BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

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OCTOBER, 1943

A., II.—ORGANIC CHEMISTRY

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Offices of the Bureau : 56 Victoria Street, London, S.W.1

Publishers : THE CHEMICAL SOCIETY, Burlington House, Piccadilly, London, W.1.

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A., II.—Organic Chemistry

OCTOBER, 1943.

I.—ALIPHATIC.

Application of group theory to isomerism in general.—See A., 1943, I, 220.

[Rates of] organic reactions.—See A., 1943, I, 258.

Theory of racemism. C. S. Hudson (*J. Amer. Chem. Soc.*, 1943, **65**, 1239—1240).—The designation, " racemate," is definitive for substances which do not tautomerise, but is not so for tautomeric substances, for which the no. of possible racemates is the no. of tautomeric forms. Examples of the latter type are " *rac.*"-arabinose (5 possibilities) and -perseulose. R. S. C.

Deuterohexane, m.p. 18°, from αβ-dideuterononoic acid.—See A., 1943, III, 580.

Action of sodium ethyl on (−)-β-bromo-octane.—See A., 1943, II, 284.

Preparation of unsaturated hydrocarbons [from alcohols] by silica gel. A. Rollett and H. Maurer-Stroh (*Ber.*, 1940, **73**, [*B*], 740—741).—SiO_2 gel (**I**) is as good as Al_2O_3 and better than clays for prep. of olefines from alcohols. Clays vary in quality, rapidly become inactivated by deposition of C, and are not fully reactivated by burning off the C. C_2H_4 is formed by passing EtOH over (**I**) in a Cu tube at 300—550° (best 550°), fine-pored being better than coarse-pored (**I**). At 250° a little Et_2O, but no C_2H_4, is formed. At 450—550°, Et_2O gives nearly 100% of C_2H_4. At 450—500° $Pr^{\beta}OH$ gives similarly C_3H_6, $Bu^{\beta}OH$ gives a 3 : 1 and $Bu^{\alpha}OH$ gives a 2 : 1 mixture of $(CHMe{:})_2$ and $CH_2{:}CHEt$. At 300° *cyclo*hexanol gives H_2O and *cyclo*hexene, and at 600° gives $(CH_2{:}CH)_2$ and C_2H_2. R. S. C.

Rubber, polyisoprenes, and allied compounds. IV. Relative tendencies towards substitutive and additive reaction during chlorination. G. F. Bloomfield (*J.C.S.*, 1943, 289—296).—In the chlorination of CCl_4 solutions of rubber at 77° in N_2, determinations of the quantity of HCl formed and of the Cl content and I val. of the product show that the reaction is mainly substitutive during the absorption of the first Cl_2, additive and substitutive (to approx. equal extents) with the second Cl_2, and mainly substitutive with the third Cl_2 per C_5H_8 unit. The marked apparent loss of unsaturation, as shown by I val., during chlorination is probably due partly to cyclisation and partly to a steric effect of the substituted Cl atoms. The first stage of chlorination is accompanied by considerable decrease in η due (?) to autoxidation, and the products are rubber-like, but if exposed to air lose HCl and set hard. The course of the reaction is little influenced by light or change of temp., or by O_2 or anti-oxidants, though these give less stable products. The above interpretation is confirmed by the fact that the products of chlorination at −30° or −80° lose no HCl when warmed to 80° in absence of air, and by the observations that chlorination (1 mol. Cl_2 per mol.) of 1-methyl*cyclo*hexene at 80° is 79% (calc. from HCl evolution) or 76% substitutive (calc. from I val.), while the marked differences between observed and calc. I vals. of similarly chlorinated dihydromyrcene and squalene are much diminished by reduction (Zn + AcOH) of the products. *Mono-*, b.p. 88—90°/15 mm., and *dichlorodihydromyrcene*, b.p. 48—50°/0·01 mm., have been isolated. A. Lt.

Geometric isomerides of piperylene. D. Craig (*J. Amer. Chem. Soc.*, 1943, **65**, 1006—1013).—Fractional distillation of a commercial concentrate (*A*) yields *cis-* (**I**), b.p. 43·8°/750 mm., and *trans*-piperylene (**II**), b.p. 41·7°/745 mm. (cf. Dolliver *et al.*, A., 1937, II, 364). $(CH{\cdot}CO)_2O$ reacts rapidly with (**II**) at 100° to give 3-methyl-Δ^4-tetrahydrophthalic anhydride (nearly 100%), but only slowly with (**I**) to give polymeric resins (cf. Robey *et al.*, A., 1941, II, 117; Farmer *et al.*, A., 1932, 141). SO_2 and (**I**) or more readily (**II**) yield 2-methyl-2 : 5-dihydrothiophen 1 : 1-dioxide (**III**), a H_2O-sol. oil; this difference in reaction rate permits ready prep. of pure (**I**); pyrolysis of (**III**) yields pure (**II**). CuCl–NH_4Cl–H_2O–HCl–Cu wool absorbs (**I**) or (**II**) to give insol. compounds, gradual thermal decomp. (60—90°) of which affords good fractionation. Mixed tetrabromides are obtained from (**I**) or (**II**) [(**I**) gives a relatively high yield of *threo*-tetrabromide, m.p. 114°] and with Zn regenerate mixtures of (**I**) and (**II**). *n*-C_5H_{12} is obtained from (**I**) or (**II**) by H_2–Raney Ni at 29—35°/~35 atm. (**I**) is the chain and (**II**) the boat form. R. S. C.

Nitration of methane.—See B., 1943, II, 271.

Production of magnesium alkoxides.—See B., 1943, II, 272.

Optically active αγ-dimethylallyl alcohols. M. P. Balfe, H. W. J. Hills, J. Kenyon, H. Phillips, and B. C. Platt (*J.C.S.*, 1943, 348—351; cf. A., 1936, 820).—(+) and (−) refer to the sign of rotatory power of optically pure substances and *d-* and *l-* to substances of unspecified optical purity. (+)-CHMe:CH·CHMe·OH (**I**) is converted by $SOCl_2$ or (better) PCl_3–C_5H_5N into *l*-αγ-dimethylallyl chloride (**II**), which gives largely racemised products with MeOH or $Bu^{\alpha}OH$ probably because these reactions are initiated by ionisation of (**II**) and with solid KOAc or AgOAc possibly due to the heterogeneous reaction conditions. In homogeneous medium (**II**) and NaOMe give a highly racemised product, suggesting that the unimol. (ionisation) mechanism controls even the homogeneous replacement. Hydrolysis of (**I**) by H_2O gives a *lævo*-alcohol (**III**) similar in magnitude of rotatory powder to the (+)-alcohol. By methods which produce optically active derivatives from (+)- or (−)-alcohol (**III**) gives an optically inactive H phthalate and methyldibromo-*n*-propylcarbinol; it does not therefore contain the normal form of (−)-αγ-dimethylallyl alcohol. (**III**) is convertible into an acetate, α^4_{5461} −0·66° (*l* = 1), and a $CHMePr^{\alpha}{\cdot}OH$, $[\alpha]^{18}_{5461}$ +0·3° (*l* = 1), these vals. being ~2% of those of the corresponding derivatives of (**I**). It appears that the major product of the hydrolysis of (**II**) is *dl*-CHMe:CH·CHMe·OH but that an optically active impurity of unknown nature is present. A lævorotatory substance appears also to be formed during the mutarotation of (**I**) since the change, though erratic, leads to a fall in [α] with ultimate change in sign; a specimen having α^{20}_{5461} +0·70°, α^{70}_{5461} −2·66° after 48 hr. at 70° had α^{70}_{5461} −3·22° and, after cooling, α^{20}_{5461} +0·47° (*l* = 1) and the alcohol recovered from the action of (**I**) and PhNCO is lævorotatory but from (**I**) which has become lævorotatory during mutarotation the recovered alcohol is also lævorotatory. The H phthalate obtained from the alcohol at various stages of its mutarotation diminishes (by >10%) in rotatory power but this change is much less marked than that of the parent alcohol and the sign of rotation of the phthalate is always the same even when that of the alcohol from which it is obtained is reversed. A survey of the literature suggests that the mutarotation of the unsymmetrically substituted allyl alcohols is due to anionotropic rearrangement with concomitant racemisation but this explanation cannot be applied to (**I**). H. W.

Stereoisomerism of unsaturated compounds. VI. Composition of divinylglycol from acraldehyde. System *meso*–*dl*-diethylglycol. W. G. Young, S. J. Cristol, and F. T. Weiss (*J. Amer. Chem. Soc.*, 1943, **65**, 1245—1246; cf. A., 1939, II, 399).—Hydrogenation (PtO_2; 95% EtOH) of $(CH_2{:}CH{\cdot}CH{\cdot}OH)_2$ [obtained by reduction of $CH_2{:}CH{\cdot}CHO$ (**I**)] gives a mixture [whence *meso-* (**II**) and *dl*-$(CHEt{\cdot}OH)_2$ are isolated] which is shown by thermal analysis [eutectic contains 21·5% of (**II**)] to be 52 : 48 mixture. The same mixture is obtained if (**I**) was mixed with CHMe:CH·CHO. R. S. C.

Volatile borates of polyhydric alcohols and the activation of boric acid. R. E. Rippere and V. K. La Mer (*J. Physical Chem.*, 1943, **47**, 204—234).—Interaction of H_3BO_3 with polyhydric alcohols has been investigated by determining the amount of liberated H_2O. Ethylene, propylene, trimethylene, βγ-, αγ-, and *iso*-butylene glycol form *borates*, R<O>B·OH. The boiling ranges at 1 mm. or less are 176—187°, 110—114°, 147—151° (3 mm.), 112—117°, 107—109°, and 76—79° respectively. A compound with glycerol is formed but could not be isolated. Glycerol Et_1 and Bu_1 ethers and glycerol chlorohydrin form compounds of the same general type, the boiling ranges at <1 mm. being 145—150°, 162—165°, and 160—165° (decomp.) respectively. Three mols. of $OH{\cdot}[CH_2]_2{\cdot}OMe$ combine with 1 mol. of H_3BO_3 or HBO_2 to a compound of the same type as Me_3BO_3 with a boiling range 91—99° at <1 mm. Propylene and ethylene glycols " activate " H_3BO_3 in titrations in presence of H_2O, although not to the same extent as mannitol. C. R. H.

Reactions of ethers with chromous halides. F. Hein and H. Kraft (*J. pr. Chem.*, 1940, [ii], **154**, 285—308).—$CrCl_2$ or $CrBr_2$ and dioxan in N_2 give fission products which cannot be isolated; treating the reaction product with NH_3 gives *ppts.*, which after washing with Et_2O, have sometimes the composition, $3NH_3{,}CrHal_2{\cdot}O{\cdot}[CH_2]_2{\cdot}O{\cdot}CrHal_2{,}3NH_3$ containing indefinite amounts

of $Et_2O + NH_3$ of solvation (cf. A., 1930, 1019). However, the ppts. are often solvated mixtures thereof with $Cr(O\cdot[CH_2]_2\cdot O)_3Cr$. Treatment with p-$C_6H_4(NH_2)_2$ (**I**) gives similar mixed ppts. in which 1 mol. of (**I**) replaces each $3NH_3$. The double fission is proved by formation of $(CH_2\cdot OH)_2$ as sole alcohol (only $H_2C_2O_4$ formed by oxidation with HNO_3) when the NH_3 adduct is heated in H_2O. $CH_2Ph\cdot OEt$ similarly gives *products*, $CrHal_2\cdot OEt,3NH_3$, $+x Et_2O$, and mixtures thereof with $Cr(OEt)_3$. MeOH at −50° to −60° gives *products*, $CrHal_2\cdot OMe,3NH_3$, $+x Et_2O$. $(CH_2Ph)_2O$ reacts to give, presumably, $CrHal_2\cdot O\cdot CH_2Ph$, but the ppt. produced by NH_3 is difficult to analyse. Aryl alkyl and diaryl ethers and cineole do not react with $CrHal_2$. Methylfurfuraldehyde and furfuraldehyde react but the products were not investigated. The fate of the second fragment of the ethers is unknown. The ppts. formed by NH_3 are all amorphous. The first portions are greenish, the later portions reddish-violet. At −50° to −60° a liquid phase is formed containing the product in liquid $NH_3 + ROR'$; warming removes the NH_3 (and Me_2O); washing with Et_2O then give products similar in composition to those above but resinous and almost black. Fresh ppts. immediately give AgHal from $AgNO_3$, indicating their structure as $[Cr\cdot OR,5NH_3]Hal_2 + m ROR' + n NH_3$; the NH_3 of solvation is detectable by odour. Keeping over H_2SO_4 in vac. removes first the "excess" of NH_3 (giving odourless products) and then the ability to give ionisable Cl, which is interpreted as gradual conversion into $[CrHal_2\cdot OR,3NH_3] + m ROR'$; these products are odourless. Warming the products in H_2O causes the colour to change through violet-red and dark red to dark green, giving finally gels owing to hydrolysis to $CrCl(OH)_2$. Keeping the products, particularly solvated $3NH_3,CrCl_2\cdot O\cdot[CH_2]_2\cdot O\cdot CrCl_2,3NH_3$, in MeOH causes alcoholysis to $Cr(OMe)_3$. EtOH causes slower formation of $Cr(OEt)_3$. R. S. C.

Mercaptan syntheses with thioacetic acid. B. Sjöberg (*Ber.*, 1941, **74**, [*B*], 64—72; cf. A., 1939, I, 86).—Epichlorohydrin and AcSH at 60° (I uptake min. after 12 hr.) give 75% *α-acetyl-*, $SAc\cdot CH_2\cdot CH(OH)\cdot CH_2Cl$ (**I**), b.p. 94°/0·4 mm., which, on further heating at 60° or on prolonged interaction of the starting materials, is partly converted into *β-acetyl-thiochlorohydrin*, $SH\cdot CH_2\cdot CH(OAc)\cdot CH_2Cl$ (**II**), b.p. 69—70°/1 mm., which, in contrast to (**I**), consumes I; (**I**) is converted into (**II**) to the extent of 80% at room temp. in 14 days. *αγ*-Dichlorohydrin acetate (**III**), b.p. 76°/12 mm., and AcSK in EtOH at 60° give: (i) unchanged (**III**), (ii) *αβ-diacetylthiochlorohydrin* (**IV**), b.p. 105—110°/1·7 mm., 95°/0·9 mm., and (iii) *αβγ*-triacetyl-*αγ*-dithioglycerol, b.p. 135—140°/1·7 mm. (**I**) and AcCl give (**IV**), b.p. 102—103°/1 mm. (**I**), (**II**), and (**IV**), on trans-esterification (MeOH–1% HCl), afford thiochlorohydrin (**V**), b.p. 57°/1·3 mm. (CMe_2 derivative, b.p. 74—75°/15 mm.); the three specimens of (**V**) show identical unimol. decomp. coeffs. in aq. alkali. AcSH and $CH_2{:}CH\cdot CH_2Cl$ at 60° give 79% of *α-acetyl-γ-chloropropyl mercaptan*, b.p. 83—84°/10 mm., which, with MeOH–HCl, affords 81% of *γ-chloropropyl mercaptan*, b.p. 52°/12 mm., 145·5°/760 mm., also obtained from $Br\cdot[CH_2]_3\cdot Cl$ and KSH. J. Wa.

Preparation of allyl and methylallyl methylacrylates by thermal decomposition of allyl and methylallyl α-acetoxyisobutyrates. C. E. Rehberg, C. H. Fisher, and L. T. Smith (*J. Amer. Chem. Soc.*, 1943, **65**, 1003—1006).—*Allyl* (64·5%), b.p. 73°/20 mm., and *β-methylallyl α-hydroxyisobutyrate* (70%), b.p. 78°/16 mm., are obtained by boiling the acid (1 mol.), alcohol (3 mols.), and a little p-$C_6H_4Me\cdot SO_3H$ in C_6H_6 with continuous removal of H_2O. With Ac_2O at 80—100° and then 100—110° these give the *α-acetoxyisobutyrates*, b.p. 96°/19 mm., and 106°/19 mm., respectively, pyrolysis of which, best at 475—500°, yields 70—75% of allyl, b.p. 67°/50 mm., and *β*-methylallyl *β*-methylacrylate, b.p. 63°/17 mm. Pyrolysis is thus readier than that of the lactates (A., 1943, II, 251). Allyl and *β*-methylallyl α-OH-esters are more stable than the Bu or $OPh\cdot[CH_2]_2$, less stable than the Me, Et, or CH_2Ph, and as stable as the $OMe\cdot[CH_2]_2$, esters. R. S. C.

Vitamin-*E*. XLII. Long-chain compounds with recurring "isoprene" units. L. I. Smith and G. F. Rouault (*J. Amer. Chem. Soc.*, 1943, **65**, 745—750).—Methods of introducing isoprene units into aliphatic chains and of converting unsaturated alcohols into the next lower acid are described. Slow distillation of perhydrogeranyl palmitate (prep. from citronellol by H_2–catalyst and then RCOCl at 150°) at 310° gives 27% of $Pr^{\beta}\cdot[CH_2]_3\cdot CHMe\cdot CH{:}CH_2$ (**I**), b.p. 152°/740 mm., and much unchanged ester, but that of the stearate at 360° gives 84% of (**I**). $KMnO_4$ converts (**I**) in $COMe_2$–$NaHCO_3$ at 7° into *αε-dimethyl*-n-*heptoic acid* (45%), b.p. 115°/3 mm. (*S-benzylthiuronium* salt, m.p. 141—143·5°). Adding the crude derived (PCl_5) chloride (decomposes when distilled) to p-cresol and $AlCl_3$ at 145° gives 3-*αε-dimethyl*-n-*heptoyl*-p-*cresol* (69%), b.p. 144°/3 mm., which, with H_2–Raney Ni at 195°/1700—3700 lb. (in EtOH) and then 175°/1700—2400 lb. (no EtOH), gives 4-*methyl*-2-*βζ-dimethyl*-n-*heptyl*cyclo*hexanol* (96%), b.p. 133°/3 mm. (dinitrophenylurethane, an oil), dehydrated by a little p-$C_6H_4Me\cdot SO_3H$ (**II**) (not H_3PO_4) to 5-*methyl*-1-*βζ-dimethyl*-n-*heptyl*-Δ^1-cyclo*hexene* (87%), b.p. 141°/15 mm. 6% O_3 in EtBr and then 30% H_2O_2 (H_2O_2 alone gives a poor yield) in AcOH converts this into *ε-keto-γηλ-trimethyl*-n-*tridecoic acid* (92%), b.p. 170°/4 mm. With Zn–Hg and EtOH–HCl this affords *Et γηλ-trimethyl*-n-*tridecoate*, b.p. 160°/3 mm., which with H_2–Cu chromite at 250°/2800 lb. gives *δθμ-trimethyl*-n-*tridecanol* (85%), b.p. 140°/3 mm., converted by gaseous HBr at 120° into the bromide (<57%), b.p. 135°/2—3 mm., the Grignard reagent from which with MeCHO yields *ζκξ*-trimethyl-*n*-pentadecan-*β*-ol, oxidised by $Na_2Cr_2O_7$–H_2O–AcOH–H_2SO_4 to "phytol ketone" (95%). 3-*Dodecoyl*-p-*cresol*, m.p. 43—45°, b.p. 190°/3 mm., with H_2–Raney Ni in EtOH at, successively, 150°, 165°, 185°, and 200° (all at 1700—2800 lb.) yields 4-*methyl*-2-n-*dodecyl*cyclo*hexanol* (**III**) (78%), f.p. ~28°, b.p. 178°/2 mm., but in absence of a solvent at 175°/2200 lb. and then (fresh catalyst) 225° gives 1-*methyl*-3-n-*dodecyl*cyclo*hexane* (55%), b.p. 148°/2 mm. With $Na_2Cr_2O_7$–H_2SO_4–H_2O–AcOH, (**III**) gives 4-*methyl*-2-n-*dodecyl*cyclo*hexanone* (86%), b.p. 170—171°/3 mm. (semicarbazone, m.p. 86—89°; 2 : 4-dinitrophenylhydrazone, m.p. 68—72°), and with (**II**) at 180° gives 5-*methyl*-1-n-*dodecyl*-Δ^1-cyclo*hexene* (74%; $KHSO_4$ at 320° gives 60%; H_3PO_4 gives none), b.p. 190°/3 mm. This yields, as above (not by KMO_4), *ε-keto-γ-methylstearic acid* (93%), b.p. 190°/3 mm., and thence *Et γ-methylstearate*, b.p. 175°/3 mm., and *δ-methyl*-n-*octadecan-α-ol* (58%), b.p. 170°/3 mm. $Pr^{\beta}COCl$ gives only 25% of 3 : 1 : 4-$Pr^{\beta}CO\cdot C_6H_3Me\cdot OH$. R. S. C.

***sec.*-Butyl stearate, linolenate, b.p. 193—195°/<0·01 mm., and oleate, b.p. 163—165°/<0·01 mm.**—See A., 1943, III, 670.

Enol ether–acetal equilibrium in the ethyl acetoacetate series. F. Arndt, L. Loewe, and M. Ozansoy [with A. Gönenç and Z. Lugal] (*Ber.*, 1940, **73**, [*B*], 779—782).—Heating 1 mol. of AcCl with $CH_2Ac\cdot CO_2Et$ and $CH(OEt)_3$ gives $OMe\cdot CMe{:}CH\cdot CO_2Et$ (**I**), m.p. 31°, but use of 0·1 mol. of AcCl gives ~4 parts of (**I**) and 1 part of $(OEt)_2CMe\cdot CH_2\cdot CO_2Et$ (**II**) (cf. Claisen, A., 1894, i, 66; 1896, i, 463; 1898, i, 421). (**I**) or nearly pure (**II**) is converted by 2—4 mols. of NaOEt in cold or hot EtOH into a 3 : 1 mixture of (**I**) and (**II**), proving presence of an equilibrium favouring (**I**). $CH_2Ac\cdot CO_2Et$ and $OEt\cdot CH{:}NH,HCl,HgCl_2$ in EtOH at 0° and then room temp. give a mixture, whence removal of (**I**) by fractional freezing at −20° gives 80—90% pure (**II**); this boils at 81—83°/6 mm. or 68—69°/2 mm., but at 760 mm. gives (**I**) + EtOH. R. S. C.

Identification of ascorbic acid.—See A., 1943, III, 667.

Autoxidation of ascorbic acid.—See A., 1943, I, 259.

Preparation of substituted malonic esters.—See B., 1943, II, 273.

Synthesis of α-bromoadipic acid. J. von Braun and F. Meyer (*Ber.*, 1941, **74**, [*B*], 19—21).—$Br\cdot[CH_2]_3\cdot CO_2Et$ with $CHNa(CO_2Et)_2$ in Et_2O gives 61% of $CH(CO_2Et)_2\cdot[CH_2]_3\cdot CO_2Et$ (**I**), b.p. 172—174°/13 mm., and a small fraction, b.p. 200—204°/13 mm., probably $C(CO_2Et)_2([CH_2]_3\cdot CO_2Et)_2$. (**I**) and Br react readily giving Et_3 *α-bromobutane-αaδ-tricarboxylate*, b.p. 186°/12 mm., which when carefully hydrolysed with fuming HBr gives the (impure) free *bromotricarboxylic acid*, m.p. 135—148°, passing on short heating at >145°, with loss of CO_2, into α-bromoadipic acid (70%), m.p. 126° (Et_2 ester, b.p. 138°/0·6 mm.). J. Wa.

Action of diazomethane on mannosaccharic acid. O. T. Schmidt and H. Kraft (*Ber.*, 1941, **74**, [*B*], 33—49; cf. A., 1938, II, 42).—Mannosaccharic acid (**I**), m.p. 128° (obtained pure from the amide via the K and Ag salts), with dry and then moist CH_2N_2 gives a *substance* (OMe, 39·2, 39·02%), b.p. 138—142°/0·15 mm., $[\alpha]_D^{20}$ −28·1° in MeOH. Similarly, mannosaccharodilactone (**II**) affords *αδ-dimethylmannosaccharodilactone* (**III**), m.p. 143°, $[\alpha]_D^{20}$ +249° (±2·5°) → −44° (±2·2°) after 12 months (in H_2O) (*diphenylhydrazide*, m.p. 183—186°, $[\alpha]_D^{20}$ −57·54° in MeOH), stable to Fehling's solution but consuming 0·2 I per mol.; more I is consumed as NaOI, giving CHI_3. (**III**) and aq. NH_3 give *αδ-dimethylmannosaccharodiamide* (**IV**), m.p. 183—185° (decomp.), $[\alpha]_D^{20}$ −55·39° (±0·5°) (hemihydrate in H_2O). Attempts to prepare the free acid from (**IV**) via Na and Ag salts give (**III**). (**IV**) with NaOCl followed by $NH_2\cdot CO\cdot NH\cdot NH_2$ gives no $(NH_2\cdot CO\cdot NH)_2$ (**V**), whereas the diamide of (**I**) under the same conditions gives 72% of (**V**). Anhyd. (**II**) with 10—11 mols. of CH_2N_2 gives *Me₂ αα'-dimethoxymuconate* (*cis-trans* form) (**VI**), m.p. 139—140° [also obtained from (**III**) with CH_2N_2], reduced (H_2–PtO_2 in EtOAc) to a mixture of liquid racemic and meso- (**VII**) -forms of *Me₂ αα'-dimethoxyadipate*. (**VII**), m.p. 53°, is also obtained by methylating *meso-αα'*-dihydroxyadipic acid with CH_2N_2 followed by MeI–Ag_2O. *αα'-Dimethoxymuconic acid* (*cis-trans*), m.p. 196—197°, obtained from (**VI**) by alkaline hydrolysis, passes when heated with H_2O into 3-*methoxy*-2-*pyrone*-6-*carboxylic acid* (Me ester, m.p. 215°), m.p. 261° (decomp., sinters 234°). In one case the methylation product of (**II**) is distilled in a poor vac. and *Me₂ αα'-dimethoxymuconate* (*cis-cis* form?) (**VI***a*), m.p. 63—64°, b.p. 130—150°/3—5 mm. (free *acid*, m.p. 169—171°), is obtained, passing on hydrogenation into (**VII**) and its *dl*-form. (**VI***a*) decomposes on keeping to give *Me₂ αα'-diketodihydromuconate* (?), m.p. 120—121°, and on irradiation in C_6H_6 in presence of I is converted into an *isomeride* (*trans-trans* form?) (**VI***b*), m.p. 115—116°, identical with the product from CH_2N_2 and *αα'*-dihydroxymuconic acid, m.p. 226—227°. J. Wa.

Preparation of *D*-galacturonic acid from pectin. E. Rietz and W. D. Maclay (*J. Amer. Chem. Soc.*, 1943, **65**, 1242—1243).—74—80% yields are obtained by use of Pectinol 46 AP. R. S. C.

Hydrogenolysis of sulphur compounds by Raney nickel catalyst. R. Mozingo, D. E. Wolf, S. A. Harris, and K. Folkers (*J. Amer. Chem. Soc.*, 1943, **65**, 1013—1016).—Relatively large amounts of Raney Ni containing absorbed H_2, but without added H_2, convert aliphatic or aromatic RR'S, RS·SR', RR'SO, or RR'SO_2 in, *e.g.*, boiling EtOH or MeOH into RH, R'H, and (?) Ni sulphides. Thus, $S([CH_2]_4{\cdot}CO_2H)_2$ (2·5 g.) and Raney Ni (25—30 g.) in boiling 75% EtOH give 94% of Bu^aCO_2H; *γ-methylthiol*-n-*butyric acid*, b.p. 143—144°/16 mm., gives Pr^aCO_2H; *l*-(−)-[S·CH_2·CH(NHBz)·$CO_2H]_2$ gives *l*-(+)-NHBz·CHMe·CO_2H, $[\alpha]_D^{25}$ +9·7° in EtOH, thus correlating the configurations; *dl*-SMe·$[CH_2]_2$·CH(NHBz)·CO_2H gives NHBz·CHEt·CO_2H, and the derived *hydantoin*, m.p. 109—110°, behaves similarly; *p*-C_6H_4Me·SH, (*p*-C_6H_4Me·S)$_2$, or $(CH_2Ph)_2S$ gives PhMe; Ph_2S, Ph_2SO, and Ph_2SO_2 give C_6H_6. R. S. C.

Catalytic preparation of cyclic acetals of aldehydes and ketones. G. Willfang (*Ber.*, 1941, **74**, [*B*], 145—153; cf. A., 1938, II, 2).—CO-compounds, except hydroxy-carbonyl compounds such as aldol, with epichloro- and epibromo-hydrin in CCl_4 in presence of $SnCl_4$ (best), $AlCl_3$, $FeCl_3$, or $SbCl_5$ give cyclic acetals. The reaction is not particularly sensitive to moisture and, after the catalyst is destroyed with alkali or an org. base, the products are readily purified by distillation. *Acetaldehyde*, 45% yield, b.p. 158—162°/760 mm., *crotonaldehyde*, 75%, b.p. 68—70°/1·5 mm., cyclo*pentadecanone*, b.p. 100—120°/0·003—0·006 mm., m.p. ~33°, *camphor*, 83%, b.p. 114—122°/1·85 mm., *bromoacetophenone*, 65·3%, b.p. 133°/1·5 mm., and *benzophenone γ-chloropropylene acetal*, 71%, b.p. 159—167°/2—3 mm., m.p. 44·5°, and *chloral*, 54%, b.p. 94—100°/14—15 mm., and *Et$_2$ ketone γ-bromopropylene acetal*, 68·5%, b.p. 82—85°/2 mm., are described. The halogen atoms in the above compounds are very inert towards C_5H_5N, KI, anhyd. NaOAc, $AgNO_3$, Mg, and NaOH. J. Wa.

Determination of paracetaldehyde.—See B., 1943, II, 269.

Reduction of chloral by organometallic compounds. *aaa*-Trichlorobutan-*β*-ol. H. Gilman and R. K. Abbott, jun. (*J. Org. Chem.*, 1943, **8**, 224—229).—In the reaction between CCl_3·CHO and MgEtHal there is no significant production of CCl_3·CHEt·OH (**I**), the main product being CCl_3·CH_2·OH formed by reduction. (**I**) does not appear to be formed from CCl_3·CHO and $PbEt_4$. CCl_3·CHO and CH_2N_2 afford trichloropropylene oxide (**II**), b.p. 39—40°/11 mm., transformed by MgMeI in Et_2O into *aaa-trichloro-γ-iodopropan-β-ol*, m.p. 54—55°. With LiMe in Et_2O at −75° (**II**) gives (**I**), b.p. 169—171°/738 mm. (p-*nitrobenzoate*, m.p. 70—71·5°), hydrolysed by Na_2CO_3 in boiling aq. EtOH to OH·CHEt·CO_2H. In the Lucas test (**I**) passes into *aaaβ-tetrachloro*-n-*butane*, b.p. 134—135°/742 mm. CCl_3·CHO and CH_2Ph·MgCl afford CCl_3·CH_2·OH in small amount. H. W.

Catalytic degradation of heptaldehyde in the vapour phase. T. J. Suen and S. Fan (*J. Amer. Chem. Soc.*, 1943, **65**, 1243—1245).—Passing *n*-C_6H_{13}·CHO (**I**) over Ni at 250° in absence of H_2 (cf. A., 1942, I, 233; apparatus modified) gives liquids [43—67%; *n*-C_6H_{14} (**II**) including 1·9—15% of unchanged (**I**) and 24—30% of C_6H_{12}], CO 48·2—57·4, H_2O 12·0—18·9, CH_4 13·1—14·4, O_2 1·6—5·4, CO_2 0·4—1·4, unsaturated gases 0·6—1·8, and N_2 (by difference) 11·1—19·9%. Absence of H_2 causes rapid depreciation of the Ni. The C_6H_{12} is probably the Δ^β-isomeride (b.p.; *n*); it is probably the primary product, giving (**II**) by interaction with the H_2 formed. A considerable part of the (**I**) is completely converted into gases. Reaction is incomplete at 200°; ~35% of the liquid product is then C_6H_{12}. R. S. C.

Catalytic conversion of ethyl alcohol into acetone.—See B., 1943, II, 269.

Production of amines.—See B., 1943, II, 273.

Compounds of gallium.—See A., 1943, I, 233.

Stovaine analogues. W. T. Olson and F. M. Whitacre (*J. Amer. Chem. Soc.*, 1943, **65**, 1019—1020).—Passing CHEt:CH_2 (prep. by adding Bu^aI to KOH–EtOH at ~90°) into aq. HOCl gives CH_2Cl·CHEt·OH, b.p. 53—55°/17 mm., which with $NHEt_2$ in C_6H_6 at 120° yields NEt_2·CH_2·CHEt·OH, b.p. 74—75°/22 mm. [benzoate, b.p. 120—122° (corr.)/2 mm. (*hydrochloride*; picrate, m.p. 112°). *iso*Butylene oxide, $NHEt_2$, and a little H_2O at 105—110° give NEt_2·CH_2·CMe_2·OH, b.p. 65—68°/23—25 mm. (picrate, m.p. 99·2—100·2°; *benzoate hydrochloride*, m.p. 149·5—150°). NH_2·CHEt·CH_2·OH and EtBr in boiling aq. Na_2CO_3 give NEt_2·CHEt·CH_2·OH (**I**), b.p. 86—87°/25 mm. [*hydrochloride*, an oil; *benzoate*, b.p. 124—126° (corr.)/2 mm. (hydrochloride); picrate, m.p. 113—114°)]. Anæsthetic action of the above benzoate hydrochlorides (prep. by BzCl in boiling C_6H_6) and those of stovaine, NEt_2·CH_2·CMeEt·OH, and NMe_2·CH_2·CMe_2·OH are recorded; (**I**) is comparable with novocaine. Ethylation of NH_2·CMe_2·CH_2·OH gives only NHEt·CMe_2·CH_2·OH, m.p. 74·5—75° (picrate, m.p. 124·7—125·3°; *hydrochloride*, m.p. 136·5°). M.p. are corr. R. S. C.

Reaction of formaldehyde with *l*-(+)-aspartic and -glutamic acids. D. C. Carpenter and F. E. Lovelace (*J. Amer. Chem. Soc.*, 1943, **65**, 1161—1165).—Measurement of [*α*] and [H·] during interaction of CH_2O with *l*-(+)-aspartic and -glutamic acids shows 1 : 1 (mol.) interaction, followed by interaction with a second mol. of CH_2O to give unstable compounds. Equilibrium consts. are calc. The initial products are OH·CH_2 compounds (cf. A., 1943, II, 122). R. S. C.

***p*-Toluenesulphonyl-aspartic acid, m.p. 159—160° (anhydride, m.p. 158·5—160°; benzyl esters, m.p. 135·5—137° and 108·5—109°), -asparagine, m.p. 174·5—175·5°, and -*iso*asparagine, m.p. 177·5—178°.**—See A., 1943, III, 604.

New type of complex silver compounds with tervalent silver.—See A., 1943, I, 260.

II.—SUGARS AND GLUCOSIDES.

Effect of boric acid on the caramelisation of sugars. M. Niculescu (*Z. anal. Chem.*, 1941, **122**, 335—344).—Data showing the inhibiting effect of H_3BO_3 on the caramelisation of solutions of glucose, lactose, sucrose, and milk are discussed. The effect is attributed to combination between H_3BO_3 and the sugar. L. S. T.

Action of diazomethane on acyclic sugar derivatives. IV. Ketose synthesis. M. L. Wolfrom, R. L. Brown, and E. F. Evans (*J. Amer. Chem. Soc.*, 1943, **65**, 1021—1027; cf. A., 1943, II, 57).—*D*-Arabonic acid tetra-acetate and PCl_5 in Et_2O give D-*arabonyl chloride tetra-acetate* (85%), m.p. 74—75°, $[\alpha]_D^{22}$ +46° (cf. A., 1942, II, 395). Adding $KHCO_3$ and then Br to crude *aldehydo-D*-galactose penta-acetate (modified prep.) in H_2O at 25° gives *D*-galactonic acid penta-acetate (44%), m.p. 127—130°, $[\alpha]_D$ +16·5°, converted, as above, into the *chloride penta-acetate* (**I**) (90—92%), m.p. 80—81°, $[\alpha]_D^{21}$ +3° [gives the known amide and the Et ester penta-acetate, m.p. 110—111°, $[\alpha]_D^{27}$ +9·5° (cf. Kohn, A., 1895, i, 504)], which with CH_2N_2 in Et_2O at 0° gives 1-*diazo*-1-*deoxy*keto-D-*galaheptulose penta-acetate*, pale yellow, m.p. 136—137°, $[\alpha]_D^{23}$ +64° (const.). This evolves N_2 slowly in H_2O at room temp., more rapidly if heated or in presence of Cu^{++}, Ag^+, or acids, and reduces aq. $AgNO_3$ or halogens. With NH_3–MeOH at 0—5° it gives 1-*diazo*-1-*deoxy*-D-*galaheptulose* (71%), m.p. 140° (decomp.), $[\alpha]_D^{23}$ +82° in H_2O → (at 0°) +93°, unstable in H_2O at room temp. or, more so, in aq. HCO_2H, and in boiling AcOH yields keto-D-*galaheptulose hexa-acetate*, *forms*, m.p. 100—102° and 116—117°, $[\alpha]_D^{23-27}$ −1·6° in $CHCl_3$, −20° in C_6H_6 (different *X*-ray diagrams), which is the enantiomorph of *keto-L*-perseulose hexa-acetate (Khouvine *et al.*, A., 1938, II, 219) and with aq. $Ba(OH)_2$ at 0—5° gives D-*galaheptulose* [D-*perseulose*; D-*gala*-L-*fructoheptose*] (55%), +0·5H_2O, m.p. 101—102° (102—103° after drying), $[\alpha]_D^{25}$ +90·6° → +75·3° in H_2O (with *L*- gives dl-*perseulose*, m.p. 136—137°). *D*-Glucoheptulose, softens 168°, m.p. 171—173°, $[\alpha]_D^{18}$ +67° (const.) in H_2O, is obtained from its hexa-acetate in 77% yield by $Ba(OH)_2$ at 0—5°. NHPh·NH_2 and (**I**) in Et_2O give D-*galactonophenylhydrazide penta-acetate*, m.p. 136·5—137°, $[\alpha]_D^{21}$ +36°, converted by $ZnCl_2$–Ac_2O at 0° and then room temp. into D-*galactonacetphenylhydrazide penta-acetate*, m.p. 218°, $[\alpha]_D^{29}$ +23°, which is also obtained from *D*-galactonophenylhydrazide by Ac_2O–C_5H_5N at room temp. (cf. Robbins *et al.*, A., 1940, II, 266). *D*-Gluconyl chloride penta-acetate yields similarly *glucono-phenylhydrazide penta-acetate*, m.p. (anhyd.) 127·5—128·5° (128—128·5°) and (+H_2O) 86—88°, $[\alpha]_D^{22}$ +37·0° in $CHCl_3$, $[\alpha]_D^{21}$ +17·5° in EtOH, and *-acetphenylhydrazide penta-acetate*, m.p. 152—153°, $[\alpha]_D^{22}$ +33° in $CHCl_3$, +25° in EtOH (cf. Major *et al.*, A., 1937, II, 49). Unless otherwise stated, [*α*] are in $CHCl_3$. R. S. C.

Glucosidation of 2 : 3 : 6-trimethylglucose. K. Freudenberg and W. Jakob (*Ber.*, 1941, **74**, [*B*], 162—163; cf. A., 1943, II, 255).—The small amount of dimethylglucose isolated from methylated starch (**I**) owes its origin to demethylation of trimethylglucose under the conditions used for methanolysis, or hydrolysis of (**I**) and glucosidation. The following are very mild conditions. 2 : 3 : 6-Trimethylglucose affords 94% of the methylglucoside when treated with $Si(OMe)_4$, MeOH, and HCl at 80°, or 95% at 20° when HCl is replaced by AcCl. $CH(OMe)_3$ can replace $Si(OMe)_4$. J. Wa.

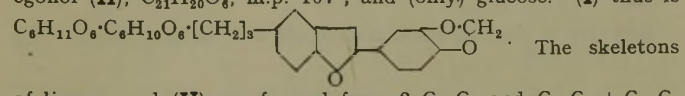
Constitution of 1-phenyl-*d*-fructosone. H. Ohle and M. Hielscher (*Ber.*, 1941, **74**, [*B*], 18—19).—1-Phenyl-*d*-fructosone (**I**) was known to react with only 1 mol. of NHPh·NH_2 and the possibility of a mol. rearrangement in its prep. had to be considered. However, (**I**) with *o*-$C_6H_4(NH_2)_2$ in boiling EtOH gives 2-*phenyl*-3-d-arabo-*tetrahydroxybutylquinoxaline* (**II**), m.p. 198°, $[\alpha]_D^{20}$ −145° in aq. C_5H_5N (1 : 1). (**II**) with 3 mols. of NHPh·NH_2 in boiling H_2O and H_2 gives much unchanged (**II**) and 2-*phenylquinoxaline*-3-*aldehydephenylhydrazone*, m.p. 176°, which shows the anticipated colour reactions. J. Wa.

Vitamin-*P*.—See A., 1943, III, 579.

Mechanism of polysaccharide production from sucrose. S. Hestrin and S. Avineri-Shapiro (*Nature*, 1943, **152**, 49—50).—Levan sucrase shows optimal activity at pH 5·5; its solutions are stable at 0° but are inactivated by boiling. Production of levan from raffinose is not regarded as proceeding by way of intermediately

formed sucrose. It ceases when levan concn. is 300—500 mg.-%; increase in initial sucrose concn. beyond a necessary min. does not shift the position of the levan end-point. Known poisons of respiration or glycolysis do not retard levan production. A. A. E.

Egonol. XII. Egonol glucoside from the fruits of "Taiwan-Egonoki." S. Kawai and K. Sugimoto (*Ber.*, 1940, **73**, [*B*], 774—776; cf. A., 1943, II, 275).—This plant is *Styrax formosanum*, Matsum (cf. A., 1939, II, 32). It yields *egonol diglucoside* (**I**), $C_{31}H_{38}O_{15}$, $+2H_2O$ (lost at 110°/12 mm.), m.p. 143° (decomp.), $[\alpha]_D^{22}$ (anhyd.) −29·8° in AcOH, which in boiling 10% H_2SO_4 gives egonol (**II**), $C_{21}H_{20}O_6$, m.p. 107°, and (only) glucose. (**I**) thus is



The skeletons of lignans and (**II**) are formed from 2 C_6–C_3 and C_6–C_3 + C_6–C_2 units, respectively. R. S. C.

Molecular constitution of amylose and amylopectin of potato starch. W. Z. Hassid and R. M. McCready (*J. Amer. Chem. Soc.*, 1943, **65**, 1157—1161).—Potato starch contains ~20% of amylose (**I**), $[\alpha]_D$ +155° in N-NaOH. Methylation and end-group analysis indicate 300—400 glucopyranose units per mol. of (**I**) but only 25 units for amylopectin (**II**), $[\alpha]_D$ +161° in N-NaOH. Hydrolysis of (**II**) by β-amylase is stopped at 54% conversion (*i.e.*, 13—15 units) by side-chains. R. S. C.

Separation and determination of amylose and amylopectin in potato starch. R. M. McCready and W. Z. Hassid (*J. Amer. Chem. Soc.*, 1943, **65**, 1154—1157).—When potato starch is treated with H_2O at 60—70°, the granules swell but do not burst. Centrifuging the filtered solution separates amylopectin (**I**). MeOH then ppts. amylose (**II**), which is insol. in H_2O, completely hydrolysed by β-amylase, and gives a brilliant blue colour with I, is identical with the amyloamylose of Samec and Mayer (A., 1921, i, 707), and resembles synthetic starch. 60—64% of whole starch is hydrolysed by β-amylase. The amounts of (**I**) and (**II**) in mixtures of starch are determined colorimetrically by I–KI. R. S. C.

Constitution of starch. E. Bois (*Canad. Chem.*, 1943, **27**, 362, 364).—The unit of the starch mol. is a pentahexose (**I**) of which successive pairs of hexoses (overlapping) represent gentiobiose, cellobiose, maltose, and sucrose; this is associated with a second similar but oppositely oriented (**I**), giving a decahexose (**II**) with OH groups blocked by oxonium linkings. Amylose comprises four (**II**) units in a closed ring, whereas amylopectin is composed of chains of (**II**) associated with P. I. A. P.

Structural difference of starches differentiated colorimetrically by iodine. M. Samec (*Ber.*, 1940, **73**, [*A*], 85—92).—A lecture summarising the differences between amylose (blue I colour) and amylopectin (red I colour) in their mol. wt., behaviour on dialysis, pptn. by EtOH and tannin, adsorption on cotton, effect on H_2O_2, oxidation by $KMnO_4$, and hydrolysis by acid and enzymes. The P content has no significance. A pictorial representation of the enzyme attack is given. R. S. C.

Dextrins from maize starch.—See A., 1943, III, 682.

Determination of carbonyl groups in chromic anhydride oxystarch and oxycellulose by means of hydroxylamine. E. K. Gladding and C. B. Purves (*Paper Trade J.*, 1943, **116**, *TAPPI Sect.*, 150—155).—The reaction $>C{:}O + NH_2OH,HCl = >C{:}N{\cdot}OH + H_2O + HCl$ is followed by titration of the liberated HCl with standard alkali. The highly buffered nature of the system renders the method unsuitable for technical oxycelluloses although massive amounts of >CO are determined with an accuracy of ~5%. Simple sugars condense in first-order reactions which are complete within either 1·5 or 18 hr. at 20° and the >CO groups are classified as fast or slow. All CHO in periodate oxycellulose (**I**) or oxystarch are fast although the reactions are not of the first order. When unswollen linters is oxidised with increasing amounts of CrO_3 in AcOH at 20° up to 28% of the oxidant is accounted for as CO_2H and "fast" CO in the insol. (**I**) and H_2O-sol. products result even with relatively small amounts of oxidant. Unswollen, powdered starch is not appreciably affected under the same conditions. With highly swollen linters duplicate oxidations proceed very much more rapidly and cause no perceptible production of H_2O-sol. material until an oxidation level of ~0·3 atom of O per glucose unit is reached. ~75% of the O consumed below this level is represented by insol. (**I**) but the recovery falls sharply thereafter. The fate of the remaining 25% is not elucidated though it may have produced slow CO groups in (**I**). The chemical course of oxidations which are not accompanied by substantial swelling may be dominated by the extent of the colloidal surface present in the original material. The colloidal condition of the latter is not nearly so crit. when the CrO_3 is dissolved in 0·2N-H_2SO_4, probably because aq. solutions exert a powerful swelling action. H. W.

Action of nitric acid on vegetable seed shells.—See A., 1943, II, 286.

III.—HOMOCYCLIC.

Halogenation of *cyclo*hexane.—See B., 1943, II, 274.

Catalytic hydrogenation of benzene over metal catalysts.—See A., 1943, I, 260.

Number of structural isomerides in simple ring compounds. I. T. L. Hill (*J. Physical Chem.*, 1943, **47**, 253—260).—Mathematical. General functions for determining the no. of possible structural isomerides in substituted symmetrical ring compounds have been derived. C. R. H.

Determination of benzene. Detection and estimation of benzene in presence of toluene, xylene, and other substances.—See B., 1943, II, 269.

Photometric determination of benzene, toluene, and their nitro-derivatives.—See B., 1943, II, 270.

Organic reactions with boron fluoride. XXVI. Friedel–Crafts type alkylations with boron trifluoride. G. F. Hennion and R. A. Kurtz (*J. Amer. Chem. Soc.*, 1943, **65**, 1001—1003; cf. A., 1942, II, 84).—*tert.*-Alkyl halides and CH_2PhCl readily alkylate C_6H_6 in presence of BF_3 if H_2O or the appropriate alcohol is also present; *sec.*-alkyl halides give low yields, raised somewhat by adding also H_2SO_4 (and H_2O); *n*-alkyl halides do not react. Small amounts of *p*-dialkylation sometimes occur. The lower reaction layer can be re-used, particularly if re-saturated with BF_3. R. S. C.

Colorimetric determination of alkylbenzenesulphonates.—See B., 1943, II, 270.

Ethylenic stereoisomerism. VI. Crystalline *cis*-stilbene. C. Weygand and I. Rettberg (*Ber.*, 1940, **73**, [*B*], 771—773).—Various old samples of *cis*-$(CHPh{:})_2$ (**I**), prepared from $(CPh{:})_2$, contained $(CPh{:})_2$, $(CH_2Ph)_2$, and/or *trans*-$(CHPh{:})_2$ (**II**), since they yield in AcOH the adducts thereof with *s*-$C_6H_3(NO_2)_3$ (**III**), m.p. 155° (lit. 96°; ? dimorphism), 102°, and —, respectively. The final filtrate is freed from (**III**) by chrysene; the residual (**I**) is fractionated; a colourless distillate, b.p. 93°/0·08 mm., crystallised (m.p. 1°) when scratched; a yellow distillate crystallised when seeded. When freshly prepared from $CHPh{:}CPh{\cdot}CO_2H$ and freed from (**II**) by (**III**), (**I**) crystallised spontaneously. R. S. C.

Tribenzylsulphonium hydrogen sulphate and hydroxide. O. Haas and G. Dougherty (*J. Amer. Chem. Soc.*, 1943, **65**, 1238—1239).—In conc. H_2SO_4 at 70—80° $(CH_2Ph)_2S$ (**I**) gives $(CH_2Ph)_3S{\cdot}HSO_4$, m.p. 171°, and thence *tribenzylsulphonium hydroxide*, m.p. 133° [when heated, gives (**I**) and $CH_2Ph{\cdot}OH$], and the additive *compound*, $(CH_2Ph)_3SI,HgI_2$, m.p. 137—138°; the nitrate is an oil. R. S. C.

Absorption of light by αε-dien-γ-inenes.—See A., 1943, I, 217.

Conversion of 2 : 7-dibromofluorene into 2 : 7-dibromophenanthrene. W. G. Brown and B. A. Bluestein (*J. Amer. Chem. Soc.*, 1943, **65**, 1235—1236).—2 : 7-Dibromo-9-formylfluorene, m.p. 171° (*acetate*, m.p. 219°), is obtained in 85% yield by boiling 2 : 7-dibromofluorene in KOEt–Et_2O and then adding HCO_2Et. It is reduced by $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ to 2 : 7-*dibromo*-9-*fluorenylcarbinol* (58%), m.p. 154° (acetate, m.p. 190°), which with P_2O_5 in boiling xylene gives 2 : 7-dibromophenanthrene, m.p. 207° (lit. 202°, [quinone, m.p. 321° (lit. 323°)] (cf. A., 1941, II, 247). R. S. C.

Dehydrogenation. III. Dehydrogenation of a methylspiran. M. Levitz and M. T. Bogert (*J. Org. Chem.*, 1943, **8**, 253—255).—1 : 1-Pentamethylene-1 : 2 : 3 : 4-tetrahydronaphthalene (Perlman *et al.*, A., 1937, II, 11) is oxidised by CrO_3 in AcOH to 4-*keto*-1 : 1-*pentamethylene*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. 140—142°/3 mm. [*semicarbazone*, m.p. 204·5—205·5° (corr.)]. This is converted by MgMeI into the corresponding carbinol, which is dehydrated by $KHSO_4$ at 150—160°/18 mm. to 1 : 1-*pentamethylene*-4-*methyl*-1 : 2-*dihydronaphthalene*, b.p. 109—110°/2 mm. This is dehydrogenated (Pd–C at 330°) to 9-methylphenanthrene, m.p. 90—91° (corr.) [picrate, m.p. 156° (corr.)]. There is no shift in the initial position of Me (cf. Marvel *et al.*, A., 1941, II, 15). H. W.

Arylnaphthacene series. III. A. Weizmann (*J. Org. Chem.*, 1943, **8**, 285—289; cf. A., 1939, II, 548).—Me_2 *benzylsuccinate*, b.p. 125—135°/1·5 mm., is converted by PhCHO and Na powder in Et_2O followed by hydrolysis into benzylbenzylidenesuccinic acid, m.p. 160—162°, which is hydrogenated (Pd–$BaSO_4$ in boiling $Pr^{\alpha}OH$ or $Pr^{\beta}OH$) to a mixture of *s*-dibenzylsuccinic acids, transformed by conc. H_2SO_4 at 100° into 5 : 11-*diketo*-5 : 5a : 6 : 11 : 11a : 12-*hexahydronaphthacene* (**I**), m.p. 220—222°. With LiPh in Et_2O under N_2 at room temp. (**I**) affords the *peroxide*, $C_{24}H_{16}O_3$, m.p. 295—298°, and with 1 : 3 : 6-Li·$C_6H_3Br{\cdot}OMe$ it gives (?) 5-*keto*-6 : 11-*di*-(5′-*bromo*-2′-*methoxyphenyl*)-5 : 5a : 6 : 11 : 11a : 12-*hexahydronaphthacene*, m.p. 278°, which is resistant towards boiling AcCl. With Li·C_6H_4Me-*p* (**I**) yields 5 : 11-*di*-p-*tolylnaphthacene*, m.p. 335—336°. H. W.

1 : 2 : 3 : 4-Dibenzphenanthrene and its derivatives. I. Synthesis with chrysene as starting material. F. Bergmann and H. E. Eschinazi (*J. Amer. Chem. Soc.*, 1943, **65**, 1413—1417).—Chrysene,

AcCl, and $AlCl_3$ in CS_2 at room temp.—60° give 2- (**I**), m.p. 145°, and some (? 4-)*acetyl-* (**II**), m.p. 254°, and x : y-*diacetyl-chrysene*, m.p. 296° (cf. Funke *et al.*, A., 1936, 472). MgMeI (3 mols.) and (**I**) in Et_2O, later boiling xylene, give 2-α-*hydroxyisopropyl-* (**III**) (60%), m.p. 172°, and 2-*isopropenyl-chrysene* (**IV**) (25%), m.p. 161°, b.p. 220°/2 mm. [*picrate*, m.p. 144°, also obtained from (**III**)]. Adding conc. H_2SO_4 to (**III**) in cold AcOH gives (**IV**), but at 100° a *dimeride*, m.p. 307°, is obtained. (**II**) gives similarly (?4-)*isopropenylchrysene*, m.p. 288°. MgEtBr and (**II**) give β-2-*chrysenyl-*Δ$^{\beta}$-n-*butene* (**V**) (68%), m.p. 159—160° [inert towards $(CH{\cdot}CO)_2O$ (**VI**); *picrate* (**VII**), m.p. 132—133°], and β-2-*chrysenyl-*n-*butan-*β-*ol* (26%), m.p. 119° [gives (**VII**)]. MgPr$^{\alpha}$Br or MgBu$^{\alpha}$Br gives similarly β-2-*chrysenyl-*Δ$^{\beta}$-n-*pentene* (67%), m.p. 102° (*picrate*, m.p. 138—140°), and -n-*hexene*, m.p. ~40° (*picrate*, m.p. 129—130°), respectively. H_2–Pd–$BaSO_4$ reduces (**IV**) or (slowly) (**V**) in EtOAc to 2-*isopropyl-*, m.p. 137° (*picrate*, m.p. 144—145°), and 2-sec.-*butyl-chrysene*, m.p. 100° (*picrate*, m.p. 133°), respectively, but the higher homologues are unaffected. In boiling Ac_2O, (**III**) or, less well, (**IV**) with (**VI**) gives 4-*methyl-*1 : 2 : 3 : 11-*tetrahydro-* (**VIII**) (80%), dimorphic, m.p. 262°, dehydrogenated by $Pb(OAc)_4$ in boiling AcOH to 4-*methyl-* (20%; Br–NaOAc–AcOH gives 30% of impure product) (**IX**), m.p. 325°, 2′ : 1′-9 : 10-*naphthophenanthrene-*1 : 2-*dicarboxylic anhydride*. Distilling (**VIII**) with Zn at 100 mm. gives (**IV**), but heating with Se at 270—310° gives 4′-*methyl-*1′ : 2′ : 3′ : 4′-*tetrahydro-*1 : 2-*benzchrysene* (**X**) (50%), m.p. 139° (*picrate*, m.p. 140°; 7 : 8-*quinone*, m.p. 178°), which with Se at 310—320° yields a small amount of a substance (picrate, m.p. 165°). Heating (**IX**) with basic Cu carbonate in quinoline gives 4-*methyl-*2′ : 1′-9 : 10-*naphthophenanthrene-*1- or -2-*carboxylic acid*, m.p. 292—293°. Carcinogenic activity is affected by alkyl side-chains in so far as they simulate, sterically, active rings. R. S. C.

Benz*cyclo*octatetraenes. III. Diphenylene and tetraphenylene. W. S. Rapson, R. G. Shuttleworth, and (in part) J. N. van Niekerk (*J.C.S.*, 1943, 326—327).—The Grignard reagent from 2 : 2′-$(C_6H_4Br)_2$ with $CuCl_2$ in Et_2O yields diphenylene and 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*tetrabenz-*Δ$^{1:3:5:7}$-cyclo*octatetraene*, m.p. 233° [*Br-* (Br and a trace of Fe in CCl_4), m.p. 182°, and $(NO_2)_4$-derivative (HNO_3, *d* 1·5, +H_2SO_4 on the CCl_4 solution), m.p. 195—197°], which is unaffected by $KMnO_4$ in boiling $COMe_2$, and forms no additive compounds with picric or styphnic acid or $C_6H_3(NO_2)_3$. Crystallographic data confirm the constitution. A. Li.

Perylene and its derivatives. LII. A. Zinke and H. Troger [in part with E. Posch]. **LIII. Synthesis of 2 : 3 : 10 : 11-dibenzoperylene.** A. Zinke and E. Ziegler (*Ber.*, 1941, **74**, [*B*], 107—115, 115—118).—LII. Perylene (**I**) with Br vapour or with Br in C_6H_6 gives an unstable *compound*, $C_{20}H_{10}Br_4$, readily passing with loss of Br into a mixture of 3 : 9- (**II**), m.p. 287°, and 3 : 10-dibromoperylene (**III**), m.p. 221°. (**III**) with conc. H_2SO_4, then H_2O, gives 3 : 10-perylenequinone. (**II**) and (**III**) with Br vapour give unstable Br_2-derivatives which decompose on keeping, heating to 140—150°, or treatment with KI, with regeneration of (**II**) and (**III**). 3 : 9-Dibenzoylperylene readily absorbs ~8 Br. The unstable dark additive compound readily loses Br to give 3 : 9-dibromo-4 : 10-dibenzoylperylene, m.p. 355°, converted by KOH in boiling NH_2Ph or quinoline into *iso*violanthrone. The amount of I taken up by (**I**) depends on concn. in C_6H_6. 3 : 9-Dinitro- and 3 : 9-dicyanoperylene do not react with Br and 3 : 9-dichloroperylene reacts only in solution with Br and not with the vapour.

LIII. 9 : 9′-*Diphenanthryl*, m.p. 188—189°, from 9-bromophenanthrene and Cu powder at 330—350°, with $AlCl_3$–NaCl at 120—130° gives 2 : 3 : 10 : 11-dibenzoperylene (**IV**) [1 (or 4) : 12 (or 9)-*quinone*, m.p. 330° (darkening)], m.p. 343—345° (sinters at 327°) and 299—300° in admixture with the supposed (**IV**) of Brass *et al.* (A., 1939, II, 207). J. Wa.

Synthesis of physiologically active amines. Amines derived from phenyl styryl ketones. J. Algar, A. Hickey, and P. G. Sherry (*Proc. Roy. Irish Acad.*, 1943, **49**, **B**, 109—119).—*Ph* α-*chloro-*β-*amino-*β-*phenylethyl ketone hydrochloride*, m.p. 195°, is prepared from $COPh{\cdot}CHBr{\cdot}CHPhBr$ (**I**) by EtOH–NH_3 followed by EtOH–HCl. *Ph* α-*chloro-*β-*methylamino-*β-*phenylethyl ketone hydrochloride*, m.p. 169°, similarly prepared from (**I**) and aq. NH_2Me, yields *Ph* β-*methylamino-*β-*phenylethyl ketone hydrochloride*, m.p. 191°, with Pt–H_2–H_2O. *Ph* α-*chloro-*β-*methylamino-*β-p-*anisyl-*, m.p. 170°, and -β-3 : 4-*methylenedioxyphenyl-ethyl ketone hydrochloride*, m.p. 174°, are similarly prepared. Reduction (H_2, Pt, EtOH–HCl) of $COPh{\cdot}C(:N{\cdot}OH){\cdot}CH_2Ph$ gives β-*amino-*αγ-*diphenyl-*n-*propyl alcohol hydrochloride* (**II**), m.p. 250° (decomp.) (free *amine*, m.p. 115°). β-*Amino-*α-*phenyl-*γ-3 : 4-*methylenedioxyphenyl-*n-*propyl alcohol*, m.p. 142° [*hydrochloride* (**III**), m.p. 197° (decomp.)], is similarly obtained. *Ph* 3 : 4-*methylenedioxystyryl ketone oxide*, m.p. 96°, yields an *oxime* (poor yield), m.p. 169°, which could not be reduced by Pt–H_2 or Na–Hg and EtOH. $COPh{\cdot}CH_2{\cdot}NMe_3Cl$ (+H_2O), new m.p. 204° (decomp.), is obtained from the oxides of Ph styryl or *p*-methoxystyryl ketone and EtOH–NMe_3. In general only the compounds having NH_2 α to CO or OH [(**II**) and (**III**)] have marked physiological action and cause a reduction in blood pressure. J. H. Ba.

Synthesis of 4 : 5-trimethylene*iso*quinoline etc.—See A., 1943, II, 278.

Monoreduction of dinitronaphthalenes in acid solution and of 1 : 5- and 1 : 6-dinitronaphthalene by aqueous sodium sulphide. H. H. Hodgson and H. S. Turner (*J.C.S.*, 1943, 318—319).—Reduction of 1 : 6-$C_{10}H_6(NO_2)_2$ with $SnCl_2$ in AcOH–HCl yields 6 : 1-$NO_2{\cdot}C_{10}H_6{\cdot}NH_2$ whilst aq. EtOH–Na_2S gives 5 : 2-$NO_2{\cdot}C_{10}H_6{\cdot}NH_2$. 1 : 3-$C_{10}H_6(NO_2)_2$ with $SnCl_2$ gives 3 : 1- and 4 : 2-$NO_2{\cdot}C_{10}H_6{\cdot}NH_2$. 1 : 5-$C_{10}H_6(NO_2)_2$ with Na_2S gives 5 : 1-$NO_2{\cdot}C_{10}H_6{\cdot}NH_2$, whilst 1 : 5- and 1 : 8-$C_{10}H_6(NO_2)_2$ with $SnCl_2$ (excess or deficit) afford the $C_{10}H_6(NH_2)_2$. J. H. Ba.

New reaction of sulphanilamide. W. T. Somerville (*J. Chem. Educ.*, 1943, **20**, 238).—Sulphanilamide gives a bright orange coloration with substances containing lignin (**I**). The reaction detects the presence of (**I**) in paper, wood, and various vegetable fibres. Manila hemp (no reaction) can be easily distinguished from sisal fibres by this reaction, which is better than that for (**I**) with aniline sulphate. L. S. T.

Preparation of phenols.—See B., 1943, II, 275.

Separation of individual cresols and xylenols from their mixtures.—See B., 1943, II, 270.

Stimulation of formation of additive compounds between bases and phenol derivatives by lipoid solvent.—See A., 1943, I, 259.

Preparation of pentabromophenol and bromanil from phenol. M. Kohn (*J. Chem. Educ.*, 1943, **20**, 117).—Working details are given. L. S. T.

Halogeno-*p-tert.*-octylphenols.—See B., 1943, II, 275.

Long-chain compounds with recurring "isoprene" units.—See A., 1943, II, 291.

Formation of phenols by ozonisation of benzene derivatives. II. E. Späth, M. Pailer, and G. Gergely (*Ber.*, 1940, **73**, [*B*], 795—804; cf. A., 1943, II, 227).—Phenols, as well as acids and aldehydes, are often obtained when substituted CHPh:CHR (R usually = CO_2Me) or PhCHO are treated with O_3 (1·5 mols.) in $CHCl_3$ at 0° and the product is boiled with Zn dust and a little $AgNO_3$ in H_2O. The OH replaces the CH:CHR or CHO. OAlk, probably best *o-* or *p-*, or other accelerating substituents must be present, but general rules cannot be laid down. The following are yields of phenol, acid, and aldehyde, respectively, from $CHPh{:}CH{\cdot}CO_2Me$, having the named substituents: 2 : 4 : 5-$(OMe)_3$ 48·2, 2·4, 7·8; 3 : 4-$(OMe)_2$-6-Et 46·4, 5·1, 11·5; 2 : 4-$(OMe)_2$-6-Me 27·1, trace, 72·0; 4-OMe-2 : 5-Me_2 22·0, 5·2, 61·7; 6-OMe-3 : 4-Me_2 15·9, 15·0, 54·0; 2 : 4-$(OMe)_2$ 15·0, 2·2, 28·8; 2 : 3 : 4-$(OMe)_3$ 13·7, 17·1, 45·6; 3 : 4-$(OMe)_2$ trace, 22·3, 59·0; 5-Br-3 : 4-$(OMe)_2$ trace, 15·0, 83·5%; *p*-Me and 4 : α-Me_2 trace, —, —. *iso*Apiol give 5·0, 2·3, and 54·3%, respectively. $(CHPh:)_2$ gives no PhOH. Yields of phenol and acid, respectively, from substituted PhCHO are: 2 : 3 : 4- 20·1, 43·0, and 2 : 4 : 5-$(OMe)_3$ 4·1, 3·1; 3 : 4-$(OMe)_2$-6-Et 14·5, 21·0; 2 : 4-$(OMe)_2$ 14·0, 39·1; 2 : 4-$(OMe)_2$-6-Me 8·0, 11·6; 4-OMe-2 : 5-Me_2 4·4, 14·5; 6-OMe-3 : 4-Me_2 3·9, 18·0; 5-Br-3 : 4-$(OMe)_2$ trace, 15·1%. 6-*Methoxy-*3 : 4-*dimethylbenzaldehyde* (prep. from 6 : 3 : 4 : 1-$OH{\cdot}C_6H_2Me_2{\cdot}CHO$ by Me_2SO_4–KOH–MeOH), m.p. 66°, with $CH_2(CO_2H)_2$ and piperidine at 100° gives 6-*methoxy-*3 : 4-*dimethylcinnamic acid*, m.p. 168° (*Me* ester, m.p. 64—66°). Similarly are prepared 4-methoxy-2 : 5-dimethyl-, m.p. 205° (lit. 200—202°) (*Me* ester, m.p. 81°), 2 : 4-*dimethoxy-*6-*methyl-*, m.p. 190° (*Me* ester, m.p. 101°), 2 : 3 : 4-trimethoxy-, m.p. 173° (lit. 172°) (*Me* ester, m.p. 55°), and 5-*bromo-*3 : 4-*dimethoxy-cinnamic acid*, m.p. 142° (*Me* ester, m.p. 78°). The following are also described: 6 : 3 : 4 : 1-, m.p. 146° (lit. 142·5—143·5°), and 4 : 2 : 5 : 1-$OMe{\cdot}C_6H_2Me_2{\cdot}CO_2H$, m.p. 168° (lit. 163—165°); 5-*methoxy-*o-4-*xylenol*, m.p. 69—70°; 3 : 5-*dimethoxy-*o-*cresol*, m.p. 107°; 2 : 4 : 6 : 1-$(OMe)_2C_6H_2Me{\cdot}CHO$, m.p. 62°; 2 : 3 : 4 : 1-$(OMe)_3C_6H_2{\cdot}CO_2H$, m.p. 100—102° (lit. 99°, 100°); 2 : 4 : 1-$(OMe)_2C_6H_3{\cdot}OH$, m.p. 28° (*benzoate*, m.p. 90); 2 : 4 : 5-*trimethoxyphenol*, m.p. 59—61°; 2 : 5-*dimethoxy-*3 : 4-*methylenedioxyphenol*, m.p. 84°; 2 : 3 : 4-*trimethoxyphenyl benzoate*, dimorphic, m.p. 70° and 80° R. S. C.

Ethylenic stereoisomerism. V. Molecular compounds of stereoisomeric ethylenes [stilbenes]. C. Weygand and T. Siebenmark (*Ber.*, 1940, **73**, [*B*], 765—770; cf. A., 1939, II, 36).—*cis-*(*p*-$OMe{\cdot}C_6H_4{\cdot}CH:)_2$, prepared by half-reduction of (*p*-$OMe{\cdot}C_6H_4{\cdot}C:)_2$, is contaminated with the *trans*-form and (*p*-$OMe{\cdot}C_6H_4{\cdot}CH_2)_2$; it exists in a stable, m.p. 37°, and metastable form, m.p. 36°. m-*Methoxy-*α-m-*anisylcinnamic acid* (prep. from m-$OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO_2Na$, m-$OMe{\cdot}C_6H_4{\cdot}CHO$, and Ac_2O at 90° and then 160—170°), m.p. 167°, with Cu chromite in quinoline at 230° gives cis-3 : 3′-*dimethoxystilbene* (**I**), b.p. 133°/0·2 mm., converted by illumination (ultra-violet) in C_6H_6 into the *trans*-isomeride, m.p. 165°. 2 : 2′-*Dimethoxybenzildihydrazone*, m.p. ~230° (decomp.), and HgO in boiling xylene (not C_6H_6) give 2 : 2′-o-*anisylosotetrazine*, $N<\begin{matrix}CR-CR\\NH{\cdot}NH\end{matrix}>N$ (R = *o*-anisyl), m.p. 138°, and a small amount of 2 : 2′-*dimethoxytolane*, m.p. 126°. o-*Methoxy-*α-o-*anisylcinnamic acid* (prep. as above), m.p. 210°, gives, as above, cis-2 : 2′-*dimethoxy-*

tilbene (**II**), m.p. 86—88°, and thence (irradiation) the *trans*-form (together with a substance, m.p. 193°). Methoxystilbenes and *s*-$C_6H_3(NO_2)_3$ (**III**) in AcOH give additive *compounds* as follows: 2(**III**) + 1 mol. of *cis*-2 : 2′-, m.p. 102—103° (**IV**), *cis*-4 : 4′-, m.p. 62—90°, *trans*-3 : 3′-, m.p. 137—138°, and *trans*-4 : 4′-$(OMe)_2$, m.p. 155°; 1(**III**) + 1 mol. of *trans*-2 : 2′-$(OMe)_2$, m.p. 102—103°. With $C_{10}H_8$ in EtOH, (**IV**) ppts. the additive compound, $C_{10}H_8$ + (**III**), and the filtrate yields (**II**). *trans*-$(CHBz{:})_2$ and its 4 : 4′-Me_2, 4 : 4′-Et_2, and 4-Me derivatives give additive compounds, containing 2 mols. of 2 : 4 : 6 : 1-$(NO_2)_3C_6H_2{\cdot}OH$; no such compounds are obtained from the *cis*-isomerides, nor from the *cis*- or *trans*-4 : 4′-Pr^{α}_2 or 4-Et derivative. The theoretical expectation that the *cis*-forms, richer in energy, would combine with more (**III**) etc. is not justified. Steric causes may play a predominant rôle. R. S. C.

Phenolic constituents of pine heart-wood. Synthesis of pinosylvin dimethyl ether [3 : 5-dimethoxystilbene]. G. Aulin-Erdtman and H. Erdtman (*Ber.*, 1941, **74**, [*B*], 50—56; cf. A., 1939, II, 259). —2 : 6-*Dibromopinosylvin* Me_2 *ether* (**I**) [from pinosylvin Me_2 ether (**II**) and Br in $CHCl_3$], m.p. 135—136°, on oxidation ($KMnO_4$) affords BzOH (85%) and 3 : 5 : 2 : 6 : 1-$(OMe)_2C_6HBr_2{\cdot}CO_2H$ (**III**). (**I**) or (**II**) is further brominated to *tetrabromopinosylvin* Me_2 *ether, forms*, m.p. 195—197° (**IV**) and 172—173°, which give no colour with $C(NO_2)_4$ or conc. H_2SO_4. 3 : 4 : 1-$(OMe)_2C_6H_3{\cdot}CH{:}CPh{\cdot}CO_2H$ is decarboxylated (Cu chromite in boiling quinoline) to 3 : 4 : 1-$(OMe)_2C_6H_3{\cdot}CH{:}CHPh$ (45%), m.p. 111°; 3 : 5-*dimethoxy-α-phenylcinnamic acid* (70%), m.p. 202—204° [from 3 : 5 : 1-$(OMe)_2C_6H_3{\cdot}CHO$ and $CH_2Ph{\cdot}CO_2H$, and PbO in boiling Ac_2O], similarly gives (mainly) iso*pinosylvin* Me_2 *ether* (**V**), b.p. 150° (bath)/0·2 mm., oxidised to BzOH (54%) and 3 : 5 : 1-$(OMe)_2C_6H_3{\cdot}CO_2H$ (32%)' The 2 : 6-Br_2-derivative (**VI**), m.p. 173—174°, of (**V**) is oxidised to BzOH (67%) and (**III**) (48%). (**V**) or (**VI**) is brominated to (**IV**). When (**V**) is heated to the b.p. (>350°), (**II**) is formed in practically 100% yield. J. Wa.

Preparation of diazonaphthols and nitration of 4-bromoacet-1-naphthalide. H. H. Hodgson and S. Birtwell (*J.C.S.*, 1943, 321—322).—4-Nitro-, m.p. 130—133° (decomp.), 4-bromo-, m.p. 133° (decomp.), 4-*chloro*-, m.p. 138° (decomp.), and 4-*iodo-naphthalene*-1 : 2-*diazo-oxide*, m.p. 142° (decomp.), are prepared from 2 : 4 : 1-$NO_2{\cdot}C_{10}H_5R{\cdot}NH_2$ by one or more of four methods given for "diazotisation." Nitration [HNO_3 (*d* 1·42)–AcOH at 50—65°] of 4 : 1-$C_{10}H_6Br{\cdot}NHAc$ is inhibited by $CO(NH_2)_2$; 2 : 4 : 1-$NO_2{\cdot}C_{10}H_5Br{\cdot}NHAc$ has new m.p. 231—233°. 2 : 4 : 1-$NO_2{\cdot}C_{10}H_5Cl{\cdot}NH_2$ and -$NO_2{\cdot}C_{10}H_5Br{\cdot}NH_2$ (improved preps.) exhibit chromoisomerism. J. H. Ba.

Nuclear alkylation of amino-substituted aromatic ethers.—See B., 1943, II, 275.

4 : 4′-Diaminodiphenyl sulphone-2-sulphonamide.—See B., 1943, III, 225.

Synthesis and rearrangement of deca- and tetra-hydronaphthalene diols. J. English, jun., and G. Cavaglieri (*J. Amer. Chem. Soc.*, 1943, **65**, 1085—1089).—1-Keto-*cis*-decahydronaphthalene [does not rearrange under the conditions of Hückel (A., 1925, i, 258)] and MgMeI in Et_2O give 1-*methyl*-cis-*decahydro*-1-*naphthol* (90%), b.p. 76—77°/12 mm. 1-Methyl-*trans*-decahydro-1-naphthol, b.p. 93°/5 mm., is dehydrated by $KHSO_4$ at 120—130° to mixed 1-*methyl*-$\Delta^{1:2}$-trans- and -$\Delta^{1:9}$-*octahydronaphthalene*, b.p. 65°/5 mm., which with BzO_2H in $CHCl_3$ at 0° give mixed *epoxides*, b.p. 83°/7 mm. The mixture is hydrated by 10% H_2SO_4 at 0—10° to 1 : 2-trans-*dihydroxy*-1-*methyl*-trans- (**I**) (36%), +$3H_2O$, m.p. 79, and 1 : 9-trans-*dihydroxy*-1-*methyl-decahydronaphthalene* (**II**) (15%), m.p. 97°, converted by $Pb(OAc)_4$–AcOH at 40—45° into β-2-*acetyl*cyclo*hexyl-propionic acid*, cryst. (ψ-benzylthiocarbamide salt, m.p. 156·5—157·5°; with some -propaldehyde), and 2-δ-*keto*-n-*amyl*cyclo*hexanone*, an oil [*disemicarbazone*, m.p. 207—209° (decomp.)], respectively. In boiling 30% H_2SO_4, (**I**) gives 2-*keto*-1-*methyl*-trans-*decahydronaphthalene* (**III**), b.p. 98°/10 mm. [*semicarbazone*, m.p. 208—209° (decomp.); oxime, m.p. 149°; 2 : 4-dinitrophenylhydrazone, m.p. 170—171° (decomp.)], and a small amount of (?) 1-*methyl*-3 : 4 : 5 : 6 : 7 : 10-*hexahydronaphthalene* (**IV**), b.p. 82°/7 mm. The structure of (**III**) is proved by Clemmensen reduction to 1-methyl-*trans*-decahydronaphthalene, b.p. 54°/4 mm., which with Pd–C–H_2 at 350° gives 1-$C_{10}H_7Me$. In boiling 30% H_2SO_4, (**II**) gives (**IV**) and a small amount of (?) 1-keto-9-methyldecahydronaphthalene [semicarbazone, m.p. 200—202° (decomp.)]. $KHSO_4$ at 120—130° dehydrates 1-methyl-1 : 2 : 3 : 4-tetrahydro-1-naphthol to 1-*methyl*-3 : 4-*dihydronaphthalene*, b.p. 84°/5 mm., which with BzO_2H in $CHCl_3$ at 0°, gives, by oxidation and rearrangement, 2-keto-1-methyl-3 : 4-dihydronaphthalene, b.p. 103°/3 mm. {semicarbazone, m.p. 194° (decomp.) [lit. 200—202° (decomp.)]} (and polymerides), and with $KMnO_4$ in $COMe_2$ at −40° (later room temp.) gives 1 : 2-cis-*dihydroxy*-1-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (~60%, variable), b.p. 135—140°/4 mm., rearranged in boiling 30% H_2SO_4 to 2-keto-1-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 105—107°/3 mm. [semicarbazone, m.p. 194° (decomp.)]. 1-Keto-2-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene (*semicarbazone*, m.p. 199°) has b.p. 98°/3 mm. Contrary to Musser *et al.* (A., 1938, II, 182), hydrogenation of α-$C_{10}H_7{\cdot}OH$ gives mainly the *trans*-decahydro-1-naphthol. R. S. C.

Synthesis of camphononic acid and *dl*-pinonic acid.—See A., 1943, II, 306.

Course of reaction in the transformation of αα-dibromoacetophenone into mandelic acid by aqueous alkali. E. B. Ayres and C. R. Hauser (*J. Amer. Chem. Soc.*, 1943, **65**, 1095—1096).—Passing 5% NaOH through $COPh{\cdot}CHBr_2$ at 15° and then immediately into 10% AcOH gives 15% of BzCHO, which is thus an intermediate in the formation of $OH{\cdot}CHPh{\cdot}CO_2H$. The reaction mechanism is discussed. R. S. C.

Methoxyphenylacetic acids. H. A. Weidlich and M. Meyer-Delius (*Ber.*, 1940, **73**, [*B*], 631; cf. A., 1943, II, 229).—The methods used in the prep. of methoxyphenylacetic acids (*loc. cit.*) have been described by Hahn *et al.* (A., 1939, II, 368). A. T. P.

Wandering of halogen atoms in carbon chains and rings.—See A., 1943, II, 216.

Catalytic dehydrogenation of 2-substituted 5 : 6 : 7 : 8-tetrahydronaphthalene derivatives. M. S. Newman and H. V. Zahm (*J. Amer. Chem. Soc.*, 1943, **65**, 1097—1101).—Dehydrogenations below are effected by 20% Pd–C (prep. described) at 210—310° (N_2). CO_2Me in a side-chain is unaffected by dehydrogenation; thus $R{\cdot}[CH_2]_n{\cdot}CO_2Me$ (R = 5 : 6 : 7 : 8-tetrahydro-2-naphthyl here and below) (*n* = 0—3) gives 2-$C_{10}H_7{\cdot}[CH_2]_n{\cdot}CO_2Me$. Ketonic CO adjacent to R is reduced to CH_2; thus COMeR (prep. by a Friedel–Crafts reaction in CS_2 at <10°), b.p. 132·5—134·5°/3·5—4 mm., gives 63% of 2-$C_{10}H_7Et$ and some 2-$C_{10}H_7{\cdot}COMe$ [*semicarbazone*, m.p. 222—223° (decomp.)], and *Me γ-keto-γ*-5 : 6 : 7 : 8-*tetrahydro*-2-*naphthylbutyrate* [prep. by $(CH_2{\cdot}CO)_2O$–$AlCl_3$–C_6H_6 and subsequent esterification of the acid (**I**), m.p. 114—116°], f.p. 31·0°, b.p. 170—172°/1·5—2 mm., gives 70% of 2-$C_{10}H_7{\cdot}[CH_2]_3{\cdot}CO_2Me$ + the derived acid [obtained by reduction of the OH-ester, which then (*a*) is dehydrated and reduced and (*b*) lactonises by loss of MeOH and is then hydrogenolysed (see below)]. C·O·X adjacent to R is hydrogenolysed; thus γ-5 : 6 : 7 : 8-*tetrahydro*-2-*naphthyl-γ-butyrolactone* [obtained from (**I**) by Na–Hg], f.p. 33·2°, b.p. 173—175°/1 mm., gives 71% of 2-$C_{10}H_7{\cdot}[CH_2]_3{\cdot}CO_2H$, and $CH_2R{\cdot}OH$ gives 67% of 2-$C_{10}H_7Me$ + RMe. 5 : 6 : 7 : 8-Tetrahydro-2-naphthaldehyde (**II**) (prep. by Rosenmund reduction of the acid chloride in cymene), b.p. 116—119°/3 mm. [*semicarbazone*, m.p. 223—224° (decomp.)], gives $C_{10}H_8$ and tetrahydronaphthalene. *Me* β-5 : 6 : 7 : 8-*tetrahydro*-2-*naphthylacrylate* [(**II**) and $CH_2(CO_2H)_2$ in C_5H_5N at 100° afford the *acid* (**III**), m.p. 170·8—171·8°], m.p. 40°, b.p. 157—158°/2·5—3 mm., gives 2-$C_{10}H_7{\cdot}[CH_2]_2{\cdot}CO_2Me$ (89%). α-5 : 6 : 7 : 8-*Tetrahydro*-2-*naphthylethyl alcohol* [prep. from COMeR by $Al(OPr^{\beta})_3$ in $Pr^{\beta}OH$; if the reaction mixture is allowed to become hot during isolation 2-*vinyl*-5 : 6 : 7 : 8-*tetrahydronaphthalene*, b.p. 96°/2 mm., results], b.p. 120—121°/2 mm., gives a polymeride and a little 2-$C_{10}H_7Et$. RCOCl gives a mixture. The following are incidentally described. RCO_2H [prep. from COMeR by $Ca(OCl)_2$–Na_2CO_3–NaOH–H_2O–dioxan at 100°], m.p. 154—155° (chloride, b.p. 121—122°/2 mm.; Me ester, b.p. 149—150°/4—4·5 mm.). $CH_2R{\cdot}OH$ [from RCHO by H_2–PtO_2–$FeCl_2$ (trace) in EtOH], b.p. 133—134°/4 mm. *Me* 5 : 6 : 7 : 8-*tetrahydro*-2-*naphthylacetate* (from $CH_2R{\cdot}OH$ by, successively, $SOCl_2$, NaCN–MeOH–H_2O, H_2SO_4–H_2O–AcOH, and HCl–MeOH), b.p. 141—143°/4 mm. (*acid*, m.p. 97—97·5°). *Me* β-5 : 6 : 7 : 8-*tetrahydro*-2-*naphthylpropionate*, b.p. 136—137·5°/2·5—3 mm. [acid, m.p. 81—82° (cf. lit.)], obtained with some bimol. product from (**III**) by Na–Hg–Ni (trace) in neutral solution and subsequent esterification. γ-5 : 6 : 7 : 8-Tetrahydro-2-naphthylbutyric acid [from (**I**) by Clemmensen reduction], m.p. 47—49°, b.p. 195—200°/4·5—5 mm. (*Me* ester, b.p. 181—184°/3·5—4 mm.). M.p. are corr. R. S. C.

Preparation of aminobenzoic acid esters of substituted monoalkylamino-alcohols. W. F. Ringk and E. Epstein (*J. Amer. Chem. Soc.*, 1943, **65**, 1222—1226).—$NHR{\cdot}CH_2{\cdot}CMe_2{\cdot}OH$ (R = *n*-hexyl, b.p. 224—228°, *n*-heptyl, b.p. 242—246°, β-octyl, b.p. 245—248°, and β-ethyl-*n*-hexyl, b.p. 245—248°) (prep. as A., 1940, II, 85, but in 50% $Pr^{\beta}OH$; yields ~45%) with *p*-$NO_2{\cdot}C_6H_4{\cdot}COCl$ (**I**) in aq. alkali give solid esters, reduced by Fe–HCl etc. to β-n-*hexyl*-, m.p. 169—171°, β-n-*heptyl*-, m.p. 169—172°, *β-β′-octyl*-, +0·5H_2O, m.p. 154—156°, and *β-β′-ethyl*-n-*hexyl*-, m.p. 141—143°, -*amino*-tert.-*butyl* p-*aminobenzoate sulphate*, B_2,H_2SO_4 (corresponding hydrochlorides are oils). $NH_2{\cdot}CMe_2{\cdot}CH_2{\cdot}OH$ with AlkHal in boiling $Pr^{\beta}OH$ gives 20—60% of β-ethyl-, m.p. 72—73°, b.p. 167—169°, *β-n*-, m.p. 55—57°, b.p. 183—186°, and -*iso*-propyl-, m.p. 40—42°, b.p. 172—175°, *β-n*-, m.p. 68—69°, b.p. 200—203°, -*iso*-, m.p. 45—46°, b.p. 192—194°, and -*sec*.-butyl-, b.p. 186—190°, *β-n*-, m.p. 59—60°, and -*iso*-amyl-, m.p. 73—74°, b.p. 211—215°, *β-n*-hexyl-, m.p. 62—63°, b.p. 235—238°, *β-x*-ethylbutyl-, b.p. 220—226°, *β-n*-heptyl-, m.p. 50—52°, b.p. 253—258°, *β-β′*-octyl-, b.p. 250—255°, *β-β′*-ethyl-*n*-hexyl-, m.p. 15—17°, b.p. 249—255°, and *β-n*-decyl-, m.p. 55—57°, b.p. 295—300°, -*iso*butyl alcohol, converted by (**I**) in aq. NaOH at 35—40° and then Fe–HCl into *β-ethyl*-, m.p. 245—246·5°, β-n-, m.p. 239—240°, and -iso-*propyl*-, m.p. 234·5—236°, β-n-, m.p. 192—192·5°,

-iso-, m.p. 225·8—228°, and -sec.-*butyl*-, $+H_2O$, m.p. 202—205°, β-n-, m.p. 209—211·8°, and -iso-*amyl*-, m.p. 202—203°, β-n-*hexyl*-, m.p. 212·5—213·5°, β-x-*ethylbutyl*-, m.p. 198—199·5°, β-n-*heptyl*-, m.p. 197—198°, β-β′-*octyl*- (**II**), $+0·5H_2O$, m.p. 137—140°, β-β′-*ethyl*-n-*hexyl*-, m.p. 154—158°, and β-n-*decyl*-, m.p. 141—142°, -iso-*butyl* p-*aminobenzoate hydrochloride*. β-Ethyl- (*sulphate*, m.p. 223—224°), β-n- (*hydrochloride*, m.p. 192—194°) and -iso-propyl- (*sulphate*, m.p. 188—189°), β-n- (*hydrochloride*, m.p. 205—208°) and -iso-butyl- (*sulphate* and *hydrochloride*, oils) -aminoisobutyl *m*- and β-n-butyl-aminoisobutyl *o*-aminobenzoate, m.p. 68—69° (hydrochloride, sulphate, and phosphate, oils), are similarly prepared. *p*-NO_2·C_6H_4·CO_2·$[CH_2]_2$·NHBu[a], when kept for several weeks, isomerises to p-*nitrobenz*-N-β-*hydroxyethyl*-N-*butylamide*, m.p. 195—196° (cf. Kremer *et al.*, A., 1942, II, 283). Pharmacological data are reported for the esters. The *iso*- are very potent anæsthetics and less toxic than the *tert.*-butyl esters. They are vasodilators in cats (intravenous injection), but are synergistic with adrenaline. The most effective product is (**II**), which is 24 times as effective as cocaine for surface anæsthesia and 8 times as effective as procaine for conductive anæsthesia. R. S. C.

βγ-Diaryladipic acids.—See B., 1943, II, 276.

Conversion of an alcohol into the corresponding aldehyde by a less volatile aldehyde with the aluminium alkoxide as catalyst. Influence of an ethylene linking in the reactant aldehyde. R. R. Davies and H. H. Hodgson (*J.S.C.I.*, 1943, **62**, 109—110).—Al alkoxides act as catalysts for the conversion of the alcohol into the corresponding aldehyde through reaction with a less volatile aldehyde. Cinnamaldehyde is a more reactive aldehyde than PhCHO due to its ethylenic linking. An explanation of the reaction is given based on H bonding.

Alkylation and other reactions of 9-formylfluorene. W. G. Brown and B. A. Bluestein (*J. Amer. Chem. Soc.*, 1943, **65**, 1082—1084).—9-Formylfluorene (**I**) [prep. from fluorene by HCO_2Et and KOEt (80—90%) or NaOEt (65%) in Et_2O], b.p. 189—192°/10 mm., unstable, with Me_2SO_4–KOH–H_2O gives 62% of the *enol Me ether*, m.p. 104°, but with MeI–KOH–H_2O gives 9-methyl- (**II**), and with $Pr^{\beta}Br$, *cyclo*hexyl bromide, or CH_2PhCl in KOH–aq. EtOH gives 9-*iso*propyl-, m.p. 54—55°, 9-*cyclo*hexyl-, m.p. 115—116° [not identical with the compound, m.p. 102—103°, of Miller *et al.* (A., 1935, 741)], or 9-benzyl-fluorene (77%), m.p. 132—133° (also obtained from Et 9-fluorenylglyoxylate and CH_2PhCl in boiling NaOH–H_2O–EtOH), respectively. With CH_2O in aq. NaOH, (**I**) gives 9-fluorenylcarbinol (**III**). Hydrogenation (PtO_2; EtOH; 3 atm.) of the enol acetate or benzoate of (**I**) gives (**II**) and the acetate or benzoate, respectively, of (**III**). The K salt of (**I**) with $ClCO_2$·CH_2Ph in H_2O gives *CH_2Ph ββ-2 : 2′-diphenylenevinyl carbonate*, m.p. 149·5°, hydrogenated very slowly to (**II**) (poor yield). R. S. C.

Lignin and related compounds. LXIV. Synthesis and properties of γ-hydroxy-γ-4-hydroxy-3-methoxyphenylpropan-α-one. K. A. West and H. Hibbert. **LXVIII. Synthesis and properties of α- and γ-ethoxy-α-4-hydroxy-3-methoxyphenylpropan-β-one and their methyl ethers.** M. Kulka and H. Hibbert (*J. Amer. Chem. Soc.*, 1943, **65**, 1170—1172, 1185—1187; cf. A., 1942, II, 158).—LXIV. Veratrole, Cl·$[CH_2]_2$·COCl, and $AlCl_3$ (4 mols.) in CS_2 at 50° and then at 100° (no solvent) give *4-hydroxy-3-methoxy-β-chloropropiophenone* (**I**) (60%), m.p. 101—102°, converted by KOAc–AcOH at 100° into *4-hydroxy-3-methoxy-β-acetoxy-* (**II**) (67%), m.p. 80—81°, and thence ($BaCO_3$ in boiling H_2O) *-β-hydroxy-propiophenone* (**III**) (55%), m.p. 109—110°. CH_2N_2–Et_2O converts (**I**), (**II**), and (**III**) into the known veratrole derivatives. With Et_2SO_4–1·5% NaOH at the b.p., (**II**) gives the Et ether, oxidised by $KMnO_4$ to 3 : 4 : 1-OMe·C_6H_3(OEt)·CO_2H. With 2% HCl–EtOH, (**III**) gives *4-hydroxy-3-methoxy-β-ethoxypropiophenone, forms*, m.p. 72—74° and 35—37° (with CH_2N_2 gives the veratrole derivative). 72% H_2SO_4 at room temp. or boiling 5% H_2SO_4 or 1% NaOH converts (**III**) into lignin-like products.

LXVIII. *α-Ethoxy-α-4-acetoxy-* (prep. from the 4-Br-compound by AgOAc in boiling EtOH), an oil, with NaOEt–EtOH at room temp. gives *α-ethoxy-α-4-hydroxy-3-methoxyphenylpropan-β-one* (80%), m.p. 62—63° (*semicarbazone*, m.p. 173·5—174·5°), methylated by CH_2N_2 to *α-ethoxy-α-3 : 4-dimethoxyphenylpropan-β-one* (2 : 4-*dinitrophenylhydrazone*, m.p. 141—142°). *β-Nitro-γ-ethoxy-α-4-hydroxy-3-methoxyphenyl-Δ[α]-propene* (from vanillin by NO_2·$[CH_2]_2$·OEt, a little NH_2Me,HCl, and Na_2CO_3 in EtOH at room temp.; 30% yield), m.p. 78—79°, with Fe–$FeCl_3$–HCl–EtOH–H_2O at the b.p. and then 7N-H_2SO_4 at room temp. gives *γ-ethoxy-α-4-hydroxy-3-methoxyphenylpropan-β-one* (68%), an oil (*semicarbazone*, m.p. 144—144·5°). 3 : 4 : 1-$(OMe)_2C_6H_3$·CHO gives similarly *β-nitro-γ-ethoxy-α-3 : 4-dimethoxyphenyl-Δ[α]-propene*, m.p. 90—91°, and *γ-ethoxy-α-3 : 4-dimethoxyphenylpropan-β-one* (67%) (2 : 4-*dinitrophenylhydrazone*, m.p. 114—116°). R. S. C.

Synthesis of α-acyltetronic acids.—See A., 1943, II, 217.

Friedel–Crafts reaction of lactones. III. Dehydrogenations with aluminium chloride. H. Beyer and H. Schulte (*Ber.*, 1941, **74**, [*B*], 98—106; cf. A., 1937, II, 291, 377).—CH_2Bz·CO_2Et, NaOEt, and epichlorohydrin in EtOH afford δ-chloro-α-benzoyl-γ-valerolactone (**I**), m.p. 105—106° (p-*nitrophenylhydrazone*, m.p. 159°), which with C_6H_6 and $AlCl_3$ at 80—90° for 1 week gives acidic products (*A*), 1-*benzoyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (**II**), b.p. 182—183°/0·5 mm. (*semicarbazone*, sinters at 168°, m.p. 171°), and *Ph γδ-diphenyl-n-butyl ketone* (**III**), m.p. 108—109° (*semicarbazone*, m.p. 180—181°; p-*nitrophenylhydrazone*, m.p. 137—138°). (**II**) is reduced (H_2, PtO_2) to *phenyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthylcarbinol*, b.p. 186—187°/0·6 mm., m.p. 101°, and (Clemmensen) to 1-*benzyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. 145—146°/0·6 mm., which is also obtained by Clemmensen reduction of 1-keto-4-benzyl-1 : 2 : 3 : 4-tetrahydronaphthalene. Clemmensen reduction of (**III**) gives *αβε-triphenylpentane*, b.p. 206—207°/0·18 mm., m.p. 39—40°. (*A*) contains 1 : 2-OH·$C_{10}H_6$·CO_2H (*hydrazide*, m.p. 212—213°) which must be formed from (**I**) by loss of PhMe. J. Wa.

Properties of 4-methoxydibenzoylmethane [benzoylanisoylmethane]. R. P. Barnes and A. Brandon (*J. Amer. Chem. Soc.*, 1943, **65**, 1070—1072).—*p*-OMe·C_6H_4·CO·CH:CHPh and Br in CS_2–CCl_4 give the *dibromide* (**I**), m.p. 162°, converted by KOAc in boiling AcOH into p-*α-bromo-*, an oil, which with boiling NaOMe–MeOH gives p-*β-methoxy-*, semi-cryst., *-cinnamoylanisole*. With conc. HCl–MeOH this gives p-*β-hydroxycinnamoylanisole* (**II**), m.p. 128—129°, which with NH_2OH,HCl in boiling aq. MeOH yields *5-phenyl*-3-p-*anisylisooxazole* (**III**), m.p. 119°, also obtained from (**I**) by NH_2OH,HCl–EtOH–H_2O and then KOH. Identity of (**III**) with the misnamed *iso*oxazole of Pond *et al.* (A., 1901, i, 35) is due to the compound considered to be *p*-OMe·C_6H_4·C(OH):CH·COPh reacting as and being identical with (**II**). R. S. C.

Optical activity in the *trans*-hydrindane and -decahydronaphthalene series. W. Hückel and H. Sowa (*Ber.*, 1941, **74**, [*B*], 57—63).—The remarkable high rotation of optically active *trans*-β-hydrindanone (**I**) suggested investigating whether a symmetrical ring system with *trans*-fusion of the rings gave rise to so high a rotation or whether it was to be attributed to the induced dissymmetry of the CO group. Distillation of (+)-*cyclo*hexane-1 : 2-diacetic acid (**II**), $[\alpha]_D^{19}$ +48·35° in EtOH, affords (−)-(**I**), $[\alpha]_D^{19·5}$ −301·8° in C_6H_6, which is reduced (H_2, Pt-black, AcOH) to a mixture of (−)-*trans*-hydrindane, b.p. 159°/760 mm., $[\alpha]_D^{21}$ −5·98°, and (−)-*trans*-β-hydrindanol, m.p. 12°, $[\alpha]_D^{17}$ −12·46° (homogeneous), −7·83° in C_6H_6, −9·77° in tetrahydronaphthalene, −11·95° in *cyclo*hexane, −14·07° in EtOH (*phenylurethane*, m.p. 131—132°, $[\alpha]_D^{18·5}$ −18·67° in EtOH), isolated as the H succinate, m.p. 48—50°. Impure *trans*-decahydro-β-naphthylamine II (**III**) and HCO_2H at 120° afford the *formate*, m.p. 124°, and *formyl* derivative, m.p. 84°, hydrolysed to pure (**III**), m.p. 15° (Ac derivative, m.p. 163°). (**III**) is resolved through the *α-bromo-d-camphorsulphonate*, m.p. 158°, $[\alpha]_D^{18}$ +71·7° in EtOH, to (+)-(**III**), m.p. 10·6°, $[\alpha]_D^{22}$ +2·14° (hydrochloride, $[\alpha]_D^{22}$ +0·92° in H_2O; Ac, m.p. 175—176°, $[\alpha]_D^{23}$ +25·3° in EtOH, and Bz derivative, m.p. 174°, $[\alpha]_D^{20}$ +1·89° in EtOH). Impure (−)-(**III**) is isolated from the mother-liquors as the H tartrate and consists of 75% of (−)- and 25% of (+)-base. (+)-(**III**) with $NaNO_2$ in 10% AcOH gives (?) decahydro-β-naphthol II (**IV**), m.p. 72°, $[\alpha]_D^{16·5}$ +0° in EtOH, −2·7° in (?) *cyclo*hexane, −1·8° in tetrahydrofuran (toluenesulphonate, m.p. 63°, $[\alpha]_D^{20}$ −1·75° in EtOH), after purification through the H phthalate, m.p. 173°, $[\alpha]_D^{20}$ −1·4° in EtOH. The toluenesulphonate of (**IV**) and NaOEt give a mixture of (**IV**), decahydronaphthyl Et ether (formed with Walden inversion), b.p. 100°/15 mm., and (−)-*trans*-Δ²-octahydronaphthalene, b.p. 72°/13 mm., $[\alpha]_D^{21}$ −26·2°, which is oxidised ($KMnO_4$) to optically impure (**II**), m.p. 151°, $[\alpha]_D^{20}$ +40·5°, containing ~10% of (−)-(**II**), indicating ~90% resolution of (**III**). J. Wa.

Oxido-ketones in the indene series. C. F. H. Allen and J. W. Gates, jun. (*J. Amer. Chem. Soc.*, 1943, **65**, 1230—1235).—4 : 5-*Dibromo-α-benzylidene-*, m.p. 244°, and *α-benzylidene*-4 : 5-*dimethylphthalide*, m.p. 166°, and thence 5 : 6-*dibromo*-2 : 3-*diphenyl-*, m.p. 196°, and 2 : 3-*diphenyl*-5 : 6-*dimethyl*-1-*indenone*, m.p. 229°, are prepared (method : A., 1943, II, 196). Adding 15% H_2O_2 to the appropriate indenone and aq. NaOH in EtOH at, usually, 60—70° gives 2 : 3-*epoxy*-2 : 3-*diphenyl*-5 : 6-*dimethyl-*, m.p. 197°, 5 : 6-*dibromo*-2 : 3-*epoxy*-2 : 3-*diphenyl-*, m.p. 178°, and 2 : 3-*epoxy*-2 : 3 : 5 : 6-*tetraphenyl-* (**I**), m.p. 199—200°, -1-*indanone*, but 2 : 3 : 5 : 6-tetraphenyl-4 : 7-dimethyl- and 2 : 3 : 4 : 7-tetraphenylindenone do not thus react. The epoxy-compounds are peroxidic, liberating I from KI–AcOH; with dry HCl–AcOH at room temp., hydrolysis to 2 : 3-*dihydroxy*-2 : 3-*diphenyl*-5 : 6-*dimethyl-* (**II**), m.p. 145°, -2 : 3 : 5 : 6-*tetraphenyl-* (**III**), m.p. 215°, and 4 : 5-dibromo-2 : 3-dihydroxy-2 : 3-diphenyl-1-indanone, m.p. 166°, occurs, but in hot HCl–AcOH or usually, very slowly, AcOH alone 3 : 4-*diphenyl*-6 : 7-*dimethyl-* (**IV**), m.p. 208°, 3 : 4 : 6 : 7-*tetraphenyl-* (**V**), m.p. 230°, and 6 : 7-*dibromo*-3 : 4-*diphenyl*-iso*coumarin*, m.p. 229°, are obtained. (**IV**) and (**V**) are similarly obtained from (**II**) and (**III**), respectively; (**II**) and (**III**) are thus intermediates, others being the 1 : 2-epoxy-1 : 3-dihydroxyindanes (*A*) and 4-hydroxy-3 : 4-dihydro*iso*coumarins. (**V**) dissolves in aq. NaOH (not Na_2CO_3) and then, by careful acidification, yields *Ph* 2-*carboxy-α* : 4 : 5-*triphenylbenzyl ketone* (**VI**), m.p. 244°, whence it is regenerated by warming alone or in solution. Structures are proved by oxidation of (**V** or

(**VI**) by CrO_3 or $KMnO_4$ to BzOH and 4 : 5 : 2 : I-$C_6H_2Ph_2Bz{\cdot}CO_2H$. 2 mols. of MgMeI add (Grignard machine) to (**V**), but the product is dehydrated to give *Ph α* : 4 : 5-*triphenyl*-2-iso*propenylbenzyl ketone*, m.p. 256°; MgPhBr and (**V**) give *Ph α* : 4 : 5-*triphenyl*-2-α-*hydroxybenzhydrylbenzyl ketone*, m.p. 186°. The other *iso*coumarins are stated (no details) to behave similarly. Weitz *et al.* (A., 1921, i, 869) misinterpreted the similar reactions of 2 : 3-diphenyl-1-indenone. This yields an epoxide, glycol (**VII**) (adds 1 MgMeI; 2 active H), lactone [which, like (**VII**), is oxidised to BzOH and *o*-$C_6H_4Bz{\cdot}CO_2H$], and derived acid. Warm alkali destroys (**III**), but converts (**II**) or (**VII**) into respectively 1-*benzoyl*-2-*phenyl*-4 : 5-*dimethyl*-, m.p. 132°, or 1-*benzoyl*-2-*phenyl*-iso*benzfuran* (**VIII**) (the " yellow substance " of Weitz *et al.*). (**VIII**) is unimol., adds 1 MgMeI, contains no active H, does not form a quinoxaline, resists H_2O_2, but is oxidised by CrO_3 to BzOH and *o*-$C_6H_4Bz{\cdot}CO_2H$ and by $KMnO_4$ or HNO_3 to *o*-$COPh{\cdot}C_6H_4{\cdot}CO{\cdot}COPh$. Its structure is thus established. Its formation from (**VII**) occurs by way of *o*-$OH{\cdot}CHPh{\cdot}C_6H_4{\cdot}CO{\cdot}COPh$ and *o*-$C_6H_4{<}^{CHPh}_{CBz(OH)}{>}O$. Only the epoxide (**IX**), new m.p. 58—59°, is formed from 3-phenyl-2-ethyl-1-indenone by alkaline H_2O_2. This yields, as above, 2 : 3-*dihydroxy*-3-*phenyl*-2-*ethyl*-1-*indanone*, m.p. 122°, and 4-*phenyl*-3-*ethyl*isocoumarin, m.p. 101°. With 30—32% HBr–AcOH at 10—15°, (**IX**) gives 3-*bromo*-2-*hydroxy*-3-*phenyl*-2-*ethyl*-1-*indanone* (80%), m.p. 129°, whence MgMeI does not remove the Br. In boiling AcOH (6 hr.) or 15% HBr– or 30%H_2SO_4–AcOH (10 min.), (**I**) gives 4-*benzoyl*-4-*phenyl*-2 : 3-4′ : 5′-*diphenylbenz*-Δ^2-cyclo*butenone* (**X**), brick-red, m.p. 219—220°, which adds 2 MgMeI, contains no active H, is oxidised to BzOH and 4 : 5 : 2 : I-$C_6H_2Ph_2Bz{\cdot}CO_2H$, in boiling KOH–EtOH gives (**VI**), and with $Zn(OAc)_2$, KOAc, or NH_2OH,HCl in hot AcOH gives (**V**) (reaction mechanism discussed). The CO of epoxy-ketones is very reactive; *e.g.*, *αβ*-epoxy-*β*-phenylpropiophenone rapidly gives a 2 : 4-*dinitrophenylhydrazone*, m.p. 205°. The labile grouping, $\cdot{}^{CH}_{O}{>}C(OH)\cdot$ (*B*), as in (*A*) (above), is held to explain various " rearrangements." *E.g.*, oxidation of cyclic ketones to lactones by Caro's acid involves the reactions, $\cdot CH_2{\cdot}CO_2 \rightarrow \cdot CH(OH){\cdot}CO\cdot \rightarrow$ (*B*) $\rightarrow \cdot CH_2{\cdot}O{\cdot}CO\cdot$; (*B*) is also an intermediate in the conversion of $CHBz_2{\cdot}OH$ into $CH_2Bz{\cdot}OBz$ by distillation and of $CPhBz_2{\cdot}OH$ into $CHPhBz{\cdot}OBz$. R. S. C.

Simple and practical preparation of 2-methyl-1 : 4-naphthaquinone from naphthalene. P. P. T. Sah, W. Brüll, and H. Holzen (*Ber.*, 1940, **73**, [*B*], 762).—The following reaction series is recommended. 2-$C_{10}H_7{\cdot}SO_3Na$ + $K_4Fe(CN)_6$ in Cu at <1 atm. → 2-$C_{10}H_7{\cdot}CN$ → (KOH– or NaOH–EtOH) 2-$C_{10}H_7{\cdot}CO_2H$ → [Ba salt + $(HCO_2)_2Ba$ in Cu at <1 atm.] 2-$C_{10}H_7{\cdot}CHO$ (50—60%) → (Clemmensen) 2-$C_{10}H_7Me$ → 1 : 2 : 4-O:$C_{10}H_5$Me:O, m.p. 105—106° (quinol diacetate, m.p. 112—113°). R. S. C.

Water-soluble derivatives of menadione [2-methyl-1 : 4-naphthaquinone]. A. R. Menotti (*J. Amer. Chem. Soc.*, 1943, **65**, 1209—1211).—1 : 2 : 4-O:$C_{10}H_5$Me:O (**I**) with aq. $NaHSO_3$ at 0° gives the insol., hygroscopic additive compound (**II**), $+3H_2O$, m.p. (capillary) ~126° (immersed at 115°) or (micro) loses solvent at 100° and melts at 154—157° (decomp.) (benzyl*iso*thiocarbamide salt, m.p. 126·5—128°), but at 90—100° slowly gives 2-methyl-1 : 4-naphthaquinol-3-sulphonic acid (sol. Na salt), isolated as *K* salt (**III**), $+2H_2O$, loses solvent at 100° and melts at 193—196° (decomp.) [also obtained with much 2 : 1 : 4-$C_{10}H_5Me(OH)_2$ from (**II**) in boiling H_2O]. With Ac_2O–AcOH, (**III**) gives the *K* salt *diacetate* (**IV**), m.p. >205° (decomp.). 2 : 1 : 4-$C_{10}H_5Me(OAc)_2$ and $ClSO_3H$ in $CHCl_3$ at 25° give, after treatment with KCl, *K* 2-*methyl*-1 : 4-*naphthaquinol*-3-*sulphonate monoacetate*, $+H_2O$, m.p. (micro) 168—170° (decomp.; after loss of solvent at ~100°), and some (**IV**). (**II**) is identified by conversion into (**I**) (95—98%) by 10% aq. NH_3, by Craven's test, or crystallo-optical properties (detailed). (**III**) is identified by formation of a scarlet ppt. with the $Fe^{\cdot\cdot}$ *o*-phenanthroline complex, formation of a red colour in dil. alkali, or crystallo-optical properties (detailed). R. S. C.

Model experiments on the use of *cyclo*pentadiene in the synthesis of sterol-like compounds. C. F. Koelsch and F. J. Lucht (*J. Amer. Chem. Soc.*, 1943, **65**, 1240—1242).—3-Methyl*cyclo*hexenone does not react with *cyclo*pentadiene (**I**). 1 : 2 : 4-O:C_6H_3Ph:O (improved prep.) and (**I**) in warm MeOH give (?) 2-*phenyl*-5 : 8-endo*methylene*-5 : 8 : 9 : 10-*tetrahydro*-1 : 4-*naphthaquinone* (88%), m.p. 70·5—71°, reduced by Zn dust in AcOH at 70° to the 2 : 3 : 5 : 8 : 9 : 10-*H*$_6$-*quinone* (75%), m.p. 149·5—152°, which by Clemmensen reduction gives a *substance*, $C_{17}H_{20}$, b.p. 136—138°/4 mm. Contrary to Niederl *et al.* (A., 1939, II, 416), *cyclo*hexanone and *m*-cresol give 4-cyclo*hexenyl*-m-*cresol* (14%), b.p. 180—190°/25 mm. [and a *dimeride*, m.p. 142—143° or (+$COMe_2$) softens 106°, m.p. 111—113° (decomp.)], hydrogenated (PtO_2; AcOH) to 4-cyclo*hexyl*-m-*cresol*, m.p. 69—70°, b.p. 166—169°/19 mm. Coupling with *p*-$SO_3H{\cdot}C_6H_4{\cdot}N_2Cl$ and reduction by $Na_2S_2O_4$ then yields 6-*amino*-4-cyclo*hexyl*-m-*cresol* (78%), pink at 170°, m.p. 182°, oxidised by $K_2Cr_2O_7$–H_2SO_4 to 2-cyclo*hexyl*-5-*methylbenzoquinone*, m.p. 60—61° (derived *quinol*, m.p. 146—148°), which with (**I**) in boiling MeOH gives 2-cyclo*hexyl*-10-*methyl*-5 : 8-endo*methylene*-5 : 8 : 9 : 10-*tetrahydro*-1 : 4-*naphthaquinone* (96%), m.p. 75—77° (with Zn–AcOH gives a substance, m.p. 71—78°). R. S. C.

IV.—STEROLS AND STEROID SAPOGENINS.

Formation of ergostatetraene-*B* during the acetylation of ergosterol. H. A. Stansbury, jun. (*J. Amer. Chem. Soc.*, 1943, **65**, 1243).—Ergosteryl acetate, prepared from ergosterol by boiling Ac_2O, is accompanied by a small amount of ergostatetraene-*B*. R. S. C.

Thiocholesterol. T. Wagner-Jauregg and T. Lennartz (*Ber.*, 1941, **74**, [*B*], 27—32).—The " thiocholesterol " of Montignie (A., 1931, 481) is a dithiocholesteryl phosphate (S : P = ~2 : 1). Cholesteryl bromide and NaCNS in boiling aq. EtOH give cholesteryl thiocyanate (**I**), m.p. 129°, $[\alpha]_D$ −10·97°, reduced (Zn–Hg, aq. HCl) to *thiocholesterol* (**II**), m.p. 99·5°, $[\alpha]_D$ −23·85° [*cinnamate*, m.p. 141—142° (turbid), 224—226° (clear), $[\alpha]_D$ −9·96°; *chaulmoograte*, m.p. 67—69°, $[\alpha]_D$ −9·28°; CH_2Ph *ether*, m.p. 98·5°, $[\alpha]_D$ −31·7°]. (**I**) with NaOEt–EtOH, KOH–aq. EtOH, or K_2CO_3–$C_5H_{11}{\cdot}OH$ affords *dicholesteryl disulphide*, m.p. 144·5°, $[\alpha]_D$ −41·78°, which is reduced (Zn–Hg, aq. HCl, PhMe) to (**II**). $[\alpha]$ are in $CHCl_3$. J. Wa.

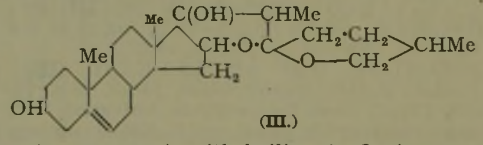
Deoxycholic acid. Preparation from cholic acid. G. A. D. Haslewood (*Chem. Products*, 1943, **6**, 65—66).—An account of work previously abstracted (A., 1942, II, 365; 1943, II, 199). Lithocholic acid is a by-product and arises from 3-hydroxy-7 : 12-diketocholanic acid. S. A. M.

Bile acids. LX. M. Schenck (*Z. physiol. Chem.*, 1940, **264**, 267—273).—When 7-nitrodeoxybilienic acid (**I**) is treated with HNO_3 (*d* 1·4) for 48 hr. at room temp., 6-nitrobilianic acid (**II**) is formed. (**II**) is also formed from bilianic acid dioxime and HNO_3; in this case (**I**) is an intermediate. 6-Aminobilianic acid, which reduces $AgNO_3$–NH_3 on heating, is oxidised to cilianic acid by Fehling's solution. J. N. A.

Behaviour of Δ¹-unsaturated steroid ketones on reduction by fermenting yeast. A. Butenandt, H. Dannenberg, and L. A. Surányi (*Ber.*, 1940, **73**, [*B*], 818—820).—Yeast fermenting in aq. sucrose reduces Δ¹-androstene-3 : 17-dione or Δ¹-androsten-17-ol-3-one to *iso*androstane-3 : 17-diol, but does not affect Δ¹-cholestenone or Δ¹-*allo*pregnenedione. The position of the C:C and the nature of the $C_{(17)}$-substituent thus both affect the reducibility of the Δ$^\alpha$-ketones. R. S. C.

Sterols. CLIV—CLVII. Sapogenins. LXVI. Sapogenin of *Trigonella foenum-graecum*. LXVII. Pennogenin, nologenin, and fesogenin, three new sapogenins from *Beth* root. LXVIII. Steroidal sapogenin from *Balanites aegyptica*, Wall. R. E. Marker, R. B. Wagner, D. P. J. Goldsmith, P. R. Ulshafer, and C. H. Ruof. **LXIX. Isolation and structures of thirteen new steroidal sapogenins. New sources for known sapogenins.** R. E. Marker, R. B. Wagner, P. R. Ulshafer, E. L. Wittbecker, D. P. J. Goldsmith, and C. H. Ruof (*J. Amer. Chem. Soc.*, 1943, **65**, 1247, 1248, 1248—1249, 1199—1209).—LXVI. The sterol from the seed of *T. foenum-graecum* is diosgenin (**I**) (cf. Soliman *et al.*, A., 1943, II, 99).

LXVII. (Cf. A., 1943, II, 239.) The sterols from *Beth* root yield (**I**) (35—60% isolated as acetate), kryptogenin (**II**) (20—40% isolated as acetate), *pennogenin* (**III**), $C_{27}H_{42}O_4$ (10—20%), m.p. 247°, and small amounts of *nologenin* (**IV**), $C_{27}H_{44}O_5$, m.p. 265°, unsaturated (*diacetate*, m.p. 180°), and *fesogenin* (**V**), $C_{27}H_{40}O_3$, m.p. 180°, unsaturated. (**III**) has the structure shown, for it contains 2 OH, no

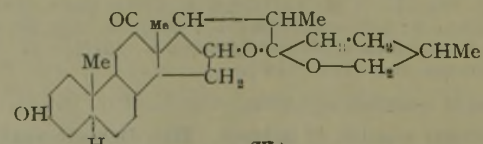


(**III.**)

CO (absorption spectrum), with boiling Ac_2O gives a *monoacetate*, m.p. 200°, and after prolonged treatment with HCl–EtOH yields (**II**). (**V**) contains a conjugated system, since with H_2–Pd–$BaSO_4$ it gives a H_2-, m.p. 213°, and with Na–EtOH a H_4-derivative, m.p. 240°.

LXVIII. " Nitogenin " (Kon *et al.*, A., 1939, II, 332) from *Balanites aegyptica* is really (**I**).

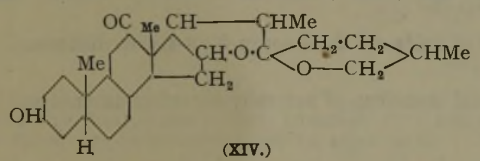
LXIX. Isolation of thirteen new sapogenins and new sources of known sapogenins from Mexican and U.S. plants are briefly recorded. *Hecogenin* (**VI**), $C_{27}H_{42}O_4$, *forms*, m.p. 245°, 253°, and 268°, is obtained from 22 plants [1·3% from *Agave toumeyana*, Trel.; 0·7% from *A. gracilipes*, Trel.; >0·33% (dry wt. in all cases) from the others]. The structure



(**VI.**)

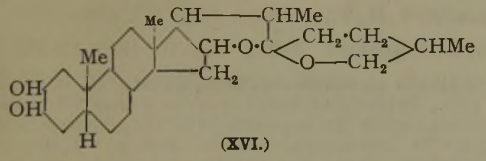
follows from its conversion by boiling Ac_2O into a *monoacetate*,

forms, m.p. 243° and 252°, resistance to Clemmensen reduction, formation of a semicarbazone, oxidation by CrO_3 to *hecogenone* (**VII**), $C_{27}H_{40}O_4$, m.p. 240° (CO at $C_{(3)}$), and then to *hecogenic acid* (**VIII**), $C_{27}H_{40}O_7$, m.p. 268° (decomp.) (fission between $C_{(2)}$ and $C_{(3)}$; Me_2 ester, m.p. 187°), and Wolff–Kishner reduction to tigogenin. *Manogenin* (**IX**), $C_{27}H_{42}O_5$, *forms*, m.p. 241—243°, 254°, and 264° (*diacetate, forms*, m.p. 215°, 242°, and 255°), is isolated from 25 plants [abundantly in *Manfreda maculosa*, Hook; 0·53% from *A. huachucensis*, Baker; >0·17% from other plants]; it is the 2-OH-derivative of (**VI**), since with CrO_3 it gives (**VIII**) and by Wolff–Kishner reduction gives gitogenin (**X**). *Yucca schottii*, Engelm., *Y. elata*, Engelm., and *Y. flaccida*, Haw., yield *yuccagenin* (**XI**), $C_{27}H_{42}O_4$, *forms*, m.p. 246° and 252° (*diacetate*, m.p. 178°), which with H_2–PtO_2 and a little AcOH in Et_2O gives (**X**), with H_2O_2 gives a *tetraol*, $C_{27}H_{44}O_6$, m.p. 350° [with CrO_3–AcOH and then, after dehydration, Zn–AcOH gives chlorogenic acid], and is thus the $\Delta^{5:6}$-derivative of (**X**). *Y. brevifolia*, Engelm., *Y. harrimanii*, Trel., and *Samuela carnerosana*, Trel., contain *kammogenin* (**XII**), $C_{27}H_{40}O_5$, m.p. 242° [*diacetate, forms*, m.p. 243° and 260°; also present in the mother-liquors from (**XI**) obtained from *Y. schottii*], which gives a semicarbazone but resists Clemmensen reduction, gives (**XI**) by Wolff–Kishner reduction, is hydrogenated (PtO_2; Et_2O + a little AcOH) as diacetate to the diacetate of (**IX**), and is thus the 12-CO derivative of (**XI**). *Rockogenin*, $C_{27}H_{44}O_4$, m.p. 221° (*acetate*, m.p. 206°), is isolated with much (**VI**) from *A. gracilipes*, Trel.; it is 12-dihydrohecogenin, being obtained from (**VI**) by H_2–PtO_2 or Na–EtOH and oxidised to (**VII**) by CrO_3–AcOH. The saponins from *A. huachucensis*, Baker (1360 kg.), yield (**IX**) (22%), (**X**) (50%), (**VI**) (22%), and *agavogenin* (**XIII**) (5%), $C_{27}H_{44}O_5$, m.p. 242° (*triacetate*, m.p. 228°). (**XIII**) is 12-dihydromanogenin, being obtained from (**IX**) by H_2–PtO_2 or Na–EtOH and oxidised by CrO_3 to (**VIII**). *Furcogenin* (**XIV**), $C_{27}H_{42}O_4$, m.p. 225°, is obtained from *Furcræa selloa* and, with much smilagenin (**XV**) and little (**XI**), from *Y. flaccida*, Haw. It has the β-configuration at $C_{(3)}$, giving a ppt. with digitonin in EtOH. It gives a *monoacetate*, m.p. 225°, is reduced (Wolff–Kishner) to (**XV**), but resists Clemmensen reduction, and thus has the formula shown. *Samuela carnerosana*, Trel., and *Y. schottii*,



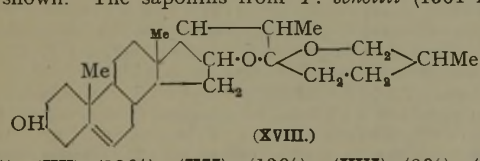
(**XIV.**)

Engel., contain *samogenin* (**XVI**), $C_{27}H_{44}O_4$, m.p. 210—212° (*diacetate*, m.p. 195—198°; digitonide), and *mexogenin* (**XVII**), $C_{27}H_{42}O_5$, m.p. 246° (*diacetate*, m.p. 208°). (**XVI**) is unaffected by boiling HCl–EtOH, is converted by NaOEt at 200° into epi*samogenin* (α-configuration at $C_{(3)}$), m.p. 235—237°, and is oxidised by CrO_3–AcOH to *samogenic acid*, m.p. 264° (decomp.), isomeric with gitogenic acid; the reactions indicate the structure shown. (**XVII**) gives a semi-



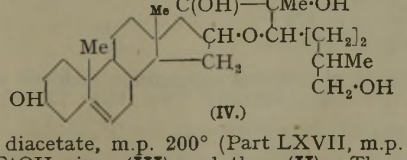
(**XVI.**)

carbazone but resists Clemmensen reduction, by Wolff–Kishner reduction gives (**XVI**), and is thus the 12-CO-derivative of (**XVI**). *Dioscorea testudinaria* and 12 other plants yield (**I**) and *yamogenin* (**XVIII**), $C_{27}H_{42}O_3$, m.p. 200—201° (*acetate*, m.p. 180—182°); this yields (**I**) by isomerisation of the side-chain, is hydrogenated as acetate in Et_2O + AcOH to neotigogenin acetate, and thus has the structure shown. The saponins from *Y. schottii* (1364 kg.) yield



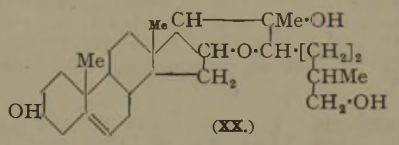
(**XVIII.**)

(**XI**) (59%), (**XV**) (13%), (**XII**) (13%), (**XVI**) (8%), (**X**) (2%), (**XVII**) (1%), and *texogenin* (**XIX**) (4%), $C_{27}H_{44}O_4$, m.p. 171—172° (*diacetate*, m.p. 170—172°). (**XIX**) is converted into (**XVI**) by boiling HCl–EtOH and is thus the $C_{(22)}$-epimeride of (**XVI**). The annexed structure is suggested for (**IV**), since it contains 4 OH, with boiling



(**IV.**)

Ac_2O gives a diacetate, m.p. 200° (Part LXVII, m.p. 180°), and in boiling HCl–EtOH gives (**III**) and then (**II**). The mother-liquor from (**IV**) (from *Beth* root) yields *kappogenin* (**XX**), $C_{27}H_{44}O_4$, m.p. 230°, the structure of which is proved because it possesses 3 OH, gives a *diacetate*, m.p. 178°, with boiling 2N-HCl–EtOH gives (**I**), and



(**XX.**)

with CrO_3 at 25°, followed by hydrolysis, gives $\Delta^{5:16}$-pregnadien-3(β)-ol-20-one. Sarsasapogenin is isolated from 26 (1% from *Y. elata*, Engelm.), (**XV**) from 28 (0·8% from *Y. flaccida*, Haw.; 0·75% from *A. lophantha*), (**X**) from 16 (1—1·1% in *A. schottii*, *Y. filamentosa*, L., and *Manfreda virginica*, L.), chlorogenin from 2, tigogenin from 10 (0·88% from *Y. whipplei typica*), (**I**) from 29, (**II**) from 12, and sitosterol from 18 new sources (0·14% from *Y. arizonica*, McKel.).

R. S. C.

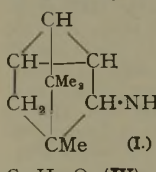
Steroid glucuronide, m.p. 267—269°, from human urine [steroid, m.p. 212—213° (corr.) (acetate, m.p. 192—194°; oxime, m.p. 223—225°)].—See A., 1943, III, 656.

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Unambiguous synthesis of camphor. I. Synthesis of camphononic acid. N. C. Ganguly (*J. Indian Chem. Soc.*, 1943, **20**, 101—104).—$CMe_2Ac{\cdot}CO_2Et$ (100 g.), condensed with $CN{\cdot}CH_2{\cdot}CO_2Et$ in AcOH–NH_2Ac, gives *Et α-cyano-βγγ-trimethylglutaconate*, b.p. 145°/4 mm., which adds HCN to give *Et αβ-dicyano-βγγ-trimethylglutarate*, b.p. 170°/5 mm. Boiling for 30 hr. with 72% H_2SO_4 hydrolyses this to 20 g. of camphoronic acid, m.p. 168°. Me_3 camphoronate (b.p. 134°/3 mm.), obtained using CH_2N_2, is partly hydrolysed (on the primary CO_2Me) by NaOH–MeOH; the mono-acid is then converted into its chloride by $SOCl_2$ in C_6H_6 in presence of C_5H_5N. Following the technique of Bachmann *et al.* (A., 1940, II, 225), the acid chloride in C_6H_6 is treated successively with CH_2N_2 in Et_2O and Ag_2O in MeOH, thus giving Me_3 homocamphoronate, b.p. 150°/5 mm. This with Na dust and a trace of EtOH in C_6H_6 gives *Me_2 2 : 2 : 3-trimethylcyclopentanone-3 : 5-dicarboxylate*, b.p. 157°/9—10 mm., which, when refluxed for 20 hr. with 20% H_2SO_4, gives camphononic acid, m.p. 230—231° (lit. 232°) [oxime, m.p. 189—190° (lit. 186—187°); *Et* ester, b.p. 106—110°/8 mm.]. S. A. M.

Synthesis of *dl*-pinonic acid. F. L. N. Rao (*J. Indian Chem. Soc.*, 1943, **20**, 97—100).—*trans*-Pinic acid (for synthesis cf. A., 1937, II, 377) is converted into *trans*-1-carbethoxy-2 : 2-dimethyl*cyclo*butane-3-acetyl chloride (A., 1938, II, 283, 412), which, with $NHPh_2$ in C_5H_5N, gives the *-3-acetdiphenylamide*, m.p. 99—100°. 95% H_2SO_4, at 60—65°, gives the corresponding *-1-carboxy*-compound (m.p. 139—140°), the acid chloride of which (prepared by using $SOCl_2$) with CdMeCl in Et_2O gives trans-dl-*pinondiphenylamide* (yield 30%) (*semicarbazone*, m.p. 204—205°, undepressed by adding a sample, m.p. 205—206°, prepared from pinonic acid). Boiling MeOH–KOH gives *dl*-pinonic acid, m.p. 103—105°. S. A. M.

Attempted preparation of a tetracyclic hydrocarbon of the camphane series. M. Lipp (née Bredt-Savelsberg) [with N. Proth] (*Ber.*, 1941, **74**, [*B*], 1—6).—2-Amino*cyclo*camphane (**I**), b.p. 125—132°/12 mm. (*phenylcarbamido*cyclo*camphane*, no m.p., sublimes ~150°), is obtained by reduction ($Na + C_5H_{11}{\cdot}OH$) of *cyclo*camphanoneoxime.



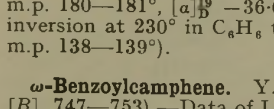
(**I.**)

The hydrochloride of (**I**), KOH, and excess of $ClCO_2Et$ afford the *urethane* (**II**), b.p. 142°/9 mm., $[\alpha]_D^{12}$ −3·06° in EtOH. Because of the instability of the NO-compound obtained when (**II**) is treated with dry N_2O_3 in Et_2O at <−20°, the dried solution is used directly. NaOMe (excess) at −20° affords: (i) not quite pure cyclo*camphanyl Me ether* (**III**), b.p. 64°/12 mm.; (ii) $C_{10}H_{16}O$ (**IV**), sublimes at 82—84°, m.p. (not sharp) 160—163°, $[\alpha]_D^{20}$ +27·72°; (iii) unchanged (**II**). When MeOH-free NaOMe is used (**III**) is not formed. (**IV**) gives an inhomogeneous 3 : 5-dinitrobenzoate (different fractions, m.p. 126—134°). (**IV**) with CrO_3 gives *cyclo*camphane-2-one and is a mixture of *cyclo*camphan-2-ol (3 : 5-dinitrobenzoate, m.p. 138°) and its epimeride. The formation of these products is attributed to the production from the nitroso-urethane of a diazotate, instead of a diazo-compound, which loses N_2 to give the Na-derivative of (**IV**) and reacts with MeOH to give (**III**). J. Wa.

***iso*Alcohols of the camphane series. II. 2-*iso*Hydroxy*cyclo*camphane.** M. Lipp (née Bredt-Savelsberg) [with E. Oeckinghaus and C. L. Conze] (*Ber.*, 1941, **74**, [*B*], 6—12; cf. A., 1935, 496).—Hydrogenations are carried out in a Au-plated steel autoclave. Camphor is completely reduced (H_2–Pt-black–AcOH) at 40—50 atm. and room temp. to 20% of *iso*bornyl acetate and 80% of *iso*borneol (3 : 5-dinitrobenzoate, m.p. 139°; previously recorded m.p. 133° is a misprint; A., 1931, 1068). Camphor and *epi*camphor reduced in methyl*cyclo*hexane (**I**) give respectively *iso*borneol and

>90% of epi-iso*bornyl* 3 : 5-*dinitrobenzoate*, m.p. 118—119°. *cyclo*-Camphan-2-one, purified through the semicarbazone, reduced in (I) gives iso-cyclo*camphanol* 3 : 5-*dinitrobenzoate*, m.p. 112—113° (Kofler micro-m.p. 116°), $[\alpha]_D^{22}$ −75·65° in PhMe (additive compound with α-$C_{10}H_7$·NH_2, m.p. 163—164°). iso-cyclo*Camphanol*, m.p. 180—181°, $[\alpha]_D^{19}$ −36·07° in C_6H_6, as Na-derivative, undergoes inversion at 230° in C_6H_6 to *cyclo*camphanol (3 : 5-dinitrobenzoate. m.p. 138—139°). J. Wa.

ω-Benzoylcamphene. Y. Asahina and T. Sano (*Ber.*, 1940, **73**, [*B*], 747—753).—Data of Lipp *et al.* (A., 1927, 883; 1929, 1308) are modified and extended. The product (**I**), b.p. 145—150°/4 mm., obtained from ω-benzoylborneol by $KHSO_4$ at 180—190°, consists mainly of ω-benzoylcamphene (**II**) with a little *ω-benzoyltricyclene* (**III**). It gives a small amount of the *semicarbazone* (**IV**), m.p. 210—211°, of (**III**). With $KMnO_4$ in $COMe_2$, (**I**) gives BzOH, camphenilone, and a little (**III**), m.p. 59—60°, b.p. ~115°/5 mm. [semicarbazone = (**IV**)]. MgPhBr in boiling Et_2O, followed by aq. NH_4Cl, converts (**III**) into αα-diphenyl-β-tricyclenylethylene (**V**), m.p. 70—71°, b.p. ~154°/0·06 mm. With MgPhBr in boiling Et_2O, (**I**) gives the *diphenylcarbinol*, $C_{23}H_{26}O$, b.p. 174°/0·06 mm., dehydrated by twice boiling with Ac_2O into a (? mixed) hydrocarbon, $C_{23}H_{24}$, b.p. 172—173°/0·08 mm., which with O_3 in $CHCl_3$ gives *tricyclenic acid*, $C_{10}H_{14}O_2$, sinters 149°, m.p. 151°, and with $COPh_2$, and with $KMnO_4$ in $COMe_2$ gives much (**V**) and *substances*, $C_{23}H_{26}O_2$, m.p. 160°, and $C_{23}H_{24}O_3$, m.p. 196—198°, and an *acid*, $C_{10}H_{16}O_3$, m.p. 190—192°. Camphenylideneacetonitrile (**VI**), b.p. 128°/14 mm., with MgPhBr in boiling Et_2O and then aq. NH_4Cl gives (**II**), b.p. 125—127°/0·03 mm. [containing a little (**III**), present in (**VI**)], which with $KMnO_4$ or MgPhBr (and then O_3 or $KMnO_4$) gives the same products as does (**I**). No hydrocarbon, $C_{23}H_{24}$, m.p. 83—84°, could be obtained. R. S. C.


(III.)

Cafesterol. II. P. N. Chakravorty, (Miss) M. M. Wesner, and R. H. Levin (*J. Amer. Chem. Soc.*, 1943, **65**, 929—932; cf. A., 1943, II, 40).—Cafesterol (**I**) which is probably diterpenoid (prep. described), has m.p. 147—151°, $[\alpha]_D^{30}$ −156° in $CHCl_3$; the solution darkens and [α] becomes −161° in 2 weeks. The acetate, m.p. 162—165° (160—165°) [absorption max. at 290 mμ. (ε 6300, decreases on irradiation)], with H_2–Pd–C in EtOH at 34 lb. gives tetrahydrocafesteryl acetate (**II**), m.p. 152—154·5°, $[\alpha]_D^{29}$ −20·4° in $CHCl_3$, and thence tetrahydrocafesterol (**III**), m.p. 154·5—157° (cf. Wettstein *et al.*, A., 1942, II, 198, 371). (:CH·CO)$_2$O combines with (**I**) in C_6H_6 at 35—40° in 0·5 hr. or slowly at room temp. to give the *adduct*, $C_{24}H_{30}O_6$, m.p. 190—192°, $[\alpha]_D^{29}$ −43° in $COMe_2$, wherefore (**I**) contains C:C·C:C. With Zn dust at 180—200°/1·5 mm. (20 min.), followed by distillation at 0·02 mm., (**II**) gives oxcafestanaldehyde, $C_{18}H_{28}O$>CH·CHO, amorphous (*semicarbazone*, m.p. 217—218°; p-*nitrophenylhydrazone*, m.p. 231—233°), converted by $KMnO_4$–$COMe_2$ into *oxcafestanic acid* (**IV**), m.p. 260—262°, $[\alpha]_D^{30}$ −39·7° in $CHCl_3$ (*Me* ester, m.p. 123·5—124·5°), which is unaffected by H_2–PtO_2–HCl–AcOH at 60°/50 lb. (**I**) and (**III**) are œstrogenic (Kahnt–Doisy) in 2-mg. doses. In 20-mg. doses (**IV**) has no cortin activity (Ingle) and contains <1 œstrogenic rat unit per 5 mg. R. S. C.

Cafesterol. III. *iso***Cafesterol.** P. N. Chakravorty, R. H. Levin, (Miss) M. M. Wesner, and G. Reed (*J. Amer. Chem. Soc.*, 1943, **65**, 1325—1328; cf. *supra*).—Adding Na to cafesterol (**I**) in boiling EtOH gives iso*cafesterol* (**II**), m.p. 156—159° [not depressed by (**I**)], $[\alpha]_D^{30}$ −108° in $CHCl_3$, −114° in $COMe_2$ [*acetate* (**III**), m.p. 163—167°, not depressed by the acetate of (**I**)]. (**I**) absorbs 2 and (**II**) absorbs 2·5 O from *o*-CO_2H·C_6H_4·CO_3H in Et_2O; both absorb 8 Br; in presence of Pd–C in EtOH they give the same H_4-derivative. With (:CH·CO)$_2$O in warm C_6H_6, (**II**) gives an *adduct*, m.p. 177—180° (decomp.), $[\alpha]_D^{30}$ −45° in $COMe_2$, converted into (**III**) by Ac_2O–C_5H_5N, and regenerating (**II**) at 130—160°/0·01 mm.; the adduct from (**I**) similarly regenerates (**I**) at 125—145°/0·008 mm., so that the adducts also differ. Boiling NaOMe–MeOH does not convert (**I**) into (**II**). In conc. HCl, (**I**) gives a blue and (**II**) a pink colour, so that acid does not reverse the change. In Pr$^\beta$OH, (**I**) has an absorption max. at 292 mμ. (ε ~6500) and (**II**) at 226 mμ. (ε ~8300); thus the ethylenic linkings in (**I**), but not in (**II**), are probably in the same ring; partial structures are suggested. R. S. C.

Rubber, polyisoprenes, and allied compounds. IV. Relative tendencies towards substitutive and additive reaction during chlorination.—See A., 1943, II, 289.

Constitution of *l*-pimaric acid. W. Sandermann (*Ber.*, 1941, **74**, [*B*], 154—161).—A mixture of pine rosin acid [crude l-pimaric acid (**I**)] and (:C·CO_2Me)$_2$ (**II**) in Et_2O has $[\alpha]_D$ −75° → +87·5° (const.) in 46 hr., indicating, together with the absorption spectrum of (**I**), that the two double linkings of (**I**) are in the same ring. (**I**) and (**II**) at 180° afford no volatile unsaturated hydrocarbon and the adduct gives no definite product with Pd–C at 300°, whilst (**I**) alone gives 80% of retene. The "residual acid," m.p. 162—168°, $[\alpha]_D$ +55° in Et_2O, is obtained from crude (**I**) after removal of (**I**) as the benzoquinone adduct and contains 50% of *d* pimaric acid, abietic acid, and "proabietic" acid. J. Wa.

VI.—HETEROCYCLIC.

Tetrahydrofurfuryl ethers etc.—See B., 1943, II, 283.

3-Chloro-2-ethoxy-2-methyltetrahydrofuran.—See B., 1943, II, 277.

Condensation of pyromucic acid with *N*-methylolamides. R. O. Cinneide (*Proc. Roy. Irish Acad.*, 1943, **49**, **B**, 143—150).—Pyromucic acid and OH·CH_2·NHBz in conc. H_2SO_4 give 5-N-*benzamidomethylfuran*-2-*carboxylic acid* (**I**), m.p. 168—169·5° and 191—192° (two forms) (*Et* ester: labile m.p. 95—96°; stable m.p. 125—127°). Oxidation of (**I**) with $K_3Fe(CN)_6$ gives furan-2 : 5-dicarboxylic acid; (**I**) with boiling $HgCl_2$–H_2O (or H_2O at 150—170° in sealed tube) gives 2-benzamidomethylfuran (**II**) and tetra(chloromercuri)-furan. The Na salt of (**I**) with boiling $HgCl_2$–H_2O yields 5-*benzamidomethyl*-2-*chloromercurifuran*, m.p. 162—164°, which with boiling aq. HCl gives (**II**). Pyromucic acid and OH·CH_2·NH·CO·C_6H_4Me-*p* (prep. described) give 5-p-*toluamidomethylfuran*-2-*carboxylic acid* (**III**), m.p. 195—198°, which reacts like (**II**) with $HgCl_2$–H_2O on heating in a sealed tube. Pyromucic acid and o-*nitrobenzhydroxymethylamide*, m.p. 114—117° (prep. described), give 5-N-o-*nitrobenzamidomethylfuran*-2-*carboxylic acid* (**IV**), m.p. 195—198°, which reacts like (**I**). Preps. of 2-p-*tolu*-, m.p. 102°, 2-*benz*-, m.p. 101—102°, and 2-o-*nitrobenz*-*amidomethylfuran*, m.p. 107—108°, are also given. J. H. Ba.

Pyrones and related compounds. II. New reaction product of acetonedicarboxylic acid and acetic anhydride. R. Kaushal, P. B. Bhisse, and S. S. Deshapande (*J. Indian Chem. Soc.*, 1943, **20**, 51—53).—CO(CH_2·CO_2H)$_2$ is converted by Ac_2O into 2 : 6-dihydroxy-1 : 4-pyrone and 3′-*keto*-6-*methyl*-3′ : 4′-*dihydro*cyclo*butadieno*-1′ : 2′-2 : 3-1 : 4-*pyrone*-5-*carboxylic acid* (**I**), m.p. 157° (*NH_2Ph* salt, m.p. 185°). If a considerable excess of Ac_2O is used (**I**) is the sole product. Its structure is confirmed by its production from Ac_2O and dehydracetocarboxylic acid. H. W.

Action of acids on 2 : 3-epoxy-2 : 3-diphenylindanone.—See A., 1943, II, 266.

Structural chemistry of naturally occurring flavones and flavonols. P. S. Rao and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1943, **17**, **A**, 119—141).—An account of the chemistry of the members of the group. H. W.

Isomorphous replacement of bivalent atoms and ψ-atoms [groups] in organic compounds. G. Bruni (*Ber.*, 1940, **73**, [*B*], 763—764).—The work of Lüttringhaus *et al.* (A., 1940, II, 305) and Rheinboldt *et al.* (A., 1943, II, 263) was anticipated on a much wider scale by Garelli *et al.* (A., 1894, i, 157; 1895, ii, 205) and Bruni (*Ahrens Sammlung*, 1901, **6**, 415), whose results are briefly recapitulated. R. S. C.

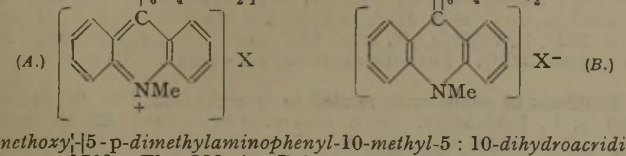
Rubrofusarin, $C_{15}H_{12}O_5$.—See A., 1943, III, 600.

Esters of 1 : 4-dioxan-2 : 3-diol.—See B., 1943, II, 277.

Action of alkalis on substituted benzdioxins. H. Irving and E. G. Curtis (*J.C.S.*, 1943, 319—321).—8-*Nitro*-6-*methyl*-2 : 4-*bistrichloromethyl*-1 : 3-*benzdioxin* (**I**), m.p. 175—176°, is prepared from 3 : 1 : 4-NO_2·C_6H_3Me·OH and chloral hydrate in conc. H_2SO_4. It is unaffected by EtOH–KOAc but EtOH–KOH opens the hetero ring, giving 5-*nitro*-4-*ethoxy*-m-*toluic acid* (**II**), m.p. 148—149°. 7-*Nitro*-6-*methyl*-2 : 4-*bistrichloromethyl*-1 : 3-*benzdioxin*, m.p. 143°, gives the 2 : 4-*bisdichloromethylene* compound, m.p. 101°, with EtOH–KOH. (**I**) with $SnCl_2$ in Ac_2O–AcOH–HCl gives 8-*amino*-6-*methyl*-2 : 4-*bistrichloromethyl*-1 : 3-*benzdioxin*, m.p. 140° (*Ac* derivative, m.p. 171·5°), which with EtOH–KOH gives the 2 : 4-*bisdichloromethylene* compound, m.p. 121° (*Ac* derivative, m.p. 201°). 5 : 7-*Dichloro*-6-*methoxy*-2 : 4-*bistrichloromethyl*-1 : 3-*benzdioxin*, m.p. 189—190° (from the OH-derivative and Me_2SO_4–aq. KOH), gives the 2 : 4-*bisdichloromethylene* derivative, m.p. 114·5°, with EtOH–KOH. 6-*p*-Toluneazo-2 : 4-bistrichloromethyl-1 : 3-benzdioxin with EtOH–KOH also gives the 2 : 4-*bisdichloromethylene* derivative, m.p. 147—148°. Di-(6-nitrobenzdioxinyl)-8 : 8′-ketone with aq, NaOH gives CH_2O and 5 : 5′-*dinitro*-2 : 2′-*dihydroxy*-3 : 3′-*bishydroxymethylbenzophenone*, m.p. 260° (*phenylhydrazone*, m.p. 226—227°). These results confirm the mechanisms previously (A., 1934, 531) proposed. 4 : 1 : 3-OEt·C_6H_3Me·CO_2Et [from 4 : 1 : 3-OH·C_6H_3Me·CO_2H (**III**), Et_2SO_4, and K_2CO_3 in $COMe_2$ or from the Et ester of (**III**), EtBr, and NaOEt] is hydrolysed (aq. EtOH–KOH) to the *acid*, m.p. 76—78°, which is nitrated to (**II**). Nitration of (**III**) gives the 5-NO_2-derivative, new m.p. 176—177°, decarboxylated (boiling quinoline) to 3 : 1 : 4-NO_2·C_6H_3Me·OH. J. H. Ba.

Condensation of phosphorus oxychloride–acridone with dimethylaniline. K. Gleu and A. Schubert (*Ber.*, 1940, **73**, [*B*], 757—761).—Acridones and $POCl_3$ give compounds, [*o*-C_6H_4<CCl=NR>C_6H_4-*o*]PO_2Cl_2, in which the Cl at $C_{(5)}$ is very reactive. Thus, melting 10-methyl-

acridone, $POCl_3$, and $NPhMe_2$ gives a blue melt (*A*) (X = PO_2Cl_2), which in ice gives the carbinol, converted by boiling MeOH into



5-*methoxy*-|5-p-*dimethylaminophenyl*-10-*methyl*-5 : 10-*dihydroacridine* (**I**), m.p. 170°. The OMe in (**I**) is mobile, for, with boiling EtOH, (**I**) gives 5-*ethoxy*-, m.p. 139°, with dil. HCl and then NaOH gives impure 5-hydroxy- (**II**), m.p. 129°, unstable, and with 13N-aq. NH_3 gives 5-*amino*-, m.p. 146°, -5-p-*dimethylaminophenyl*-10-*methyl*-5 : 10-*dihydroacridine*. Treating (**I**) with 2N-HCl and then with NaOH until pptn. of (**II**) begins, heating at 60°, and saturating with NaCl yields the blue 5-p-*dimethylaminophenyl*-10-*methylacridinium chloride* (*A* ⟷ *B*) (X = Cl) +2·5H_2O, which in an excess of mineral acid gives pale yellow, non-resonating, sol. salts in which both N are combined with acid; a *nitrate*, $[C_{22}H_{21}N_2]NO_3,2HNO_3$, is isolated. 10-Phenylacridone similarly yields 5-*methoxy*-, m.p. 210—211°, 5-*ethoxy*-, m.p. 154°, and 5-*amino*-, m.p. 181°, -10-*phenyl*-5-p-*dimethylaminophenyl*-5 : 10-*dihydroacridine*, and a blue acridinium chloride. R. S. C.

Interaction of phosphorus oxychloride–acridone with Grignard reagents. K. Gleu and A. Schubert (*Ber.*, 1940, **73**, [*B*], 805—811).—The compound obtained from acridone and $POCl_3$ with MgPhBr in Et_2O gives PPh_2O_2H, 5 : 5′-diacridyl, and Ph_2. With 10-substituted acridones further reduction occurs. Thus, 10-methyl- or 10-phenyl-acridone gives 10 : 10′-dimethyl- or 10 : 10′-diphenyl-5 : 5′-diacridylidene with, after treatment with HNO_3, 10 : 10′-dimethyl- or 10 : 10′-diphenyl-diacridylium dinitrate. R. S. C.

Diketopyrazolidines. H. Ruhkopf (*Ber.*, 1940, **73**, [*B*], 820—822).—Diketopyrazolidines are obtained from (*a*) N_2H_4,H_2O (excess), $CR_2(CO_2Et)_2$ (R = H, alkyl, or aryl), (*b*) NHPh·NH_2, $CR_2(CO_2Et)_2$ (R = H or alkyl, not aryl), or (*c*) $(NHPh)_2$, $CH_2(CO_2Et)_2$ (not its derivatives), and, in all cases, NaOEt in EtOH at 180—200°. The products containing no, or one, substituent on N are acetylated by boiling Ac_2O, but di-*N*-substituted products are unaffected. Thus are prepared 3 : 5-diketo-4 : 4-diethyl- (90%), m.p. 270° (lit. 256°, 260—261°), -4 : 4-*di*-n-*propyl*- (70%), m.p. 256° [some $CPr^n_2(CO_2H)_2$ is also formed], -4-*phenyl*-4-*ethyl*- (**I**) (70%), m.p. 198° (3-O-*Ac* derivative, m.p. 159·5°), -4-*ethyl*-4-n-*propyl*- (70%), m.p. 232·5°, -4 : 4-*diallyl*- (70%), m.p. 280°, and -1 : 2-*diphenyl*- (90%), m.p. 173·5°, -1 : 2-*pyrazolidine*. These products are fairly sol. in H_2O and stable to acid and alkali (*e.g.*, boiling 50% KOH for 50 hr. or autoclaving at 10 atm.); they have no, or a weakly acid, taste, never a bitter one, and resemble pyrazolones in physiological action but have no advantage thereover. With Br in hot AcOH, (**I**) gives 3 : 5-*diketo*-1 : 2-*phenylethylmalonyl*-4-*phenyl*-4-*ethylpyrazolidine* (40%), CPhEt<CO·N·CO / CO·N·CO>CPhEt, m.p. 238°, and some $CPhEt(CO_2H)_2$. R. S. C.

Bacterial inhibition by metabolite analogues. V. Reactions and antibacterial properties of *p*-diazine di-*N*-oxides. H. McIlwain (*J.C.S.*, 1943, 322—325).—The *di-N-oxides* of the following have been prepared by treatment of the appropriate base in AcOH with 100-vol. H_2O_2: *quinoxaline*, m.p. 238—239°, 2-*methylquinoxaline* (**I**), m.p. 180—181°, 2-*methyl*-3-n-*amylquinoxaline*, m.p. 107°, and 1 : 2 : 3 : 4-*tetrahydrophenazine*, m.p. 188°. Iodinin [di-*N*-oxide of the dihydroxyphenazine obtained fron *Chromobacterium iodinum* (cf. Clemo *et al.*, A., 1938, II, 248)] could only be prepared using BzO_2H–C_6H_6. The oxides retain the basic characters of the diazines, but those with saturated 2-substituents have also acidic properties, explained as due to tautomeric oxime forms. (**I**) changes in alkali to a blue product, the conversion being accelerated by light. Two quinoxaline di-*N*-oxides characterised by unsubstituted 2-positions react with keto-methylene compounds in dil. alkaline solution. All the di-*N*-oxides are readily reduced to the diazines, whilst quinoxalines, but not phenazines, undergo further fission (Zn–H_2SO_4) to *o*-$C_6H_4(NH_2)_2$ and monoketones. All the di-*N*-oxides are inhibitory to bacterial growth in concns. in which their parent diazines are inactive. F. R. S.

Preparation and cleavage of *d-arabo*-tetrahydroxybutylquinoxaline. H. Ohle and M. Hielscher (*Ber.*, 1941, **74**, [*B*], 13—17; cf. A., 1934, 392).—Optimal conditions for the prep. of 3-*d-arabo*-tetrahydroxybutylquinoxaline (**I**) from fructose (62% yield) are given. Glucose and mannose give only 35% yields. Cleavage of (**I**) with 5 mols. of NHPh·NH_2 in boiling H_2O (H_2 atm.) proceeds slowly, giving a ppt. of quinoxaline-3-aldehydephenylhydrazone (**II**) (9%), m.p. 234°, NH_3 (18·4%), unchanged (**I**) (73%), and NH_2Ph (11%). Cleavage in alkaline solution shows that 2·79 mols. of NHPh·NH_2 are consumed per mol. of (**I**), but no H_2O-insol. material is produced. Cleavage in boiling dil. AcOH (H_2 atm.) gives unchanged (**I**) (60%) and a *compound*, $C_{18}H_{16}O_3N_4$ (**III**) (29·5%), m.p. 218°, $[\alpha]_D^{23}$ −19·1° in C_5H_5N; repetition on a large scale gives a small amount of (**II**). (**III**) with Ac_2O–C_5H_5N gives a *triacetate*, m.p. 123—124°, $[\alpha]_D^{22}$ +81·5° in C_5H_5N, $[\alpha]_D^{21}$ +64·4° in $CHCl_3$. Catalytic deacetylation (Zemplén) regenerates (**III**), which thus retains the side-chain of (**I**). J. Wa.

New syntheses of heterocyclic compounds. II. 2-Phenyl-3 : 4 : 6 : 7-dibenzo-1 : 5-naphthyridine. V. A. Petrow, M. V. Stack, and W. R. Wragg (*J.C.S.*, 1943, 316—318).—2-(o-*Benzamidophenyl*)*pyridine* (**I**), m.p. 117° [*picrate*, m.p. 155° (decomp.)], is obtained from the corresponding NH_2-compound [*picrate*, m.p. 185—186° (decomp.)], and the 3-*o*-*derivative* (**II**), m.p. 132° [*picrate*, m.p. 168° (decomp.)], is similarly prepared from the NH_2-compound [*picrate*, m.p. 164° (decomp.)]. 2-Amino- furnishes 2-*acetamido*-3-*phenylquinoline* (**III**), m.p. 107—108°. 2-(o-*Benzamidophenyl*)-*quinoline* (**IV**), m.p. 124°, is obtained by benzoylation of the NH_2-derivative. Attempts to cyclise compounds (**I**)—(**IV**) have not been successful. *Benzoylphenacylamine*, m.p. 125—126°, prepared along with the *Bz*$_2$ compound, m.p. 173—174°, from the corresponding amine, condenses with isatin in EtOH–KOH to form 3-*benzamido*-2-*phenylquinoline*-4-*carboxylic acid*, m.p. 254—255°, which with H_3PO_4 gives 3-amino-2-phenylquinoline [3-*NHBz*- (**V**), m.p. 179—180°, and 3-p-*nitrobenzamido*-derivatives, m.p. 223°]. Cyclisation of (**V**) with P_2O_5 affords 2-*phenyl*-3 : 4 : 6 : 7-*dibenzo*-1 : 5-*naphthyridine*, m.p. 197—198° (*monopicrate*, m.p. 240—241°), whilst the corresponding Ac derivative yields an unidentified *product*, m.p, 199°. F. R. S.

Synthesis of nitrogenous hetero-rings. XX. Synthesis of dibenzpyridocoline derivatives. III. Synthesis of 3′ : 4′ : 3″ : 4″-tetramethoxy-1 : 4 : 5 : 8-tetrahydro-2 : 3 : 6 : 7-dibenzpyridocoline [etc.]. S. Sugasawa, K. Kakemi, and H. Kazumi (*Ber.*, 1940, **73**, [*B*], 782—789; cf. A., 1939, II, 281).—*Diveratryl ketone* (prep. from *Pb homoveratrate* at 240—270°/vac.; not from alkaline-earth salts), m.p. 98—99° (*oxime*, m.p. 108—111°), with $(NH_4)_2CO_3$ and HCO_2H at 170—175° gives the N-*CHO* derivative, m.p. 129—130°, hydrolysed by hot 20% HCl to *ββ′-di*-3 : 4-*dimethoxyphenylisopropylamine* (**I**), m.p. 88—89° (*picrate*, decomp. 147—149°; *Bz* derivative, m.p. 156°), and cyclised by $POCl_3$ in xylene at 100° to 6 : 7-dimethoxy-3-veratryl-3 : 4-dihydro*iso*quinoline (**II**), an oil (*perchlorate*, m.p. 230—232°). H_2 converts (**II**) in presence of PtO_2 and a little HCl in EtOH into 6 : 7-*dimethoxy*-3-*veratryl*-1 : 2 : 3 : 4-*tetrahydroisoquinoline hydrochloride*, m.p. 206° [*Bz* derivative, m.p. 149—150°, of the base (**III**)], which with CH_2O in aq. HCl at 100° gives 3′ : 4′ : 3″ : 4″-*tetramethoxy*-1 : 4 : 5 : 8-*tetrahydro*-2 : 3 : 6 : 7-*dibenz-quinolizine* [*-pyridocoline*] (**IV**), m.p. 283—284° (decomp.) [*hydrochloride*, +0·5H_2O, m.p. 272° (decomp.); *methiodide*, +4H_2O, brown at ~250°, decomp. 266°]. Heating (**III**) in 90% HCO_2H, treating the product with $POCl_3$ at room temp. and then 100° and finally with KI in dil. HCl gives 3′ : 4′ : 3″ : 4″-*tetramethoxy*-1 : 4 : 4a : 8-*tetrahydro*-2 : 3 : 6 : 7-*dibenzpyridocolinium iodide*, +H_2O, m.p. 190—192° (decomp.), which absorbs 2 H (catalyst) to give (**IV**) and with I in EtOH gives the 1 : 4 : 5 : 8-H_4-isomeride, m.p. 225—226° [also gives (**IV**) by hydrogenation (2 H)]. (**I**) gives (Schotten–Baumann) the N-*homoveratryl* derivative, m.p. 138—139°, converted (PCl_5–xylene) into 6 : 7-*dimethoxy*-1 : 3-*diveratryl*-3 : 4-*di*-, +H_2O, m.p. 150° (*hydrochloride*, +1·5H_2O, decomp. 180°; *picrate*, +1·5H_2O, decomp. 196—197°), and thence -1 : 2 : 3 : 4-*tetra-hydroisoquinoline* (**V**), m.p. 134—135° (*hydrochloride*, +0·5H_2O, decomp. 214—215°). CH_2O–aq. HCl at 100° converts (**V**) into a mixture, which by chromatography (Al_2O_3–C_6H_6) gives 3′ : 4′ : 3″ : 4″-*tetramethoxy*-1-*veratryl*-1 : 4 : 5 : 8-*tetrahydropyridocoline* (**VI**), m.p. 172° (*hydrochloride*, decomp. 229—230°), and a mixture, m.p. 110—130°, possibly containing veratryltetrahydro*isopalmitin*. With, successively, 3 : 4 : 1-$(OMe)_2C_6H_3$·CH_2·COCl–NaOH, $POCl_3$–xylene, and KI, (**III**) gives 3′ : 4′ : 3″ : 4″-*tetramethoxy*-1-*veratryl*-4 : 4a : 5 : 8-*tetrahydro*-2 : 3 : 6 : 7-*dibenzpyridocolinium iodide*, +2H_2O, decomp. 183—184°, hydrogenated (2 H) in EtOH to (**VI**). R. S. C.

Pyrazoles, pyridylpyrazoles, etc.—See B., 1943, II, 302.

Constitution of 1-phenyl-*d*-fructosone.—See A., 1943, II, 294.

Effect of caffeine and other iminazole compounds on hæmatins and their derivatives. J. Keilin (*Biochem. J.*, 1943, **37**, 281—289).—When caffeine (**I**) is added to an alkaline solution of protohæm, the solution turns from reddish-brown to red and the two diffuse absorption bands are replaced by much stronger bands of shorter λ; the solution is no longer opalescent, and no ppt. is formed on keeping. A similar effect is produced by (**I**) on meso-, deutero-, and hæmatohæm. The product so obtained is not a caffeine-hæmochromogen since the (**I**) combines with the porphyrin and not with the Fe$^{\cdot\cdot}$. ~20 mols. of (**I**) per mol. of hæm or prophyrin are required for complete transformation. (**I**) also reacts with CO-protohæm (**II**), and the two absorption bands at 565 and 542 mμ. are shifted to 590 and 551 mμ., respectively. Only 1 mol. of (**I**) per mol. of (**II**) is required to produce this change. (**I**) gives no reaction of this type with CO-hæms such as those derived from hæmato-, deutero-, and meso-hæmatin. It is suggested that a CO-caffeine-hæmochromogen may be formed, or the (**I**) may react with the porphyrin. Only (**I**) and chlorocaffeine (**III**) out of a large no. of purines including theo-

bromine, theophylline, and 1 : 3 : 7-trimethyluric acid react in this way with hæm, (**II**), porphyrin, and metallo-porphyrins. The fact that (**III**) behaves like (**I**) shows that the H in position 8 can be replaced by Cl, but not by O. Thymine, cytosine, and uracil are without effect on various hæms or their porphyrins. Of all the glyoxaline compounds tested only pilocarpine, and to a smaller extent 1-methylglyoxaline, react like (**I**) with the porphyrin, but, in contrast to (**I**), they yield parahæmatin, hæmochromogen, and CO-hæmochromogen compounds with hæmatin, hæm, and CO-hæm respectively. Globin and certain serum-proteins react with porphyrin in the same manner as (**I**) does, whilst none of their constituent NH_2-acids including histidine gives the reaction, and it is suggested that either these proteins contain another, not yet isolated, constituent having the above properties, or that the glyoxaline ring of histidine, when it is part of a polypeptide chain, may have some of the properties of the glyoxaline rings of (**I**) and pilocarpine. The bearing of the results on the physico-chemical properties and pharmacology of (**I**), and on the mechanism of (**I**) diuresis, is discussed. J. N. A.

Chlorophyll-*c*.—See A., 1943, III, 703.

Benzthiazoles.—See B., 1943, II, 302.

Aldehydo-methylene derivatives of quinolines, benzoxazolines, and thiazolines.—See B., 1943, II, 278.

Quinolines ox- and thi-azolines.—See B., 1943, II, 278.

Thiazinocyanines. II. Cyanines containing the dihydro-1 : 3-thiazine nucleus. (Miss) F. M. Hamer and R. J. Rathbone (*J.C.S.*, 1943, 243—249; cf. A., 1942, II, 182).—2-Thiotetrahydro-1 : 3-diazine with Me_2SO_4 gives the 2-*Me*, b.p. 155—160°/50 mm., and with Et_2SO_4 affords the 2-*Et* derivative, b.p. 145—150°/40 mm. The Me compound with MeI yields 2-*methylthioldihydro*-1 : 3-*diazine methiodide* (**I**), m.p. 132—133°, with considerable loss on crystallisation; the 2-*Et ethiodide* (**II**), m.p. 98°, is similarly obtained. C_5H_5N and (**I**) form 2-*thio*-3-*methyltetrahydro*-1 : 3-*thiazine*, m.p. 88°, and the 3-*Et* compound, similarly obtained, has m.p. 68°. 2-Methyldihydro-1 : 3-thiazine methiodide with NPh:CH·NHPh gives 2-*β-anilinovinyldihydro*-1 : 3-*thiazine methiodide*, m.p. 165° (*Ac* derivative, m.p. 180—185°). 2-Methylbenzoxazole ethiodide, NEt_3, and (**II**) in EtOH afford [2-(3-*ethyldihydro*-1 : 3-*thiazine*)][2-(3-*ethylbenzoxazole*)]-, m.p. 260° (decomp.), and [2-(3-*methyldihydro*-1 : 3-*thiazine*)][2-(3-*ethyl*-6 : 7-*benzbenzoxazole*)]-*methincyanine iodide*, m.p. 264° (decomp.) is prepared from (**I**), NEt_3, and 2-methyl-6 : 7-benzbenzoxazole ethiodide. [2-(3-*Methyldihydro*-1 : 3-*thiazine*)][2-(3-*methylbenzthiazole*)]-*methincyanine iodide*, m.p. 283° (decomp.), is obtained from (**I**), 2-methylbenzthiazole methiodide, and K_2CO_3, whilst the corresponding Et derivative, m.p. 265° (decomp.) (lit. decomp. 238°), is prepared from (**II**) and the ethiodide. Similar preps. are made from (**I**) or (**II**) with the appropriate benzthiazole derivative: [2-(3-*methyldihydro*-1 : 3-*thiazine*)][2-(3-*methyl*-4 : 5-, m.p. 226° (decomp.) [*Et* compound, m.p. 238° (decomp.)], and -6 : 7-*benzbenzthiazole*)]-*methincyanine iodide*, m.p. 267° (decomp.) [*Et* compound, m.p. 254° (decomp.)]; [2-(3-*ethyldihydro*-1 : 3-*thiazine*)][2-(5-*chloro*-3-*ethylbenzthiazole*)]-, m.p. 251° (decomp.), [2-(3-*methyldihydro*-1 : 3-*thiazine*)][2-(6-*chloro*-, m.p. 283° (decomp.), -(6-*acetamido*-, m.p. 279° (decomp.), and -(3-*ethylbenzthiazole*)]-*methincyanine iodide*, decomp. 249°; [2-(3-*ethyldihydro*-1 : 3-*thiazine*)]-[2-(3-*ethylbenzselenazole*)]*methincyanine iodide*, m.p. 264° (decomp.), and the corresponding *Me* derivative, m.p. 271° (decomp.); [2-(3-*methyldihydro*-1 : 3-*thiazine*)][2-(1-*methylquinoline*)]-, m.p. 225°/decomp.), [2-(1-*ethylquinoline*)-, m.p. 189° (decomp.) [*Et* derivative, m.p. 169° (decomp.)], [4-(1-*methylquinoline*)]-, m.p. 164—165° (decomp.), and [4-(1-*ethylquinoline*)]-*methincyanine iodide*, m.p. 202° (decomp.) [*Et* derivative, m.p. 191° (decomp.); *bis*-2-(3-*methyldihydro*-1 : 3-*thiazine*)*trimethincyanine iodide*, m.p. 188° (decomp.), and the *Et* derivative, m.p. 243° (decomp.); [2-(3-*methyldihydro*-1 : 3-*thiazine*)][2-(3-*ethylbenzoxazole*)]-, m.p. 270° (decomp.), and -3(-*ethylbenzthiazole*)]-*trimethincyanine iodide*, m.p. 275° (decomp.); 5 : 2′-(3′-*ethyltetrahydro*-1′ : 3′-*thiazyl*)-3-*ethylrhodanine*, m.p. 102°; 5 : 2′-(3′-*methyltetrahydro*-1′ : 3′-*thiazyl*)*ethylidene*-3-*rhodanine*, m.p. 195° (decomp.); and 5 : 2′-(3′-*methyltetrahydrothiazolyl*)*ethylidene*-3-*ethylrhodanine*, m.p. 219° (decomp.). Absorption max. of the various dyes have been compared. Replacement of the thiazoline by the dihydro-1 : 3-thiazine nucleus produces a bathochromic shift. F. R. S.

VII.—ALKALOIDS.

Alkaloids of *Thermopsis rhombifolia* (Nutt.), Richards. R. H. F. Manske and L. Marion (*Canad. J. Res.*, 1943, **21**, **B**, 144—148; cf. A., 1943, III, 294).—*T. rhombifolia* (excluding roots) contains *N*-methylcystisine (0·107), thermopsine (0·048), 3-methoxypyridine, rhombifoline (0·022), $C_{15}H_{20}O_2N_2$ (?) (*perchlorate*, m.p. 242°; *picrate*, m.p. 207°), cytisine (0·009), rhombinine (0·004%), $C_{16}H_{22}O_2N_2$ (?) [*perchlorate*, m.p. 313° (bath preheated to 305°); *picrate*, m.p. 253°], and neutral *compounds A*, $C_{19}H_{20}O_{10}$, m.p. 218—220°, and *B*, $C_{22}H_{16}O_6$, m.p. 257°. All m.p. are corr. A. Li.

Alkaloids of papaveraceous plants. XXXVIII. *Bocconia arborea*, **Wats.** R. H. F. Manske (*Canad. J. Res.*, 1943, **21**, **B**, 140—143).—*B. arborea* (excluding roots) contains chelerythrine (0·86), protopine (0·04%), *allo*cryptopine, *alkaloid P*61, $C_{21}H_{19}O_5N$ (? 2 OMe and 1 NMe groups), m.p. 210°, and neutral *compounds A*, $C_{20}H_{17}O_4N$, m.p. 302°, *B*, $C_{20}H_{15}O_4N$, m.p. 191°, and *C*, $C_{31}H_{33}O_5N$, m.p. 332° (shrinks at 327°). Phenolic alkaloids are absent. All m.p. are corr. A. Li.

Synthesis of compounds related to lysergic acid. H. W. Murphy and G. L. Jenkins (*J. Amer. Pharm. Assoc.*, 1943, **32**, 83—89).—Aq. *p*-NH_2·NH·C_6H_4·CO_2H,HCl (**I**) with $COMe_2$ gives acetone-*p*-carboxyphenylhydrazone, m.p. 230° (decomp.), which, when heated with anhyd. $ZnCl_2$ to 175—185°, yields 2-methylindole and not the expected 2-methylindole-5-carboxylic acid. Similarly, n-*butaldehyde*-p-*carboxyphenylhydrazone*, m.p. 170°, failed to yield the expected indole derivative. Na 1 : 2 : 3 : 4-tetrahydrocarbazole-6-carboxylic acid (1 mol.) [from *cyclo*hexanone-*p*-carboxyphenylhydrazone (Collar and Plant, A., 1926, 735)] with dry Cl·$[CH_2]_2$·$NHEt_2$Cl (**II**) (1 mol.) (Gough and King, A., 1928, 1231) at 150° for 1½ hr., liberation of base by aq. NH_3, and treatment with Et_2O–HCl affords *β-diethylaminoethyl*-1 : 2 : 3 : 4-*tetrahydrocarbazole*-6-*carboxylate hydrochloride*, m.p. 241—242°. *cyclo*Hexanone-*m*-carboxyphenylhydrazone yields on cyclisation with 20% H_2SO_4 two acids, m.p. 286° and 212°, probably 1 : 2 : 3 : 4-tetrahydrocarbazole-5- and -7-carboxylic acid, but neither gave the corresponding acid chloride with $SOCl_2$ or $SOCl_2$–C_5H_5N. *o*-NH_2·NH·C_6H_4·CO_2H (from anthranilic acid) is freed from *o*-diazobenzimide by reduction with Zn–AcOH, addition of HCl, and removal of the imide by filtration; with *cyclo*hexanone, the acid (warm, aq. hydrochloride) gives *cyclo*hexanone-*o*-carboxyphenylhydrazone, m.p. 162°, cyclised by 20% H_2SO_4 to 1 : 2 : 3 : 4-*tetrahydrocarbazole*-8-*carboxylic acid*, m.p. 203° (*Et* ester, m.p. 76°), the Na salt of which with dry (**II**) at 150° for 2 hr. and treatment as above gives *β-diethylaminoethyl*-1 : 2 : 3 : 4-*tetrahydrocarbazole*-8-*carboxylate hydrochloride*, m.p. 208°. In an attempt to prepare 4-chloro-1 : 2 : 3 : 4-tetrahydrocarbazole-6-carboxylic acid, 2-chloro*cyclo*hexanone is treated with excess of $NHEt_2$ in presence of NaI at room temp., giving (2-*keto*-1-*cyclohexyl*)*diethylamine* [2-*diethylamino*cyclo*hexanone*], b.p. 188°/742 mm. (*hydrochloride*, m.p. 226—228°). Camphor in EtOH, refluxed with (**I**) and NaOAc for 2 hr., gives *camphor*-p-*carboxyphenylhydrazone*, m.p. 251°; attempts to cyclise this to 1-methyl-1 : 4-(dimethylmethylene)-1 : 2 : 3 : 4-tetrahydrocarbazole-6-carboxylic acid failed, as did attempts to prepare the corresponding -8-carboxylic acid from *camphor*-o-*carboxyphenylhydrazone*, m.p. 224—226° (decomp.). Et *cyclo*hexan-2-one-1-carboxylate with diazotised *p*-phenetidine gives 1-*Et* 2-*ketopimelate* p-*ethoxyphenylhydrazone*, m.p. 114°, cyclised by 10% H_2SO_4 in EtOH to *Et*$_2$ γ-(2-*carboxy*-5-*ethoxy*-3-*indolyl*)*butyrate*, m.p. 93°; the free *acid*, m.p. 206°, is decarboxylated by heating with a small amount of powdered glass to 220—230° to γ-(5-*ethoxy*-3-*indolyl*)*butyric acid*, m.p. 133° [*Et* (**III**), m.p. 69°, and *Me* ester (**IV**), m.p. 84°] (**III**) is reduced (EtOH–Na) to δ-5-*ethoxy*-3-*indolylbutyl alcohol*, b.p. 215°/2 mm. (*phenylurethane*, m.p. 117—118°). (**IV**) with N_2H_4,H_2O–EtOH at 130—145° yields γ-(5-*ethoxy*-3-*indolyl*)-*butyrhydrazide*, m.p. 157°, which with aq. HNO_2 at 0° gives the corresponding azide; this added in small amounts to H_2O at 100° fails to yield *NN′*-bis-(5-ethoxy-3-indolyl)propylcarbamide, but the waste liquor affords γ-(5-*ethoxy*-3-*indolyl*)*propylammonium chloride*, m.p. 205°. F. O. H.

Strychnine alkaloids. CX. Strychnone and ψ-strychnone as by-products of the preparation of ψ-strychnine. Further experiments in the series. CXI. Transformations of dihydro-ψ-strychnine. H. Leuchs and F. Räck (*Ber.*, 1940, **73**, [*B*], 731—739, 811—817).—CX. The neutral by-products (10—15%) obtained during oxidation of strychnine (**I**) in $CHCl_3$ by Fehling's solution (A., 1937, II, 435) contain *strychnone* (**II**) (3—4·5%), $C_{21}H_{20}O_3N_2$, sinters 240°, m.p. ~268° (decomp.; vac.), [α] −667°/*d* in $CHCl_3$, and *ψ-strychnone* (**III**) (~0·5%), $C_{21}H_{20}O_4N_2$, m.p. 315—317° (decomp.; vac.), [α] +33·3°/*d* in $CHCl_3$. In (**II**) the CH_2 next to N-*b* has been oxidised to CO, so that (**II**) is " diamidostrychnine " and its neutral properties are accounted for. H_2–PtO_2 converts (**II**) in 50% AcOH into a H_2-derivative, m.p. 165—175° (vac.), [α] −365°/*d* in $CHCl_3$. 12N-HCl at room temp. hydrolyses (**II**) to the NH_2-acid, " *strychnone hydrate* " (**IV**), sinters 200°, m.p. 220—225° (vac.), and an amorphous, blue *product*, $C_{42}H_{38}O_6N_2$,HCl. (**IV**) is sol. in NH_3 or HCl; its hydrochloride is readily hydrolysed. Ac_2O at 100° reconverts (**IV**) into (**II**). H_2–PtO_2 converts (**III**) in 50% AcOH into its H_2-derivative, sinters 290°, m.p. ~330° (decomp.; vac.), [α] +116°/*d* in AcOH, previously obtained as an impurity in dihydro-ψ-strychnine. Adding SO_2 to strychnine oxide in warm aq. HCl gives (**I**) and an inner *salt*, $C_{21}H_{22}O_2N_2,SO_3$, m.p. 270—275° (decomp.; vac.), containing a semipolar N–S linking. ψ-Strychnine reacts with aq. SO_2 only in presence of pptd. MnO_2; warming this mixture gives C-*sulphonic acids*, (*a*) decomp. 280—305°, [α] −150°/*d* in 0·1N-NaOH, and (*b*) +5H_2O, [α] (anhyd.) −189°/*d* in 0·1N-NaOH. At 100—125°/vac., (*b*) becomes orange and loses >5 H_2O, presumably forming an anhydro-salt or lactone. Zn dust in boiling 50% AcOH converts (*a*) into strychninesulphonic acid-I, [α] −230° in 0·1N-NaOH. *N*-Methyl-*sec.*-ψ-strychnine (**V**), with SO_2–MnO_2 also gives a mixture;

a *sulphonic acid*, $[\alpha]$ −128·0°/*d*, and a mixture, $[\alpha]$ −31·8°/*d* in 0·1N-NaOH, are isolated. Although a ketone, (**V**) gives no oxime and in aq. HBr (1 mol.) gives only a Br_1-compound (50%) [*perchlorate* (**VI**); Br is attached to a C_6H_5 nucleus]. Only amorphous material is obtained from (**V**) by $KMnO_4$–$COMe_2$. The methoperchlorate (**VII**) of (**V**) and Br (4 atoms) in H_2O give similarly only a perbromide, whence SO_2 yields the Br_1-derivative *methoperchlorate*, $C_{22}H_{24}O_3N_2,MeClO_4$, m.p. 290—295° (decomp.). With Br–$CHCl_3$ at 0° and then aq. $HClO_4$, (**VIII**) gives a perbromide and thence a Br_2-derivative *methoperchlorate*, $C_{22}H_{22}O_3N_2Br_2,MeClO_4$, decomp. 260—330°. Reduction of the methiodide of (**VIII**) by Na–Hg in H_2O gives an amorphous mixture, whence MeI yields a small amount of a *salt*, $C_{24}H_{30}O_3N_2,MeI$, m.p. 275—278° (decomp.); Na–Hg reduces (**VIII**) in MeOH to a product, m.p. 170—172° (vac.). Oxidation of (**VIII**) by $KMnO_4$–$COMe_2$ gives no identifiable products; that of the ether, $C_{24}H_{32}O_3N_2$ (**IX**), results only in hydrolysis to the base, $C_{23}H_{30}O_3N_2$ (*perchlorate*). The base, $C_{24}H_{34}O_3N_2$, m.p. 128° (A., 1938, II, 208), with CNBr in C_6H_6 gives the quaternary salt (derived perchlorate, m.p. ~280°) and *cyanoamide*, $C_{24}H_{31}O_3N_2$, m.p. 110° (decomp.); (**IX**) gives similarly a quaternary salt [derived *methoperchlorate*, $C_{23}H_{30}O_3N_2,MeClO_4$, m.p. 295—300° (decomp.)] and *cyanoamide*, $C_{24}H_{29}O_3N_3$, sinters 155°, m.p. 165—166°. The base, $C_{23}H_{28}O_3N_2$, obtained by reducing the methiodide of (**V**) by Na–Hg, with $KMnO_4$ in $COMe_2$ at 0° gives 10% of a neutral *substance*, $C_{23}H_{28}O_4N_2$, m.p. 295° (vac.), containing CO·N(*b*).

CXI. H_2–PtO_2 converts *ψ*-strychnine in HCl–H_2O–AcOH partly into dihydro-*ψ*-strychnine (**X**), $C_{21}H_{24}O_3N_2$, m.p. 240—243° (vac.), $[\alpha]$ +38·7°/*d* (lit. +34·5°) in $CHCl_3$, which is purified as hydrochloride or hydrobromide and gives the Me ether (**XI**), m.p. ~209° (vac.). With Cl_2–CCl_4, (**X**) in HCl gives a Cl_1-derivative, sinters 270°, m.p. 280—282° (decomp.; vac.), $[\alpha]$ −59·7°/*d* in $CHCl_3$, best isolated by way of the *Me ether*, m.p. 212—215° (vac.), $[\alpha]$ +51°/*d* in $CHCl_3$. With aq. Br–HBr, (**X**) gives the Br_1-derivative, m.p. 240—244° (decomp.; vac.), $[\alpha]$ −61° in $CHCl_3$ [Me ether, m.p. 205—207° (vac.)]. With PhCHO and NaOMe–MeOH, (**XI**) gives a little *benzylidene-*, m.p. 209—215°, $[\alpha]$ −108°/*d* in $CHCl_3$ (positive Otto reaction) (much *ψ*-derivative is formed), and thence (Na–Hg in HCl–MeOH–H_2O) *benzyl-ψ-dihydrostrychnine*, m.p. 208—212° (vac.), decomp. 220° [m.p. 235—238° (decomp.; vac.)] (hydrochloride), which is also obtained by catalytic hydrogenation of benzylidene- or *benzyl-ψ-strychnine*, m.p. 125—135° (vac.), decomp. 145°. Boiling NaOMe–MeOH converts (**X**) into iso*dihydro-ψ-strychnine Me ether* (**XII**), sinters at 325°, m.p. ~345° (decomp.; block), $[\alpha]$ +116°/*d* in $CHCl_3$, which yields iso*dihydro-ψ-strychnine*, m.p. 332—334° (decomp.; vac.) [*CHPh*: derivative, m.p. 190—192° (decomp.) (negative Otto reaction)]; this absorbs 6 H (PtO_2; HCl–AcOH–H_2O), yielding 13·4% of a base, $C_{21}H_{26}O_2N_2$, m.p. 226—228°, $[\alpha]$ −42° in $CHCl_3$ (perchlorate, sinters ~141°), previously (A., 1934, 312) obtained from *iso*dihydrostrychnine and in which N(*a*)·CO·CH_2·CH·O·CH_2 has been converted into N·CO·CH:CH + OH·CH_2·. In Ac_2O (blue solution) or Ac_2O–C_5H_5N at 100°, (**XII**) gives the ON-*Ac*$_2$ derivative, m.p. 248—250° (decomp.; vac.). In Ac_2O at 100°, (**X**) or (**XI**) gives a *salt*, $C_{23}H_{27}O_4N_2ClO_4$, m.p. ~280—285° (decomp. from 270°; block), and ~10% of the N-*Ac* derivative, m.p. 267—269° (decomp.; vac.) (the main product formed by Ac_2O–C_5H_5N); this salt absorbs 6 H (PtO_2–H_2O) to give a product, m.p. ~290° (decomp.), of uncertain composition. $[\alpha]$ are $[\alpha]_D^{20}$. R. S. C.

Veratrine alkaloids. XIX. Protoveratrine and its alkamine, protoverine. W. A. Jacobs and L. C. Craig (*J. Biol. Chem.*, 1943, **149**, 271—279; cf. A., 1942, II, 240).—Protoveratrine (**I**), $C_{39}H_{61}O_{13}N$, decomp. 275° (depends on rate of heating) after darkening and sintering, and warm aq. NaOH–MeOH, followed by $CHCl_3$ extraction and saturation with CO_2 [limits formation of (**III**)], give, after decomp. of the $CHCl_3$ compound, *protoverine* (**II**), $C_{27}H_{43}O_9N$, anhyd. (dried at 120°/2 mm.) or +H_2O, slowly softens and melts at 210—216°, or +2MeOH, softens to a resin at 195—200°, $[\alpha]_D^{25}$ −12° in C_5H_5N. A little iso*protoverine* (**III**), decomp. 264° after sintering and darkening, $[\alpha]_D^{28}$ −42° in C_5H_5N, is also isolated, and it can be obtained by isomerisation of (**II**) with aq. MeOH–NaOH at 50°. (**II**) and $COMe_2$–HCl–MeOH yield *acetonylprotoverine*, $C_{30}H_{47}O_9N$, sinters and colours at >235°, and gradually melts to a dark mass at 253—256° [*hydrochloride*, m.p. 278—281° (decomp.), after sintering]; (**I**) does not give a similar derivative. (**II**) and Na–BuOH (but not H_2–PtO_2) afford a H_2-compound, decomp. >300°, increasing decomp. at 330—335°, $[\alpha]_D^{25}$ −54° in C_5H_5N. (**III**) and H_2–MeOH–PtO_2 yield a H_2-derivative, slow decomp. at 315—320° after softening and discoloration, $[\alpha]_D^{28}$ −49° in C_5H_5N. (**II**) behaves as a *tert.* base, and contains a double linking and probably 9 OH groups, and is a hexacyclic *tert.* sterol base. Structures of (**I**) and (**II**) are discussed, and the relation between veratrine and potato alkaloids is noted (cf. Prelog *et al.*, A., 1943, II, 106). A. T. P.

Lunamaridine, $C_{16}H_{15}O_2N$, m.p. 209—210°, from bark of *Lunasia amara*.—See A., 1943, III, 675.

VIII.—ORGANO-METALLIC COMPOUNDS.

Mercurated aryl alkyl ketones.—See B., 1943, III, 225.

IX.—PROTEINS.

Polarographic researches on proteins. I. Polarography as a research method. C. Tropp. **II. Application to changes of state of fibrinogen.** L. Jühling, C. Tropp, and E. Wöhlisch. **III. Albumin, globulin, fibrinogen, plasma, and serum.** C. Tropp, L. Jühling, and F. Geiger (*Z. physiol. Chem.*, 1939, **262**, 199—209, 210—224, 225—242).—I. An exposition of the method and its application to proteins.

II. Pure fibrinogen (**I**) behaves polarographically like other S-containing proteins, giving the typical double step curve. Heat-denaturation of (**I**) in 10% $CO(NH_2)_2$ solution causes elevation of both protein steps. When treated with thrombin in 10% $CO(NH_2)_2$ the corresponding elevation of both steps is only seen after dilution of the $CO(NH_2)_2$ content to 3%. Trypsin elevates both protein steps at room temp. and at 40°. When the action of the enzyme is prolonged, the first step disappears and the second is flattened. The first step is correlated with the acid–amide linking. The elevation of the second step marks the increase in cystine materials due to enzyme action. The flattening of the second step denotes that under the influence of continued alkaline enzymic hydrolysis the liberated cystine escapes detection owing to oxidation.

III. Albumin and globulin (**II**), like (**I**), show a definite elevation of both protein steps on heat-denaturation. The max. protein concn. permitting polarographic analysis is for (**II**) 3·2%, for (**I**) 0·48%, for other proteins intermediate concns. The polarographic dilution curves are shown as plane diagrams which differ for each protein. All show a " cross-over effect " due to the lowering of the second below the first step. At high dilutions all the protein systems show similar behaviour. The plasma and serum diagrams are interpreted as interference diagrams of the corresponding basal proteins. The proteins examined can all be differentiated polarographically. J. H. B.

Fractionation of protein mixtures by electrophoresis. H. Gutfreund (*Biochem. J.*, 1943, **37**, 186—189).—Proteins are separated by electrodialysis in a buffer at the isoelectric point of the one to be purified. The others collect at the top or bottom of the cell, and are separated by carefully removing suitable portions of the cell contents, leaving the desired protein electrically homogeneous. R. L. E.

Iron proteins of spleen. Structure of ferritin. R. Kuhn, N. A. Sörensen, and L. Birkofer (*Ber.*, 1940, **73**, [*B*], 823—837).—Ferritin (**I**) is obtained by Laufberger's method (A., 1938, III, 208) from the spleen of horses, dogs, cats, or jackals, but not from that of guinea-pigs, rabbits, or a whale, although the spleen of the latter group was rich in Fe. Spleen containing (**I**) is stable at 80°; others coagulate. (**I**) is dimorphic, and has $[\alpha]_{Cd}^{21}$ ±30° in H_2O. All the Fe is $Fe^{...}$, being liberated as $Fe^{...}$ by dil. HCl but unaffected by 2 : 2′-dipyridyl. Reduction to $Fe^{..}$ is impossible without removal of Fe from the mol. (**I**) has no catalase, peroxidase, tyrosinase, aldehyde-dehydrase or -mutase action, confirming the view that biological catalysts function only when a change of valency is possible. The Fe content of (**I**) can usually be raised to ~21% (cf. *loc. cit.*), but occasionally to 24%. Dialysis against N-HCl removes the Fe and all the P. The S is entirely accounted for as cysteine (**II**) and methionine (**III**). Hydrolysis by boiling 6N-H_2SO_4 gives $Fe_2(SO_4)_3$, H_3PO_4, guanine, adenine, thymine, cytosine, a reducing sugar (**IV**) (? deoxyribose; gives no pentose reaction), and NH_2-acids. Determination of the N content of the purines, the reducing power of (**IV**), and the H_3PO_4 indicate that these ingredients are totally accounted for as the thymonucleic acid of Levene *et al.* (cf. A., 1908, i, 587). (**I**) containing 21·1% of Fe contains also 54·5% of protein and 12·1% of nucleic acid; the residual 33·4% necessitates the Fe being present as FeO_2H (theory 33·6%) and excludes its presence as $Fe(OH)_3$. The absorption spectrum of (**I**) (steady rise in ε from 0 at 600 mμ. to ~2300 at ~380 mμ.; no max.) resembles that of $Fe(NO_3)_3$ at pH 6·6 (acetate buffer), confirming the presence of $Fe^{...}$. Quant. measurement of the pptn. by $(NH_4)_2SO_4$ confirms the homogeneity of (**I**). Determination of various NH_2-acids shows that no one NH_2-acid can be attached to all the Fe; the following mol. composition is indicated by these analyses: arginine 72, histidine 2, lysine 24, glycine 18, phenylalanine 6 or 8, tyrosine 48, tryptophan ? 6, (**II**) 12, (**III**) 12, S 24, P 48, Fe 470 (? 2 × 288 = 576). It is thus probable that for (**I**) containing 24% of Fe each peptide linking corresponds to 1 Fe atom. R. S. C.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Lichen substances. XCV. Zeorin group. II. Y. Asahina and I. Yosioka (*Ber.*, 1940, **73**, [*B*], 742—747; cf. A., 1938, II, 289).—Yields of atranorin and zeorin (**I**), respectively, are from *Anaptychia*

speciosa, Mass., 4·1 and 1·0, *A. hypoleuca* (Muelenb.), Wain., 3·4 and 1·4, and *A. heterochroa*, Wain., 1·2 and 0·45% [contains also a (? hydroxyanthraquinone) dye, ? blastenin, m.p. 278°]. In Ac_2O–C_5H_5N at 75°, (**I**) gives the acetate, m.p. 225—227° (*loc. cit.*, m.p. 178°), which gives no colour with $C(NO_2)_4$. Boiling AcOH dehydrates (**I**) to anhydrozeorin acetate (**II**), m.p. 211—215° (*loc. cit.*, 158°), $[\alpha]_D^{20}$ +94·52° in $CHCl_3$, and mixed isomerides (**III**), m.p. 65—75°. Crude (**II**) and (**III**) are hydrolysed by boiling 20% KOH–MeOH to pure (m.p. 211—214°) and impure anhydrozeorin, $C_{30}H_{50}O$, respectively. HCl–EtOH dehydrates (**I**) to *zeorinin* (**IV**), $C_{30}H_{50}O$, m.p. 181—183°, $[\alpha]_D^{20}$ +50·0° in $CHCl_3$ [yellow in $C(NO_2)_4$; *acetate* (**V**), m.p. 197—200°; reddish-violet Liebermann reaction]. $Na_2Cr_2O_7$ oxidises (**IV**) in AcOH at >60° to *zeorinone*, $C_{30}H_{48}O$ (CO in place of CH_2), m.p. 184° (no acetate or oxime). With CrO_3–AcOH at 60—65°, (**V**) gives a saturated $[C(NO_2)_4]$ *acetate*, $C_{32}H_{52}O_4$, m.p. 230—236° [*oxime*, m.p. 293° (decomp.)], containing CO in place of CH_2 and CH·C·OH in place of C:C. Bz_2O_2H–$CHCl_3$ or 30% aq. H_2O_2 in AcOH converts (**IV**) into *zeorinin oxide* (**VI**), m.p. 286—289° (289°), $[\alpha]_D^{20}$ +62·5° in $CHCl_3$ [*acetate*, m.p. 255—257°, also obtained from (**V**) and hydrolysed by KOH–MeOH to (**VI**)], which with conc. HCl–EtOH at 100° gives iso*dehydrozeorinin* (**VII**), m.p. 183—185·5° [reddish-violet Liebermann reaction; orange red in $C(NO_2)_4$; *acetate*, m.p. 223—227°]. (**VII**) contains 2 C:C and, when hydrogenated (Pt–black; AcOH), slowly absorbs 2 H to regenerate (**IV**) having the difficultly reducible C:C. H_2–Pd-black reduces (**IV**) to *deoxyzeorin* (**VIII**), $C_{30}H_{52}O$, m.p. 166—167°, $[\alpha]_D^{20}$ +48·62° in $CHCl_3$ (red Liebermann reaction; no colour in $C(NO_2)_4$; *acetate*, m.p. 182—183°], oxidised by CrO_3–AcOH at room temp. to *deoxyzeorinone*, $C_{30}H_{50}O$, m.p. 164—165°, $[\alpha]_D^{20}$ +16·87°, unchanged by SeO_2 at 100° and reduced by Na–EtOH to (**VIII**). R. S. C.

Mould tissue. XVI. Isolation of fungus cerebrin from the mycelium of *Aspergillus sydowi*. N. Bohonos and W. H. Peterson (*J. Biol. Chem.*, 1943, **149**, 295—300; cf. A., 1938, III, 151).—A cryst. lipin (**I**), $C_{46}H_{93}O_5N$, m.p. 142·5—143°, $[\alpha]_D^{22}$ +11·9° in C_5H_5N, obtained from *A. sydowi*, is probably identical with fungus cerebrin (Reindel *et al.*, *Annalen*, 1940, **544**, 116). (**I**), obtained by Et_2O extraction of the insol. residue after autolysis and alkali extraction of the mycelium, is purified through the *tetra-acetate*, $C_{54}H_{101}O_9N$, m.p. 67—67·5°, $[\alpha]_D^{23}$ +20·6° in $CHCl_3$. (**I**) appears to be bound in mould tissue, as it is not obtained from unautolysed mycelium. It is degraded at 235°, H_2O is lost, and a product, m.p. 74—75° (softens at 71°), is obtained. (**I**) and $Pb(OAc)_4$–$CHCl_3$–AcOH at 40—50° yield (*a*) a ketone, $C_{16}H_{32}O$ (*dinitrophenylhydrazone*, m.p. 94—95°), and (*b*) a product hydrolysed by boiling HCl–MeOH to (probably) a compound, $C_4H_8O_3$ (2 : 4-dinitrophenylhydrazone, decomp. 270—280°), and (mainly) the Me ester, m.p. 68—71°, of a OH-acid; the free acid (**II**), $C_{26}H_{52}O_3$, m.p. 102·5—104·5° (NH_4 salt; chloral derivative, m.p. 65—66°), is obtained by boiling KOH–EtOH. (**II**) and $Pb(OAc)_4$–AcOH give (probably) an aldehyde (semicarbazone, m.p. 113·5—114°). Data confirm the structure suggested for fungus cerebrin by Reindel *et al.*, who also prepared similar derivatives. A. T. P.

Caneine, $C_{12}H_{24}O_3N_2$, m.p. 188—189° (picrate, m.p. 120—121°), and kitagine, $C_7H_7O_3N$, m.p. 240—242°, from jack beans.—See A., 1943, III, 702.

Lignin. XL. Enzymic degradation of polymeric carbohydrates. VII. Fractionation of linden wood and enzymic degradation of the fractions. T. Ploetz (*Ber.*, 1940, **73**, [*B*], 790—794).—When linden wood (*Tilea tomentosa*) is digested for 14 days with $(CH_2{\cdot}NH_2)_2$–CuO, ~34% of a residue (*A*) is obtained. Acid ppts. ~42% from the solution; ~24% remains sol. The components of lower OMe content are preferentially dissolved. A fraction containing 75% of pentosan had 3·28% of OMe, indicating that the OMe of the sugars occurs mainly in the pentosans. (*A*) is rapidly attacked by snake venom (cf. *loc. cit.*); up to 50% degradation the loss in wt. is accounted for by the sugar in solution; thereafter discrepancies occur. 58·5% degradation is finally achieved; the insol. material (*B*) is then a 1 : 1 lignin–sugar complex, containing only a little pentose. Treatment of (*B*) with $(CH_2{\cdot}NH_2)_2$–CuO leaves 8·8% of residue, containing 78·9% of lignin; acid ppts. from the solution a small amount of material which is degraded enzymically to the 1 : 1 complex, which now contains no pentose. Treating the solution from (*B*) with acid gives a product, which suffers 62·1% of enzymic degradation, the insol. portion (*C*) then containing 39% of lignin. Repetition on (*C*) of the two degradative procedures gives an insol. material containing 53·8% of lignin, *i.e.*, the 1 : 1 complex. R. S. C.

Reaction of sulphanilamide [with lignin].—See A., 1943, II, 298.

Lignin esters.—See B., 1943, II, 281.

XI.—ANALYSIS.

New technique for ultimate micro-analysis of organic compounds. R. Belcher and C. E. Spooner (*J.C.S.*, 1943, 313—316).—A technique is described for the micro-determination of C, H, S, and halogens in org. compounds, by combustion at 800° in a rapid stream of O_2 (50 ml. per min.) without catalysts. Ag gauze near the exit absorbs interfering acid gases, S being determined gravimetrically in the aq. extract of this. Halogens and N oxides are absorbed in external absorbents, halogens being determined titrimetrically. A. Li.

Micro-determination of nitrogen in organic compounds by Kjeldahl's method. E. I. Aizenschtadt (*Zavod. Lab.*, 1940, **9**, 233—234).—Reduction of NO_2- and NO-compounds by glucose often requires boiling for 3—5 hr. J. J. B.

Semi-micro-analysis of anions.—See A., 1943, I, 262.

Tentative method for the determination of mono- and di-unsaturated glycerides. A. R. S. Kartha and K. N. Menon (*Proc. Indian Acad. Sci.*, 1943, **17**, **A**, 114—118).—The fat or oil is oxidised by $KMnO_4$–$COMe_2$ and tri-saturated glycerides are removed. The mixture of mono- (**I**), di- (**II**), and tri-azelaoglycerides, dissolved in Et_2O, is washed 5 or 6 times with 5% aq. Na_2CO_3 and the extract and washings are rejected, thus removing all the monobasic acids, triazelain, and a portion of the (**II**). The solution is cautiously extracted with 10% aq. K_2CO_3 and H_2O to extract (**I**) and (**II**). The combined extract and washings are acidified with dil. H_2SO_4 to Congo-red and thoroughly extracted with Et_2O. The extract is dried over anhyd. $MgSO_4$ and the solvent is removed completely under reduced pressure at a very low water-bath temp. The sap. val. of a portion of the residue is determined, this corresponding with a mixture of (**I**) and (**II**). The remaining residue is dissolved in Et_2O and washed alternately with $NaHCO_3$ and H_2O; the combined washings and extract are acidified with dil. H_2SO_4 and the pure (**II**), after being dried, are used for determination of sap. val. The method is applied to the oils of *Mimusops elangi* and *Jatropha curcas*. H. W.

Polarographic determination of small concentrations of aldehydes and peroxides. M. N. Michailova and M. B. Neiman (*Zavod. Lab.*, 1940, **9**, 166—168).—10^{-8} g. of MeCHO or H_2O_2 can be estimated in presence of a large excess of O_2 by the height of the polarographic wave. J. J. B.

Identification and determination of β-phenyl*iso*propylamine and β-phenyl*iso*propylmethylamine. G. Dultz (*Z. anal. Chem.*, 1940, **120**, 84—88).—The two compounds are detected by the use of Kofler's micro-m.p. and sublimation procedure (cf. A., 1942, II, 1). For the determination tablets are extracted with $CHCl_3$ in presence of NaOH, excess of 0·01N-H_2SO_4 is added, the $CHCl_3$ removed, and the excess of H_2SO_4 titrated with NaOH using Tashiro's indicator (100 c.c. of 0·03% Me-red + 15 c.c. of 0·1% methylene-blue). F. N.

Determination of nicotinic acid. R. G. Martinek, E. R. Kirch, and G. L. Webster (*J. Biol. Chem.*, 1943, **149**, 245—249).—3 : 4 : 1-$NH_2{\cdot}C_6H_3(OH){\cdot}CO_2H$ is preferred to NH_2Ph etc. as chromogenic amine in the CNBr–nicotinic acid reaction; the method is less crit. with respect to pH control and time of comparison of colour; the colour reaches a max. in 5 min. and is stable for <15 min. A. T. P.

Determination of nicotinic acid; modifications of the microbiological method.—See A., 1943, III, 753.

Determination of nicotinic acid and its amide.—See A., 1943, III, 684.

Determination of nicotine and nornicotine in mixtures. L. N. Markwood (*J. Assoc. Off. Agric. Chem.*, 1943, **26**, 283—289).—Nornicotine (**I**) is converted into nitrosonornicotine and unchanged nicotine (**II**) is removed by steam-distillation at pH 10. The procedure is repeated after methylation of (**I**) to (**II**) with CH_2O–HCO_2H. Recoveries of 97—98% are recorded. A. A. E.

Spectrophotometric methods. Determination of quinine by absorption spectrophotometry. J. Carol (*J. Assoc. Off. Agric. Chem.*, 1943, **26**, 238—241).—With the aid of a Beckmann quartz spectrophotometer quant. measurements could be made at 250·5, 318·0, and 347·5 mμ. Many compounds frequently present in preps. of quinine show no absorption at 347·5 mμ., so that separation is frequently unnecessary. Separation from aloin, podophyllin, anthraquinone derivatives, other cinchona alkaloids, and yellow dyes is necessary. A. A. E.

Lignin. XXXVIII. Determination of lignin. K. Freudenberg and T. Ploetz (*Ber.*, 1940, **73**, [*B*], 754—757).—The concn. of H_2SO_4 used in determining lignin can be that which gives the min. yield, but sometimes, *e.g.*, with linden, no such min. exists. It is thus better to use that concn. which gives a "lignin" having max. OMe content, *i.e.*, for *Picea excelsa* and *Tilea tomentosa* 75 and for *Fagus silvatica* and *Sambucus nigra* 66·4—66·5%. The analytical method is detailed. R. S. C.

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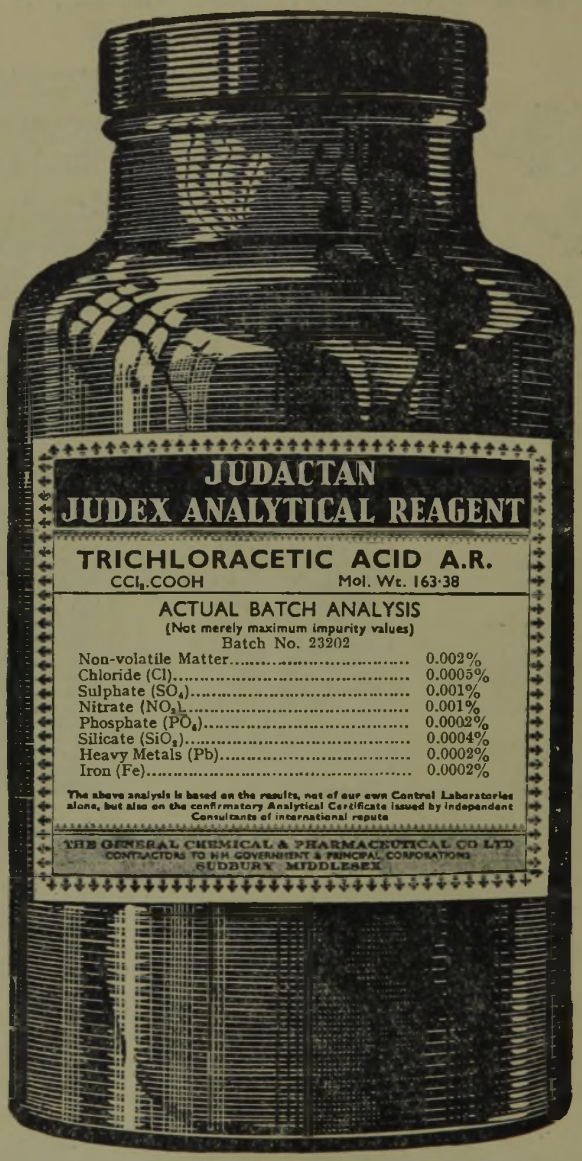
JUDACTAN

ANALYTICAL REAGENTS WITH ACTUAL BATCH ANALYSIS

ACTUAL

BATCH

ANALYSIS



Each Batch subjected to INDEPENDENT ANALYSIS before label is printed

You are invited to compare the above actual batch analysis with the purities guaranteed by the specifications of any competing maker in this Country or abroad

THE GENERAL CHEMICAL & PHARMACEUTICAL CO. LTD.

Chemical Manufacturers, Judex Works, Sudbury, Middlesex

PRINTED IN GREAT BRITAIN BY RICHARD CLAY AND COMPANY, LTD, BUNGAY, SUFFOLK.