *Ac* derivative, m.p. 272—273°, of (V) with Me_2SO_4 and EtOH–alkali gives a *Me* deriv-

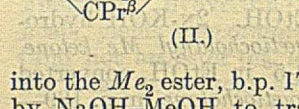
ative, m.p. 195—200° (decomp.). (IV) and (VI) arise from secondary oxidations. (II) is transformed by NH_3 under pressure and in the absence of a reducing agent into (V) (yield about 25%) whilst about 50% of (II) is recovered [as (I)]; (VI) and 9 : 9′-*di-imino*-10 : 10′-*dihydrodianthryl*, m.p. 204—205°, but not (III), are also formed in small proportion. Increase in the amount of $Na_2S_2O_4$ causes diminution in the total yield and in that of (V), reduction proceeding extensively to the anthracene stage before reaction with NH_3 occurs. Under similar conditions halogeno- or sulpho-anthraquinones give the corresponding amines without loss of the usually mobile substituent. The behaviour of Na_2SO_3 resembles that of $Na_2S_2O_4$. H. W.

Synthesis of polycyclic compounds from di-*cyclo*hexenyl. C. Weizmann, E. Bergmann, and T. Berlin (J. Amer. Chem. Soc., 1938, **60**, 1331—1334).—The adduct, m.p. 113—115°, of di-Δ^1-*cyclo*hexenyl (I) and (:CH·CO)$_2$O is dehydrogenated by S at 245° to phenanthrene-9 : 10-dicarboxylic anhydride (II), m.p. 312°, but by $Pb(OAc)_4$ only to the 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-H_8-*anhydride*, m.p. 305°. With MgPhBr (II) gives 9-benzoylphenanthrene-10-carboxylic acid, m.p. 218°, and thence (P_2O_5 on chloride in decahydronaphthalene) 1 : 2 : 3 : 4-dibenzanthraquinone (III), m.p. 180°. *o*-9-Phenanthroylbenzoic acid [prep. from $C_{14}H_9$·MgBr and *o*-$C_6H_4(CO)_2O$ with, in some cases, *di*-9-*phenanthrylphthalide*, m.p. 239°, as a by-product] gives the impure *chloride*, m.p. 165—166° (decomp.), which is converted (as above) into (III). CHPh:CH·CO_2H and (I) at 180° give 9-*phenyl*-$\Delta^{12:13}$-*dodecahydrophenanthrene*-10-*carboxylic acid*, m.p. 221°; CHPh:CH·CO_2Et gives the corresponding *Et* ester, m.p. 85—86°, which is resistant to hydrolysis; the acid with Se at 300—320° gives 9-phenylphenanthrene, m.p. 113°, but with S at 260° yields 9-phenylphenanthrene-10-carboxylic acid. With *p*-O:C_6H_4:O at 140° (I) gives the normal adduct, *eicositetrahydrotetrabenzanthraquinone*, m.p. 247°, together with *p*-$C_6H_4(OH)_2$ and (?) s-*tetra*(*tetramethylene*)-1 : 4 : 5 : 8-*tetrahydroanthraquinone*, m.p. 297°. The product, m.p. 315° (decomp.), described by Barnett and Lawrence (A., 1935, 1243) was not obtained. The normal adduct is not obtained from (I) and α-naphthaquinone, but, instead, the partly dehydrogenated deca-, m.p. 254°, and *octa-hydro*-1 : 2 : 3 : 4-*dibenzanthraquinone*, m.p. 238—239°, and 1 : 4-$C_{10}H_6(OH)_2$ are formed. 1-Cyano-Δ^1-*cyclo*pentene and (I) at 150—160° give only a trace of the *adduct* (IV), b.p. 210—220°/1·5 mm. Mg 9-phenanthryl bromide and $CH(OEt)_3$ give *phenanthrene*-9-*aldehyde Et*$_2$ *acetal*, b.p. 175°/0·75 mm., hydrolysed to the free aldehyde, m.p. 98°, b.p. 200°/1·5 mm., which leads to β-9-phenanthryl-acrylic, m.p. 255°, and -propionic acid, m.p. 178°, cyclised by P_2O_5 in PhMe at 100° to 4 : 5 : 6 : 7-*dibenzhydrindone*, m.p. 164°; Clemmensen reduction then yields 9 : 10-*cyclo*pentenophenanthrene, m.p. 154°. With phenyl-*p*-benzoquinone at 120—125° (I) gives 2-*phenyl*-5 : 6 : 7 : 8-*bistetramethylene*-5 : 8 : 9 : 10-*tetrahydronaphtha*-1 : 4-*quinone*, m.p. 207—208°, but in $PhNO_2$ dehydrogenation to 2-*phenyl*-5 : 6 : 7 : 8-*bistetramethylene*-5 : 8-*dihydronaphtha*-1 : 4-*quinone*, m.p. 140—141°, occurs simultaneously. 2 : 3-Dimethylindone and (I) in PhMe at 200° give 9 : 10-*dimethyl*-s-*dodecahydrophenanthreno*-[9 : 10-2 : 3]-*hydrindone*, b.p. 165—175°/0·1 mm., reduced (Clemmensen) to the corresponding *hydrindene* derivative, b.p. 240—245°/0·1 mm., dehydrogenation of which at 300° gives traces of a substance, m.p. >300°, and an oil (picrate, m.p. 210°). R. S. C.


(IV.)

Chenopodium oil. III. Ascaridole. H. Paget (J.C.S., 1938, 829—833).—Ascaridole (I) has m.p. 2°, b.p. 113—114°/20 mm., $[\alpha]_D$ −0·03°; repeated crystallisation has not indicated any separation. Reduction ($TiCl_3$) gives C_3H_8 and *p*-cresol, together with very small amounts of an unsaturated *glycol*, $C_{10}H_{18}O_2$, m.p. 84°, a *chlorotrihydroxymenthane* (?), m.p. 191° (*mono*-p-*nitrobenzoate*, m.p. 124°), and ascaridole ω-glycol (*mono*-, m.p. 150°, and *di*-p-*nitrobenzoate*, m.p. 174°). Hydrogenation (Pd) of (I) affords *cis*-1 : 4-terpin (*mono*-, m.p. 117°, and *di*-p-*nitrobenzoate*, m.p. 172°), whilst with PtO_2–H_2 *dihydroascaridole*, m.p. 19·5°, $[\alpha]_D$ ±0°, is obtained. This is reduced ($TiCl_3$) to 1-*methyl*cyclo*hexan*-1-*ol* 3 : 4-*oxide* (?), m.p. 45° (*mono*-p-*nitrobenzoate*, m.p. 157°), and C_3H_8. Partial hydrogenation (Pd–C) of (I) yields Δ^2-*p*-menthene-1 : 4-diol (*di*-p-*nitrobenzoate*, m.p. 130°). F. R. S.

Diene synthesis. XXIX. α-Terpinene. O. Diels, W. Koch, and H. Frost (Ber., 1938, **71**, [*B*], 1163—1172).—α-Terpinene (I) and maleic anhydride give cis-3-*methyl*-6-iso*propyl*endo*ethylenetetrahydrophthalic anhydride* (II), b.p. 195°/12 mm., m.p. 66—67° [corresponding *acid* (III), m.p. 158° (decomp.), and its *Na* salt]. (II) is converted by MeOH–H_2SO_4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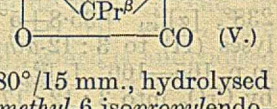
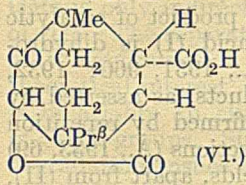
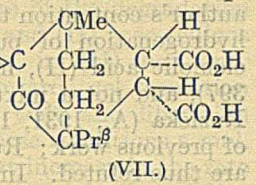

(V.)

into the *Me*$_2$ ester, b.p. 175—180°/15 mm., hydrolysed by NaOH–MeOH to trans-3-*methyl*-6-iso*propyl*endo-*ethylenetetrahydrophthalic acid* (IV), m.p. 203°. Hydrogenation (colloidal Pd–MeOH) followed by distillation of (III) gives cis-3-*methyl*-6-iso*propyl*endo*ethylene-hexahydrophthalic anhydride*, m.p. 54°, identical with the product obtained directly from (II). Similarly (IV) is reduced to trans-3-*methyl*-6-iso*propyl*endo-*ethylenehexahydrophthalic acid*, m.p. 218°. There is therefore no need to doubt the structure already assigned to (I). Lactonisation of (II) or (III) proceeds with exceptional difficulty (50% H_2SO_4 at 100° for 6 days for a partial change) and is accompanied by a *trans*-isomerisation of the free CO_2H, the product therefore being the *lactonic acid* (V), m.p. 169—170°. The cis-*lactonic acid*, m.p. 185°, is obtained by debromination of the *monobromolactonic acid* (VI), m.p. 178° (slight decomp.), obtained by the action of Br–H_2O on (III); it is isomerised to (V) by treatment with CH_2N_2 followed by alkaline hydrolysis. KOH–MeOH–H_2O followed by Ac_2O transform (VI) into the *dilactone*, $C_{14}H_{18}O_4$, m.p. 235°. Oxidation of (II) with

$KMnO_4$ gives in small amount a *ketocislactonic acid* (VI), m.p. 218°, characterised as the *Me* ester, m.p.



(VI.)



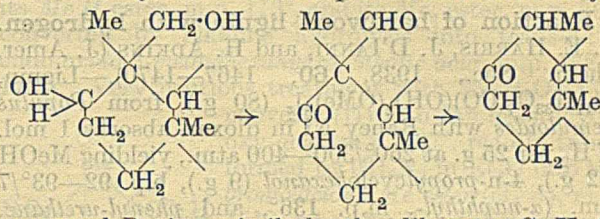
(VII.)

161°, whilst a second oxidation product is a *hydroxyketodicarboxylic acid* (VII), m.p. 216° (decomp.) (*Me_2* ester, m.p. 150°; *anhydride*, m.p. 198°). No evidence of the formation of the expected $(CO_2H)_4$ acid was obtained. Ozonisation of (II) in EtOAc and treatment of the product with H_2–Pd–$CaCO_3$ affords a neutral *compound*, m.p. 214°, which cannot be esterified and does not give the customary reactions for ketones. Δ^3-Carene (VIII) differs from (I) in containing a 3-membered ring in place of a double linking so that the conjugation in (I) is replaced by that of a double linking and a 3-membered ring; this is frequently ruptured during additive reactions and behaves as a double linking. If this is here the case (II) must also result from (VIII) and maleic anhydride. Actually a well-defined adduct is obtained, converted by NaOH into an acid, $C_{14}H_{20}O_4$, m.p. 184° (decomp.) (*Na* salt), which is not identical with (III) and of which the structure is not established. H. W.

Anomalous mutarotation of salts of Reychler's acid. V. Comparison of the absorption spectrum of 2-*N*-methylimino-*d*-camphane-10-sulphonic acid with the spectra of other camphane derivatives. R. L. Shriner and H. Sutherland (J. Amer. Chem. Soc., 1938, **60**, 1314—1316; cf. A., 1936, 339).—The ketimine structure of 2-methylimino-*d*-camphane-10-sulphonic acid (modified prep.), m.p. 312—313° (block), $[\alpha]_D$ −137·6° in EtOH, is confirmed by the close resemblance of its absorption spectrum in 95% EtOH (absorption only at <2700 A.) to that of the 2-N·OH-compound and the difference thereof from those of camphor and Reychler's acid (max. at 2870 A.). R. S. C.

Myrcenal and myrcenol. R. Delaby and E. Dupin (Bull. Soc. chim., 1938, [v], **5**, 931—938). The products of interaction of myrcene and SeO_2 in EtOH at 80° for 2 hr. and then at 95—96° for 1 hr. are examined. Fractions, b.p. 101—111°/9·5 mm. (*semicarbazone*, $C_{11}H_{17}ON_3$, m.p. 168—169°), b.p. 113—116°/17 mm. (2 : 4-*dinitrophenylhydrazone*, $C_{16}H_{18}O_4N_4$, m.p. 129·5—130°), and b.p. 108—113°/11·5 mm. [Ag_2O gives an acid, $C_{10}H_{14}O_2$ (*Ba* salt)], indicate the presence of an aldehyde, *myrcenal* (I), $C_{10}H_{14}O$, b.p. 116—119°/17 mm., and some ketones (*myrcenones*). A primary alcohol, *myrcenol*, $C_{10}H_{16}O$, b.p. 123—128°/17 mm. (*allophanate*, m.p. 110—111°), converted into (I) by SeO_2–EtOH at 93—95° for 1½ hr., and an *alcohol*, b.p. 140—145°/17 mm., are also obtained. Raman spectra of many fractions are examined; the myrcene skeleton is intact. A. T. P.

Dehydrogenation of triterpene alcohols by means of finely divided copper. K. Tsuda and S. Kitagawa (Proc. Imp. Acad. Tokyo, 1938, **14**, 182—183).—Triterpene alcohols are dehydrogenated (annexed scheme) by heating with Cu as by treating with CrO_3, but usually with better yield. Thus, heating hederagenin Me ester with Cu-bronze at 300° and distilling in vac. gives CH_2O and methylhederagenone, m.p. 203°, $[\alpha]_D^{19}$ +104·9°, the reaction occurring as shown by the annexed partial formulæ. Soja-



sapogenol-*B* gives similarly the diketone, $C_{19}H_{44}O_2$ (A., 1938, II, 729). Betulin is, however, unchanged; dihydrobetulin requires repeated distillation to give a small yield of a *keto-aldehyde*, $C_{30}H_{48}O_2$, m.p. 183—185°, $[\alpha]_D^{25}$ +11·45° (*dioxime*, decomp. 275°).

R. S. C.

Lignin. D. Krüger (Zellstoff u. Papier, 1938, **18**, 305—311).—Recent advances in the chemistry of lignin are reviewed. All lignins probably have the same fundamental structure, although their properties vary somewhat with the method of isolation. The aromatic nature of lignin is suggested by the formation of veratric and protocatechuic acids by fusion with alkali, although lignin–carbohydrate complexes appear to be present in nature. D. A. C.

Lignin. XI. Action of amidosulphonic acid on pine wood. H. Friese and H. Ademeit (Ber., 1938, **71**, [*B*], 1307—1312).—The use of H_2SO_4–Ac_2O–AcOH in the treatment of lignin has the disadvantage that the sulphoacetic acid (I) produced is very difficult to separate from the ligninsulphonic acid. Attempts are therefore made to replace it by $NH_2{\cdot}SO_3H$; this reacts rapidly with boiling AcOH–Ac_2O giving NH_4 sulphoacetate, but below 50° the change is much slower than the formation of (I) from H_2SO_4–Ac_2O–AcOH. According to conditions $NH_2{\cdot}SO_3H$ degrades cellulose (II) to lower sugar acetates or gives sol. complex products containing about 13% of Ac. The reaction between pine wood and $NH_2{\cdot}SO_3H$–Ac_2O–AcOH at about 50° proceeds with feeble disengagement of heat but complete dissolution is never attained. The residue is filtered and washed with AcOH and H_2O. The acid solution contains sugar acetates and NH_4OAc. Ultrafiltration of the aq. solution gives a brown residue which is doubtless a lignin–carbohydrate compound. The residue yields to hot H_2O a dark brown powder intermediate in composition between lignin and polysaccharide which does not contain N or S; the undissolved portion (42% of the wood) does not contain N or S and after hydrolysis with NaOMe yields a material with the analytical data of (II). Hydrolysis with 66% H_2SO_4 establishes the presence of >90% of carbohydrates. Treatment of wood with $NH_2{\cdot}SO_3H$, therefore, resembles sulphite boiling rather than sulphacetolysis. The lignin is not sulphonated, whereas if it had an aromatic and hence phenolic nature its sulphonation is certain. Further the C content of the so-called lignin substance is ≪ that customary for acid lignin and points rather to the addition of H_2O to a C_9 complex. All the reactions of native lignin (towards

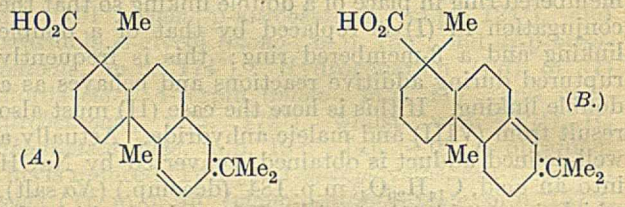
H_2SO_4, H_2SO_3, HNO_3, and $NH_2{\cdot}SO_3H$) and its behaviour towards conc. mineral acids are not due to an aromatic nature but to an ill-understood at. grouping which is also responsible for the union of lignin in wood with the polysaccharide portions. H. W.

Reaction of hardwood lignin with hydrogen. E. E. Harris, J. D'Ianni, and H. Adkins (J. Amer. Chem. Soc., 1938, **60**, 1467—1470).—Lignin, $[C_{41}H_{33}O_7(CO)(OH)_2(OMe)_8]_x$ (80 g.), from *Populus tremuloides* with Raney Ni in dioxan absorbs 1 mol. of H_2 per 25 g. at 260°/300—400 atm., yielding MeOH (22 g.), 4-n-*propyl*cyclo*hexanol* (9 g.), b.p. 92—93°/7 mm. (*α-naphthyl-*, m.p. 136°, and *phenyl-urethane*, m.p. 131°; also prepared by H_2–Raney Ni at 100—200° from *p*-OH·C_6H_4·OEt), (?) *γ-4-hydroxy*cyclo*hexylpropyl alcohol* (20 g.), b.p. 125—127°/1 mm. [3 : 5-*dinitrobenzoate*, m.p. 130—144°; oxidised by $Na_2Cr_2O_7$–H_2SO_4 at 65° or CrO_3–aq. AcOH–C_6H_6 at room temp. to an *acid*, $C_9H_{14}O_3$, b.p. about 280°/740 mm., m.p. 55—60° (2 : 4-, m.p. 80°, and 3 : 5-*dinitrophenylhydrazone*, m.p. 90—93°)], 4-n-*propyl*cyclo*hexane*-1 : 2-*diol* (3 g.), b.p. 107—110°/1 mm. [*di*-(*α-naphthylurethane*), m.p. 218—219°; also obtained by hydrogenation (Raney Ni) of 3 : 4-$(OH)_2C_6H_3$·COEt, prepared from 1 : 2-OH·C_6H_4·O·COEt], a mixture (I) (18 g.), b.p. 130—260°/ 1 mm., compounds (5 g.), b.p. >260°/1 mm., and intermediate fractions (4 g.). Analysis of (I) indicates the formula $(C_6H_{11}O)_n$, *n* being 3—5; dehydration by Al_2O_3–pumice in H_2 at 400°, followed by hydrogenation (Raney Ni) at 200°/300 atm., gives hydrocarbons, C_nH_{2n-2} or C_nH_{2n-4}, which from the b.p. (mostly 90—140°/1 atm.) must contain >9C. The presence of units larger than C_9 in lignin is certain. Ether linkings are probable. The relative amounts of the products may be due to the relative ease of hydrogenation and hydrogenolysis and may not indicate differences in structure. Cleavage of C·C linkings is inferred from the large yield of MeOH. The very large absorption of H_2 is noteworthy. R. S. C.

Cativic acid. Its preparation, properties, and derivatives. N. L. Kalman (J. Amer. Chem. Soc., 1938, **60**, 1423—1425).—The oleo-resinous exudate ("cativo") from *Prioria copaifera*, Griseb., contains 0·5% of H_2O, <2% of volatile oil, and >95% of *cativic acid* and its *cativyl* ester. The acid, $C_{20}H_{34}O_2$, b.p. 194—195°/1 mm., is obtained by distillation in vac. or dissolution in EtOH, in which the ester is insol. The ester cannot be distilled, but yields, when hydrolysed, *cativyl alcohol*, $C_{20}H_{36}O$, b.p. 208·5—209·5° (slight decomp.)/4·5 mm. [*acetate*, b.p. 191° (slight decomp.)/2·5 mm.]. The alkali *salts* of the acid have detergent action and are pptd. by electrolytes as jellies; other metallic *salts* are thermoplastic and sol. in hydrocarbons etc. *Me*, b.p. 200°/1 mm., *Et*, b.p. 206°/2·5 mm., *Bu*^{a}, b.p. 208°/2·75 mm., iso-*amyl*, b.p. 221°/3·5 mm., *β-methoxyethyl*, b.p. 243°/23 mm., *β-hydroxyethyl*, b.p. 212°/1·75 mm., and *β-butoxyethyl cativate*, b.p. 240°/2·5 mm., and *triethyleneglycol di-*, b.p. 312°/1·5 mm., and *glyceryl tri-cativate* are described. Cold $KMnO_4$ converts the acid into *dihydroxycativic acid*, m.p. 158°, the *Me* ester, m.p. 64°, of which loses H_2O when heated, yielding an oily ester, $C_{21}H_{36}O_3$. R. S. C.

Dihydroelemolic acid. M. Mladenović (Bull. Soc. Chim. Yougoslav., 1937, **8**, 169—174).—The author's contention that the sole product of catalytic hydrogenation of pure elemic acid (I) is dihydroelemolic acid (II), m.p. 238° (A., 1931, 960; 1932, 397), and not a mixture of products, as asserted by Ruzicka (A., 1931, 1067), is confirmed by repetition of previous work; Ruzicka's objections (A., 1933, 69) are thus refuted. Impure (I) yields, apart from (II), only tetrahydro-β-elemonic acid, whereas Ruzicka reported formation of two other acids, in addition to the three dihydroelemolic acids obtained from pure (I). R. T.

Abietic acid. H. Raudnitz, N. Lederer, and E. Kahn (Ber., 1938, **71**, [*B*], 1273—1274).—Ozonisation of abietic acid gives $COMe_2$ in about 3% yield, whence it appears that about 3% of an impurity of structure *A* or *B* is present. To this is probably due



the occurrence of the characteristic absorption max. at 237·5 mμ. whereas the main acid possibly shows no absorption in this region. H. W.

Resin acids. Action of palladium on abietic acid. E. R. Littmann (J. Amer. Chem. Soc., 1938, **60**, 1419—1421).—With 4% Pd-activated Al_2O_3 or 60% Pd-asbestos at 230° Me abietate gives 30—45% of Me dehydroabietate (I), m.p. 60—61° (CNS no. 7—8), which gives an aromatic $(NO_2)_2$-derivative, m.p. 192—193°, reduced (H_2–Cu–Cr_2O_3 at 150°/133 atm.) to *Me diaminodehydroabietate*, m.p. 133—134°, which, after diazotisation, couples with β-$C_{10}H_7{\cdot}NH_2$, R-salt, and PhOH. Abietic acid gives similarly dehydroabietic acid, m.p. 166—167° [converted into (I) by Me_2SO_4], and tetrahydroabietic acid, m.p. 159° (Me ester, b.p. 185—190°/5·7 mm. (CNS no. 5). Fieser's view (A., 1938, II, 108) that disproportionation to an aromatic and reduced acid occurs is thus supported. R. S. C.

Acetylation of Congo copal. E. Mertens and L. Hellinckx (Congr. Chim. ind. Bruxelles, 1935, **15**, II, 813—816; Chem. Zentr., 1936, ii, 1804).—Treatment of transparent Congo copal with AcOH–Ac_2O (4 : 1) for 5 days yields 30% of resinous *acetocopal*, $C_{24}H_{36}O_4$, m.p. 66°. A. H. C.

Constitution of pectin substances. II. Constitution and gel formation. G. G. Schneider and H. Bock (Ber., 1938, **71**, [*B*], 1353—1362; cf. A., 1937, II, 383).—In acid solution the gel is formed of pectin (I) whereas in an alkaline medium (I) suffers rapid removal of the OMe groups with production of insol. pectic acids or their Na salts which are pptd. by Na. The solidity of a (I) gel is a direct function of the mol. size. In addition to mean mol. wt. the proportion of particularly large mols. has an outstanding influence on the elasticity of the gel. In general, the OMe content of pure pectic substances (II) ∝ the mol.

wt. Usually the OMe content is determined on a mixture of (II) and pentosans (III) so that the % OMe is only indirectly a measure of the degradation of (II). The separation of (III) and (II) is so tedious that determination of % OMe in (II) has only theoretical interest. Impulse towards gel formation is invariably an elimination of OMe and liberation of CO_2H groups. Since under these conditions a mol. degradation ensues it follows that increase in the rate of gelation is accompanied by decrease in the solidity of the gel. Measurements of the acidity of solutions of (I) with exact control of the mol. size show that on treatment with acid of varied concn. the elimination of OMe is nearly parallel to fission of the mol. If, however, (I) is treated with cold, very dil. NaOH at p_H 8—9 OMe is almost completely eliminated within 1 hr. whereas the mol size decreases only very slowly. It is therefore obvious that the CO_2H groups are not concerned with the union of the (I) chains but are free. The parallelism between acidity and OMe content shows that the latter is located at the CO_2H group. The view that (I) is composed of esterified polygalacturonic acids involved with arabinose and galactose must be abandoned in favour of the conception that Me polygalacturonates themselves constitute (I). The nature of the (I) gel is discussed.

H. W.

Snake poisons.—See A., 1938, III, 669.

Pechmann dyes. P. Chovin (Ann. Chim., 1938, [xi], **9**, 447—553).—A fuller account of work already abstracted (A., 1937, II, 150, 294, 512; 1938, II, 110).

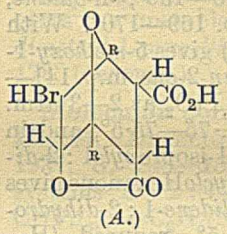
H. W.

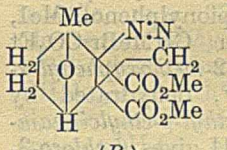
Enlargement of ring accompanying dehydration of tetrahydrofurfurylmethylcarbinol. R. Paul (Bull. Soc. chim., 1938, [v], **5**, 919—929; cf. A., 1933, 831).—Dehydration of tetrahydrofurfurylmethylcarbinol over Al_2O_3 (CO_2) at 400° yields mainly 2-methyl-Δ^2-dihydropyran (I), b.p. 105—106°/742 mm. Possible alternative structures are discussed; decomp. of the ozonide, and lability of Br in the bromination products, favour the pyran configuration. Further, aq. mineral acid affords hexan-α-ol-ε-one. (I) and H_2–Pt-black give 2-methyltetrahydropyran, b.p. 104—106°/770 mm., converted by HBr–AcOH at 150° into αε-dibromohexane, which with NH_2Ph–EtOH forms 1-phenyl-2-methylpiperidine (picrate, m.p. 157—158°; cf. isomeric picrate of 1-phenyl-2-ethylpyrrolidine, m.p. 126°) and with piperidine in $CHCl_3$ affords 1-pentamethylene-2-methylpiperidinobromide. The results of Connor *et al.* (A., 1936, 340) are discussed.

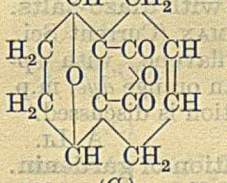
A. T. P.

Diene synthesis. V. Steric course of the diene synthesis in the furan series. Diene syntheses of furan and its homologues with acetylenedicarboxylic esters. K. Alder and K. H. Backendorf (Annalen, 1938, **535**, 101—113).—The diene syntheses with furan and its homologues proceed normally. As with *cyclo*pentadiene and *cyclo*hexadiene and their derivatives the addition is sterically selective and the adducts have the *endo* configuration. *trans-endo*-Oxidohexahydrophthalic acid, m.p. 179—180°, is obtained by hydrolysing the Me_2 ester of the corresponding *cis*-acid with saturated KOH–MeOH at 100°. Addition of sylvan to maleic anhydride (I) in Et_2O at room temp. affords 3 : 6-endo-*oxido*-3-*methyl*-Δ^4-*tetrahydrophthalic anhydride* (II), m.p. 84° (free *acid*, m.p. 145—146°), hydrogenated (Pd–$CaCO_3$ in EtOAc) to 3 : 6-endo-*oxido*-3-*methylhexahydrophthalic anhydride*, m.p. 105—106° (corresponding free *acid*, m.p. 158°, its *Me H* ester, m.p. 118°, and its *Me*$_2$ ester, m.p. 76°, converted by alkaline hydrolysis into trans-3 : 6-endo-*oxido*-3-*methylhexahydrophthalic acid*, m.p. 172—173°). Very cautious treatment with Br–H_2O at 0° converts (II) into the bromohydroxy-*acid*, m.p. 127°, readily transformed by CH_2N_2 in Et_2O into the *bromolactone Me ester* (cf. *A*), m.p. 151°, whereby its configuration is established. Similarly 3 : 6-*endo*-oxido-3 : 6-dimethyl-Δ^4-tetrahydrophthalic anhydride, from (I) and 2 : 5-dimethylfuran (III), is transformed into the *bromolactonic acid*, m.p. 168° (*Me* ester, $C_{11}H_{13}O_5Br$, m.p. 155—156°), and 3 : 6-*endo*-oxido-3 : 6-dimethylhexahydrophthalic anhydride is converted by boiling MeOH into *Me H* 3 : 6-endo-*oxido*-3 : 6-*dimethylhexahydrophthalate*, m.p. 106—108°, whence the *Me*$_2$ ester, m.p. 83—84°, hydrolysed by alkali to trans-3 : 6-endo-*oxido*-3 : 6-*dimethylhexahydrophthalic acid*, m.p. 212—213° (decomp.). Me_2 3 : 6-*endo*-oxido-Δ^1-tetrahydrophthalate is hydrolysed by KOH–MeOH to 3 : 6-endo-*oxido*-Δ^1-*tetrahydrophthalic acid* (IV), m.p. 168—170° (*K* salt), and 3 : 6-endo-*oxido*-1-*methoxyhexahydrophthalic acid*, m.p. 188—190°, which is stable towards alkaline $KMnO_4$ and does not give an anhydride with boiling AcCl. Sylvan and (:C·CO_2Me)$_2$ at 100° give the non-cryst. *Me*$_2$ 3 : 6-endo-*oxido*-3-*methyl*-$\Delta^{1:4}$-*dihydrophthalate*, hydrogenated (Pd–$CaCO_3$ in EtOAc) to the non-cryst. *Me*$_2$ 3 : 6-endo-*oxido*-3-*methyl*-Δ^1-*tetrahydrophthalate*, whence the corresponding unsaturated *acid* (V), m.p. 151—152° (decomp.); this is converted by the prolonged action of an excess of CH_2N_2 into the *ester adduct* (*B*), m.p. 95°. (:C·CO_2Me)$_2$ and (III) give the non-cryst. *Me*$_2$ 3 : 6-endo-*oxido*-3 : 6-*dimethyl*-$\Delta^{1:4}$-*dihydrophthalate*, reduced to the non-cryst. *Me*$_2$ 3 : 6-endo-*oxido*-3 : 6-*dimethyl*-Δ^1-*tetrahydrophthalate*, whence the free *acid*, m.p. 173—174° (decomp.), which is unstable towards Na_2CO_3–$KMnO_4$. This with an excess of CH_2N_2 gives the *adduct*, $C_{13}H_{18}O_5N_2$ (cf. *B*), m.p. 78—79°. Butadiene (VI) and (IV) at 170—180° give the *anhydride* (cf. *C*), m.p. 164°, hydrogenated (Pd–C in EtOAc) to the saturated *product*, $C_{12}H_{14}O_4$, m.p. 189—190°. The *adduct*, $C_{13}H_{14}O_4$, m.p. 132—133°, is derived from (V) and (VI).

H. W.


(*A.*)


(*B.*)


(*C.*)

Derivatives of coumaran. II. Condensation of aliphatic aldehydes and ketones with 5-methoxycoumaran-2-one. Reduction of 5-methoxy-1-*iso*propylidenecoumaran-2-one. III. *O*-Acetylation of 5-methoxycoumaran-2-one. R. L. Shriner and J. Anderson (J. Amer. Chem. Soc.,

1938, **60**, 1415—1417, 1418—1419; cf. A., 1938, I, 240).—II. 5-Methoxybenz-1 : 2-dihydrofuran-2-one (I) and the appropriate ketone in HCl–AcOH give ββ-*di*-5-*methoxy*-1 : 2-*dihydrobenzfuran*-2-*onyl*-*propane*, m.p. 209—210°, and -*butane*, m.p. 194°, and γγ-*di*-5-*methoxy*-1 : 2-*dihydrobenzfuran*-2-*onyl*-n-*pentane*, m.p. 231·5—232·5°. By interaction with the appropriate aldehyde, HCl, and $ZnCl_2$ in hot MeOH are obtained αα-*di*-5-*methoxy*-1 : 2-*dihydrobenzfuran*-2-*onyl*-*ethane*, m.p. 167—168°, -*propane*, m.p. 135—136°, -n-*butane*, m.p. 141—142°, and -*methane*, m.p. 169—170°. With $COMe_2$ and $ZnCl_2$ in hot EtOH (I) gives 5-*methoxy*-1-iso*propylidene*-1 : 2-*dihydrobenzfuran*-2-*one*, m.p. 141—142°, hydrogenated in presence of PtO_2 at 2—3 atm. in EtOH to the 1-*Pr*$^{\beta}$ *ketone*, m.p. 75—75·5°, and in presence of Pd–C to 5-*methoxy*-1-iso*propyl*-1 : 2-*dihydrobenzfuran*, b.p. 149°/19 mm. *cyclo*Hexanone gives similarly 5-*methoxy*-1-cyclo*hexylidene*-1 : 2-*dihydrobenzfuran*-2-*one*, m.p. 146·5—147·5°, reduced (H_2–PtO_2) to 5-*methoxy*-1-cyclo*hexyl*-1 : 2-*dihydrobenzfuran*-2-*one*, m.p. 86·5—87·5°, but higher aliphatic ketones do not react with (I) under these conditions. M.p. are corr.

III. Although (I) is completely ketonic, giving no colour with $FeCl_3$ until after 2 hr., it is converted by Ac_2O–AcOH at 100° into 2-acetoxy-5-methoxybenzfuran, m.p. 74—75° (cf. Sonn *et al.*, A., 1922, i, 1164), the structure of which is proved by hydrolysis by very dil. H_2SO_4–EtOH to (I) and by hydrogenation (PtO_2; 2—3 atm.; EtOH) to the 1 : 2-H_2-compound, which decomposes, when distilled, into 5-methoxybenzfuran and AcOH (identified as piperazonium diacetate). R. S. C.

Synthesis of coumarins from o-hydroxyarylalkyl ketones. I. D. Chakravarti and B. Majumdar (J. Indian Chem. Soc., 1938, **15**, 136—138).—2-*Methoxy*-5-*chlorophenyl Et ketone*, m.p. 41—42°, obtained from 4-chloro-2-propionylphenol, MeI, and NaOEt–EtOH, yields with $CHMeBr{\cdot}CO_2Et$ and Zn *Et* β-*hydroxy*-β-5-*chloro*-2-*methoxyphenyl*-α-*methyl*-β-*ethylpropionate*, m.p. 71°, dehydrated by $SOCl_2$ to *Et* 5-*chloro*-2-*methoxy*-α-*methyl*-β-*ethylcinnamate*, b.p. 163°/6 mm., which with HI gives 6-*chloro*-3-*methyl*-4-*ethylcoumarin*, m.p. 94°. 5-*Chloro*-2-*methoxy*-4-*methylphenyl Et ketone*, m.p. 74°, with $CHMeBr{\cdot}CO_2Et$ similarly yields 6-*chloro*-3 : 7-*dimethyl*-4-*ethylcoumarin*, m.p. 121°. A. L.

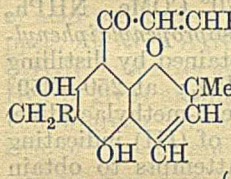
Coupling of 6-hydroxyflavone with diazo-salts. H. S. Mahal and K. Venkataraman (Current Sci., 1938, **6**, 450).—Na 6-hydroxyflavone with *p*-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ and NaOAc gives an orange *dye*, m.p. 256°. The significance of the reaction is discussed. A. Li.

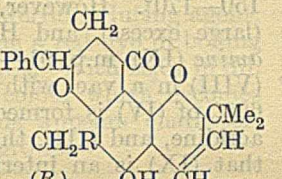
Natural flavones. I. Constitution of gardenin. P. K. Bose and R. Nath (J. Indian Chem. Soc., 1938, **15**, 139—148).—The formula $C_{21}H_{22}O_9$ is preferred for gardenin (I), the yellow colouring matter in Dikamali gum from *Gardenia gummifera*, Linn. (I) with Ac_2O gives *acetylgardenin*, m.p. 136°, and with EtOH–KOH yields trimethylgallic acid, and a phenolic *substance*, $C_9H_8O_6$, m.p. 158—160°, which when reduced with SO_2 affords a *substance*, $C_9H_{10}O_6$, m.p. 175—176°. With HNO_3 (I) yields *gardeninone* (II), $C_{20}H_{18}O_9$, m.p. 222—224°, 1 : 3 : 4 : 5-$NO_2{\cdot}C_6H_2(OMe)_3$, and 1 : 2 : 3 : 4 : 5-$(NO_2)_2C_6H(OMe)_3$. With SO_2 (II) gives *gardeninol*, $C_{20}H_{20}O_9$, m.p. 184—185° (Ac_2 derivative, m.p. 146—147°). Since (I) contains 1 OH and 6 OMe and forms a double compound with $SnCl_4$ in which the ratio Sn/Cl is 1 : 3, the OH is probably at 5 in a flavone nucleus. (I) is either 5-hydroxy-3 : 6 : 8 : 3′ : 4′ : 5′- or -3 : 7 : 8 : 3′ : 4′ : 5′-hexamethoxyflavone. A. L.

Synthesis of wogonin [5 : 7-dihydroxy-8-methoxyflavone]. R. C. Shah, C. R. Mehta, and T. S. Wheeler (Current Sci., 1938, **6**, 503).—Condensation of 2 : 4-dihydroxy-3 : 6-dimethoxyacetophenone (Baker *et al.*, A., 1929, 326) with NaOBz and Bz_2O yields 7-*hydroxy*-5 : 8-*dimethoxyflavone*. HI converts this into 5 : 6 : 7-trihydroxyflavone, and $AlCl_3$ into a trihydroxyflavone, m.p. 251—252°, or under mild conditions into wogonin (Hattori, A., 1931, 493). A. Li.

Rottlerin. H. Brockmann and K. Maier (Annalen, 1938, **535**, 149—175; cf. A., 1937, II, 429; 1938, II, 108).—Rottlerin (I), m.p. 201—202° (Berl), is $C_{30}H_{28}O_8$. It contains four active H (Zerevitinov–Roth) and when treated with O_3–$KMnO_4$ gives 0·2 mol. of $COMe_2$ indicating the presence of Pr^{β} or *gem*-Me. It gives a penta-acetate, m.p. 211·5—212·5°. With CH_2N_2 (I) yields a *Me*$_2$ *ether* (II), m.p. 245—246° (decomp.), converted into a *Me*$_5$ *ether* (III), $C_{30}H_{23}O_3(OMe)_5$, m.p. 142·5°, identical with the compound $C_{27}H_{22}O_3(OMe)_4$ of Ray *et al.* Hydrogenation (Pd–C in $COMe_2$) of (I) affords tetrahydrorottlerin (IV), $C_{30}H_{32}O_8$, m.p. 211° (*penta-acetate*, m.p. 188°). Similarly (II) affords *tetrahydrorottlerin Me*$_2$ *ether*, m.p. 193—194°, also obtained by methylation of (IV) and transformed by Me_2SO_4 and K_2CO_3 in boiling $COMe_2$ into *tetrahydrorottlerin Me*$_5$ *ether*, m.p. 108—108·5°, also obtained by hydrogenation of (III). Treatment of (I) with H_2O_2 in alkaline solution gives $CHPh{:}CH{\cdot}CO_2H$ whilst PhCHO is obtained by degradation with O_3 or when (I) is boiled with dil. NaOH, thus disclosing the presence of the $CHPh{:}CH{\cdot}$ group. The formation of *o*- or *p*-$C_6H_4(CO_2H)_2$ by the oxidation of (I) could not be confirmed. Diazoaminobenzene and (I) in boiling EtOH gives 2 : 4 : 6-*trihydroxy*-3-*acetyl*-5-*methylazobenzene*, m.p. 206°, which contains 2—3 active H (Zerevitinov–Roth) and gives 1·6 mols. of AcOH when oxidised by CrO_3 (Kuhn–Roth); it is obtained synthetically from methylphloracetophenone (V), m.p. 213—214°. (Analogously, *methylphlorpropiophenone*, m.p. 205°, is transformed into 2 : 4 : 6-*trihydroxy*-3-*propionyl*-5-*methylazobenzene*, m.p. 211°.) (V) is also obtained by the thermal decomp. of (I). Very prolonged treatment of (I) with boiling EtOH leads to iso*rottlerin* (VI), $C_{30}H_{28}O_8$, m.p. 180°, the production of which is accelerated by H_3PO_4 or *d*-camphorsulphonic acid, also obtained in boiling PhMe or, preferably, in boiling AcOH. It contains 2—3 active H and yields 0·48 mol. of $COMe_2$ when degraded by O_3–$KMnO_4$. Acetylation and methylation give only amorphous or oily products. Hydrogenation (Pd–C in $COMe_2$) of (VI) gives *dihydro*iso*rottlerin*, m.p. 210—211°, so that the isomerisation of (I) is accompanied by the loss of a double linking; if this is absent, as in (IV), isomerisation does not take place. In contrast with (I), (VI) does not yield a dye

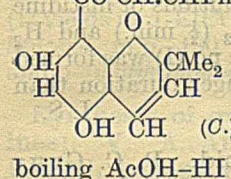
when treated with NPh:N·NHPh although the presence of a methylphloracetone residue is betrayed by the formation of (V) by the thermal decomp. of (VI). The presence of the Ph residue of the CHPh:CH· group is established by the formation of BzOH but the residue CHPh:CH is not present as such since PhCHO is not formed by ozonolysis. To (I) and (VI) the constitutions *A* and *B* respectively are ascribed.


(*A*.)


(*B*.)

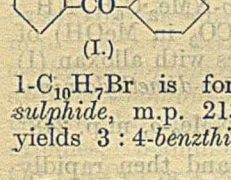
[R = 2 : 4 : 6 : 3 : 5-$(OH)_3C_6$AcMe.]

These are in harmony with the reactions described above and with the absorption spectra of (I) and (VI) in $CHCl_3$. (II), like (IV), is not isomerised by boiling AcOH. This may be due to the etherification of OH required for ring closure or to the diminised activity of (II). It does not appear possible to convert 2-*hydroxy*-4 : 6-*dimethoxy*-3-*methylchalkone*, m.p. 142°, or 2-hydroxy-4 : 6 : 4′-trimethoxy-3-methylchalkone into the corresponding flavanones by the prolonged action of AcOH. Attempts to transform (I) by *d*-camphor-sulphonic acid into an optically active flavanone derivative led only to optically inactive (VI). Rottlerone, to which the constitution *C* is ascribed, is dissolved by boiling AcOH with marked lightening of colour but does not appear to give well-defined products. With boiling AcOH–HI (IV) gives a *substance*, $C_{30}H_{30}O_7$, m.p. 169—170°, which has not been completely investigated.


(*C*.)

H. W.

New ring systems. V. Phenyl 2-methoxy-8-naphthyl ketone *o* : 1-sulphide. W. Knapp (Monatsh., 1938, **71**, 440—443; cf. A., 1938, II, 59).—1 : 2-$C_{10}H_6$Br·OMe and *o*-SH·C_6H_4·CO_2H with anhyd. K_2CO_3 and Cu powder in boiling *n*-C_5H_{11}·OH give 2-*carboxyphenyl* 2′-*methoxy*-1′-*naphthyl sulphide*, m.p. 226—228°, which with P_2O_5 in boiling PhMe yields the 1 : 8-cyclic *sulphide ketone* (I), m.p. 184—185°. Similarly from 1-$C_{10}H_7$Br is formed 2-*carboxyphenyl* 1′-*naphthyl sulphide*, m.p. 213—215°, which with P_2O_5–PhMe yields 3 : 4-*benzthioxanthone*, m.p. 193—194°.


(I.)

J. D. R.

Pyrrole–indole group. Series II. XXIII. Derivatives of pyrrole-1- and -2-carboxylic acid. B. Oddo and C. Alberti (Gazzetta, 1938, **68**, 204—214).—The K derivative of pyrrole (I) and CS_2 in PhMe yield *K pyrrole*-1-*dithiocarboxylate* (II) (*Cu*, *Hg*, *Ag*, and *Pb* salts described), which with dil. H_2SO_4 gives the oily *acid* (III); this is very unstable, and spontaneously oxidises to *bis*-1-*pyrrylthiocarboxyl disulphide*, $(C_4H_4N·CS·S)_2$, m.p. 95—96° (decomp.). With EtI in EtOH, and with PhN_2Cl in aq. EtOH, (II) gives the *Et*, b.p. 162—164°/33 mm., and *Ph*, b.p. 180—200° (bath)/30 mm. (decomp. to Ph_2S, Ph_2S_2 and a *product*, m.p. 147—148°) *esters* of (III). $C_4H_3NH·CS_2MgBr$ (IV), from the MgBr derivative of (I) and CS_2, with EtI yields *Et pyrrole*-2-*dithiocarboxylate*, b.p. 60°/60 mm., and, with AcCl, S-*acetylpyrrole*-2-*dithiocarboxylic acid*, $C_4H_3NH·CS·SAc$, m.p. 87—88°. The K derivative of 2 : 5-dimethylpyrrole with CS_2 forms *K* 2 : 5-*dimethylpyrrole*-1-*dithiocarboxylate* (*Ag*, *Cu*, *Ni*, *Co*, and *Pb* salts), which with PhN_2Cl gives the *Ph* ester, and with dil. H_2SO_4 gives the unstable *acid*, rapidly oxidised to *bis*-2 : 5-*dimethyl*-1-*pyrrylthiocarboxyl disulphide*, m.p. 177—178° (decomp.).

E. W. W.

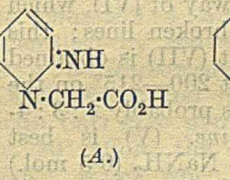
Molecular compounds of pyrrole derivatives. II. M. Deželić (Bull. Soc. Chim. Yougoslav., 1937, **8**, 145—156).—The fusion diagrams of the systems Et 2 : 4-dimethylpyrrole-5-carboxylate (I)–$CHPh_3$, –*o*-$C_6H_4(NH_2)_2$, and -quinine, and Et 2 : 4-dimethylpyrrole-3 : 5-dicarboxylate (II)–$CH_2Cl·CO_2H$, –PhOH, –*m*-, –*o*-, and –*p*-$C_6H_4(OH)_2$, –salicylic acid, and –$CHPh_3$ do not suggest compound formation. 1 : 1 *compounds* are described in the systems (I)–$CCl_3·CO_2H$, transition point 35·5°, (II)–$CCl_3·CO_2H$, transition point 79°, and (II)–picric acid, m.p. 107·2°.

R. T.

Reaction between amines and unsaturated compounds containing halogen attached to one of the ethylenic carbon atoms. II. Preparation and constitution of some new diamines. J. C. Roberts (J.C.S., 1938, 963—965; cf. A., 1936, 1236).—CHMe:CCl·CO_2Et and piperidine in EtOH yield *Et* αβ-*dipiperidinobutyrate*, b.p. 181—183°/14 mm. CHPh:CBr·CO_2Et with piperidine yields *Et* αβ-*dipiperidino*-, m.p. 74—75° (*dihydrochloride* readily loses HCl; *picrate*, m.p. 122—123°), and with $NHMe_2$ gives *Et* αβ-*bis*(*dimethylamino*)-β-*phenylpropionate*, b.p. 154—155°/8 mm., solidifying after several months, m.p. 37—38° [*platinichloride*, m.p. 185° (decomp.); *dihydrochloride*; *picrate*, m.p. 148—149°], which when boiled with aq. KOH yields some $NHMe_2$, and with dil. H_2SO_4 gives a mixture of phenylglycidic acid and $CH_2Ph·CO·CO_2H$ (formed by the action of H_2SO_4 on the former).

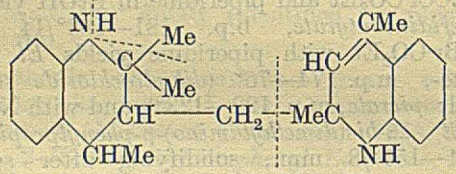
A. Li.

Pyridinium compounds and betaines. A. Kirpal and B. Wojnar (Ber., 1938, **61**, [*B*], 1261—1266).—Pyridylglycine (I) is converted by boiling, dil. aq. alkali or by HNO_2 into pyrid-2-oneacetic acid, thus establishing the constitution *A* or *B*. With warm conc. alkali hydroxide (I) yields *Na* 2-*iminopyridineacetate*. C_5H_5N and $CH_2Cl·CH_2·CO_2H$ afford the *compound* $C_5H_5N(Cl)·CH_2·CH_2·CO_2H$, m.p. 160°, which decomposes when heated into C_5H_5N,HCl and CH_2:CH·CO_2H. It is transformed by Ag_2O into the very hygroscopic 1-β-*carboxyethylpyridinium hydroxide*, m.p. 90°. 2-*Hydroxy*-1-β-*carboxyethylpyridinium chloride*, m.p. 96°, is decomposed by boiling aq. alkali into OH·C_5H_4N, and CH_2:CH·CO_2H. 3-*Hydroxy*-1-β-*carboxyethylpyridinium chloride*, m.p. 183°, is converted by NaOH into 3-*hydroxy*-1-β-*carboxyethylpyridinium hydroxide*, m.p. 184° or (+1H_2O), m.p.


(*A*.) (*B*.)

180°, which when heated above its m.p. passes partly into 3-OH·C_5H_4N and CH_2:CH·CO_2H but mainly yields the anhydride. *4-Hydroxy-1-β-carboxyethylpyridinium chloride* has m.p. 196°. 2-Aminopyridine and $CH_2Cl·CH_2·CO_2H$ at 100° afford *2-amino-1-β-carboxyethylpyridinium chloride*, decomp. 285°, which with moist Ag_2O yields *2-amino-1-β-carboxyethylpyridinium hydroxide*, m.p. 156° (decomp.); this loses H_2O at 120° with formation of *pyridone-2-imidepropionic acid*, which slowly absorbs $1H_2O$ when exposed to air. H. W.

Reaction of acetone with aniline. D. Craig (J. Amer. Chem. Soc., 1938, **60**, 1458—1465).—NH_2Ph, $COMe_2$, and a trace of HCl at 100° give 68% of "acetoneanil" (I), m.p. 26—27°, b.p. 255—260°/743 mm. (slight decomp.) (*hydrochloride*, m.p. 214—216°, partly hydrolysed by H_2O) (cf. Reddelien and Thurm, A., 1932, 1142), and 31% of a resin. At 120—150° $NHPh_2$ is the main by-product, but under other conditions (p-$NH_2·C_6H_4)_2CMe_2$ (II), p-$C_6H_4Pr^β·NH_2$, *phenyl-p-cumylamine* (III), m.p. 70—72° (*Ac* derivative, m.p. 94—95°), 5 : 5-*dimethylacridane* (IV), 5-methylacridine, 2 : 4-dimethylquinoline (V), and polymeric quinoline derivatives are obtained. The structure of (I) as 2 : 2 : 4-trimethyl-1 : 2-dihydroquinoline is probable (cf. *loc. cit.*), but 2 : 4 : 4-trimethyl-1 : 4-dihydroquinoline is also a possibility. With conc. HCl (0·1 mol.) at 100° (I) gives a *dimeride*, b.p. 215—220°/2·5 mm. (*Ac_2* derivative, m.p. 185—186°), believed to be (VI), and higher



(VI.)

polymerides; these products are depolymerised by Cu–Cr_2O_3 or by distilling in vac. with a trace of a strong acid, and are converted by H_2–Raney Ni into the H_2-derivative of (I). 2 : 4-Dimethylquinoline methiodide, new m.p. 263—265° (decomp.), and MgMeI give the *N*-Me derivative, b.p. 105—115°/1·5 mm. (*zincichloride*, m.p. 195—197°; picrate, m.p. 147—148°), of (I). Acid decomp. (NH_2Ph,HCl at the b.p.) of (I) gives (V) and 2 : 3 : 4-trimethylquinoline (VII), m.p. 91—92°, probably by way of (VI), which decomposes by fission along the broken lines; this view is supported by the fact that (VII) is obtained with C_2H_6 by the action of HCl at 200—215° on the "anil" from COMeEt; this anil is probably 2 : 3 : 4-*trimethyl-2-ethyl*-1 : 2-*dihydroquinoline*. (V) is best (86% yield) obtained from (I) by $NaNH_2$ (0·5 mol.) at 150—210°, about 1 mol. of CH_4 being liberated; this reaction does not occur by way of (VI), since (VI) gives <0·5 mol. of CH_4 at a much higher temp. The H_2-derivative of (I) is stable to $NaNH_2$. 6 : 6′-Methylenebis-2 : 2 : 4-trimethyl-1 : 2-dihydroquinoline is obtained from (I) and CH_2O, having m.p. 153—154°. The formation of $NHPh_2$ from NH_2Ph, $COMe_2$, and HCl probably occurs by way of (II) thus: (II) $+2NH_2Ph \rightarrow 2NH_3 + (p$-$NHPh·C_6H_4)_2CMe_2$ (VIII) $\rightarrow NHPh_2 + p$-$NHPh·C_6H_4·CMe$:CH_2 (IX); (IX) with $2NH_2Ph$ then re-forms (VIII). In confirmation of this view, 1 mol. of (II) with 8 of NH_2Ph and 5 of NH_2Ph,HCl at about 195° give 2·2 mols. of $NHPh_2$ with some (III) and (V). ββ-*Di*-p-*anilinodiphenylpropane* (VIII), m.p. 99—100°, is obtained (*a*) from $NHPh_2$, $COMe_2$, and conc. HCl at 120—135°, (*b*) with NH_2Ph and (IV) from (II) (0·1), $NHPh_2$ (0·5), and $NHPh_2$,HCl (0·1 mol.) at about 240°, and (*c*) from (II), o-$C_6H_4Cl·CO_2H$, K_2CO_3, and a trace of CuI at 150—170°. However, at 160—170° $COMe_2$, $NHPh_2$ (large excess), and HCl give p-iso*propenyldiphenylamine* (IX), m.p. 91—92°, best obtained by distilling (VIII) in a vac. with a little H_3PO_4; at 250—259° 60% of (IV) is formed, with some 5-methylacridine, acridine, and (III), the formation of (III) indicating that (IX) is an intermediate. Attempts to obtain (VIII) directly from $COMe_2$, NH_2Ph, and HCl failed. R. S. C.

Formation and destruction of histamine by ascorbic acid and thiol compounds. P. Holtz and R. Heise (Arch. exp. Path. Pharm., 1937, **187**, 581—588).—Histamine (I) was formed from histidine (II) by addition of ascorbic acid or cysteine by slow oxidation in the air, but not in an O_2 atm. A min. concn. of (II) was necessary to obtain (I). Formation of (I) was inhibited by Fe (cf. A., 1937, III, 210). I. S.

Formation of histamine from histidine by oxido-reductive catalytic processes. P. Holtz (Arch. exp. Path. Pharm., 1937, **187**, 589—593).—Histamine (I) was formed in aq. solutions of histidine when alternately perfused with O_2 (½ min.) and H_2 (2 min.) in presence of Pd. Less or no (I) was formed when perfusion with O_2 was of longer duration than that with H_2. I. S.

Synthesis of umbellulonic acid. P. C. Guha and M. S. Muthanna (Current Sci., 1938, **6**, 449).—Diazoacetone with CH_2:$CPr^β·CO_2Et$ gives 5-*carbethoxy-3-acetyl*-5-iso*propylpyrazoline*, b.p. 130—135°/3 mm., which when heated to 180° loses N_2 giving the *Et* ester, b.p. 233—235°/685 mm., of *cis*-umbellulonic acid (oxime, m.p. 145—146°; *semicarbazone*, m.p. 170°), oxidised to *cis*-umbellularic acid. A. Li.

Alloxandimethylaminoanil. Constitution of the dinuclear compounds of alloxan with aromatic *o*-diamines. H. Rudy and K. E. Cramer (Ber., 1938, **71**, [*B*], 1234—1242).—*o*-$NMe_2·C_6H_4·NH_2$, obtained by reduction (H_2–Pd–$CaCO_3$ in MeOH) of *o*-$NMe_2·C_6H_4·NO_2$, readily condenses with alloxan (I) in boiling EtOH–H_2O to *alloxan-5-o-dimethylaminoanil* (II), $CO<^{NH·CO}_{NH·CO}>C$:N·$C_6H_4·NMe_2$-*o*, m.p. 248° when brought into bath at 220° and then rapidly heated or decomp. without melting at >300° when slowly heated. The properties of (II) resemble so closely those of the compounds obtained by condensing (I) with *o*-$C_6H_4(NH_2)_2$ and *o*-$NH_2·C_6H_4·NHMe$, respectively, that there can be no doubt that all are anils and that Hinsberg's formulation N:$C(OH)>_{C_6H_4—N}>C·CO·NH·CO·NH_2$ is incorrect. (I) is amphoteric, being sol. in warm aq. Na_2CO_3 and yielding a *hydrochloride*, m.p. 236° (decomp.), stable only in presence of an excess of acid. In conc. H_2SO_4 it

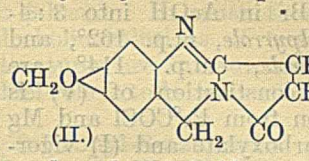
gives a colourless solution. In conc. NaOH (I) gives a sparingly sol. *Na* salt but NH_3 is readily evolved with production of *o-dimethylaminoanilomalonimide*, *o*-$NMe_2 \cdot C_6H_4 \cdot N{:}C\langle^{CO}_{CO}\rangle NH$, m.p. 239° (decomp.). This is stable towards 50% NaOH and hot conc. HCl. With CH_2N_2 it affords the corresponding *methylimide*, m.p. 156—157° (*picrate*, m.p. 133°), which is devoid of acid properties. (II) is a powerful reducing agent, pptg. Ag from $AgNO_3$ and giving a red dye in boiling C_5H_5N, best after addition of H_2O_2. With H_2O_2 in dil. HCl it gives an intense violet colour which becomes yellow-green on warming; this appears characteristic of all substances with the group,

o-$NMe_2 \cdot C_6H_4 \cdot N{:}C\langle^{C\cdot}_{C\cdot}$ H. W.

Formula of indigotin. J. VAN ALPHEN (Chem. Weekblad, 1938, **35**, 435—439).—The various formulæ for indigotin are discussed. Its colour, stability and the influence of various substituents are explained by its being a resonance-hybrid of at least six different structures. S. C.

Glyoxaline group. VII. Opening of the benziminazole ring. B. ODDO and (SIGNA.) L. RAFFA (Gazzetta, 1938, **68**, 199—204).—The MgBr derivative of benziminazole (I) with Pr^aCOCl (II) in Et_2O gives 1-butyrylbenziminazole (II) (A., 1933, 285), not altered by boiling with (II). With boiling $(EtCO)_2O$, (I) yields its 1-EtCO derivative, and *o-dipropionamidobenzene*, m.p. 130°. Similarly $(Pr^aCO)_2O$ gives (II) and *o-dibutyramidobenzene*, m.p. 132°. E. W. W.

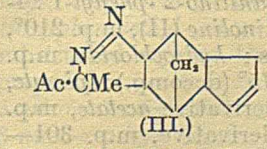
Synthesis of quinazolines (and benzoglyoxalines). V. A. AHMED, K. S. NARANG, and J. N. RAY (J. Indian Chem. Soc., 1938, **15**, 152—159).—*o*-Nitrochloroacetanilide and piperidine in C_6H_6 give o-*nitro*-ω-*piperidinoacetanilide*, m.p. 83°, reduced by Zn–HCl to o-*amino*-ω-*piperidinoacetanilide*, m.p. 173°; this with AcOH–NaOAc gives 2-*piperidinomethylbenziminazole*, m.p. 201°. Similarly o-*nitro*-ω-*diethylaminoacetanilide*, m.p. 70°, affords o-*amino*-ω-*diethylaminoacetanilide*, m.p. 81°, ring-closure of which yields 2-α-*diethylaminomethylbenziminazole*, m.p. 169°, and o-*nitro*-β-*chloropropionanilide*, m.p. 85° gives o-*nitro*-β-*piperidinopropionanilide*, m.p. 44°, leading to o-*amino*-β-*piperidinopropionanilide*, m.p. 110. Ring-closure of this substance, however, gave a *polymeride*, m.p. 290°, of 2-vinylbenziminazole (I). o-*Nitro*-β-*diethylaminopropionanilide* is reduced to o-*amino*-β-*diethylaminopropionanilide*, m.p. 56°, which on ring-closure also affords (I). For the synthesis of quinazolines, *o*-aminobenzamide is condensed with $CH_2Cl \cdot COCl$ or $Cl \cdot [CH_2]_2 \cdot COCl$ and the products are condensed with $NHEt_2$ or piperidine and treated with KOH to give the quinazolone. The following are prepared: o-ω-*chloroacetamidobenzamide*, m.p. 171°, o-α-*piperidinoacetamidobenzamide*, m.p. 186°; 2-*piperidinomethyl*-, m.p. 170°, and 2-α-*diethylaminomethyl-quinazol*-4-*one*, m.p. 85°; o-β-*piperidinopropionamidobenzamide*, m.p. 140°, 2-β-*piperidinoethylquinazol*-4-*one*, m.p. 148°, o-β-*diethylaminopropionamidobenzamide*, m.p. 99°, 2-β-*diethylaminoethylquinazol*-4-*one*, m.p. 122°, 6-*nitro*-N-3 : 4-*methylenedioxybenzylphthalimide*, m.p. 218°, 6-*nitro*-3 : 4-*methylenedioxybenzylamine*, m.p. 105°, 6-*nitro*-, m.p. 204°, and 6-*amino*-3 : 4-*methylenedioxyacetbenzylamide*, m.p. 126° (ring-closure of this substance could not be effected), N-6-*nitro*-3 : 4-*methylenedioxybenzylsuccinimide*, m.p. 175°; *methylenedioxy*iso*vasicone* (II), m.p. 267°. A. L.

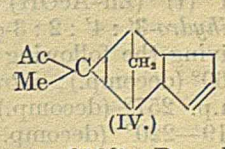

(II.)

Chemiluminescent organic compounds. VI. Isolation of peroxide derivatives of phthalaz-1 : 4-diones. H. D. K. DREW and R. F. GARWOOD (J.C.S., 1938, 791—793).—The Na salt of 5-aminophthalaz-1 : 4-dione in H_2O_2 gives the *Na* salt of 5-*amino*-1 : 4-*dihydroxy*-2 : 3-*dihydrophthalazine peroxide* (+H_2O); the *Ba* salt of 1 : 4-*dihydroxy*-2 : 3-*dihydrophthalazine peroxide* is similarly obtained. These are chemiluminescent and are probable intermediates in the luminescing reactions of the diones. By the use of duroquinol, atm. O_2 may be used in these reactions of the diones. F. R. S.

Stereochemistry of diphenyls. XLV. Stereoisomeric dipyrryldiphenyls. R. ADAMS and R. M. JOYCE, jun. (J. Amer. Chem. Soc., 1938, **60**, 1491—1492).—$CH_2Ac \cdot CHAc \cdot CO_2Et$ (I) and benzidine in AcOH at 100° give 4 : 4′-*bis*-(3-*carbethoxy*-2 : 5-*dimethyl*-1-*pyrryl*)*diphenyl*, m.p. 182—183°, which could not be smoothly hydrolysed. NaOAc, *o*-tolidine, and (I) in hot AcOH give 4 : 4′-*bis*-(3-*carbethoxy*-2 : 5-*dimethyl*-1-*pyrryl*)-3 : 3′-*dimethyldiphenyl*, (?) dl-, m.p. 172—174°, and (?) meso-*form*, m.p. 142—144°. Dianisidine similarly gives 3 : 3′-*dimethoxy*-4 : 4′-*bis*-(3-*carbethoxy*-2 : 5-*dimethyl*-1-*pyrryl*)*diphenyl*, *forms*, m.p. 185—187° and 168—170°, respectively. M.p. are corr. R. S. C.

Diene syntheses. XXXI. Behaviour of azibutanone towards unsaturated systems. O. DIELS and H. KÖNIG (Ber., 1938, **71**, [*B*], 1179—1185).—Azibutanone (I) does not react with aliphatic dienes or with monomeric *cyclo*pentadiene. With $(:C \cdot CO_2Et)_2$ in abs. Et_2O it affords *Et*$_2$ 3-*acetyl*-3-*methylpyrazole*-4 : 5-*dicarboxylate*, b.p. 180—181°/13 mm. (corresponding *Me*$_2$ ester, m.p. 65°), hydrolysed by KOH–MeOH to 3-*methylpyrazole*-4 : 5-*dicarboxylic acid* (+1H_2O) (II), m.p. 239° (decomp.) [*Et H* ester, m.p. 213° (decomp.)]. (II) is oxidised ($KMnO_4$–Na_2CO_3) to *pyrazole*-3 : 4 : 5-*tricarboxylic acid* (III), m.p. 234°, identified by conversion into *Me*$_3$ 1-*methylpyrazole*-3 : 4 : 5-*tricarboxylate*, m.p. 100°, obtained also from $CHN_2 \cdot CO_2Et$ and $(:C \cdot CO_2Et)_2$. Distillation of (III) with CaO give pyrazole. Di*cyclo*pentadiene and (I) at 80° afford the *adduct* (III) (*semicarbazone*, m.p. 218°), which when distilled under 13 mm. gives a liquid *ketone* (IV), b.p. 155—158°/13 mm. (*semicarbazone*, m.p. 254°), and is hydrogenated (PtO_2 in EtOAc) to the corresponding saturated *ketone*, b.p.

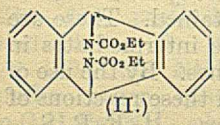

(III.)


(IV.)

148—150°/13 mm. (*semicarbazone*, m.p. 218°). Pyrrole and (I) in presence of Cu powder give 2-iso*butyryl*-

pyrrole (V), m.p. 85°. 5-iso*Butyryl*-2-*methylpyrrole*, m.p. 106°, converted by Br in AcOH into 3 : 4-*dibromo*-5-iso*butyryl*-2-*methylpyrrole*, m.p. 162°, and 5-iso*butyryl*-2 : 4-*dimethylpyrrole*, m.p. 114°, are obtained similarly. The constitution of (V) is established by its formation from $Pr^{\beta}COCl$ and Mg pyrryl iodide. Et_2 azodicarboxylate and (I) vigorously give *Et*$_2$ *acetylmethylhydrazomethanedicarboxylate*, CAcMe$<^{N\cdot CO_2Et}_{N\cdot CO_2Et}$, b.p. 180—184°/14 mm., m.p. 44—46°, readily converted into Ac_2 and $(\cdot NH\cdot CO_2Et)_2$. H. W.

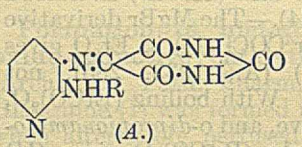
Diene syntheses. XXXII. Anthracene and azodicarboxylic ester. O. Diels, S. Schmidt and W. Witte (Ber., 1938, **71**, [*B*], 1186—1189).—Anthracene (I) and $(:N\cdot CO_2Et)_2$ in boiling PhMe give the labile *adduct* (II), m.p. 138°, hydrolysed (KOH–MeOH or EtOH) to K_2CO_3 and (I) and thermally decomposed into its components. It is converted by dil. HCl in lukewarm AcOH or by HCO_2H at room temp. into the stable *adduct*, (?) 9 : 10-*dicarbethoxylaminoanthracene*, m.p. 242°, which could not be satisfactorily hydrolysed. Similarly, $(:N\cdot CO_2Me)_2$ affords a labile *adduct*, $C_{18}H_{16}O_4N_2$, m.p. 192°, thermally decomposed into its components and transformed by acid into the stable (?) 9 : 10-*dicarbomethoxylaminoanthracene*, m.p. 267°, which is very resistant towards hydrolysis. H. W.



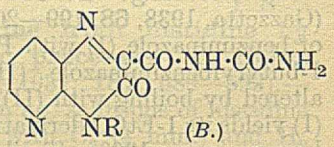
(II.)

Synthesis of compounds related to 2′-phenyl-3′ : 4′ : 2 : 3-quinolinoquinoline. J. Moszew (Bull. Acad. Polonaise, 1938, **A**, 98—115).—4-*Anilo*-2′-*phenyl*-3′ : 4′ : 2 : 3-*quinolino*-4-*quinolone* (I), m.p. 245—246° [*picrate*, m.p. 245° (decomp.); *hydrochloride*, m.p. 252° (decomp.); *nitrate*, m.p. 137—138° (decomp.)], a by-product in the reaction of COPhMe with $CS(NHPh)_2$ (A., 1932, 1039), is hydrolysed by EtOH–HCl to the corresponding *quinolone*, m.p. 365° (*hydrochloride* and *nitrate* lose acid at >200° and melt at 365°), or by EtOH–KOH under pressure to 4-*hydroxy*-2′-*phenyl*-3′ : 4′ : 2 : 3-*quinolinoquinoline*, m.p. 324—325° [*picrate*, m.p. 240° (decomp.); *hydrochloride*, m.p. 275° (decomp.)]. The latter is converted by HCl into the quinolone, whilst EtOH–KOH effects the reverse process. Either isomeride when heated with Zn dust yields 2′-*phenyl*-3′ : 4′ : 2 : 3-*quinolinoquinoline*, m.p. 300—301° [*hydrochloride*, loses HCl at >200°, m.p. 300°; *picrate*, m.p. 260—261° (decomp.)], also obtained by heating 4-anilino-2-phenyl-3-methylquinoline (A., 1933, 956) with Zn dust, an intermediate product being 2′-*phenyl*-1 : 4-*dihydro*-3′ : 4′ : 2 : 3-*quinolinoquinoline*, m.p. 202° [*hydrochloride*, m.p. 240° (decomp.); *picrate*, m.p. 265—266° (decomp.)]. With dil. HNO_3, (I) is partly oxidised to N-*phenyl*-2 : 3 : 4-*diquinolinoquinoline*, m.p. 245° [*nitrate*, m.p. 152° (decomp.); *picrate*, m.p. 280° (decomp.)]. Reduction of (I) (Zn–AcOH) yields 4-*anilino*-2′-*phenyl*-1 : 4-*dihydro*-3′ : 4′ : 2 : 3-*quinolinoquinoline* (II), m.p. 210°, giving the following derivatives: *hydrochloride*, m.p. 360° (decomp.); *nitrate*, m.p. 175° (decomp.); *picrate*, m.p. 257° (decomp.); N-*NO*-derivative *acetate*, m.p. 219—220° (decomp.); N-*Ac* derivative, m.p. 301—302°; *methosulphate*, m.p. 247° (decomp.); *methiodide*, m.p. 255° (decomp.), hydrolysed by EtOH–KOH to 4-*anilino*-2′-*ethoxy*-2′-*phenyl*-1′-*methyl*-1 : 4-*dihydro*-3′ : 4′ : 2 : 3-*quinolinoquinoline*, m.p. 105—106° (decomp.) [*picrate*, m.p. 278—279° (decomp.)], which with HCl yields the *methochloride*, m.p. 220° (decomp.), of (II). (II) is hydrolysed by EtOH–KOH to the 4-OH-compound. Both this and the isomeric ketone are reduced (Na–C_5H_{11}·OH) to the 1′ : 2′ : 3′ : 4′-*tetrahydro-ketone*, m.p. 308—309° [*picrate*, m.p. 224° (decomp.)]. A. Li.

Dinuclear alloxan derivatives of 2 : 3-diaminopyridines. H. Rudy and O. Majer (Ber., 1938, **71**, [*B*], 1323—1332).—2-Chloro-3-aminopyridine is converted by 33% $NHMe_2$ and $CuSO_4$ at 170° into the very unstable 3-*amino*-2-*dimethylaminopyridine*, b.p. 110—111°/12 mm., m.p. (indef.) 60° (*hydrochloride*, m.p. 202°; *picrate*, m.p. 139°), which with alloxan (I) in dil. HCl gives a very small yield of the *compound*, $C_{15}H_{13}O_7N_7$ or $C_{15}H_{15}O_8N_7$, m.p. 308°. 3-Amino-2-propylaminopyridine (II) and (I) in boiling dil. AcOH afford the yellow *alloxan*-2-*propylamino*-3-*pyridylimide* (cf. *A*), m.p. 243° (decomp.) when brought into bath at 200°, whereas in H_2O, MeOH, or EtOH the product is 2-*keto*-1-*propyl*-1 : 2-*dihydro*-8-*azaquinoxaline*-3-*carboxureide* (III) (cf. *B*), m.p. 243° (decomp.) when



(*A*.)



(*B*.)

introduced into a bath at 200° and then rapidly heated. Boiling 20% Na_2CO_3 or short treatment with 10% NaOH does not affect (III) whereas with boiling 30% NaOH it affords (II). *Alloxan*-2-*methylamino*-3-*pyridylimide*, m.p. 235—236° (decomp.), is somewhat more stable than the Pr derivative and can be crystallised at will from AcOH. It is isomerised by boiling 20% Na_2CO_3 or by 2N-NaOH at room temp. to 2-*keto*-1-*methyl*-1 : 2-*dihydro*-8-*azaquinoxaline*-3-*carboxureide*, m.p. 239° (decomp.), also obtained from 3-amino-2-methylaminopyridine (IV) and (I) in dil. HCl; it is stable towards Na_2CO_3 but decomposed by 30% NaOH with formation of (IV). 2 : 3-Diaminopyridine and (I) give *alloxan*-2-*amino*-3-*pyridylimide*, m.p. 280—285° (*Na* salt), whence 2-*hydroxy*-8-*azaquinoxaline*-3-*carboxureide*, m.p. 306° (decomp.) when rapidly heated, converted by short treatment with boiling 4N-NaOH into 2-*hydroxy*-8-*azaquinoxaline*-3-*carboxylic acid*, m.p. 235°. H. W.

Synthesis of 5-5′-5′-phenylhydantoinyl-5-ethylbarbituric acid. S. L. Ruskin and M. Pfalz (J. Amer. Chem. Soc., 1938, **60**, 1471—1472).—Prep. of OH·CHPh·CN and therefrom of 5-phenylhydantoin and its 5-Br-derivative (I) is modified to give 86, 90, and 37% yield, respectively. Na 5-ethylbarbiturate and (I) in AcOH at room temp. give 5-5′-5′-*phenylhydantoinyl*-5-*ethylbarbituric acid*, m.p. 215—218°. R. S. C.

Nucleic acids. IX. Preparation of adenosine. H. Bredereck (Ber., 1938, **71**, [*B*], 1013—1014).—Adenosine picrate (A., 1938, III, 343) suspended in warm H_2O is treated with KOH and the solution is cooled to room temp. and then to 0° to complete the

separation of the K picrate. This is filtered off and the filtrate is seeded with adenosine, which crystallises in 85% yield. H. W.

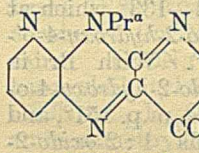
Synthesis in the alloxazine, *iso*alloxazine (flavin), and lumazine groups. III. Synthesis of some acid derivatives. K. GANAPATI (J. Indian Chem. Soc., 1938, **15**, 121—128).—1 : 2 : 4-$C_6H_3(NH_2)_2$·SO_3H and 1 : 2 : 4-$C_{10}H_5(NH_2)_2$·SO_3H with alloxan yield *alloxazine*-6- *or* -7-*sulphonic acid* and 7 : 8-*benzalloxazine*-6-*sulphonic acid* or 5 : 6-*benzalloxazine*-7-*sulphonic acid*, respectively. No condensation takes place with β-naphthoquinone-4-sulphonic acid and uracil. β-*o*-Nitroanilinopropionic acid, obtained from *o*-NO_2·C_6H_4·NH_2 and Br·$[CH]_2$·CO_2H, when reduced with $NaHSnO_2$ and condensed with alloxan in AcOH yields flavin-9-(β-)propionic acid and a *substance*, m.p. 219°. β-2-*Nitro*-4-*methylanilinopropionic acid*, m.p. 148—149°, obtained as above from 3 : 1 : 4-NO_2·C_6H_3Me·NH_2, when reduced and condensed with alloxan gives no flavinpropionic acid, but a *substance*, m.p. 225°. 3 : 4-Diaminocinnamic acid with alloxan affords alloxazine-7- or -8-(β-)acrylic acid. A. L.

Mercury phthalocyanine.—See B., 1938, 765.

Determination of the m.p. of porphyrins and other darkly-coloured substances with the use of polarised light.—See A., 1938, I, 418.

Complex chemistry of iron in α-hæmins. A. F. RICHTER (Z. physiol. Chem., 1938, **253**, 193—216).—In the addition to Fe of protohæmin, mols. with semipolar groups are favoured (*e.g.*, acetono-, acetaldehydo-, acetico-, and, possibly, the cyanico-adduct). The tenacity of acetone in the acetonohæmins depends on the nature of the polar component and the region of existence differs with the various compounds. The apparent impossibility of preparing alcoholo- and ethero-adducts proves the importance of polar components in the orientation of the prosthetic group of the hypothetical protoporphyrinio-iron $[C_{34}H_{32}O_4N_4Fe^+]$. The different orientation and polarity is designated as α-, β-, and meta-structure. In the case of the induced polarity of the alcoholic group, the binuclear complex, an ethanolodihæmin, must also be considered. The individuality of the β-modification appears to be established by the method of prep. and systematic crystallographical investigation. Küster's conception of the difference of the carboxyls in the symmetrical structure of the mol. finds no support and the representation that different demands are made on them by the free, non-coordinated basic N atoms contravenes the generally adopted constitutional formula of H. Fischer. It is therefore necessary to assume another course of the conjugated cyclus and explanation of the different polarity the existence of which and the consequent transformations are governed by the central Fe, since it has been shown that α- and β-protoporphyrin are only different modifications of the same substance. Further insight in this direction is obtained by the prep. of pure β-hæmins or metahæmins in alcohol in which the C_H influence is reduced to a min. and in which the betainising influence can be kept within bounds by the choice of added anions. Addition of I′ leads to α-hæmin, of H_2PO_2' to metahæmin, and of Cl′ to β-hæmin. It must therefore be assumed that in alcoholic solutions of oxalatohæmin the respective structures are in tautomeric equilibrium unless the chief rôle is to be assigned to the anion. H. W.

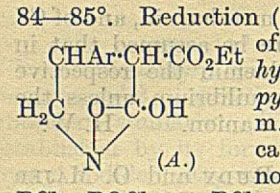
9-Propyl-8-azaflavin. H. RUDY and O. MAJER (Ber., 1938, **71**, [*B*], 1243—1248).—2-Chloro-3-aminopyridine is converted by NH_2Pr^{α}, $CuSO_4$, and H_2O at 180° into 3-amino-2-propylaminopyridine, m.p. 58°, which readily condenses with alloxan in AcOH containing $ZnCl_2$ and H_3BO_3 to 9-*propyl*-8-*azaflavin* (I), decomp. 345—350° after darkening above 300° when rapidly heated. It shows all the typical flavin properties and resembles very closely the 9-alkylflavins (II). Its neutral solution is yellow with intense green fluorescence which is proper to the zwitterion since the salts with mineral acid or alkali are non-fluorescent. The absorption spectrum of (I) coincides very nearly with those of (II) or lactoflavin. Irradiation of (I) with the unfiltered light of the Hg-vapour lamp decomposes (I); in daylight the fluorescence slowly disappears. The alkali salts of (I) are freely sol., whilst the *Ag* salt is orange-red and suitable for the separation of (I). Conc. HCl, HNO_3, Br–H_2O, and HCl + H_2O_2 are almost without action. Dil. alkali causes rapid decomp. giving a compound with blue fluorescence. $Na_2S_2O_4$ decolorises and reduces (I) but the colour returns immediately on contact with air. The redox potential is distinctly negative and apparently not greatly different from that of the flavins. Reduction with Zn and HCl causes the appearance of a red radical as intermediate. Apparently replacement of the C_6H_6 nucleus by a C_5H_5N ring does not cause marked alteration of the flavin characteristics, at any rate as far as the 8-azaflavins are concerned. H. W.


(I).

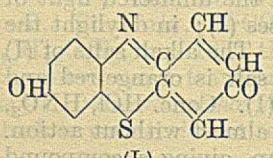
Alkyloxymethyl*iso*oxazoles. C. MUSANTE (Gazzetta, 1938, **68**, 240—246).—OEt·CH_2·CO·CH_2·COMe and NH_2OH yield (NaOEt–EtOH) 5-*methyl*-3-*ethoxymethyl*isooxazole, b.p. 90°/15 mm., oxidised (AcOH–H_2O_2) to 5-methyl*iso*oxazole-3-carboxylic acid (I). OMe·CH_2·C(NH)·CH_2·COMe and NH_2OH give 5-*methyl*-3-*methoxymethyl*isooxazole, b.p. 80—82°/15 mm., also oxidised to (I). E. W. W.

β-Nitrodicarboxylic esters and their transformation into oxidopyrrolidines. B. REICHERT and E. WEGNER (Ber., 1938, **71**, [*B*], 1254—1259).—Condensation (NaOEt–EtOH) of $CH_2(CO_2Et)_2$ and NO_2·CPh:CHPh gives *Et*$_2$ β-*nitro*-αβ-*diphenylethylmalonate*, m.p. 132—133°. The following *Et*$_2$ *-malonates* are obtained similarly: β-*nitro*-β-*phenyl*-α-p-*anisylethyl*, m.p. 127°; β-*nitro*-β-*phenyl*-α-3 : 4-*methylenedioxyphenylethyl*-, m.p. 136—138°. From the requisite substituted styrene the following *Et*$_2$ *-malonates* are prepared: β-*nitro*-α-o-*methoxyphenylethyl*-, m.p. 53°; β-*nitro*-α-2 : 4-*dimethoxyphenylethyl*- (I), m.p. 59°; β-*nitro*-α-o-*hydroxyphenylethyl*-, m.p. 92°; β-*nitro*-α-3 : 4-*methylenedioxyphenylethyl*-, m.p. 66°; (β-*nitro*-α-3 : 4-*methylenedioxyphenylethyl*)*ethyl*-, m.p.

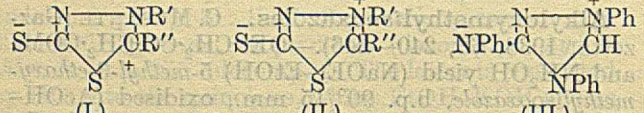
84—85°. Reduction (Pd–C in C_5H_5N) at about 50° of (I) leads to *Et* 1 : 2-*oxido*-2-*hydroxy*-4-2′ : 4′-*dimethoxyphenylpyrrolidine*-3-*carboxylate* (cf. *A*), m.p. 145°, which appears incapable of reduction and does not appear to react with $SOCl_2$, PCl_3, $POCl_3$, or PCl_5. *Et* 1 : 2-*oxido*-2-*hydroxy*-4-*o*′-*methoxyphenylpyrrolidine*-3-*carboxylate*, m.p. 106°, is hydrolysed by 10% HCl at 100° to the corresponding *acid*, m.p. 141° or (+1H_2O), m.p. 132—133° which at 160—170° gives CO_2 and 1 : 2-*oxido*-2-*hydroxy*-4-*o*′-*methoxyphenylpyrrolidine*, m.p. 139°. With Br in $CHCl_3$ it gives *Et* 3-*bromo*-1 : 2-*oxido*-2-*hydroxy*-4-*o*-*methoxyphenylpyrrolidine*-3-*carboxylate*, m.p. 151°, and with NaOH and Me_2SO_4 it yields 1 : 2-*oxido*-2-*methoxy*-4-*o*′-*methoxyphenylpyrrolidine*-3-*carboxylic acid*, m.p. 144—145°. Phenanthrene-9-aldehyde, $MeNO_2$, and KOH in EtOH afford 9-β-*nitrovinylphenanthrene*, m.p. 173°. H. W.


(*A*.)

Phenothiazine. III. Conversion of phenothiazine to thionol. F. De Eds and C. W. Eddy (J. Amer. Chem. Soc., 1938, **60**, 1446—1447).—The prep. of thionol (I) from phenthiazine and H_2O_2–HCl–aq. EtOH is improved (80% yield). With boiling Ac_2O it gives the triacetate, m.p. 136·5°, and *diacetate*, m.p. 212°, of the leuco-base, which, when pure, has an oxidation–reduction potential of 0·3019 v. at 21° and p_H 4·47. This potential is used as a criterion of purity. R. S. C.


(I.)

Constitution and isomerism of certain triazole derivatives of the nitron type in the light of the Bredt rule and the theory of resonance. A. Schönberg (J.C.S., 1938, 824—825).—It is suggested that the *endo*thiodihydrothiodiazoles are resonance hybrids of (I) and (II), that nitron is (III), and that,


(I.) (II.) (III.)

in the *endo*thio- and *endo*oxy-triazolines, each of the classical formulæ must be replaced by two betaine formulæ, which explains the existence of isomerides. F. R. S.

New heterocyclic syntheses. I. Triazoles and thiodiazoles. R. Fusco and C. Musante (Gazzetta, 1938, **68**, 147—156).—NHPh·N:CPhCl (I) and 2 : 4 : 1-$C_6H_3Br_2$·NH·N:CPhBr (II) with NH_2·CPh:NH in cold Et_2O give 1 : 3 : 5-triphenyl- and 3 : 5-*diphenyl*-1-(2′ : 4′-*dibromophenyl*)-1 : 2 : 4-*triazole*, m.p. 147°, respectively. With KCNO in boiling 80% EtOH, (I) gives 1 : 3-diphenyl-1 : 2 : 4-triazol-5-one and (II) the *K* salt, m.p. 271°, of 3-*phenyl*-1-(2′ : 4′-*dibromophenyl*)-1 : 2 : 4-*triazole*-5-*one*, m.p. 274°. With $CS(NH_2)_2$, 3 : 5-*diphenyl*-, m.p. 97° [*hydrochloride*, m.p. 247—248°; *Ac*, m.p. 157°, and *Bz*, m.p. 166°, derivatives; *NO*-derivative, m.p. 144° (decomp.), which in xylene at 150° yields 2-*keto*-3 : 5-*diphenyl*-1 : 3 : 4-*thiodiazoline*, m.p. 85—86°], and 2-*imino*-5-*phenyl*-3-(2′ : 4′-*dibromophenyl*)-1 : 3 : 4-*thiodiazoline*, m.p. 98—100° [*hydrochloride*, m.p. 246°; *Ac*, m.p. 175—176°, and *Bz*, m.p. 198°, derivatives; *NO*-derivative, m.p. 144°, decomp. to 2-*keto*-5-*phenyl*-3-(2′ : 4′-*dibromophenyl*)-1 : 3 : 4-*thiodiazoline*, m.p. 148—150°], are obtained. The same products are formed from KSCN. E. W. W.

Acridine derivatives as antimalarials. II. V. P. Basu and S. J. Das-Gupta (J. Indian Chem. Soc., 1938, **15**, 160—164).—2 : 5-Dichloro-7-methoxyacridine with 4-aminoantipyrine affords 2-*chloro*-7-*methoxy*-5-(1′-*phenyl*-2′ : 3′-*dimethyl*-5′-*pyrazolonylamino*)*acridine*, m.p. 248°. In a similar way from the 5-chloroacridine and the aminoantipyrine or the thiazole derivative the following are obtained: 2-*chloro*-5-(1′-*phenyl*-2′ : 3′-*dimethyl*-5′-*pyrazolonylamino*)-7-*methylacridine*, m.p. 257°, 3-*nitro*-5-(1′-*phenyl*-2′ : 3′-*dimethyl*-5′-*pyrazolonylamino*)-7-*methoxyacridine*, m.p. 278—279°, 2 : 7-*dichloro*-5-(1′-*phenyl*-2′ : 3′-*dimethyl*-5′-*pyrazolonylamino*)*acridine*, m.p. 276—277°, 2-*chloro*-5-(4′-*phenylthiazolylamino*)-7-*methoxyacridine*, m.p. 246—247°, 2-*chloro*-5-(4′-*phenylthiazolylamino*)-7-*methylacridine*, m.p. 263—264°, 2 : 7-*dichloro*-5-(4′-*phenylthiazolylamino*)*acridine*, m.p. 269—270°, 3-*nitro*-5-(4′-*phenylthiazolylamino*)-7-*methoxyacridine*, m.p. 264—265°, 2-*chloro*-5-(4′-*methyl*-5′-β-*hydroxyethylthiazolylamino*)-7-*methoxyacridine*, m.p. 256° (from 2-*amino*-4-*methyl*-5-β-*hydroxyethylthiazole*, m.p. 138°), 2-*chloro*-5-(4′-*methyl*-5′-β-*hydroxyethylthiazolylamino*)-7-*methylacridine*, m.p. 254°, 2 : 7-*dichloro*-5-(4′-*methyl*-5′-β-*hydroxyethylthiazolylamino*)*acridine*, m.p. 273°, 3-*nitro*-5-(4′-*methyl*-5′-β-*hydroxyethylthiazolylamino*)-7-*methoxyacridine*, m.p. 261—262°. A. L.

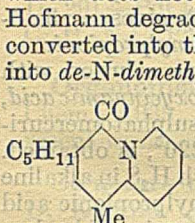
Priority in the synthesis of vitamin-B_1. H. Hörlein (Z. physiol. Chem., 1938, **253**, 80—82). W. McC.

***Cactus* alkaloids. XIX. *N*-Acetylmezcaline as component of mezcal buttons.** E. Späth and J. Bruck (Ber, 1938, **71**, [*B*], 1275—1276).—The isolation of N-*acetylmezcaline* [*acet*-β-3 : 4 : 5-*trimethoxyphenylethylamide*], m.p. 93—94°, from mezcal buttons is described. H. W.

Tobacco alkaloids. XV. Pictet's nicotine synthesis. E. Späth and P. Kainrath (Ber., 1938, **71**, [*B*], 1276—1281).—An abbreviation and an emendation of Pictet's nicotine synthesis are described. 3-Aminopyridine (I) and mucic acid are distilled mainly at 250—300° and the 3′-pyridyl-1-pyrrole thus obtained, after removal of unchanged (I) by light petroleum, is isomerised to nornicotyrine (II) by passage through a tube packed with pumice at 700°. The crude product is separated by crystallisation into (II) and 3′-pyridyl-3-pyrrole (III), m.p. 140° [*picrate*, m.p. 198—199° (vac.; decomp.)], which gives nicotinic acid when oxidised. Catalytic hydrogenation (Pd sponge) of (II) gives nornicotine (dipicrate, m.p. 194°), methylated (CH_2O–HCO_2H) to *dl*-nicotine. Hydrogenation of (III) affords 3-*pyridyltetrahydropyrrole* [*dipicrate*, m.p. 239° (vac.; decomp.)], methylated to 3′-*pyridyl*-1-*methyltetrahydropyrrole* (*dipicrate*, m.p. 193—195°). H. W.

Sparteine. Hofmann degradation of oxysparteine. E. Späth and F. Galinovsky (Ber., 1938,

71, [*B*], 1282—1287).—Oxysparteine is converted by MeI in MeOH at 100° into the *methiodide*, m.p. 223—225° (vac.), converted by Ag_2O followed by distillation into *de*-N-*methyloxysparteine* (I), m.p. 89—90°, $[\alpha]_D^{18}$ −17·13° in MeOH (mutarotation), $[\alpha]_D^{18}$ +4·82° (const.) in C_6H_6. This is reduced (PtO_2 in HCl) to *de*-N-*methyldihydro-oxysparteine* (*picrate*, m.p. indef. 129—132°), which affords an amorphous *methiodide* which does not give satisfactory results when the Hofmann degradation is attempted. (I) is therefore converted into the amorphous methiodide and thence into *de*-N-*dimethyloxysparteine* (*perchlorate*, m.p. 209—210°; *picrate*, m.p. 135—136°, $[\alpha]_D^{18}$ −0·63° in MeOH), which yields the optically inactive *de*-N-*dimethyltetrahydro-oxysparteine*. The corresponding *methiodide*, m.p. 185—187° (vac.; indef.), is converted through the hydroxide into *tetrahydrohemioxysparteylene*, whence *hexahydrohemioxysparteylene* (*A*), b.p. 130—140° (bath)/0·01 mm., which is optically inactive and does not yield cryst. salts or derivatives.


(*A*.)

H. W.

Absorption of the chief cinchona alkaloids in the ultra-violet. L. Fuchs and A. Kampitsch (Sci. pharm., 1935, 6, 113—122; Chem. Zentr., 1936, ii, 818).—Ultra-violet absorption spectra in H_2O and EtOH of quinine, cinchonidine, cinchonine, quinidine, of their neutral salts (spectrum type I), and of their acid salts (type II) are determined. The first pair under comparable conditions show almost identical spectra as do also the second pair, but the chromophoric OMe differentiates the quinine from the cinchonine spectrum. Minor solvent effects are also noted. A. H. C.

So-called 2-nitrosomorphine. E. Ochiai and T. Nakamura (Proc. Imp. Acad., Tokyo, 1938, 14, 134—136).—The 2-nitrosomorphine of Wieland *et al.* (A., 1911, i, 743) is shown to be 2-*nitromorphine* by analysis of its *forms*, anhyd. and $+H_2O$, and of its *hydrochloride*, anhyd. and $+2{\cdot}5H_2O$, by hydrogenation (3 H_2 absorbed) in dil. HCl in presence of Pd–C to non-phenolic 2-*aminodihydromorphine* (*dihydrochloride*, decomp. 325°; Bz_3 derivative, m.p. 185°), by absence of a Liebermann reaction, and indifference to HI.

R. S. C.

Oxidation of mesaconitine, aconitine, and their oxidation product, oxonitine. H. Suginome (J. Fac. Sci. Hokkaido Univ., III, 1937, 2, 95—114).—Details are given of results already reviewed (A., 1938, II, 74). Triacetyloxonitine contains xH_2O of crystallisation. Nitronitrosoaconitinic acid crystallises from aq. $COMe_2$ with H_2O and 0·5 or $1H_2O$. Ba nitronitrosoaconitinate contains $8H_2O$. AcCl introduces 2 Ac into nitronitrosoaconitinic acid, one replacing the NO, which (not the NO_2; cf. *loc. cit.*) is attached to N. Aconitine (I) is $C_{18}H_{17}(OMe)_4(OH)_3(OAc)(OBz)(NEt{\cdot}CH_2)$; mesaconitine (II) is $C_{18}H_{17}(OMe)_4(OH)_3(OAc)(OBz)(NMe{\cdot}CH_2)$. Oxonitine is prepared from (II) in 79% yield by $KMnO_4$ (4 O), but only in 30% yield from (I) (best with 6 O). R. S. C.

Hydrocyanic acid compounds of alkaloids and organic bases. P. Mesnard (Bull. Trav. Soc. Pharm. Bordeaux, 1936, 74, 35—56; Chem. Zentr., 1936, ii, 1732).—The compounds are prepared by slowly crystallising (nicotine and atropine compounds are not cryst.) a solution of a salt of the base with a neutralised (H_2SO_4) mixture of equal vols. of 5% $CuSO_4{,}5H_2O$ and 6% KCN solutions. The base in these compounds is determined by pptg. with NaOH, extracting, and weighing or titrating. The compounds are of three types: xCuCN,y(*B*,HCN); xCuCN,y(*B*,HCN),zHCN; xCuCN,y(*B*,HCN),z*B* (*B*= base). Derivatives of the following bases are described: cocaine, $CuCN{,}4(C_{17}H_{21}O_4N{,}HCN){,}4HCN$; novocaine, $CuCN{,}(C_{13}H_{20}O_2N_2{,}HCN){,}HCN$; *p*-aminobenzoyldibutylaminoethanol, $CuCN{,}2(C_{18}H_{30}O_2N_2{,}HCN){,}HCN$; benzoyldiethylaminodimethylethylcarbinol, $3CuCN{,}4(C_{16}H_{25}O_3N{,}HCN){,}HCN$; morphine, $CuCN{,}9(C_{17}H_{19}O_3N{,}HCN){,}7HCN$; codeine, $CuCN{,}4(C_{18}H_{21}O_3N{,}HCN){,}3HCN$; ethylmorphine, $CuCN{,}5(C_{19}H_{23}O_3N{,}HCN){,}2HCN$; benzoylmorphine, $CuCN{,}4(C_{24}H_{25}O_3N{,}HCN){,}HCN$; diacetylmorphine, $CuCN{,}5(C_{21}H_{23}O_5N{,}HCN){,}2HCN$; $NHPh{\cdot}NH_2$, $3CuCN{,}4(C_6H_8N_2{,}HCN){,}HCN$; sparteine, $3CuCN{,}2(C_{15}H_{26}N_2{,}2HCN)$; quinine, $CuCN{,}4(C_{20}H_{24}O_2N_2{,}HCN)$; cinchonidine, $CuCN{,}8(C_{19}H_{22}ON_2{,}HCN)$; strychnine, $CuCN{,}2(C_{21}H_{22}O_2N_2{,}HCN)$; brucine, $2CuCN{,}5(C_{23}H_{26}O_4N_2{,}HCN)$; piperidine, $CuCN{,}5(C_5H_{11}N{,}HCN)$; methylene-blue, $2CuCN{,}13(C_{16}H_{18}N_3SCl{,}HCN){,}5HCN$; nicotine, $CuCN{,}2(C_{10}H_{14}N_2{,}HCN){,}1{\cdot}5HCN$; atropine, $2CuCN{,}3(C_{17}H_{23}O_3N{,}HCN){,}3HCN$; hordenine, $CuCN{,}(C_{10}H_{15}ON{,}HCN){,}HCN$; *l*-ephedrine, $CuCN{,}6(C_{10}H_{15}ON{,}HCN){,}5HCN$; caffeine, $4CuCN{,}(C_8H_{10}O_2N_4{,}HCN)$; $CuCN{,}9(NH_2Ph{,}HCN)$; pyramidone, $CuCN{,}4(C_{13}H_{17}ON_3{,}HCN){,}3HCN$; $4CuCN{,}3(C_5H_5N{,}HCN){,}9HCN$; $CuCN{,}5[(CH_2)_6N_4{,}HCN]$; antipyrine, $6CuCN{,}(C_{11}H_{12}ON_2{,}HCN){,}12C_{11}H_{12}ON_2$; quinoline, $5CuCN{,}(C_9H_7N{,}HCN){,}4C_9H_7N$. A. H. C.

Cinchona alkaloids in pneumonia. VI. Hydroxyalkylation of phenolic cinchona alkaloids. C. L. Butler and (Miss) A. G. Renfrew (J. Amer. Chem. Soc., 1938, 60, 1473—1475; cf. A., 1937, II, 171).—*p*-$C_6H_4Me{\cdot}SO_3{\cdot}[CH_2]_2{\cdot}O{\cdot}CH_2Ph$, *apo*cupreine, and KOH–EtOH at 100° give β-*benzyloxyethyl*apo-*cupreine* (I), m.p. 115°, $[\alpha]_D$ −155°, obtained also from the β-*chloroethyl ether* (*dihydrochloride*, $[\alpha]_D$ −205°). The product is stable to NaOH, but is hydrolysed by 11% HCl to β-*hydroxyethyl*apo*cupreine* (II) (*dihydrochloride*, $[\alpha]_D$ −228°; Ac_2 derivative, amorphous). Isolation of (I) is unnecessary for the prep. of (II), and β-*hydroxyethylcupreine*, $[\alpha]_D$ −131° (*dihydrochloride*, $[\alpha]_D$ −181°; amorphous Ac_2 derivative, $[\alpha]_D$ −30°), γ-*hydroxypropyl*-, m.p. 140°, $[\alpha]_D$ −181° (*dihydrochloride*, $[\alpha]_D$ −225°; Ac_2 derivative, $[\alpha]_D$ −69°), β-*hydroxyisopropyl*- (III), m.p. 105—108°, $[\alpha]_D$ −180° (*dihydrochloride*, $[\alpha]_D$ −224°; Ac_2 derivative, a gum, $[\alpha]_D$ −61°), and ββ′-*dihydroxyisopropyl*-apo*cupreine*, m.p. 128°, $[\alpha]_D$ −177° (*dihydrochloride*, $[\alpha]_D$ −203°; Ac_3 derivative, amorphous, $[\alpha]_D$ −46°), are thus prepared. These OH-ethers, especially (III), have high toxicity to pneumococci *in vitro*, but cause little eye-damage to dogs. [α] are in EtOH. R. S. C.

Arsenated derivatives of mixed ketones. II. Arsenicals of pæonol. C. K. BANKS and C. S. HAMILTON (J. Amer. Chem. Soc., 1938, **60**, 1370—1371; cf. A., 1937, II, 267).—5-Nitro-2-hydroxy-4-methoxyacetophenone [prep. in 80% yield by HNO_3 (*d* 1·42) at 15—10°], m.p. 155°, is reduced quantitatively by H_2–Raney Ni in $COMe_2$ (only with difficulty by H_2–PtO_2) to the unstable 5-NH_2-compound, m.p. 115° (*hydrochloride*, m.p. 250°), which by a diazo-reaction affords 2-*hydroxy*-4-*methoxyacetophenone*-5-*arsinic acid*, m.p. 225° (decomp.). HCl–NaI–SO_2 then affords the *arsenious oxide*, m.p. 260° (decomp.), reduced by HPO_2 to 4 : 4′-*dihydroxy*-5 : 5′-*diacetyl*-2 : 2′-*dimethoxyarsenobenzene*, m.p. 228° (decomp.). R. S. C.

Antimony compounds of 8-hydroxyquinoline. M. DENAYER (Cong. Chim. ind. Bruxelles, 1935, **15**, I, 387—391; Chem. Zentr., 1936, ii, 1926).—Whilst Sb_2O_3 yields with Na 8-hydroxyquinoline-5-sulphonate the ester $(C_9H_5O_4NSNa)_3Sb$, which is hydrolysed by alkali, Na 7 : 8-dihydroxy- and 7-amino-8-hydroxy-(but not 7-acetamido-8-hydroxy-)quinoline-5-sulphonates yield alkali-stable compounds. Compounds of Sb^V are also described. A. H. C.

Phenylmercuric compounds. J. K. GJALDBÆK and V. H. MIKKELSEN (Arch. Pharm. Chem., 1938, **11**, 1—100).—A complete crit. review of the literature on the prep., properties, qual. and quant. analysis, and pharmacological applications of HgPh salts. Many consts. have been determined and errors corr. HgPh salts when warmed with aq. KI_3 give PhI. HgPh salts insol. in H_2O are determined by dissolution in excess of 0·1N-NaOH in $COMe_2$–EtOH and back-titration. Their reactions with Cu, Zn, Sn, Na_2S, $(NH_4)_2S_x$, and $Na_2S_2O_3$ have been investigated. The dissociation and hydrolysis of HgPh·OH and HgPh·OAc in aq. solution have been studied. *Hg^{II} Ph thiosulphate*, m.p. >270°, and *metaborate*, m.p. 185—190°, and *HgPh·BO_2*,*HgPh·OH*, m.p. 120°, have been prepared. M. H. M. A.

Introduction of the MgBr group into anisole and phenetole. F. CHALLENGER and S. A. MILLER (J.C.S., 1938, 894—899).—2-Thienylmagnesium bromide, S, and PhOEt (I) give a product, which on reduction (Zn–HCl) and treatment with $CH_2Cl·CO_2H$ affords *phenetylthiolacetic acid*, m.p. 64—65°. MgEtBr and (I), followed by $HgBr_2$, yield *o*-phenetylmercury bromide, converted into di-*o*-phenetylmercury. PhOMe with MgEtBr or $MgPr^aBr$ similarly gives *o*-anisylmercury bromide: no *p*-compounds are formed. (I) does not react appreciably with S at its b.p., nor is (I) or PhOMe mercurated by $HgCl_2$ or $HgBr_2$. *o*-Anisidine, $HgBr_2$, HBr, and $NaNO_2$ give o-*anisyldiazonium-mercury tribromide*, m.p. 117—118°, which with Cu affords *o*-anisylmercury bromide; the corresponding p-*diazonium* compound, m.p. 138—139°, similarly yields *p*-anisylmercury bromide, also obtained from *p*-$C_6H_4Br·OMe$. $NPhMe_2$, MgEtBr, and CO_2 give dimethylanthranilic acid. F. R. S.

Reactivity of the double linking in coumarins and related αβ-unsaturated carbonyl compounds. VI. Action of mercuric acetate on the methyl ethers of coumarinic and coumaric acids. S. RANGASWAMI, V. S. RAO, and T. R. SESHADRI (Proc. Indian Acad. Sci., 1938, **7**, **A**, 312—318; cf. A., 1938, II, 300).—The Me ether (I) of coumarinic acid with $Hg(OAc)_2$ in MeOH at 28° gives *α-acetoxymercuri-β : 2-dimethoxy-β-phenylpropionic acid*, decomp. 204°, which loses AcOH giving an anhydride (Biilmann, A., 1912, i, 461) when a solution in aq. NaOH is acidified with dil. H_2SO_4; with dil. HCl removal of the addenda occurs with the formation of the isomeric Me ether of coumaric acid. When heated with >3 mols. of $Hg(OAc)_2$ in MeOH (20 hr.) (I) gives *α : 3 : 5-triacetoxymercuri-β : 2-dimethoxy-β-phenylpropionic acid*, decomp. 220—221°; an alkaline solution with HCl gives *3 : 5-dichloromercuri-2-methoxycinnamic acid*, decomp. 216°, whereas with H_2SO_4 a sulphatomercuri-*compound*, $C_{11}H_{10}O_8SHg_3$, decomp. 226°, is obtained. The foregoing mercuri-compounds with H_2S in alkaline solutions give β : 2-dimethoxy-β-phenylpropionic acid (cf. *loc. cit.*). The Me ether of coumaric acid when treated with $Hg(OAc)_2$ in MeOH in the cold gives an indefinite, partly mercurated additive product, but with >3 mols. of $Hg(OAc)_2$ in boiling MeOH (20 hr.) the compounds obtained are identical with those from (I). By similar methods the Me ether (II) of 5-nitrocoumarinic acid first gives its *Hg* salt, decomp. 141—142°, which slowly changes into *α-acetoxymercuri-5-nitro-β : 2-dimethoxycinnamic acid* (III), decomp. 199°, converted (H_2SO_4 on alkaline solution) into the *anhydride* form (IV), decomp. 210°, also obtained from (II) and $Hg(OAc)_2$ in MeOH (100°; 5 hr.). Acidification of a solution of (III) or (IV) in aq. NaOH with HCl gives the Me ether of 5-nitrocoumaric acid. This with $Hg(OAc)_2$ gives its *Hg* salt, decomp. 205°, which changes slowly into (III). Alkaline solutions of (III) and (IV) with H_2S give *5-nitro-β : 2-dimethoxy-β-phenylpropionic acid*, m.p. 158°. The NO_2-acids undergo addition only; elimination of the addenda by dil. HCl gives the *trans*-form in each case. H. G. M.

Decomposition reactions of aromatic diazo-compounds. IV. New synthesis of aromatic antimony compounds. F. B. MAKIN and W. A. WATERS (J.C.S., 1938, 843—848; cf. A., 1938, II, 52).—Solid *p*-$C_6H_4Cl·N_2Cl$ and *p*-$C_6H_4Br·N_2Cl$ with $COMe_2$ at 50°, with or without $CaCO_3$, yield PhCl and PhBr, respectively, and $CH_2Cl·COMe$, whilst with Hg and $CaCO_3$ in $COMe_2$, *p*-$C_6H_4Hal·HgCl$ are obtained. In EtOAc with $CaCO_3$ at 60°, *p*-$C_6H_4Cl·N_2Cl$ yields *p*-$C_6H_4Cl_2$, but no PhCl; it is decomposed in the cold by Pb, Ag, or Bi, in $COMe_2$ or EtOAc. Decomp. of ArN_2Cl by Sb in presence of $CaCO_3$, in $COMe_2$ or AcOEt (but not in H_2O, EtOH, *cyclo*hexane, C_6H_6, CCl_4, CS_2, Et_2O, or dioxan), yields mixtures of $SbAr_3Cl_2$, $SbAr_3$, and $SbAr_2Cl$; it is inferred that reaction occurs only after tautomeric change to the wholly covalent NAr:NCl. $ArN_2Cl,SbCl_3$ and $ArN_2Cl,ZnCl_2$ give similar results in $COMe_2$. In this way the following compounds have been prepared: *tri*-p-*chloro*- (in $COMe_2$), m.p. 193°, and (in $COMe_2$ or EtOAc) -p-*bromo-phenyl*-, m.p. 200°, *tri*-(4- (from $ZnCl_2$ double salt in $COMe_2$), m.p. 264°, and (in EtOAc) -(5-*chloro*-o-*tolyl*)-, m.p. 238°, and (in EtOAc) *tri*-(5-*chloro*-2-*methoxyphenyl*)-*stibine dichloride*, m.p. 281° (decomp.) (the last three also obtained from the stibine and Cl_2 in CCl_4); *tri*-(4-, m.p. 226°, and -(5-*chloro*-o-*tolyl*)-, m.p. 176° (both in $COMe_2$ or EtOAc),

and (in EtOAc) *tri-(5-chloro-2-methoxyphenyl)-stibine*, m.p. 188°; *di-(5-chloro-2-methoxyphenyl)-* (in $COMe_2$), m.p. 144°, and (from the $ZnCl_2$ double salt in $COMe_2$) *di-(4-chloro-o-tolyl)-stibinous chloride*, m.p. 131°. The last with Cl_2 in CCl_4 gives the *stibinic trichloride*, m.p. 162°. A. Li.

Di-indolepalladium hydrochloride. L. Delavigne (Gazzetta, 1938, **68**, 271—272; cf. A., 1938, II, 29).—$PdCl_2$ and indole in H_2O give the *compound*, $C_{16}H_{14}N_2Cl_2Pd$ (? di-2-indolylpalladium +2HCl). E. W. W.

Organometallic compounds. F. Hein (Angew. Chem., 1938, **51**, 503—508).—A lecture reviewing recent work.

Structure of proteins (wool, fibroin, gelatin). D. Krüger (Chem.-Ztg., 1938, **62**, 533—535).—A review.

Copper tube preheater [for micro-analyses of carbon and hydrogen]. W. MacNevin and H. S. Clark (Ind. Eng. Chem. [Anal.], 1938, **10**, 338).—The preheater consists of Cu tubing wound for a part of its length into the form of a coil which is heated by means of a batswing burner. Air saturated with colloidal oil and other org. impurities gave a negligible blank when this heater was used. L. S. T.

Nitrogen determinations by the micro-Dumas method.—See A., 1938, I, 414.

Determination of active hydrogen in organic compounds. E. J. Schtuber and A. V. Dobromislova (J. Appl. Chem. Russ., 1938, **11**, 704—706).—Labile H is determined by a modified Tschugaev–Zerevitinov method, involving exclusion of atm. O_2, and replacement of *iso*-C_5H_{11}·OH by xylene. R. T.

Colorimetric determination of small amounts of chloropicrin in air, water, and foodstuffs. W. Deckert and B. Prathithavanija (Z. anal. Chem., 1938, **113**, 182—189).—The yellow colour formed by CCl_3·NO_2 (I) and $NPhMe_2$ (50% in C_6H_6 solution) in presence of O_2 (H_2O_2) forms the basis of the colorimetric determination of 10 to 5000 μg. of (I) in air, H_2O, and foodstuffs. (I) is extracted from H_2O by shaking with a 50% solution of $NPhMe_2$ in C_6H_6, and from dry foodstuffs such as bread, potatoes, flour, and corn by extraction with C_6H_6. Distillation with xylene is used for separating (I) from fatty substances, and distillation in xylene vapour for separation from milk etc. The application of the reaction to the detection of traces of (I) in air using the Dräger–Schröter apparatus is also described. L. S. T.

Determination of glycerol and some other hydroxyl compounds. S. H. Bertram and R. Rutgers (Rec. trav. chim., 1938, **57**, 681—687).—Glycerol (I) is determined by means of the Cu Na compound, $+1{\cdot}5H_2O$, which is sol. in aq. EtOH. $CuCl_2$–EtOH is added to (I) and NaOH in aq. EtOH until a ppt. is just formed, the mixture centrifuged, and the Cu in the supernatant liquor determined by $Na_2S_2O_3$. The technique needed for determining the (I) liberated by hydrolysis of oils and fats is also detailed. Slight variation in temp., concn. of NaOH or EtOH, or time of keeping does not vitiate the result. The (I) content may be 0—0·9 g. per 10 c.c. A blank determination is necessary. Three technical samples of (I) were 84, 91·65, and 86·5% pure. Glucose, sucrose, lactose, etc. and $CH_2(CH_2{\cdot}OH)_2$ do not interfere. Mannitol and sorbitol (2 Cu per mol.), and $(OH{\cdot}CH{\cdot}CO_2H)_2$ (1 Cu per mol.) are similarly determined. R. S. C.

Manganese as catalyst and redox indicator in the cerimetric determination of oxalate. L. Szebellédy and S. Tanay (Pharm. Zentr., 1938, **79**, 441—447).—$Mn^{\cdot\cdot}$ ions catalyse the reaction between C_2O_4'' and $Ce^{\cdot\cdot\cdot\cdot}$. The solution containing C_2O_4'' is mixed with 10 c.c. of 5N-H_2SO_4 or 5 c.c. of conc. HCl, and diluted to 50 c.c. 1 g. of $MnSO_4,5H_2O$ or $MnCl_2,4H_2O$ and 0·05 c.c. of ferroin indicator solution (1·624 g. of *o*-phenanthroline hydrochloride and 0·695 g. of $FeSO_4,7H_2O$ in 100 c.c. of H_2O) are added, and the solution is titrated (pale blue) with 0·1N-$Ce(SO_4)_2$ solution. The results agree wtih those obtained potentiometrically, by titration with $Ce(SO_4)_2$ using ICl as catalyst, and by direct titration with $KMnO_4$. The Mn salt can also serve as a redox indicator, and, in daylight, the use of ferroin is unnecessary. For micro-determinations, the C_2O_4'' solution is mixed with 1 c.c. of 5N-H_2SO_4 (or HCl) and 0·10 g. of $MnSO_4,5H_2O$ (or $MnCl_2,4H_2O$), 0·01 c.c. of ferroin solution, which is indispensable in this case, diluted to 5 c.c., and titrated with 0·1N-$Ce(SO_4)_2$ solution at 40—50°. L. S. T.

Polarographic analysis of mixtures of *cis*- and *trans*-aconitic acids. G. Semerano and L. Sartori (Mikrochem., 1938, **24**, 130—133).—These acids can be detected and determined as their Ca salts in a solution of NH_4Cl. The reduction potentials of the acids are sufficiently different; the strength of the diffusion current ∝ concn. Since at a given concn. the current with the *cis*-salt is somewhat > that with the *trans*-compound, the detection of the *cis*-acid in presence of much *trans*-acid is easier than the reverse. The Li salts serve for the detection of the *trans*- in presence of the *cis*-acid but not vice versa. L. S. T.

Organic acid–ferrous complex as a disturbing factor in the titrimetric determination of ascorbic acid. K. P. Basu and M. C. Nath (J. Indian Chem. Soc., 1938, **15**, 133—135).—Organic acid–Fe^{II} complexes exert a powerful reducing action on 2 : 6-dichlorophenol-indophenol used in the determination of ascorbic acid. The reducing power has been determined for oxalic, malonic, succinic, malic, tartaric, and citric acids; neither $Fe^{\cdot\cdot}$ nor the acid alone reduces the reagent. For the dibasic acids the reducing power of the complex decreases as the no. of C atoms in the acid increases. The citric acid–Fe^{II} complex is incompletely removed by $Hg(OAc)_2$. E. S. H.

Thioketonic esters. VII. Thio-thiol estimation. S. K. Mitra (J. Indian Chem. Soc., 1938, **15**, 205—210).—Determination of thiol in $CSMe{\cdot}CH_2{\cdot}CO_2Et$, $CSMe{\cdot}CHMe{\cdot}CO_2Et$, $CSMe{\cdot}CHBu^{\beta}{\cdot}CO_2Et$, and $CSMe{\cdot}CH(CO_2Et)_2$ by adding the ester to an excess of EtOH–I at −7° and titrating with $Na_2S_2O_3$ shows that α-substitution increases the percentage of the SH form. A. Li.

Use of glycerol instead of Seignette salt in determination of sugars by Bertrand's method. M. N. Tultschinski (J. Appl. Chem. Russ., 1938, **11**, 707—710).—5 ml. of 21·2% glycerol, 15 ml. of 20% KOH, and 20 ml. of 4% $CuSO_4 5H_2O$ are added to 20 ml. of solution, and determination of sugar is conducted further according to Bertrand. The results deviate from those given by the original method, to an extent ∝ sugar content, and require the application of an empirical correction. R. T.

Determination of choline and acetylcholine.—See A., 1938, III, 706.

Determination of amino-acids. T. Laine (Suomen Kem., 1938, **11**, A, 50—52, 65—67).—A review of methods. The determination of naturally occurring NH_2-acids is discussed in detail. M. H. M. A.

Derivatives of the indane group as reagents for amines. I. Detection of primary monoamines with bindone. G. Wanag (Z. anal. Chem., 1938, **113**, 21—34).—Primary aromatic amines yield with bindone in glacial AcOH a blue colour which furnishes a delicate test for traces of such amines. A similar colour is given with monoalkylarylamines, but the test is much less sensitive. Primary aliphatic and alicyclic amines yield a violet colour, whilst *sec.* aliphatic amines give this colour only in very conc. solution. Di- and tri-aryl-, diarylalkyl-, and trialkyl-amines, C_5H_5N, quinoline, pyrrole, and alkaloids give no characteristic colour. J. W. S.

Identification of sulphanilamide. J. V. Scudi (Ind. Eng. Chem. [Anal.], 1938, **10**, 346—347).—A solution of sulphanilamide (I) (1 drop containing 0·04 mg.) with 40% CH_2O (1 drop) and 10% Na_2CO_3 (1 drop) affords a *polymeride*, $(C_8H_8O_2N_2S)_x$, m.p. 235—240° (decomp.); 0·012 mg. of (I) can be detected microscopically. (I) (1 drop containing 0·02—0·04 mg.) with ICl (1 drop) affords 3 : 5-di-iodo-4-aminobenzenesulphonamide (cf. A., 1937, II, 409). (I) (as hydrochloride) affords a *picrate*, m.p. 179—180°; 0·012 mg. can be detected microscopically. (I) (1 drop containing 0·04 mg.) with $Hg(NO_3)_2$ (1 drop) and 10% Na_2CO_3 (1 drop) affords a flocculent ppt. best seen with dark background illumination. Equimol. amounts of (I) and $AgNO_3$ in the presence of aq. NH_3 afford a white *compound*, $C_6H_7O_2N_2SAg$, but the test is insensitive. With $(NH_4)_2S_2O_8$, (I) affords evanescent colours. (I) when boiled with conc. HNO_3 and then made alkaline with NaOH affords an intense yellow colour with concns. >10%. A few mg. of (I) with cold Ac_2O afford acetylsulphanilamide (cf. *loc. cit.*) but with boiling Ac_2O, *diacetylsulphanilamide*, m.p. 242—244° (decomp.), is formed. s-*Diphenylcarbamide*-4 : 4′-*disulphonamide* has m.p. 270—271° (decomp.). J. L. D.

Optical crystallographic studies with the polarising microscope. I. Identification and semi-quantitative determination of acetic and propionic *p*-bromoanilides in their binary mixtures. W. M. D. Bryant (J. Amer. Chem. Soc., 1938, **60**, 1394—1399).—The optical crystallographic consts. of three forms of acet-*p*-bromoanilide (I) and of two forms of propion-*p*-bromoanilide (II) have been determined. The acute and obtuse optic axial angles in cedar oil have also been measured. Optic axial angles of mixed crystals of (I) and (II) have been determined for five monochromatic radiations of the Hg arc. M.p. of mixtures of (I) and (II) of different composition have been determined; the system apparently fails to form a eutectic. The above data serve as the basis of a method for the identification of small amounts of AcOH and $EtCO_2H$ and for determining roughly the composition of their mixtures. The mixed crystal system of (I) and (II) shows three types of crystal dispersion: axial, crossed axial plane, and monoclinic crossed dispersion. The first and second are functions of composition. E. S. H.

Detection and determination of ouabain and strophanthin. W. D. Raymond (Analyst, 1938, **63**, 478—482).—The colour given by ouabain (I) with conc. H_2SO_4 and Ac_2O cannot be used to evaluate the drug quantitatively. (I) with naphthoresorcinol–conc. HCl at 50° affords a pink colour after 10 min. [strophanthin-*k* (II) and -*e* similarly afford green and red colours, respectively]; an amyl-alcoholic extract of the diluted solution shows a green fluorescence with >0·004 mg. of (I), but not with (II). (I) with $COMe_2$–conc. HCl at 100°, followed by extraction with $CHCl_3$, affords a pink colour. (II) does not give the reaction. (I) or (II) with *m*-$C_6H_4(NO_2)_2$ or *o*-$NO_2{\cdot}C_6H_4{\cdot}CHO$ (III) in EtOH at 0° followed by treatment with 20% NaOH gives an indigo-blue or violet colour with the former reagent and a red with the latter. With (III) the colour is sufficiently stable to allow quant. measurements. (I) or (II) in boiling AcOH containing furfuraldehyde and $ZnCl_2$ affords a blue colour. Anhyd. (I) with $ZnCl_2$–Ac_2O at 70° affords *hepta-acetyl-anhydro-ouabain*, m.p. 283—284°. J. L. D.

Microchemistry of methylxanthines (caffeine, theobromine, theophylline). G. Denigès (Bull. Trav. Soc. Pharm. Bordeaux, 1936, **74**, 5—11; Chem. Zentr., 1936, ii, 505).—A reaction of the hydrochlorides with NaBr–NaOBr is described. H. N. R.

Volumetric determination of diethyl- or diallyl-barbituric acid. Determination of barbituric acid derivatives in presence of acetic, salicylic, and phenylcinchonic acids, theobromine, and theophylline. E. Schulek and P. Rózsa (Z. anal. Chem., 1938, **112**, 404—415).—A wt. of substance corresponding with 0·1 to 0·15 g. of diethyl- or diallyl-barbituric acid is dissolved in 5% borax solution, K_2CrO_4 solution is added as indicator, and the hot solution titrated with 0·1N-$AgNO_3$. The method is not suitable for phenylethylbarbituric acid and other barbiturates. For the separation of these derivatives from various org. acids and from theobromine the procedure described utilises the fact that the alkali barbiturates are decomposed by H_2CO_3 to give the cryst. acids sol. in Et_2O. A method for the determination of diethylbarbituric acid in urine in presence of salicylic acid is also described. L. S. T.

Determination of flavin.—See A., III, 676.

Separation and determination of phytin.—See A., III, 706.

Microchemical determination of chlorophyll and of cuprophyll.—See A., 1938, III, 706.