BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

APRIL, 1939.

Hydrocarbon, $C_{28}H_{58}$, m.p. 63°, and acid, $C_{18}H_{36}O_2$, m.p. 55°, from cow's pregnancy urine. —See A., 1939, III, 144.

Influence of substituents on additive reactivity of ethylene derivatives.—See A., 1939, I, 206.

Oxidation of ethylenic hydrocarbons by selenious anhydride. A. GUILLEMONAT (Ann. Chim., 1939, [xi], 143—211; cf. A., 1936, 51; 1937, II, 405; 1938, II, 268).—The oxidation is effected by the gradual addition of finely divided SeO_2 to a solution of the hydrocarbon in AcOH–Ac_2O. With hydrocarbons CRMe:CHMe a considerable proportion of the initial material always remains. Oxidation occurs at the most substituted C atoms vicinal to the C having the ethylenic linking, thus giving OH·CHR·CMe:CHMe where R may be H. The radicals form the series CH_2:, Me, CH: in order of decreasing facility of oxidation; this effect is so marked that one product usually results in overwhelming proportion, *e.g.*, CMeEt:CHMe gives 34% of OH·CHMe·CMe:CHMe and only 1% of OH·CH_2·CEt:CHMe, and CMe_2:CHEt gives only OH·CH_2·CMe:CHEt. Steric influences appear without effect since CMeBu$^\gamma$:CHMe and CPhEt:CHMe afford OH·CH_2·CBu$^\gamma$:CHMe and OH·CHMe·CPh:CHMe in good yield. CMe_2:CHMe is oxidised to β-*methyl*-Δ^β-*butenyl acetate*, b.p. 148—150°, hydrolysed [$Ba(OH)_2$] to β-methyl-Δ^β-buten-α-ol, b.p. 136—138°, identified by hydrogenation to CHMeEt·CH_2·OH and by oxidation to tiglaldehyde, b.p. 114—118° (semicarbazone, m.p. 225°). CMeEt:CHMe yields β-*acetoxy*-γ-*methyl*-Δ^γ-*pentene*, b.p. 57—59°/19 mm., hydrolysed to γ-methyl-Δ^β-penten-δ-ol, b.p. 54—56°/18 mm., and γ-*acetoxymethyl*-Δ^β-*pentene*, b.p. 65—67°/19 mm., hydrolysed to γ-*hydroxymethyl*-Δ^β-*pentene*, b.p. 149—150°/760 mm., oxidised to the corresponding aldehyde (semicarbazone, m.p. 198°; *p*-nitrophenylhydrazone, m.p. 154—155°). β-*Bromo*-γ-*methyl*-Δ^γ-*pentene*, b.p. 62—64°/32 mm., from the corresponding alcohol and PBr_3, is transformed by MgMeBr into βγ-*dimethyl*-Δ^γ-*pentene*, b.p. 91°/760 mm., oxidised by SeO_2 to unchanged material possibly containing a little βγ-dimethyl-$\Delta^{\alpha\gamma}$-pentadiene, and β-iso*propyl*-Δ^β-*butenyl acetate*, b.p. 75—77°/28 mm., hydrolysed to β-iso*propyl*-Δ^β-*buten*-α-*ol*, b.p. 65—67°/24 mm.; this is reduced (Adams) to β-*iso*propylbutyl alcohol and oxidised to α-*iso*propylbutaldehyde (semicarbazone, m.p. 125°). CMeBu$^\gamma$:CHMe yields β-tert.-*butyl*-Δ^β-*butenyl acetate*, b.p. 82°/22 mm., hydrolysed to β-tert.-*butyl*-Δ^β-*buten*-α-*ol*, b.p. 82°/22 mm., which affords MeCHO when ozonised. β-Methyl-Δ^β-pentene gives β-*methyl*-Δ^β-*pentenyl acetate*, b.p. 61—63°/12 mm., whence β-methyl-Δ^β-penten-α-ol, b.p. 61—63°/14 mm., identical with the product of the reduction of methylethylacraldehyde. γ-*Phenyl*-Δ^γ-*pentene*, b.p. 87—89°/17 mm., obtained by dehydration of $CPhEt_2$·OH derived from EtOBz and MgEtBr, is oxidised to β-*acetoxy*-γ-*phenyl*-Δ^γ-*pentene*, b.p. 127—130°/20 mm., hydrolysed to γ-*phenyl*-Δ^γ-*penten*-β-*ol*, b.p. 122°/18 mm.

In the case of cyclic hydrocarbons with a double linking in the ring, oxidation results in the replacement by OH of H attached to C in the α-position to the double linking and always occurs in the ring if there is a possibility of oxidation. In consequence of dehydration of the *tert.* alcohol formed initially, the oxidation of CH leads to a diene with conjugated double linkings; these are also produced by oxidation of hydrocarbons with a cyclic, di-*tert.* double linking. Ethyl-Δ^1-*cyclo*hexene is oxidised to 2-*ethyl*-Δ^2-cyclo*hexenyl acetate*, b.p. 89—90°/15 mm., hydrolysed to 2-*ethyl*-Δ^2-cyclo*hexen*-1-*ol*, b.p. 82—83°/12 mm., which is oxidised to 2-*ethyl*-Δ^2-cyclo*hexenone*, b.p. 78—80°/15 mm. (*semicarbazone*, m.p. 175°). *Ethyl*-Δ^1-cyclo*pentene*, b.p. 105—106°, gives 2-*ethyl*-Δ^2-cyclo*pentenyl acetate*, b.p. 75—77°/20 mm., whence 2-*ethyl*-Δ^2-cyclo*pentenol*, b.p. 74—75°/20 mm., oxidised to 2-*ethyl*-Δ^2-cyclo*pentenone*, b.p. 78°/27 mm. (*semicarbazone*, m.p. 190°). 1-Methyl-Δ^1-*cyclo*hexene is oxidised to 2-methyl-Δ^2-*cyclo*hexenol, which is converted by PBr_3 into 1-*bromo*-2-*methyl*-Δ^2-cyclo*hexene*, b.p. 78—79°/26 mm., transformed by MgMeBr into 1 : 2-*dimethyl*-Δ^2-cyclo*hexene*, b.p. 130—131°/768 mm. This is oxidised by SeO_2 to *o*-xylene and 2 : 3-dimethyl-$\Delta^{1:3}$-*cyclo*hexadiene (I), hydrogenated to 1 : 2-*dimethyl*-Δ^1-cyclo*hexene* (II) and transformed by maleic anhydride into the *adduct*, $C_{12}H_{16}O_3$, m.p. 122—123°. (II), b.p. 135—137°/760 mm., is oxidised to (I), further identified by condensation with (:C·CO_2Me)$_2$ to Me_2 4 : 5-dimethyl-1 : 4-*endo*ethylene-1 : 4-dihydrophthalate, pyrolysed to C_2H_4 and an ester hydrolysed to 4 : 5 : 1 : 2-$C_6H_2Me_2(CO_2H)_2$.

Oxidation of aliphatic hydrocarbons with a di-*sec.* double linking occurs generally to only a slight extent and gives very little identifiable product. Little or no pptn. of Se occurs. Oxidation occurs at the C in the α-position to the double linking. CH_2 is more readily oxidised than Me. A double linking at the end of a chain is as active as a di-*sec.* double linking but in consequence of rearrangement a primary and not a *sec.* alcohol is obtained. If radicals CH_2 are present on each side of the ethylenic carbons, both radicals are oxidised and mixtures of alcohols are obtained which may become complicated further as a consequence of rearrangements. Δ^β-Pentene is oxidised to β-*acetoxy*-Δ^γ-*pentene*, b.p. 135—137°, hydrolysed to Δ^γ-*penten*-β-*ol*, b.p. 118—121°, which is hydrogenated (Adams) to pentan-β-ol, b.p. 116—118°.

Δ^{α}-Hexene is transformed into Δ^{β}-hexenyl acetate, b.p. 165—170°, hydrolysed to Δ^{β}-hexen-α-ol, b.p. 156°. Oxidation of Δ^{δ}-nonene gives an acetate, b.p. 89—91°/15 mm., giving a nonenol, b.p. 85—87°/11 mm., hydrogenated to a nonanol, b.p. 90—91°/18 mm.; since a cryst. derivative of this alcohol could not be obtained it is probable that the product is a mixture. Similarly, Δ^{γ}-nonene appears to yield mixtures of nonenyl acetates, b.p. 99—100°/17 mm., nonenols, b.p. 93—95°/15 mm., and nonanols, b.p. 93°/17 mm. Cyclic hydrocarbons with doubly linked *tert.* C are somewhat less readily oxidised than those with a di-*sec.* ethylenic linking but give yields of the order 30—40%; the general behaviour is similar to that of the corresponding aliphatic compounds. Thus *cyclo*hexene yields Δ^{2}-*cyclo*hexenyl acetate, b.p. 68—70°/15 mm., hydrolysed to Δ^{1}-*cyclo*hexen-1-ol (phenylurethane, m.p. 106·5—107·5°). 3-Methyl-Δ^{1}-*cyclo*hexene, b.p. 102°/760 mm., yields 4-*methyl*-Δ^{2}-cyclo*hexenyl acetate*, b.p. 88—90°/20 mm., hydrolysed to 4-*methyl*-Δ^{2}-cyclo*hexen*-1-*ol*, b.p. 65—66°/6 mm. [identified by hydrogenation to 4-methyl*cyclo*hexanol, b.p. 169°/760 mm. (phenylurethane, m.p. 122°)], and 2-*methyl*-Δ^{5}-cyclo*hexenyl acetate*, b.p. 82—84°/17 mm., hydrolysed to 2-*methyl*-Δ^{5}-cyclo*hexenol*, b.p. 72—74°/15 mm. [identified by oxidation to 2-methyl-Δ^{5}-*cyclo*hexenone, b.p. 70°/15 mm. (semicarbazone, m.p. 178—180°)]. 4-Methyl-Δ^{1}-*cyclo*hexene is oxidised to a mixture of the acetates of 6-, 4-, and 5-methyl-Δ^{2}-*cyclo*hexenol.

The possibility that selenides are intermediate products of the reaction is established by the isolation of isoprene, tiglaldehyde, tiglic acid, and *di*-β-*methyl*-Δ^{β}-*butenyl selenide*, b.p. 97°/8 mm., by the action of SeO_2 on CHMe:CMe_2 in C_6H_6 at room temp.; this is characterised by the ppts. it gives with $H_4Fe(CN)_6$ and with $HgCl_2$, by conversion by O_3 into Se and MeCHO, and by pyrolysis under atm. pressure into Se, isoprene, and CHMe:CMe_2 and their polymerides and by pyrolysis in AcOH into Se and tiglyl alcohol. The Raman spectra of most of the substances mentioned are recorded. H. W.

Composition of primary polymerisation products of propene and the butenes. H. Hoog, J. Smittenberg, and G. H. Vissen (II Congr. mond. Pétrole, 1937, **2**, 489—495).—Propene, Δ^{α}-, Δ^{β}-, and *iso*-butene were polymerised under mild conditions by passage over a solid H_3PO_4 catalyst, the olefine polymerides were hydrogenated, and the resulting paraffins analysed. It is concluded that quaternary C do not take part in the polymerisation, but a regrouping may occur which will produce a *tert.* C. Couplings between similar C occur only to a slight degree, if at all. Coupling between *tert.* and primary C takes preference of any other possible combination. These conclusions may not be valid at high temp., which promote secondary reactions. R. B. C.

Spectroscopic and chemical study of aliphatic terpenes. V. Hydrocarbons derived from aliphatic alcohols. G. Dupont, R. Dulou, and V. Desreux (Bull. Soc. chim., 1939, [v], **6**, 83—91; cf. A., 1936, 1514; 1938, II, 80).—Raman spectra of the products show that reduction ($NaNH_2$ in liquid NH_3) of β-geraniol or β-linalool, or (Na + EtOH) of myrcene, yields only β-methylgeraniolene. Cyclisation (AcOH–50% H_2SO_4) of this yields chiefly α-methyl*cyclo*geraniolene (A., 1926, 1238), whilst dehydration (anhyd. $H_2C_2O_4$) of dihydrolinalool (I) yields the ε-, α-, and γ-isomerides in the ratio 5 : 3 : 2, as shown by the Raman spectrum and the results of ozonolysis and of partial hydrogenation (Raney Ni). Dehydration (HPO_3 or hydrated $H_2C_2O_4$) of (I) gives mixtures of aliphatic dienes with cyclic compounds. A. Li.

Rate of the haloform reaction.—See A., 1939, I, 205.

Trichloro-bromo- and -iodo-methane. J. H. Simons, T. K. Sloat, and A. C. Meunier (J. Amer. Chem. Soc., 1939, **61**, 435—436).—CCl_3·COBr (prep. in 70% yield from CCl_3·COCl by HBr at <0°) at 400° gives 10% of CCl_3Br and 5% of C_2Et_6. Distillation/1 atm. of CCl_3·COI gives 75% of CCl_3I and 5% of C_2Et_6. CCl_3·COCl at 600° gives CCl_4 (10 parts), C_2Et_6 (1 part), CO, and $COCl_2$. Anhyd. CCl_3·CO_2Na and CCl_3·CO_2Hg do not react with Br, even at high temp. CCl_3Br and CCl_3I form at most traces of Mg derivatives. R. S. C.

Stabilised carbon tetrachloride.—See B., 1939, 240.

Promoter effect of platinic chloride on Raney nickel.—See A., 1939, I, 208.

Manufacture of alkali alkoxides.—See B., 1939, 241.

Alkyl carbonates.—See A., 1939, I, 190, 206.

Vapour-phase catalytic conversion of methyl-*tert.*-butylcarbinol and *tert.*-butylethylene. P. L. Cramer and A. L. Glasebrook (J. Amer. Chem. Soc., 1939, **61**, 230—232).—When passed over activated Al_2O_3 at 310° and 390°, CHMeBu$^{\gamma}$·OH (I) gives CH_2:$CHBu^{\gamma}$ (II) 64·2 and 61·5, CHMe:$CHPr^{\beta}$ (III) 28·2 and 21·6, and $(CMe_2{:})_2$ (IV) 7·6% and a trace, respectively. When passed over $Al_2(SO_4)_3$ at 275°, (I) or (II) gives (II) 3·5, (III) 34, and (IV) 62·5%. (II) is unaffected by Al_2O_3 at 350°. Thus, rearrangement during dehydration of (I) by acids is due to rearrangement of the (II) primarily formed. R. S. C.

A βδ-diene alcohol. C. K. Houo (Compt. rend., 1939, **208**, 40—42).—CH_2:CH·CHO and Mg allyl bromide afford (35%) vinylallylcarbinol, converted by PBr_5 into a desmotropic mixture, b.p. 52—57°/17 mm., of γ-bromo-$\Delta^{\alpha\epsilon}$- and α-bromo-$\Delta^{\beta\epsilon}$-hexadiene; this with NaOAc–AcOH or NaOAc–EtOH affords (80%) *α-acetoxy*-$\Delta^{\beta\epsilon}$-*hexadiene*, b.p. 68—70°/14 mm., hydrolysed (EtOH–KOH) to *hexa*-$\Delta^{\beta\epsilon}$-*dien*-α-*ol*, b.p. 71—72°/14 mm., which when heated (sealed tube) with dil. EtOH–KOH at 180° gives *hexa*-$\Delta^{\beta\delta}$-*dien*-α-*ol*, b.p. 77—78°/14 mm. J. L. D.

Linalool. Isomerisation of linalool by heating under pressure. I. Plinol. II. *iso*Plinol. T. Ikeda and K. Wakatsuki (J. Chem. Soc. Japan, 1936, **57**, 425—435, 435—441).—I. Linalool heated under N_2 at 250°/200 atm. for several hr. and then distilled yields in the final fraction the *tert.* alcohol, *plinol* (I), $C_{10}H_{18}O$, m.p. 94°, b.p. 209° (*phenylurethane*, m.p. 118°), which is dehydrated to the diene *plinolene* (II), $C_{10}H_{16}$. Hydrogenation (Pd) of (I) gives

dihydroplinol and of (II) *tetrahydroplinolene*. Decomp. of the ozonide of (I) furnished CH_2O, HCO_2H, and a *ketone* (III), $C_9H_{14}O$ (*semicarbazone*, m.p. 158°), hydrogenated to the saturated *ketone*, $C_9H_{16}O$ (*semicarbazone*, m.p. 178°); with H_2O the ozonide of (I) gave a saturated *ketoglycol*, $C_9H_{16}O_3$, m.p. 166°. (III) may be reduced to a H_2-derivative and this oxidised to acids, $C_6H_{10}O_2$ and $C_8H_{14}O_2$.

II. The mother-liquor from the prep. of (I) yields the *tert.* alcohol iso*plinol* (IV), m.p. 41° (*naphthylurethane*, m.p. 130°), by oxidising with CrO_3, removing citral, and distilling the residual unattacked oil. (IV) is dehydrated to iso*plinolene* and contains no 6-membered ring as it is not dehydrogenated by S or Se, but (IV) is reduced to *dihydroiso*plinol and (V) to *tetrahydroiso*plinolene. Decomp. of the ozonide of (IV) gives CH_2O and HCO_2H, indicating a $:CH_2$ group, and a *ketone*, $C_9H_{14}O$ (*semicarbazone*, m.p. 157·5°), hydrogenated to the saturated *ketone*, $C_9H_{16}O$ (*semicarbazone*, m.p. 179·5°), oxidised to ($KMnO_4$) the acids $C_6H_{10}O_2$ and $C_7H_{12}O_2$ or $C_8H_{14}O_2$. CH. ABS. (*c*)

Constitution of linoleyl alcohol prepared by sodium reduction of linoleic acid. J. P. KASS, E. S. MILLER, and G. O. BURR (J. Amer. Chem. Soc., 1939, **61**, 482—483).—Linoleyl alcohol, obtained from Me linoleate by Na–BuOH, is shown to be a mixture of Δ^{μ}- and $\Delta^{\kappa\mu}$-octadien-α-ol by its adsorption spectrum (max. at 2300—2350 A., $E^{1\%}_{1\,cm.}$ 600), oxidation by $KMnO_4$ in $COMe_2$ to hexoic, azelaic, and sebacic acids, and physical data recorded in the lit.
R. S. C.

Lano-octadecyl alcohol, $C_{18}H_{38}O$, m.p. 42—43° (phenylurethane, m.p. 79·5—80°), and lanyl alcohol, $C_{21}H_{42}O_2$, m.p. 79·5—80° (bisphenylurethane, m.p. 97°), from wool wax.—See A., 1938, III, 1018.

α-Naphthylcarbamic esters of complex aliphatic alcohols and their fission by methyl-alcoholic potassium hydroxide. J. TISCHER (Ber., 1939, **72**, [*B*], 291—297).—Complex primary alcohols with an even no. of C give α-naphthylcarbamates hydrolysed by KOH–MeOH in 60—80 min. to the corresponding alcohol, α-$C_{10}H_7$·NH_2, and a little $CO(NH{\cdot}C_{10}H_7)_2$. Under similar conditions urethanes of complex primary alcohols with an odd no. of C yield also a considerable amount of $C_{10}H_7$·$NH{\cdot}CO_2Me$. α-Naphthylurethanes of complex *sec.* alcohols are formed with much greater difficulty and are much more resistant to alkaline hydrolysis. A differentiation of the different classes of alcohol along these lines is suggested. The following are new: *pentadecyl*, m.p. 84·5—85° (corr.), *heptadecyl*, m.p. 88·5° (corr.), "*myricyl*," m.p. 80—94·5°, and *di*-n-*hexylcarbinyl*, m.p. 50—51°, α-*naphthylcarbamate*. H. W.

Partly *O*-methylated hexitols. I. 1:2:3:5:6-*O*-pentamethyl-*d*-sorbitol. P. A. LEVENE and M. KUNA (J. Biol. Chem., 1939, **127**, 49—53).—Nonamethyl-β-4-glucosidosorbitol (cf. A., 1937, II, 318) with 5% HCl at 100° under pressure affords a product which when oxidised (Willstätter–Schudel) yields 1:2:3:5:6-*O*-*pentamethylsorbitol*, b.p. 128—133°/3 mm., $[\alpha]_D^{25}$ —10·1° in EtOH, and αβγε-tetramethyl-δ-*d*-gluconolactone. J. L. D.

Non-reaction of ethylene oxide and methanol. J. L. JONES (J. Amer. Chem. Soc., 1939, **61**, 527—528).—$(CH_2)_2O$ and MeOH do not react, at least at <350°. This indicates a very small steric factor and high activation energy. The liquid-phase reaction must then be ionic. R. S. C.

Reaction of aliphatic ethers with Denigès' reagent. E. M. MARKS and D. LIPKIN (J. Org. Chem., 1939, **3**, 598—602).—None of the straight-chain ethers examined appears to react with Denigès' reagent, the no. of C and the position of O in these compounds being seemingly without influence. Compounds containing Bu^{γ} are reactive. $Bu^{\gamma}OH$ and $MeOBu^{\gamma}$ become opaque within 4 min., replacement of OH by OMe not affecting the rate of change. $EtOBu^{\gamma}$ is somewhat less reactive and examination of $PrOBu^{\gamma}$ and $Bu^{\alpha}OBu^{\gamma}$ shows that further lengthening of the straight-chain radical increases this effect greatly. $Pr^{\beta}OBu^{\gamma}$ is highly reactive. Compounds containing the *tert.*-amyl radical behave like Bu^{γ} compounds except that their rates of reaction are usually slower and they ultimately give white needle like ppts. instead of yellow, curdy deposits; the two classes of compounds may possibly be thus differentiated. Replacement of OH by OAlk in *tert.*-amyl alcohol causes a greater lowering of the reaction rate than that shown in the Bu^{γ} series. $EtOBu^{\beta}$ does not react with Denigès' reagent. Apparently the primary C connecting the O with the branched part of the Bu retards the change considerably.
$(CH_2{:}CMe{\cdot}CH_2)_2O$ is quite reactive probably by reason of the unsaturation within the mol. since a fully saturated ether with a similar structure should be quite inert towards the reagent. H. W.

Mechanisms for the rearrangements of ethers. Phenyl γ-ethylallyl [Δ^{β}-pentenyl] and vinyl γ-ethylallyl ether. C. D. HURD and M. A. POLLACK (J. Org. Chem., 1939, **3**, 550—569).—Ozonisation followed by hydrolytic oxidation with H_2O and Ag_2O of $CHEt{:}CH{\cdot}CH_2Cl$ (I), $CHEtCl{\cdot}CH{:}CH_2$ (II), and $CHMeCl{\cdot}CH{:}CHMe$ (III) gives respectively $EtCO_2H$, HCO_2H, and AcOH, separable by steam-distillation from the concurrently formed $OH{\cdot}CH_2{\cdot}CO_2H$, $OH{\cdot}CHEt{\cdot}CO_2H$, and $OH{\cdot}CHMe{\cdot}CO_2H$. In the steam distillate HCO_2H is determined by oxidation with CrO_3; $EtCO_2H$ and AcOH are distilled off and the aq. distillate is analysed by the Duclaux method. Further in the latter mixture $EtCO_2H$ is oxidised quantitatively to C_2O_4'' by hot, alkaline $KMnO_4$, leaving AcOH which is distilled off and identified by the Duclaux vals. and by conversion into *p*-bromophenacyl acetate. Analysis of the chloropentenes obtained by the method of Lauer and Filbert (A., 1936, 1244) shows the fraction of higher b.p. (IV), assumed to be pure (I), to contain 89% of (I), 11% of (II), and only a trace of (III). The fraction of lower b.p., assumed to be pure (II), is composed of 62% of (II), 36% of (I), and 2% of (III). Condensation of (IV) with PhOH gives a mixture of Ph pentenyl ethers shown by ozonolysis to consist of 90% of Ph Δ^{β}-pentenyl ether and 10% of Ph α-vinylpropyl ether. The rearrangement product formed by heating this mixture contains 56% of *o*-α-vinylpropylphenol from the normal γ-rearrange-

ment, 42% of the isomeric *o*-α-methyl-Δ^{β}-butenylphenol from the abnormal rearrangement, and a small amount of *o*-Δ^{β}-propenylphenol.

A mixture of pentenyl bromides (81·5% of $CH_2Br{\cdot}CH{:}CHEt$ and 18·5% of $CH_2{:}CH{\cdot}CHBrEt$) is condensed with $OH{\cdot}CH_2{\cdot}CH_2{\cdot}ONa$ to β-*hydroxyethyl pentenyl ether*, b.p. 85—87°/13 mm., converted by PBr_3 and anhyd. C_5H_5N into β-*bromoethyl pentenyl ether*, b.p. 79°/11 mm., and thence by KOH at 160—170° into *vinyl pentenyl ether* (V), b.p. 97—101°/atm. pressure. (V) is assumed to be a mixture of $CH_2{:}CH{\cdot}O{\cdot}CH_2{\cdot}CH{:}CHEt$ and $CH_2{:}CH{\cdot}O{\cdot}CHEt{\cdot}CH{:}CH_2$ in the ratio 81·5 : 18·5. It is readily hydrolysed to MeCHO and pentenyl alcohol. Its thermal stability is about the same as that of $CH_2{:}CH{\cdot}O{\cdot}CH_2{\cdot}CH{:}CH_2$. Short heating of the vapours at ~255° gives a 35% conversion into heptenaldehyde (VI) whereas practically complete conversion is effected in a sealed tube at 220°. Ozonolysis of (VI) yields HCO_2H, $EtCO_2H$, and AcOH in the mol. ratio 76·5 : 18·9 : 4·6, thus indicating that (VI) is a 76·5 : 18·9 : 4·6 mixture of β-ethyl-Δ^{γ}-pentenal, Δ^{γ}-heptenal, and β-methyl-Δ^{γ}-hexenal. Thus the abnormal effect which is so prominent in the case of $OPh{\cdot}CH_2{\cdot}CH{:}CHEt$ also results but to a much smaller extent with $CH_2{:}CH{\cdot}O{\cdot}CH_2{\cdot}CH{:}CHEt$. The various mechanisms which have been proposed to account for the rearrangement of ethers are examined critically. It is suggested that the initial effect of heat on the system C:C·O·C·C:C is to alter the position of the pair of electrons which bind the allyl group to O so that a semi-ionisation occurs. Actual separation into ions does not occur but the semi-ionisation promotes other ionic disturbances at the double linkings. This effect, combined with the spatial proximity of the atoms at the end of the systems, brings about temporary ring-closure and readjustment of electrons. The mechanism explains the intramol. nature of the reaction and the inversion of the "wandering" radical. The semi-ionic positive C seeks to satisfy its electron deficiency by appropriating electrons from the neighbouring double linking. This process is reversible but the next step which involves cyclisation is irreversible. Two mechanisms are suggested for the explanation of *para* rearrangements. H. W.

Ether-like compounds. XXII. Synthesis of ether acetals by aid of γ-halogeno-ethers. M. H. Palomaa and T. K. Kaski (Ber., 1939, **72**, [*B*], 317—318).—Protracted heating of $CH(OEt)_3$ with a solution of $OMe{\cdot}[CH_2]_3{\cdot}MgCl$ in C_6H_6 or PhMe gives *γ-methoxybutaldehyde Et_2 acetal*, b.p. 71—74°/5—6 mm., in about 18% yield. H. W.

Synthesis of γ-methylthiolpropyl alcohol ("methionol"). S. Akabori and T. Kaneko (Bull. Chem. Soc. Japan, 1939, **14**, 1—2).—Allyl alcohol and MeSH react (varying time periods) in air, O_2, or H_2, in presence of $Hg(SMe)_2$, in a sealed tube, to give $SMe{\cdot}[CH_2]_3{\cdot}OH$. The yield is 93% in O_2 at room temp. for one month; in H_2 there is no reaction in diffused light, but some occurs in the dark. The use of $Hg(OAc)_2$ as catalyst in air at 140—160° affords a 61% yield of the alcohol (cf. Kirner, A., 1928, 1214). A. T. P.

Instability of ammonium salts of higher fatty acids. J. E. Kench and T. Malkin (J.C.S., 1939, 230—232).—Interaction of fatty acids (C_{10}—C_{18}) and NH_3 in EtOH yields the NH_4 salts, which rapidly lose NH_3, giving the acid NH_4 salts, $RCO_2NH_4{,}RCO_2H$, which are formed directly from the acid and NH_3 in Et_2O. The following m.p. data are recorded: NH_4 H heptoate, m.p. 45°, octoate, m.p. 54°, decoate, m.p. 68°, undecoate, m.p. 72°, laurate, m.p. 77°, tridecoate, m.p. 81°, myristate, m.p. 84°, pentadecoate, m.p. 86°, palmitate, m.p. 89°, margarate, m.p. 91°, stearate, m.p. 93°. *X*-Ray data on neutral and acid salts are given. J. D. R.

Thermal decomposition of nickel and cobalt formates. F. Caujolle (Compt. rend., 1939, **208**, 445—447).—$(HCO_2)_2Ni{,}2H_2O$ when heated in vac. at 200—300° affords finely divided Ni, a mixture of gases containing CO_2 (62·85%), H_2 (25·08%), CO (11·37%), CH_4 (0·58%), and unidentified gas (0·12%), and some H_2O acid in reaction. Similarly, $(HCO_2)_2Co{,}2H_2O$ affords Co, CoO, and a mixture of gases containing CO_2 (39·97%), H_2 (27·60%), CO (31·48%), CH_4 (0·44%), and an unidentified gas (0·51%). Brochet's equation (cf. A., 1921, ii, 100) for the decomp. of the former does not account for the CO formed. The formation of CH_4 is probably due to a secondary reaction involving the finely divided metal. J. L. D.

Identity of α- and β-linoleic acids. R. W. Riemenschneider, D. H. Wheeler, and C. E. Sando (J. Biol. Chem., 1939, **127**, 391—402).—The identity of α-, β-, and natural linoleic acid is proved by their physical properties and the similar yields of tetrabromostearic and sativic acids obtained from each. The stereochemical configurations are discussed. R. S. C.

Cerebrosides. XVI. Cerebronic acid. E. Klenk and L. Clarenz (Z. physiol. Chem., 1939, **257**, 268—276; cf. Chibnall *et al.*, A., 1936, 454).—Synthetic α-hydroxy-*n*-tetracosanoic acid (I) [from erucic acid (II) by way of Et behenate, *n*-tetracosanoic and α-bromo-*n*-tetracosanoic acid] with AcCl yields *α-acetoxy-n-tetracosanoic acid*, m.p. 65·2—66·0°. Natural cerebronic acid (III) and synthetic (I) with excess of 0·1N-$Pb(OAc)_4$ in AcOH give the aldehyde, $C_{22}H_{45}{\cdot}CHO$ [*oxime*, m.p. 98—99°, which with excess of Ac_2O gives the corresponding *nitrile* (IV), m.p. 52·0—52·5°]. Hydrolysis of (IV) gives *tricosanoic acid*, m.p. 77·7—78·1° (natural), 77·5—78·0° (synthetic), not identical in crystal spacing with tricosanoic acid, m.p. 78·5—79·0°, synthesised from (II). Fractional distillation of Me tricosanoate from natural (III) does not result in isolation of other acids although the fractions have different crystal spacings. Natural (III) is probably identical with (I). W. McC.

Viscosic acid, $C_{27}H_{52}O_3$, m.p. 97° (Na, m.p. 129—130°, and Pb, m.p. 138°, salts). Dihydroxy-acid, $C_{27}H_{54}O_5$, m.p. 127°. Viscosin, $C_{15}H_6O_2(OH)_3{\cdot}OMe$, m.p. 294—295° (decomp.) (Pb and Ag salts; Ac_3 derivative, m.p. 222—223°).—See A., 1939, III, 342.

Condensation of α-keto-acids and amides. II. Pyruvic acid and acetamide. R. M. Herbst (J.

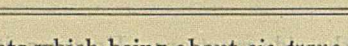
Amer. Chem. Soc., 1939, **61**, 483—486; cf. A., 1938, II, 397).—In the prep. of $(NHAc)_2CMe{\cdot}CO_2H$ (I) from $AcCO_2H$ (II) and NH_2Ac (Bergmann *et al.*, A., 1930, 585), a *compound* (III), $OH{\cdot}CMe(NHAc){\cdot}CO_2H,2NH_2Ac$, m.p. 115—116° (decomp.; corr.), is also formed. NH_2Ac and (II) in abs. EtOH also give (III). As judged by the mol. wt., (I) gives $OH{\cdot}CMe(NHAc){\cdot}CO_2H + 2NH_2Ac$ in cold, and (II) + $3NH_2Ac$ in hot, H_2O. With $NHPh{\cdot}NH_2$ (III) gives $NHPh{\cdot}N{:}CMe{\cdot}CO_2H$ slowly in cold, but rapidly in hot, H_2O, and with 2 : 4-$(NO_2)C_6H_3{\cdot}NH{\cdot}NH_2$ in EtOH it gives the corresponding hydrazone only if first boiled for a few moments with HCl. Br does not react with (III). When heated at 100°/18—20 mm., (III) gives (I) and NH_2Ac, but at 76°/0·5 mm. it gives $CH_2{:}C(NHAc){\cdot}CO_2H$ (IV) + $2NH_2Ac$. BzCl, AcCl, or PhNCO causes only dehydration. $Ba(OH)_2$ and (III) give (II) and NH_2Ac. Analogous compounds containing other amides could not be prepared. Attempts to make (IV) the main reaction product from (II) and NH_2Ac failed. R. S. C.

Isomerisation of dimethyl maleate by hydrogen bromide and by hydrogen chloride. O. Simamura (Bull. Chem. Soc. Japan, 1939, **14**, 22—28; cf. A., 1938, II, 48, 428).—Me_2 maleate and HCl or HBr, in absence of air, in the dark at room temp., afford Me_2 fumarate, the isomerisation being slower in CCl_4. O_2 or pyrocatechol has no influence on the isomerisation. A mechanism of reaction is suggested. No isomerisation of *iso*stilbene to stilbene occurs with HCl in presence of either reduced Ni or O_2. A. T. P.

Acryloxycarboxylic acids and their esters.—See B., 1939, 242.

Michael condensation. V. Influence of the experimental conditions and the structure of the acceptor on the condensation. R. Connor and W. R. McClellan (J. Org. Chem., 1939, **3**, 570—577).—*sec.* Amines (*e.g.*, piperidine) are the safest catalysts in the Michael reaction since they seldom cause change other than the normal condensation. Where ring-closure, rearrangement, or formation of termol. compounds must be avoided amines give satisfactory results. They are less potent catalysts than Na alkoxides and with them the rate of reaction is rather slow even in favourable cases. NaOEt (one sixth to one third of an equiv.) may cause condensation in cases in which amines are ineffective. The condition is less drastic and less liable to cause side reactions than the use of 1 equiv. of NaOEt. The equiv. of catalyst is most likely to cause condensation and also side reactions. If a reactant or product undergoes alcoholysis readily in the presence of alkoxides or if the Na derivative of the active CH_2 compound is not readily formed, the Na derivative may be prepared by the use of Na or $NaNH_2$. The solubility of the reactants is the chief desideratum in selecting a solvent: MeOH, EtOH, C_6H_6 Et_2O, and dioxan have given satisfactory results. With Na alkoxides as catalysts the best results are obtained by keeping the mixture at room temp. for 20—150 hr. Higher temp. may give lower yields presumably because they favour retrogression and increase the side reactions. However, if ring-closure or the formation of termol. compounds is desired, the reaction may be carried out under reflux. With *sec.* amines the change is so slow that long boiling is necessary. An arrangement of labilising groups in the order of their ability to activate the double linking of the acceptor cannot yet be given. In a system, $CH_2{:}CHL_1$, the reactivity of the acceptor diminishes as the H atoms are replaced by larger groups; this is true whether substitution is at $C_{(\alpha)}$ or $C_{(\beta)}$. The reactivity of the acceptor is decreased if the substituent is alkyl, aryl, carbethoxy, or acyl. The magnitude of this effect probably depends largely on the size of the substituent, although in the case of negative groups such as $\cdot CO_2R$ or $\cdot CN$ the spatial effect may be modified by a polar effect which renders the system less unreactive than might be expected from the size of such groups. Groups which are not attached directly to the double linking of the acceptor have a greater influence on reactivity than is generally appreciated. The magnitude of their influence cannot be estimated but in predicting reactivity the possibility that remote groups may vastly alter the nature of the acceptor cannot be dismissed. The possibility of steric hindrance would suggest that the *o*-isomeride would be the least active of the nitrocinnamic esters whereas actually the *p*-isomeride is the most turgid. Apparently steric influences by *o*-substituents are not extremely important—a fact confirmed by the reaction of benzylideneacetomesitylene. On the other hand, a *p*-NO_2-group does not always prevent reaction. In the case of 6-bromocoumarin, substitution by Br causes a decrease in reactivity. The following compounds are new: *β-hydroxy-β-phenyl-β-dicarbethoxymethylpropiolactone*, m.p. 52°, b.p. 203°/4 mm.; *Et*$_2$ *α-phenyl-ββ-dimethylpropane-αγ-dicarboxylate*, b.p. 160—163°/6 mm.; *Me* α-m-*nitrobenzylidenepropionate*, m.p. 54—55°; *Me*$_3$ β-m-*nitrophenylpropane-αγγ-tricarboxylate*, m.p. 97—98°, and the corresponding o-, m.p. 82—83°, and p-*derivatives*, m.p. 97—97·5°; *Me*$_2$ 2 : 4 : 6-*trimethylphenyl-β-phenylpropane-αγ-tricarboxylate*, m.p. 82—83°. All m.p. are corr. H. W.

Catalytic *cis–trans*-isomerisation and restricted rotation of diphenyl derivatives. W. I. Gilbert, J. Turkevich, and E. S. Wallis (J. Org. Chem., 1939, **3**, 611—617).—Experiments on the influence of Na, $AlCl_3$, $FeCl_3$, $ZnCl_2$, $CrCl_3$, Fe_3O_4, $NiCl_2$, $MgCl_2$, $HgCl_2$, Hg_2Cl_2, H_2O, and Fe_2O_3 on the isomerisation of Me_2 maleate to Me_2 fumarate show that there is no direct correlation between the magnetic character of the compound tested and its catalytic activity. Attempts are described to determine whether those experimental conditions which produce *cis–trans*-isomerism of the ethylenic double linking and those which temporarily destroy the double linking character would racemise an optically active diphenyl derivative. Et *d*-3 : 5-dinitro-6-1-naphthylbenzoate is not racemised by Pt-black, Na, or $FeCl_3$ and the acid is not racemised by exposure to sunlight in $CHCl_3$–CCl_4 or by Br in the same solvents. It is concluded that the existence of the double linking between the two Ph groups in Ph_2 derivatives cannot be detected by use of those

chemical agents which being about *cis–trans*-isomerisation. Therefore there may be no contribution of the type  to the ordinary structure for Ph_2 or this contribution may be present but, due to the size of the substituents on the Ph groups, steric factors may come into play, and prevent the catalyst from affecting the coupling between these two π electrons either by distorting their orbits or by actual bond formation with the catalyst, and thus inhibit the formation of the necessary complex which of necessity on decomp. would give an equal no. of *d*- and *l*-forms. H. W.

Synthesis of cyclic derivatives of tartaric acid. V. Optical activity and chemical structure. Y. Tsuzuki (Bull. Chem. Soc. Japan, 1939, **14**, 19—22; cf. A., 1938, II, 60).—Et_2 *d*-tartrate and the respective ketone, with P_2O_5, afford the following *Et*$_2$ *alkylidenedioxysuccinates* of type $CRR'<^{O\cdot CH\cdot CO_2Et}_{O\cdot CH\cdot CO_2Et}$: R R′ = Me Et, b.p. 158°/17 mm., $[\alpha]_D^{20}$ −40·2° in C_6H_6, −36·0° in EtOH, −31·62° in *cyclo*hexane, this order being followed with other analogues; *Me Pr*, b.p. 167·5°/20 mm., $[\alpha]_D^{20}$ −36·4°, −31·8°, −28·86°; *Et*$_2$, b.p. 169°/22 mm., $[\alpha]_D^{20}$ −33·0°, −25·3°, −20·89°; *Me amyl*, b.p. 180°/15 mm., $[\alpha]_D^{20}$ −31·13°, −27·33°, −24·19°; *Pr*$_2$, b.p. 175°/16 mm., $[\alpha]_D^{20}$ −28·47°, −22·45°, −18·17°; and *Me nonyl*, b.p. 218°/15 mm., $[\alpha]_D^{20}$ −26·03°, −21·38°, −18·93°. *Me*$_2$, b.p. 141°/15 mm., *Pr*$_2$, b.p. 167°/15 mm., and *Pr*$^\beta_2$ *methylpropylidenedioxysuccinate*, b.p. 115—117°/0·5 mm., are prepared similarly. A. T. P.

Reduction of aconitic acid at the dropping mercury cathode. A. Miolati and G. Semerano (Z. Elektrochem., 1939, **45**, 226—228).—The experiments of Siebert (cf. A., 1938, II, 471) are criticised, and views attributed by Siebert to the authors are corr. (see following abstract). C. R. H.

Reduction of aconitic acid at the dropping mercury cathode. H. Siebert (Z. Elektrochem., 1939, **45**, 228).—A reply to Miolati and Semerano (see preceding abstract). C. R. H.

Micro-determination of ascorbic and dehydroascorbic acid.—See A., 1939, III, 290.

Formation of oxamide by oxidation of dehydroascorbic acid with hydrogen peroxide in ammoniacal solution. J. Parrod (Bull. Soc. chim., 1939, [v], **6**, 392—396; cf. A., 1938, II, 307).—*l*-Ascorbic acid (I) loses 2 H with *p*-benzoquinone in Et_2O–H_2O and the resulting solution (*A*) containing dehydroascorbic acid (II) decomposes slowly. *A* on oxidation by air in presence of NH_3 gives only a little $(CO\cdot NH_2)_2$ (III); with NH_3–H_2O_2 much more (III) is formed, which increases with amount of H_2O_2, and then is approx. const. It is formed from (II). NH_3 reacts rapidly, previously to adding H_2O_2; when NH_3 and H_2O_2 are added to *A* simultaneously, the yield of (III) is ≪ that obtained if H_2O_2 is added 2—60 sec. after the NH_3. Freshly prepared *A* affords a max. yield of (III) comparable with that obtained from (I) by NH_3 + air oxidation (*loc. cit.*). The amount of (III) formed decreases as *A* is kept, as does also the amount of (I) regenerated by H_2S. A. T. P.

Methyl ethers of araboascorbic acid and their isomerism. E. G. E. Hawkins, E. L. Hirst, and J. K. N. Jones (J.C.S., 1939, 246—248).—*d*-Araboascorbic acid (I) in MeOH with CH_2N_2 in Et_2O yields 3-*methyl*-d-*araboascorbic acid*, m.p. 102°, $[\alpha]_D^{20}$ −26° in H_2O, which on further methylation with CH_2N_2 yields 2 : 3-*dimethyl*-d-*araboascorbic acid* (a syrup), $[\alpha]_D^{20}$ −20° in H_2O, −37° in MeOH, also formed from (I) with excess of CH_2N_2, which with aq. $Ba(OH)_2$ yields *dimethyl*iso-d-*araboascorbic acid* (a syrup), $[\alpha]_D$ −5° in H_2O, hydrolysed by MeOH–HCl containing 10% of H_2O to 2-*methyl*-d-*araboascorbic acid*, $[\alpha]_D$ −38° in MeOH, −19° in H_2O. J. D. R.

Intermediary metabolism of citric acid.—See A., 1939, III, 301.

Reactions of humic acids with neutral salts. II. T. A. Kucharenko (Chim. Tverd. Topl., 1937, **8**, 1064—1072).—$Ca(OAc)_2$ reacts with humic acids liberating AcOH. The reaction may be used to determine CO_2H groups titrimetrically. The determination is quicker than the standard methylation method and can be used for humic substances with small or large CO_2H content. D. G.

Preparation and determination of glyoxal tetramethyl acetal. D. H. Grangaard and C. B. Purves (J. Amer. Chem. Soc., 1939, **61**, 428—429).—$[CH(OMe)_2]_2$ (prep. from glyoxal disulphate described), b.p. 98—100°/110 mm., is quantitatively converted by 2N-HCl into $(CHO)_2$ (determined as dinitrophenylhydrazone or by Ariyama's method). Separation of the acetal from solvents is described. R. S. C.

Action of acid chlorides on aliphatic ethylenic hydrocarbons in presence of stannic chloride. I, II. J. Colonge and K. Mostafavi (Bull. Soc. chim., 1939, [v], **6**, 335—342, 342—354).—CMe_2:CHMe and EtCOCl, with $SnCl_4$ as catalyst, followed by hydrolysis (HCl), afford CMe_2EtCl, *ε-chloro-δε-dimethylhexan-γ-one* (I), b.p. 74—78°/17 mm., and *δε-dimethyl-*Δ^δ- (53% of total unsaturated ketone), b.p. 164—166°/750 mm. [*semicarbazone*, m.p. 209°; (?) 1-carbamyl-4 : 5 : 5-trimethyl-3-ethyl-2-pyrazoline, m.p. 130°], and -Δ^ϵ-*hexen-γ-one* (47%), b.p. 158—162°/750 mm. (*semicarbazone*, m.p. 108—110°). The mixed unsaturated ketones (II) are obtained from (I) by refluxing with $NPhMe_2$, and are purified by hydrolysing their semicarbazones with $H_2C_2O_4$; the α- tends to isomerise to the β-unsaturated ketone during such hydrolysis. Both ketones are hydrogenated (Pt-black) to *δε-dimethylhexan-γ-one*, b.p. 151—153°/730 mm. (*semicarbazone*, m.p. 98°). The yield of (II) is 60% with $SnCl_4$, and 40, 16, 13, and 0% with $TiCl_4$, $ZnCl_2$, $AlCl_3$, and $HgCl_2$, respectively. CMe_2:CHMe, AcCl, and $SnCl_4$ afford *δ-chloro-γδ-dimethylpentan-β-one*, b.p. 60—64°/14 mm., converted by $NPhMe_2$ into mixed unsaturated ketones, separated (as above) into *γδ-dimethyl-*Δ^γ- (III) (80%), b.p. 146—147° (*semicarbazone*, m.p. 199—200°), and -Δ^δ-*penten-β-one* (20%), b.p. 140—144° (*semicarbazone*, m.p. 112—114°), the constitutions of the semicarbazones being supported by the application of tests described by Dœuvre (A., 1936, 587) for terminal

$:CMe_2$ and $:CH_2$. (III) and NaOBr afford αββ-trimethylacrylic acid. Hydrogenation (Pt-black) of the mixed ketones gives solely γδ-dimethylpentan-β-one, b.p. 136—138°/760 mm. (*semicarbazone*, m.p. 113°). $Pr^{\beta}COCl$ similarly affords ε-*chloro*-βδε-*trimethylhexan*-γ-*one*, b.p. 74—79°/14 mm., converted into βδε-trimethyl-Δ^{δ}- (*semicarbazone*, m.p. 190°; sublimes at 188°) and -Δ^{ϵ}-hexen-γ-one (*semicarbazone*, m.p. 110—111°), which give βδε-*trimethylhexan*-γ-*one*, b.p. 162—166°/760 mm. $Bu^{\gamma}COCl$ and $CMe_2:CHMe$ also yield mixed unsaturated ketones, hydrogenated to ββδε-*tetramethylhexan*-γ-*one*, b.p. 172—175°/760 mm. With compounds CRR':CHR'', the Cl of R·COCl attaches itself to the more substituted C. β-Methylpropene and EtCOCl yield, through the chloroketone, ε-*methyl*-Δ^{δ}-*hexen*-γ-*one*, b.p. 147—148°/760 mm. (*semicarbazone*, m.p. 163°), solely. $(:CMe_2)_2$, AcCl, and $SnCl_4$ afford $CMe_2Pr^{\beta}Cl$, δ-*chloro*-γγδ-*trimethylpentan*-β-*one*, m.p. 82°, b.p. 90°/30 mm., and thence γγδ-*trimethyl*-Δ^{δ}-*penten*-β-*one*, b.p. 151°/753 mm. [ozonolysis of its *semicarbazone*, m.p. 152° (157°), indicates a terminal CH_2], hydrogenated to γγδ-*trimethylpentan*-β-*one*, b.p. 152—154°/753 mm. (semicarbazone, m.p. 150°) (cf. Whitmore *et al.*, A., 1933, 1140). β-Methyl-Δ^{β}-hexene and AcCl similarly afford mixed unsaturated ketones, hydrogenated to γ-iso*propylhexan*-β-*one*, b.p. 172—173°/744 mm. (*semicarbazone*, m.p. 129—130°). Δ^{α}-Heptene reacts with AcCl, but no unsaturated ketone was obtained. $(:CHCl)_2$ and $CH_2:CH·CH_2Cl$ do not react with AcCl.

A. T. P.

Transformation of carboxylic acids into ketones by means of their lead salts. J. Kenner and F. Morton (Ber., 1939, 72, [*B*], 452—456).—Reasons are advanced for considering the Pb salts of acids particularly suitable for the prep. of ketones. The salts of the higher fatty acids, of unsaturated acids, and of the H esters of the higher dicarboxylic acids lose CO_2 smoothly at 240—310° until about 50—70% of the theoretically possible CO_2 has been evolved. The liquid then solidifies to an intermediate product from which ketone cannot be isolated immediately. If derived from a fatty acid it gives an excellent yield of ketone when distilled. Salts of unsaturated acids give a black resinous product which gives only a little ketone when distilled under diminished pressure and is very slowly attacked by $(NH_4)_2S$. HCO_2H transforms it into a mixture of ketone and unchanged acid. The method is also applicable to salts of H esters. The method has been applied to the salts of AcOH, $EtCO_2H$, $Pr^{\alpha}CO_2H$, $C_5H_{11}·CO_2H$, $C_7H_{13}·CO_2H$, $C_8H_{15}·CO_2H$, $C_{10}H_{21}·CO_2H$, lauric and stearic acid, $CH_2Ph·CO_2H$, $CH_2Ph·CH_2·CO_2H$, $C_3H_6Ph·CO_2H$, $C_4H_8Ph·CO_2H$, undecenoic, chaulmoogric, and hydnocarpic acid, *Me H suberate*, b.p. 185—186°/18 mm., m.p. 14—15°, Me H azelaate, Me H and Et H sebacate. The following are new: *chaulmoogrone*, $C_{35}H_{62}O$, m.p. 59·5°; *hydnocarpone*, m.p. 52°; αη-*diphenylheptan*-δ-*one*, b.p. 186—187°/0·8 mm.; αι-*diphenylnonan*-ε-*one*, b.p. 205—207°/0·5 mm. (*oxime*, m.p. 43°); *Me*$_2$ θ-*ketopentadecane*-ακ-*dicarboxylate*, b.p. 242—244°/15 mm., m.p. 42° (free *acid*, m.p. 114°); ι-*ketononadecanone*-ατ-*dicarboxylic acid*, m.p. 124°; *Me H pimelate*, b.p. 168—169°/17 mm., m.p. 5°. H. W.

Symmetrical dialkoxyacetones. H. R. Henze and B. G. Rogers (J. Amer. Chem. Soc., 1939, **61**, 433—435).—$CO(CH_2·OR)_2$ (R = Alk) could not be obtained from $CO(CH_2Cl)_2$ and NaOAlk, but are prepared from $OH·CH(CH_2Cl)_2$ and NaOAlk, followed by $Na_2Cr_2O_7$–H_2SO_4 at 15—20°. $OR·CH_2·CO_2Et$ (prep. from $CH_2Cl·CO_2Et$) gives $(OR·CH_2·CO)_2CH·CO_2Et$ and thence by aq. K_2CO_3 only 10% of $CO(CH_2·OR)_2$. The following are described. n-*Amyl chloroacetate*, b.p. 198—199°/744 mm.; *Bu*$^{\alpha}$ n-*butoxy*-, b.p. 123—123·5°/30 mm., and n-*amyl* n-*amyloxy-acetate*, b.p. 148—149°/35 mm.; *glycerol* αγ-Me_2, b.p. 65·5—66°/9 mm., Et_2, b.p. 61·5—62°/2 mm., Pr^{α}_2, b.p. 82—83°/2 mm., Pr^{β}_2, b.p. 74—75°/2 mm., Bu^{α}_2, b.p. 104—105°/2 mm., Bu^{β}_2, b.p. 105—105·5°/4 mm., sec.-Bu_2, b.p. 95—96°/2 mm., di*iso*amyl, b.p. 125—126°/2 mm., and *di*-n-*amyl*, b.p. 124—125°/2 mm., *ether*; s-*dimethoxy*-, b.p. 78—78·5° (2 : 4-*dinitrophenylhydrazone*, m.p. 119·5—120·5°), -diethoxy-, b.p. 105—105·5°/35 mm. (*semicarbazone*, m.p. 90—91°), -*di*-n-, b.p. 124—125°/28 mm. (*semicarbazone*, m.p. 85·5—87°), and -*di*iso-*propoxy*-, b.p. 75—76·5°/1 mm., -*di*-n-, b.p. 111·5—112·5°/3 mm. (*semicarbazone*, m.p. 82·5—83·5°), -*di*iso-, b.p. 91—93°/1 mm., and -*di*-sec.-*butoxy*-, b.p. 88—90·5°/1 mm., -*di*-n-, b.p. 128—129·5°/1 mm., and -*di*iso-*amyloxy*-, b.p. 120—122°/1 mm., -*acetone*. *d*, *n*, γ, and parachors are given. Temp. are corr. R. S. C.

Synthesis from thujaketone of some new hydroterpenoids. J. Werner and M. T. Bogert (J. Org. Chem., 1939, **3**, 578—587).—*d*-Thujone, obtained from thuja-leaf oil (tribromide, m.p. 121—122°; 2 : 4-dinitrophenylhydrazone, m.p. 106—107°), is converted by (modified) oxidation with aq. $KMnO_4$ into α-thujaketonic acid, m.p. 74—75° (oxime, m.p. 175—176°), decarboxylated at 275—325° to thujaketone [β-methyl-γ-methyleneheptan-β-one] (I), b.p. 183—188° (semicarbazone, m.p. 141—142°; 2 : 4-*dinitrophenylhydrazone*, m.p. 73—74°). $CH_2Br·CO_2Et$ and Zn convert (I) in C_6H_6–PhMe into *Me* β-*hydroxy*-βζ-*dimethyl*-ε-*methyleneoctoate*, b.p. 113—114°/3 mm. The corresponding *acid* (II), b.p. 144—146°/3 mm., is hydrogenated (Pd–C in 80% MeOH) to β-*hydroxy*-βεζ-*trimethyloctoic acid*, b.p. 164—166°/6 mm. Dehydration of (II) by P_2O_5 in boiling C_6H_6 affords βζ-*dimethyl*-ε-*methylene*-Δ^{α}-*octenoic acid* (III), b.p. 127—128°/2 mm. Slow distillation transforms (II) into βε-*dimethyl*-δ-*methylene*-Δ^{α}-*heptene*, b.p. 158—159°, also obtained in poorer yield from (III) and oxidised by $KMnO_4$ to β-methylheptane-γζ-dione in small amount. Gradual addition of (I) to well-cooled PCl_5 gives β-*chloro*-ζ-*methyl*-ε-*methylene*-Δ^{β}-*heptene*, b.p. 95—96°/18 mm., oxidised to $COMePr^{\beta}$ in small yield. Methylheptenone (IV) is transformed by the successive action of $NaHSO_3$ and KCN into α-*hydroxy*-αε-*dimethyl*-Δ^{δ}-*heptenonitrile*, b.p. 115—117°/2 mm. Analogously, (I) affords α-*hydroxy*-αε-*dimethyl*-δ-*methyleneheptonitrile*, b.p. 116—118°/2 mm. The following alcohols are synthesised by the standard Grignard reaction either from (I) or $Bu^{\beta}CHO$ or by reduction of the corresponding unsaturated alcohol: βζ-*dimethyl*-η-*methyleneheptan*-β-*ol*, b.p. 97—99°/19 mm.; βζ-*dimethyl*-γ-*methylenedodecan*-ζ-*ol*, b.p. 150—153°/15 mm.; β-cyclo*hexyl*-ζ-*methyl*-ε-*methylene*-

heptan-β-ol, b.p. 122—124°/3 mm.; *βζ-dimethyl-γ-methylene-η-isobutyltridecan-ζ-ol*, b.p. 157—157·5°/2 mm.; *βγζ-trimethyldodecan-ζ-ol*, b.p. 149—151°/17 mm.; *β-methyldecan-δ-ol*, b.p. 123—125°/12 mm. *δ-Bromo-β-methyldecane* has b.p. 115—118°/17 mm. *Et α-cyano-βζ-dimethyl-$\Delta^{\alpha\epsilon}$-octadienoate*, b.p. 151—152°/12 mm., is obtained from (IV), $CN{\cdot}CH_2{\cdot}CO_2Et$, and NH_2Ac in AcOH–Ac_2O. The odours of these compounds differ from and are more pleasant than those of the analogously constituted compounds obtained from (IV). In the case of the *tert.* alcohols synthesised by the Grignard reaction, the agreeableness of the odour diminishes with increase in the mol. wt. of the hydrocarbon introduced. All m.p. are corr. H. W.

Degradation reaction in organic chemistry. A. Schönberg (Nature, 1939, **143**, 113).—A correction (cf. A., 1939, II, 49). L. S. T.

Acetylation of carbohydrates by keten. C. D. Hurd, S. M. Cantor, and A. S. Roe (J. Amer. Chem. Soc., 1939, **61**, 426—428).—Anhyd. glucose, keten, and a drop of H_2SO_4 in $COMe_2$ give a glass containing 4·59 Ac; *p*-$C_6H_4Me{\cdot}SO_3H$ does not catalyse acetylation in dioxan; in C_5H_5N (no acid) an impure, glassy triacetate, $[\alpha]_D^{20}$ +39·5° in $CHCl_3$ (converted by Ac_2O–C_5H_5N into a glass, $[\alpha]_D$ +48·8° in $CHCl_3$), is produced with a small amount of the compound, m.p. 204° (Wollenberg, A., 1934, 1336), formed with dehydroacetic acid (I) from C_5H_5N. In dioxan or with a drop of H_2SO_4 in AcOH an oily triacetate, converted by Ac_2O–C_5H_5N into the α-tetra-acetate, is obtained. 6-Triphenylmethyl-α-methylglucoside with Ac_2O–C_5H_5N gives only, and with keten in Ac_2O gives mainly, the 1 : 2 : 4-triacetate, m.p. 136°, and 1 : 2-*iso*propylideneglucose gives by either method the triacetate. CO:CHAc with C_5H_5N–dioxan gives (I), which is unchanged by this reagent. R. S. C.

Oxidation of aldoses by hypoiodite. I. K. Myrbäck (Svensk Kem. Tidskr., 1939, **51**, 7—11).—Errors in the determination of aldoses by NaOI are discussed, and the importance of keeping [NaOH] low is stressed. M. H. M. A.

Isolation of derivatives of 2-methylglucose and 3-methylglucose from a partly methylated cellulose. W. J. Heddle and E. G. V. Percival (J.C.S., 1939, 249—250).—Cellulose (surgical cotton) methylated by the method of Piwonka (A., 1936, 1235) yields a partly methylated cellulose from which, by hydrolysis with 1% HCl–MeOH, 2- and 3-methylglucose are isolated as the phenylhydrazone and osazone respectively. J. D. R.

Isolation of an anhydro-sugar from agar. E. G. V. Percival, J. C. Somerville, and I. A. Forbes (Nature, 1938, **142**, 797—798).—Hydrolysis of methylated agar with HCl–MeOH affords 2 : 4 : 6-trimethylmethylgalactoside and a non-homogeneous syrup from which a cryst. *dimethylanhydromethylhexoside* (X), $C_6H_7O_2(OMe)_3$, b.p. 85—90°/0·05 mm., m.p. 81°, $[\alpha]_D^{20}$ +75° in H_2O, +85° in $CHCl_3$, is isolated. This gives a strong Selivanov test and is converted by N-H_2SO_4 in 24 hr. into the *anhydrosugar* (I), $[\alpha]_D^{17}$ −23°. Direct methylation of 3 : 6-anhydro-α-methylgalactoside gives 2 : 4-*dimethyl*-3 : 6-*anhydro*-α-*methylgalactoside*, b.p. 90°/0·05 mm., $[\alpha]_D^{20}$ +87° in $CHCl_3$, which gives the Selivanov reaction and is hydrolysed by N-H_2SO_4 in 24 hr. to 2 : 4-*dimethyl*-3 : 6-*anhydro*-d-*galactose* (II), $[\alpha]_D^{18}$ +22°. It is probable that (I) and (II) are optical antipodes. H. W.

3 : 6-Anhydro-*l*-galactose in agar. E. G. V. Percival and I. A. Forbes (Nature, 1938, **142**, 1076).—The substance, X, derived from agar (preceding abstract) is shown to be 2 : 4-dimethyl-3 : 6-anhydro-β-methyl-*l*-galactoside (cf. A., 1939, II, 50). 3 : 6-*Anhydro*-β-*methyl*-d-*galactoside* (I), m.p. 118°, $[\alpha]_D^{20}$ −113° in H_2O, has been synthesised from 1-bromo-α-*d*-galactose triacetate 6-*p*-toluenesulphonate by treatment with Ag_2CO_3 + MeOH, and deacylation (NaOH). Methylation of (I) gives a quant. yield of 2 : 4-*dimethyl*-3 : 6-*anhydro*-β-*methyl*-d-*galactoside*, m.p. 82°, $[\alpha]_D^{20}$ −77° in H_2O, −86° in $CHCl_3$, which is shown to be the enantiomorph of X. L. S. T.

Crystalline β-methylmannofuranoside and mannose dimethyl acetal. E. Pacsu and A. Scattergood (J. Amer. Chem. Soc., 1939, **61**, 534—536).—*d*-Mannose Et_2 mercaptal (I) yields 60% of α- and β-*methylmannofuranoside*, m.p. 47°, $[\alpha]_D^{20}$ −107° in H_2O, the latter product being isolated as a *compound*, *X*,$CaCl_2$,$3H_2O$, $[\alpha]_D^{20}$ −58° in H_2O, which is also obtained from the syrupy reaction product of mannose and HCl–MeOH. The penta-acetate of (I) yields d-*mannose* Me_2 *acetal*, m.p. 101°, $[\alpha]_D^{20}$ +0·6° in H_2O. R. S. C.

Reaction for distinction of fructose from glucose. O. M. Tscherntsov (Compt. rend. Acad. Sci. U.R.S.S., 1938, **20**, 583—584).—The reaction suggested by Zmachinski (A., 1938, II, 172) is not sp. for fructose but proceeds readily with glucose and other aldoses, and only slightly more slowly with disaccharides. J. D. R.

Structure of γ-sugars. I. Parachors of partly and fully methylated derivatives of γ-fructose. F. Hartley and W. H. Linnell (Quart. J. Pharm., 1938, **11**, 714—721).—The vals. of [*P*] of furfuraldehyde and piperonal (305·9—307·1 for the latter) confirm that no anomaly occurs in the val. of [*P*] due to the presence of O in 5-membered rings. The vals. of [*P*] for sucrose, fructose, and glucose (in aq. solution) are anomalous and irregular, whilst those for tetramethyl-γ-fructose and -γ-methylfructoside differ significantly from the vals. calc. for either the furanose or the propylene oxide structure. F. O. H.

Ketoses. II. Structure of α-*d*-tagatose. (Mme.) Y. Khouvine, G. Arragon, and Y. Tomoda (Bull. Soc. chim., 1939, [v], **6**, 354—359; cf. A., 1938, II, 473).—α-*d*-Tagatose (I), m.p. 162° (cf. Danilow *et al.*, A., 1930, 1411; Reichstein *et al.*, A., 1934, 872), when redistilled with dry C_5H_5N and Ac_2O at 0—2° (4 hr.) gives α-d-*tagatoside penta-acetate*, m.p. 132°, $[\alpha]_{578}^{20}$ +30·2° in $CHCl_3$, −52·0° in MeOH (Raman spectrum shows no band at 2800 A.); Ac_2O with $ZnCl_2$ affords a syrup. (I) and HCl–MeOH at 28° give α-d-*methyltagatoside* (II), m.p. 128°, $[\alpha]_{578}^{20}$ +56·8° in MeOH, +47·8° in H_2O; acid hydrolysis gives (I), with mutarotation. (II) and

Ac_2O–C_5H_5N at 0°, then at room temp., give the *Ac*$_4$ derivative, m.p. 125°, $[\alpha]_{5780}^{20}$ +43·8° in C_6H_6, +23·8° in $CHCl_3$, and +6·2° in MeOH. (II) in MeOH with MeI–Ag_2O (8 to 10 successive methylations) gives *tetramethyl*-α-d-*methyltagatoside* (III), b.p. 40°/0·001 mm., $[\alpha]_{5780}^{20}$ +21·4° in MeOH (Raman spectra do not indicate CO), oxidised by HNO_3 (*d* 1·49) to *l*-dimethoxysuccinic and *d*-arabotrimethoxyglutaric acids. (II) and Me_2SO_4–NaOH–CCl_4 at 60—65° afford syrups, $[\alpha]_{5780}^{20}$ +28·7° and +30·8°, respectively, in MeOH. (I) and aq. NaOH–Me_2SO_4 at 60—70° give *tetramethyl*-β-d-*methyltagatoside*, $[\alpha]_{5780}^{20}$ +9·7° in MeOH, in poor yield. Hydrolysis of (III) with aq. HCl gives *tetramethyl*-α-d-*tagatose*, b.p. 55°/0·0001 mm., $[\alpha]_{5870}^{20}$ −3·4° in MeOH. (I) (and its derivatives) has a pyran configuration, more stable than those of β-*d*-fructose and α-*l*-sorbose. A. T. P.

Structure and configuration of perseulose (*L*-galaheptulose). R. M. Hann and C. S. Hudson (J. Amer. Chem. Soc., 1939, **61**, 336—340).—Perseulose (I) (prep. from perseitol in 91·6% yield by *Acetobacter suboxydans*), +0·5H_2O, m.p. 102—103° (corr.), $[\alpha]_D$ about −102° → −86° (anhyd.), is shown to be *L*-galaheptulose. The *phenylosazone*, decomp. 240°± 1° (block), [α] −114° → −35° in C_5H_5N, and the *penta-acetate*, m.p. 117—118° (corr.), [α] −86·8° in $CHCl_3$, thereof are enantiomorphs of the derivatives of *D*-galaheptulose. dl-*Galaheptosephenylosazone*, m.p. 222° (corr.; capillary), 259° (block), and its *penta-acetate*, m.p. 125—126° (shrinks at 116—117°), are described. Raney Ni–H_2 at 100°/167 atm. reduces (I) in H_2O to *D*-gulo-*L*-gala- and L-*gala*-D-*gluco-heptitol*, m.p. 141°, [α] −2·4° in H_2O [*hepta-acetate*, m.p. 118° (corr.), [α] −11·4° in $CHCl_3$; enantiomeride obtained by similar reduction of *D*-gala-*L*-glucoheptose]. dl-*Galaglucoheptitol*, m.p. 138° (corr.), and its *hepta-acetate*, m.p. 127° (corr.), are also described. R. S. C.

Oxidative degradation of perseulose to *L*-galactonic acid. N. K. Richtmyer, R. M. Hann, and C. S. Hudson (J. Amer. Chem. Soc., 1939, **61**, 340—343).—O_3 converts perseulose (I) in N-KOH at 23—27° in 46% yield into *K* L-*galactonate*, +H_2O, [α] −2·95° in H_2O, +12·2° → +61·2° in N-HCl, which yields the *Pb* salt, [α] +13·6° in H_2O, +14·8° → +61·2° in N-HNO_3, and thence (H_2S) γ-L-*galactonolactone*, sinters at ~ 128°, m.p. 134°, [α] +78·4° in H_2O. The *D*-salts mutarotate similarly. This confirms the structure of (I). R. S. C.

Oxidative degradation of sedoheptulose to *D*-altronic acid. N. K. Richtmyer, R. M. Hann, and C. S. Hudson (J. Amer. Chem. Soc., 1939, **61**, 343—345).—Crude sedoheptulose (prep. from *Sedum spectabile*) in N-KOH is converted by O_2 etc. into Ca *D*-altronate, +3·5H_2O, $[\alpha]_D^{20}$ +11·5° → +24·8° in N-HCl, and is thus *D*-altroheptulose (cf. Ettel, A., 1933, 47). R. S. C.

Polysaccharides synthesised by micro-organisms. IV. Molecular constitution of luteose. C. G. Anderson, W. N. Haworth, H. Raistrick, and M. Stacey (Biochem. J., 1939, **33**, 272—279).—Elimination of the malonyl residues from luteic acid, one of the metabolic products of *Penicillium luteum*, Zukal, gives rise to a polysaccharide, *luteose*; this consists of a closed chain type of mol. mainly composed of glucopyranose units linked through the 1 : 6-positions, as indicated by the isolation of 2 : 3 : 4-trimethylglucose in 85% yield from methylated luteose, together with 10% of dimethylglucose. P. G. M.

Cæsioside, $C_{26}H_{28}O_{15}$,3H_2O, m.p. 225—230°, $[\alpha]_D^{20}$ −220° in 0·1N-NaOH.—See A., 1939, III, 343.

Partial oxidation of starch by bromine. Y. Kihara (J. Agric. Chem. Soc. Japan, 1939, **15**, 107—108).—Oxidation of starch paste in presence of $CaCO_3$ by Br at room temp. produces *urondextrin*, $[\alpha]_D^{15}$ +181·72° in H_2O (*acetate*, m.p. 145°). It is sol. in H_2O and pptd. by EtOH, $Ca(OH)_2$, and $Ba(OH)_2$, but not by $CuSO_4$. It is scarcely affected by taka-diastase. J. N. A.

Constitution and enzymic degradation of starch. K. Myrbäck (Suomen Kem., 1939, **12**, A, 19—29).—A review. M. H. M. A.

Recent results in the study of starch. II. M. Samec and M. Blinc (Kolloid-Beih., 1939, **49**, 75—314; cf. A., 1938, II, 262).—A review of work on the degradation of starch by enzymes and acids. F. L. U.

[Preparation of] *sec.* amines by the Leuckart synthesis. A. Novelli (J. Amer. Chem. Soc., 1939, **61**, 520—521).—HCO·NHR and the appropriate ketone at 190—230° give 50—80% yields of the *hydrochlorides*, NHRR′,HCl, in which (*a*) R = *CHPhMe*, R′ = Me, m.p. 178—179° (lit. 173°), Et, m.p. 199—200° (lit. 201°), and *Bu*, m.p. 154—155°, (*b*) R = p-C_6H_4Me·*CHMe*, R′ = *Me*, m.p. 159—160°, *Et*, m.p. 217—218°, and *Bu*, m.p. 159—160°, (*c*) R = p-C_6H_4Cl·*CHMe*, R′ = *Me*, m.p. 199—200°, *Et*, m.p. <250°, and *Bu*, m.p. 174—175°, and (*d*) R = p-C_6H_4Br·*CHMe*, R′ = *Me*, m.p. 196—197°, *Et*, m.p. <250°, and *Bu*, m.p. 174—175°. R. S. C.

Protein metabolism. IV. Stability of nitrogen in organic compounds. A. S. Keston, D. Rittenberg, and R. Schoenheimer (J. Biol. Chem., 1939, **127**, 315—318).—When two N-containing components, one of which contained "labelled" N, were heated at 100° in aq. solution, no exchange of the N could be detected in the following systems: (*a*) NH_2-acid (I)–NH_3; (*b*) (I)–(I); (*c*) hippuric acid–(I); (*d*) $CO(NH_2)_2$–(II)–(I). Some exchange may occur between (II) and NH_3 in H_2O at 105° but in any case the reaction is a slow one. The guanido-group in arginine does not exchange N under the conditions investigated. W. O. K.

Effect of pyrrole on the oxidation of amines and the non-natural isomerides of certain amino-acids.—See A., 1939, III, 78.

Isolation of spermine as flavianate. H. Fuchs (Z. physiol. Chem., 1939, **257**, 149—150).—Spermine (I) salts yield with excess of flavianic acid (II) *spermine tetraflavianate*, decomposed by H_2O at 100° with production of the *diflavianate* (III), chars 290—300°. (III) is readily converted into the pure tetrapicrate and free base. With $CuCO_3$ at 100° (I) yields a deep lilac colour whilst putrescine yields

almost no colour and spermidine (IV) only a faint blue colour. The phosphate of (IV) gives with (II) the *triflavianate*, decomp. with frothing 249—250°. W. McC.

Complex phosphododecamolybdates.—See A., 1939, I, 212.

Phosphomolybdates of ethanolamines; triethanolamine phosphotungstate. A. Tettamanzi (Atti R. Accad. Sci. Torino, 1935, **71**, I, 116—124; Chem. Zentr., 1937, i, 554).—The following sparingly sol. yellow cryst. *compounds* have been prepared: $[NH_2{\cdot}C_2H_4{\cdot}OH]_5,H_7[P(Mo_2O_7)_6],2HNO_3,10H_2O$; $[NH_2{\cdot}C_2H_4{\cdot}OH]_5,H_7[P(Mo_2O_7)_6],1{\cdot}5HNO_3$; $[NH(C_2H_4{\cdot}OH)_2]_4,H_7[P(Mo_2O_7)_6],HNO_3$; $[N(C_2H_4{\cdot}OH)_3]_4,H_7[P(Mo_2O_7)_6],2HNO_3$; $[N(C_2H_4{\cdot}OH)_3]_5,H_7[P(Mo_2O_7)_6],1{\cdot}5HNO_3,5H_2O$; $[N(C_2H_4{\cdot}OH)_3]_3,H_7[P(W_2O_7)_6]$ (bluish-white). A. J. E. W.

Configuration of glucosamine (chitosamine). W. N. Haworth, W. H. G. Lake, and S. Peat (J.C.S., 1939, 271—274).—4 : 6-Dimethyl-2 : 3-anhydro-β-methylmannoside when heated at 130° for 30 hr. with MeOH–NH_3 yields a *dimethylmethylhexosaminide* (I), b.p. 125°/0·02 mm., $[\alpha]_D^{21}$ −103° in MeOH [*diacetate* (II), b.p. 185°/0·004 mm.]. With Ac_2O in MeOH at room temp. (I) yields a mixture, b.p. 184° (bath)/0·005 mm., of 3-*acetamido*-4 : 6-*dimethyl*-β-*methyl*-d-*altropyranoside* (III), m.p. 150°, $[\alpha]_D^{19}$ −108·0° in MeOH, and 2-*acetamido*-4 : 6-*dimethyl*-β-*methyl*-d-*glucopyranoside* (IV), m.p. 187°, $[\alpha]_D^{16}$ −21·5° in MeOH, both of which are formed from (II) with Na in EtOH. Methylation of (III) with MeI–Ag_2O yields 3-*acetamido*-2 : 4 : 6-*trimethyl*-β-*methylaltroside* (V), b.p. 160° (bath)/0·01 mm., m.p. 116°, $[\alpha]_D^{20}$ −97·7° in $CHCl_3$, −87·0° in H_2O, −83·0° in MeOH, whilst (IV) similarly treated yields 2-acetamido-3 : 4 : 6-trimethyl-β-methyl-*d*-glucopyranoside, m.p. 195—196°, identical with the *N*-acetyltrimethyl-β-glucosaminide prepared by Cutler *et al.* (A., 1938, II, 46) from natural glucosamine, which is therefore related to the parent sugar glucose. Methyl*epi*-glucosamine hydrochloride with MeOH–Ac_2O–AgOAc gives 3-acetamido-β-methylaltroside, which on methylation (MeI–Ag_2O) yields (V). J. D. R.

Derivatives of methylated glucosamine. W. O. Cutler and S. Peat (J.C.S., 1939, 274—279).—Triacetyl-β-methylglucosaminide hydrobromide with BzCl in aq. NaOH yields *tetrabenzoyl*-β-*methylglucosaminide*, m.p. 182°, $[\alpha]_D^{19}$ +18·7° in $CHCl_3$, whilst with BzCl and Ag_2CO_3 in H_2O *N*-*benzoyltriacetyl*-β-*methylglucosaminide*, m.p. 222°, $[\alpha]_D^{22}$ +29·6° in $CHCl_3$, is formed, methylated (Me_2SO_4–aq. NaOH) to *N*-*benzoyltrimethyl*-β-*methylglucosaminide* (I), m.p. 198°, $[\alpha]_D^{19}$ +29·6° in $CHCl_3$. Trimethyl-α-methylglucosaminide hydrochloride with BzCl in aq. NaOH yields *N*-*benzoyltrimethyl*-α-*methylglucosaminide* (II), m.p. 162°, $[\alpha]_D^{18}$ +122·8° in $CHCl_3$, also formed from (I) by boiling with 2% HCl–MeOH. Acetylation of triacetylbenzylglucosaminide hydrobromide (III) with Ac_2O–AgOAc in MeOH yields *tetra-acetyl*-β-*benzylglucosaminide*, m.p. 163°, $[\alpha]_D^{14}$ −38·3° in $CHCl_3$, methylated (Me_2SO_4–NaOH) to *N*-*acetyltrimethyl*-β-*benzylglucosaminide* (IV), m.p. 174°, $[\alpha]_D^{14}$ −36·2° in $CHCl_3$, converted by HCl–$CH_2Ph{\cdot}OH$ into the α-*isomeride*, m.p. 138°, $[\alpha]_D$ +118·2°. With BzCl–Ag_2CO_3 in H_2O (III) gives *N*-*benzoyltriacetyl*-β-benzylglucosaminide, m.p. 216°, $[\alpha]_D^{19}$ −6·4° in $CHCl_3$, methylated (Me_2SO_4–NaOH–$COMe_2$) to *N*-*benzoyltrimethyl*-β-*benzylglucosaminide* (V), m.p. 180°, $[\alpha]_D^{17}$ −21·75 in $CHCl_3$, converted by HCl–$CH_2Ph{\cdot}OH$ into the α-*isomeride* (VI), m.p. 184°, $[\alpha]_D^{22}$ +123·2° in $CHCl_3$. When boiled with 2% HCl–MeOH, (V) is unchanged, (VI) yields (II), and (IV) gives a mixture of trimethyl-α-methylglucosaminide and its *N*-Ac derivative. With 0·01N-HCl at 100°, *N*-acetyltrimethyl-β-methylglucosaminide (VII), (I), (IV), and (V) lose the glycosidic alkyl group, but the α-isomeride of (VII) is unchanged. Trimethyl-α-methylglucosaminide is methylated (MeI–Ag_2O) to *trimethyl*-α-*methylglucosidyl*-2-*trimethylammonium iodide*, $[\alpha]_D^{19}$ +119·1° in $CHCl_3$, which is very resistant to alkalis, and on distillation yields *trimethyldimethylaminomethylglucoside*, b.p. 160° (bath)/0·03 mm. Triacetyl-β-methylglucosaminide hydrobromide with MeI–Ag_2O yields *trimethyl*-β-*methylglucosidyl*-2-*trimethylammonium iodide*, m.p. 105°, $[\alpha]_D^{20}$ −12·9° in $CHCl_3$, which is unchanged by boiling with 1% HCl–MeOH, by which treatment 3-acetamidotrimethyl-α-methylglucoside is also unchanged. J. D. R.

Dissymmetrical synthesis in the case of complex metallic salts.—See A., 1939, I, 212.

Protein metabolism. III. Synthesis of amino-acids containing isotopic nitrogen. R. Schoenheimer and S. Ratner (J. Biol. Chem., 1939, **127**, 301—313).—Two methods for the prep. of NH_2-acids containing an excess of ^{15}N are described. (1) The corresponding keto-acids are reduced with H_2 in presence of Pd and NH_3 containing an excess of ^{15}N. In this way the following acids have been prepared: *dl*-alanine, *dl*-phenylalanine, *dl*-tyrosine, dl-*norleucine*, *dl*-glutamic acid, and *dl*-aspartic acid. (2) The appropriate α-Br-acid is treated with *o*-$C_6H_4(CO)_2NK$ prepared from *o*-$C_6H_4(CO_2H)_2$ and NH_3 containing an excess of ^{15}N. The acids prepared in this way include glycine, deuteroleucine, and lysine. Deutero-*iso*hexoic acid, b.p. 200·2°, was prepared from *iso*hexoic acid and PtO_2 saturated with D_2. Bromination by treatment with Br and red P followed by esterification yields an Et deutero-α-bromo*iso*hexoate, b.p. 83—84°/10 mm. The *dl*-leucine finally obtained contained 3·87 at.-% D and 6·49 at.-% ^{15}N excess. W. O. K.

Red coloration of ferric salts with glycine.—See A., 1939, I, 199.

***l*-(+)Citrulline.** A. G. Gornall and A. Hunter (Biochem. J., 1939, **33**, 170—172).—*l*-(+)Arginine is incubated with arginase at 37° until the arginine has disappeared. The solution, conc. in vac. and decolorised, is boiled with CuO at p_H 7·0 and $CO(NH_2)_2$ added. The citrulline–Cu is then decomposed with H_2S giving *l*(+)citrulline, $[\alpha]_D^{22}$ +3·5° in H_2O (hydrochloride, $[\alpha]_D^{22}$ +17·9° in H_2O). A. L.

Octopine. I. Synthesis and titration curve of octopine. II. Nitrogenous extractives of squid and octopus muscle. III. Precursor of octopine in autolysing scallop muscle. J. L. Irvin and D. W. Wilson (J. Biol. Chem., 1939, **127**,

555—563, 565—574, 575—579).—Synthesis of octopine (I) (A., 1937, III, 295), m.p. 265° (decomp.) [picrate, m.p. 226° (decomp.); picrolonate, m.p. 236°], is repeated using a lower temp. and Akasi's method (A., 1937, II, 403) of separating the enantiomorphs. The titration curve of (I) closely resembles that of arginine (II). *pK* of (I) for the CO_2H are 1·36 and 2·40 and for the N 8·76 and nearly 13. M.p. are corr.

II. (I) [*Cu salt*, $(C_9H_{17}O_4N_4)_2Cu$, m.p. 223—227° (decomp.); *reineckate*; *Ni* compound, m.p. >290°, containing 87·1% of (I)] and (II) are isolated from the mantle and tentacle muscle of *Loligo pealii*, and the N partition in the muscle is determined. Taurine, adenine, hypoxanthine, betaine, (II), (I), and agmatine (modified isolation as phosphotungstate) are obtained from the tentacle muscle of *Octopus vulgaris*.

III. Fresh scallop muscle contains much (II) and little (I); the amount of (I) increases during autolysis at 0° at the expense of the (II), the change being faster in sliced than in hashed muscle. R. S. C.

Synthesis of dicholylcystine and cholylcysteic acid. S. F. Velick, J. White, and H. B. Lewis (J. Biol. Chem., 1939, **127**, 477—481).—Triformylcholic acid (prep. by HCO_2H at 60°), m.p. 206°, and pure $SOCl_2$ give the acid chloride, which with cystine Me_2 ester in $CHCl_3$ gives *bistriformylcholylcystine* Me_2 ester (I), m.p. 88—90°, and thence by NaOH in aq. dioxan etc. *dicholylcystine* $(NH_4)_2$ salt and the derived acid, which is less well obtained by way of the azide. Addition of Br to (I) in H_2O gives *Me triformylcholylcysteate*, converted by NH_3–MeOH at room temp. into NH_4 β-*carbamyltaurocholate* or by NaOMe–MeOH at room temp. into Na_2 *cholylcysteate*.

R. S. C.

Oxamidedioxime. I. Determination of nickel.—See A., 1939, I, 219.

Sebacic acid methyl-, m.p. 98—99·5° (Et ester, m.p. 55°), and propyl-monoamide, m.p. 91—93°, and *NN'*-dimethyl-, m.p. 147·5—148·2°, and -dipropyl-diamide, m.p. 153—154°, and suberic propylamide, m.p. 91—92·3°.—See A., 1939, III, 172.

Monoanilide, m.p. 122° (Et ester, m.p. 65—66°), of adipic acid.—See A., 1939, III, 175.

Methyl-, m.p. 187—189°, and dimethyl-colamine phosphate, m.p. 75—80°.—See A., 1939, III, 183.

Urea derivatives. Quaternary ammonium compounds.—See B., 1939, 243.

Production of *N*-acylurethanes.—See B., 1939, 243.

Diacylcarbamides. II. Preparation and properties of diacylcarbamides derived from branched-chain aliphatic acids. R. W. Stoughton, H. L. Dickison, and O. G. Fitzhugh (J. Amer. Chem. Soc., 1939, **61**, 408—410; cf. A., 1938, II, 352). —iso*Butyryl-*, m.p. 175—176°, *iso*valeryl-, m.p. 204—205°, α-methyl-*n*-butyryl-, m.p. 179—180°, αα-*dimethyl*-n-*propionyl-*, m.p. 147—148°, α-ethylbutyryl-, m.p. 206—207°, α-*methylvaleryl-*, m.p. 152—153°, αα-, m.p. 121—122°, and ββ-*dimethyl*-n-*butyryl-*, m.p. 173—174°, αα-*dimethylvaleryl-*, m.p. 116—117°, and αα-*dimethyl*-n-*hexoyl-*, m.p. 108—109°, *-carbamide* with the appropriate acyl halides give N-*acetyl*-N'-αα-*dimethylpropionyl-*, m.p. 105—106°, -N'-αα-*dimethylbutyryl-*, m.p. 118—119°, -N'-ββ-*dimethylbutyryl-*, m.p. 120—121°, -N'-αα-*dimethylvaleryl-*, m.p. 63—64°, and -N'-αα-*dimethylhexoyl-carbamide*, m.p. 77—78°, N-iso*butyryl*-N'-α-*methylbutyryl-*, m.p. 92—93°, -N'-αα-*dimethylpropionyl-*, m.p. 170—171°, -N'-α-*ethylbutyryl-*, m.p. 75—76°, -N'-α-*methylvaleryl-*, an oil, and -N'-αα-*dimethylbutyryl-carbamide*, m.p. 147—148°, N-n-*butyryl*-N'-αα-*dimethylpropionyl-*, m.p. 71—72°, -N'-α-*ethylbutyryl-*, m.p. 57—58°, and -N'-αα-*dimethylbutyryl-carbamide*, m.p. 66—67°, N-α-*methylbutyryl*-N'-α-*ethyl-*, m.p. 77—78°, and -N'-αα-*dimethyl-butyryl-carbamide*, m.p. 130—131°, NN'-*di*iso*butyryl-*, m.p. 111—112°, NN'-*di*iso*valeryl-*, m.p. 66—67°, *NN'-di*-(α-*methylbutyryl*)-, m.p. 87—88°, NN'-*di*-(αα-*dimethylpropionyl*)-, m.p. 206—207° (decomp.), NN'-*di*-(α-*ethylbutyryl*)-, m.p. 86—87°, and NN'-*di*-(αα-*dimethylbutyryl*)-*carbamide*, m.p. 163—164°, which are readily hydrolysed and weak anæsthetics. Esters of the *sec.* and *tert.* acids with $CO(NH_2)_2$ and NaOEt give only NaCNO and the corresponding amides. Pyrolysis of $CO(NH{\cdot}COPr^{\beta})_2$ at 200° gives $Pr^{\beta}CO{\cdot}NH_2$, $Pr^{\beta}CN$, and CO_2 with smaller amounts of $NH(COPr^{\beta})_2$ and $(HCNO)_3$. M.p. are corr. R. S. C.

Preparation of amino-nitriles and their quaternary ammonium derivatives. D. B. Luten, jun. (J. Org. Chem., 1939, **3**, 588—597).—NH_2-nitriles are obtained (*a*) by adding a slight excess of $Na_2S_2O_5$ to an aq. solution of the aldehyde followed after completion of the reaction by one equiv. of the amine and then by saturated aq. KCN or (*b*) by adding a solution of KCN to a conc. aq. solution of the amine hydrochloride followed by the desired aldehyde or ketone in about 30% excess. With method (*a*) good yields are obtained only from CH_2O and the simpler amines. In cases where the method is unsuccessful the failure appears due to the low rate or adverse equilibrium of the change, $OH{\cdot}CRR'{\cdot}SO_3^- + NHR''_2 \rightleftharpoons NR''_2{\cdot}CRR'{\cdot}OH + HSO_3^-$. Under the conditions adopted method (*b*) gives a good yield in many cases in which method (*a*) fails but it also fails in certain cases. There seems to be little relationship between the mol. wts. of the reactants and the ultimate yields, although $NHEt_2$ gives a much lower yield with each of the ketones employed than does $NHMe_2$. Some of the aldehydic derivatives were obtained in low yields owing to withdrawal of the aldehydes by the competing aldol condensation reaction. The quaternary derivatives are obtained by adding the appropriate halide to the NH_2-nitrile or by adding $CH_2I{\cdot}CN$ to the appropriate *tert.* amine. The following individuals are described: $NMe_2{\cdot}CH_2{\cdot}CN$, b.p. 138°, 42°/21 mm. [methiodide, m.p. 228° (lit. 196°); *ethiodide*, m.p. 209°; n-*propiodide*, m.p. 95°; iso*propiodide*, m.p. 219°; n-*butiodide*, m.p. 86·5°; n-*hexadeciodide*]; $NEt_2{\cdot}CH_2{\cdot}CN$, b.p. 70°/23 mm., 53°/10 mm. (methiodide, m.p. 199°; ethiodide, m.p. 187°; ethobromide, m.p. 209°; n-*propiodide*, m.p. 195°; n-*butiodide*, m.p. 154°; n-*amyliodide*, m.p. 125°; *alliodide*, m.p. 162°; $NPr^{\alpha}_2{\cdot}CH_2{\cdot}CN$, b.p. 96°/23 mm., 78°/9 mm. (methiodide, m.p. 162°; *ethiodide*, m.p. 176°; n-*propiodide*, m.p. 179°); *di*-n-*butylaminoacetonitrile*,

b.p. 85°/4 mm. (*methiodide*, m.p. 104°; n-*butiodide*, m.p. 131°); NBu^{β}_2·CH_2·CN, b.p. 87°/9 mm., 78—79°/4 mm.; *di*-n-*amylaminoacetonitrile*, b.p. 102—104°/4 mm.; *diisoamylaminoacetonitrile*, b.p. 93—94°/4 mm. (*methiodide*, m.p. 109°); di-n-*octylaminoacetonitrile*, b.p. 145—150°/3 mm.; *diethylaminoacetonitrile* β-*hydroxyethiodide*; *Et diethylaminoacetate cyanomethobromide*, m.p. 128°; *Et* β-*dimethylaminopropionate cyanomethobromide*, m.p. 102°, and the corresponding *cyanomethiodide*, m.p. 122°; α-*dimethylaminopropionitrile*, b.p. 59—61°/40 mm. (*methiodide*, m.p. 204°); NEt_2·CHMe·CN, b.p. 53°/11 mm. (methiodide, m.p. 202°); β-dimethylaminopropionitrile methochloride, m.p. 230°; NMe_2·CHEt·CN, b.p. 67—68°/23 mm. (*methiodide*, m.p. 176°; *ethiodide*, m.p. 135°); α-*diethylaminobutyronitrile*, b.p. 75·5°/16 mm. (*methiodide*, m.p. 184°); NMe_2·CMe_2·CN, b.p. 57°/25 mm., 46°/13 mm. (*methiodide*, m.p. 268°; *ethiodide*, m.p. ~250°); α-*methylethylaminoisobutyronitrile*, b.p. 58°/14 mm.; NEt_2·CMe_2·CN, b.p. 72—74°/14 mm. (*methiodide*, m.p. 241°); γ-*dimethylamino*-n-*butyronitrile methobromide*, m.p. 226°; NMe_2·$CHPr^{\alpha}$·CN, b.p. 70°/14 mm. (*methiodide*, m.p. 163°; *ethiodide*, m.p. 121°); α-*diethylamino*-n-*valeronitrile*, b.p. 95°/15 mm., 78°/4 mm. (*methiodide*, m.p. 132°); α-*dimethylaminoisovaleronitrile*, b.p. 61°/14 mm. (*methiodide*, m.p. 177°); α-*diethylaminoisovaleronitrile*, b.p. 69°/4 mm. (*methiodide*, m.p. 150°); α-*dimethylamino*-α-*methyl*-n-*butyronitrile*, b.p. 63°/12 mm. (*methiodide*, m.p. 216°); α-*diethylamino*-α-*methyl*-n-*butyronitrile*, b.p. 78°/16 mm. (*methiodide*, m.p. ~220°); α-*diethylamino*-n-*hexonitrile*, b.p. 91°/9 mm. (*methiodide*, m.p. 116°); α-*dimethylamino*-α-*methyl*-n-*valeronitrile*, b.p. 75°/10 mm. (*methiodide*, m.p. 165°); α-*diethylamino*-α-*methyl*-n-*valeronitrile*, b.p. 103°/21 mm., 80—85°/5 mm. (*methiodide*, m.p. 119°); NMe_2·$CMePr^{\beta}$·CN, b.p. 63°/7 mm. (*methiodide*, m.p. 188°); NMe_2·CEt_2·CN, b.p. 69—73°/10 mm. (*methiodide*, m.p. 191°); NEt_2·CH(*n*-C_6H_{13})·CN, b.p. 113—115°/13 mm.; α-*dimethylamino*-α-*methyl*-n-*heptonitrile*, b.p. 104—105°/10 mm., (*methiodide*, m.p. 199°); NPhMe·CH_2·CN, b.p. 138—141°/9 mm., *p*-C_6H_4Me·NMe_2I·CH_2·CN; *benzylmethylaminoacetonitrile methobromide*, m.p. 158°; NMe_2·CHPh·CN, b.p. 90°/6 mm.; NEt_2·CHPh·CN, b.p. 122—124°/9 mm.; piperidinoacetonitrile, b.p. 83°/9 mm. (methiodide, m.p. 206°; *ethiodide*, m.p. 183°; n-*propiodide*, m.p. 152°); *Et piperidinoacetate cyanomethobromide*, m.p. 154°. H. W.

Reversibility of the glycerophosphoric change. —See A., 1939, I, 205.

Preparation of calcium glucose-3-phosphate from dibrucine glucose-3-phosphate. S. A. Lough and V. E. Spencer (J. Org. Chem., 1939, **3**, 541—542).—The action of $Ca(OH)_2$, dissolved or in suspension, on glucose-3-phosphoric acid gives compounds containing more Ca and less P than required for the simple salt. *Ca glucose*-3-*phosphate* is prepared by addition of the stoicheiometrical amount of solid $Ca(OH)_2$ to a well-stirred suspension of dibrucine glucose-3-phosphate in H_2O; brucine is removed by filtration and the salt is pptd. by adding EtOH to the filtrate. H. W.

Telluromercaptans. A. Baroni (R. C. Atti Accad. Lincei, 1938, [vi], **27**, 238—242).—H_2Te in EtOH–NaOEt with RBr (R = Me, Et, Pr^{α}, Bu^{α}) yields the corresponding telluromercaptan RTeH; R = *Me*, b.p. 57°, *Et*, b.p. 90°, *Pr*$^{\alpha}$, b.p. 121°, *Bu*$^{\alpha}$, b.p. 151°. An apparatus for the prep., purification, and distillation of the telluromercaptans as a continuous operation in H_2 is described. F. O. H.

Action of halides on magnesium compounds. G. Vavon, J. Calin, and J. Fouchier (Compt. rend., 1939, **208**, 203—205).—The time necessary for 40% reaction between MgEtBr and various halides and between allyl bromide and various Mg compounds in Bu^{α}_2O at 65° and 35° (equimol. concns.) is determined. MgRBr reacts much more slowly with *n*-org. halides than with *sec.* and *tert.* compounds; a double linking in the org. halide facilitates the reaction. The chlorides react least and the iodides most easily; bromides are intermediate. The difference in reaction rate using MgRBr, MgRCl, or MgRI is small, but the bromide reacts most easily. The reaction is at first rapid and then slow (migration of Mg) (cf. Prévost, A., 1932, 41; Urion, A., 1934, 640). J. L. D.

Reaction of carbon suboxide with magnesium methyl iodide. J. H. Billman and C. M. Smith (J. Amer. Chem. Soc., 1939, **61**, 457—458).—Only 1 mol. of MgMeI reacts with C_3O_2 in Et_2O, yielding CO:C:CMe·OMgI, which, after hydrolysis, condenses to give 2 : 4 : 6 : 1 : 3 : 5-$C_6Ac_3(OH)_3$ as sole product. R. S. C.

Yields of stibines and arsines. J. Seifter (J. Amer. Chem. Soc., 1939, **61**, 530—531).—A mixture of const. b.p. (min. b.p. 72—74°) was obtained by distilling the product of the prep. of $SbMe_3$ in Bu^{α}_2O. Prep. of $SbBu^{\alpha}_3$ in 70% yield and of $AsBu^{\alpha}_3$ in 50% yield is recorded. R. S. C.

Mechanism of catalytic hydrogenation of phenol [to hydrocarbons] under high pressure. IV. S. Andō (J. Soc. Chem. Ind. Japan, 1938, **41**, 386—390B; cf. A., 1933, 498).—The products of hydrogenation of PhOH, C_6H_6, and *cyclo*hexane at 430° or 471°/~240 atm. (rotating autoclave) in presence of MoO_3 or MoO_3+S indicate that *cyclo*hexane and methyl*cyclo*pentane are formed from PhOH not only via C_6H_6, but also via *cyclo*hexanol and *cyclo*hexene, although neither of these two intermediates has been isolated (cf. A., 1932, 51; B., 1932, 762; A., 1933, 1152). A. R. Pe.

Hydrogenation-cracking of diphenylene oxide and some related compounds. C. C. Hall and C. M. Cawley (J.S.C.I., 1939, **58**, 7—13).—Diphenylene oxide (I) is fairly stable at 450°/200 atm. H_2 in presence of supported Mo catalyst; 40—60% is unchanged after heating for 2 hr. Complete conversion is obtained at 500°. It is less stable in the presence of a pelleted MoS_2 catalyst, 14% remaining unchanged at 450°, and 35% at 350°. The stability of Ph_2 is very similar, but 2-hydroxydiphenyl (II) is much less stable and is completely deoxygenated at 450° in presence of the supported catalyst. 2 : 2′-Dihydroxydiphenyl (III) is readily converted into (I) and (II). At low temp. the initial decomp. product of (I) is *o-cyclo*hexylphenol (IV) and at high

temp. (II) is formed; both (II) and (IV) are converted into phenyl*cyclo*hexane (V) to a large extent, but (II) also yields some Ph_2. Ph_2 undergoes scission to C_6H_6, or is hydrogenated to (V), which undergoes scission to C_6H_6 and *cyclo*hexane (VI) or is hydrogenated to di*cyclo*hexyl which then yields (VI).

Infra-red spectra of naphthalene, 1- and 2-methylnaphthalene, quinoline, and *iso*quinoline.—See A., 1939, I, 179.

New hydrocarbon from juniper oil. P. Casparis and W. Freund (Pharm. Acta Helv., 1939, **14**, 1—8).—Oil from juniper berries collected in the Tyrol and from Italian fruits gave by fractional distillation 0·17—0·345% of *junene* (I), $C_{10}H_{16}$, b.p. 164—166°/760 mm., 53—55°/8 mm., α_D^{20} (1 dm.) +19·6° to +20·1°, possessing strong diuretic properties; a solution in Ac_2O gave a red coloration with H_2SO_4. Reduction (H_2, Pd–$BaSO_4$, AcOH) of (I) gave *dihydrojunene*, $C_{10}H_{18}$, b.p. 170°/760 mm., 58—61°/8 mm., α_D^{20} (5 cm.) −6·5°. With HCl in AcOH (I) gave an additive product, b.p. 76—86°/8 mm., α_D^{20} −0·3°, and no cryst. products with Br, NOCl, or HI, and did not react with BzO_2H. It is probably a *cyclo*pentene derivative similar to but not identical with the chamene of Kafaku *et al.* (B., 1931, 565). The juniper oils contained α-pinene, camphene, and cadinene and, from the consts. of the terpene fraction, 5—15% of (I). T. F. W.

β-Nitrostyrene in the diene synthesis. C. F. H. Allen and A. Bell (J. Amer. Chem. Soc., 1939, **61**, 521—522).—CHPh:CH·NO_2 and the appropriate diene give 4-*nitro*-5-*phenyl*-1 : 2-*dimethyl*- (I) (82%), m.p. 96°, 4-*nitro*-5-*phenyl*-1- (or 2-)*methyl*- (7%), m.p. 52°, 4-*nitro*-1 : 2 : 5-*triphenyl*- (II) (9%), m.p. 175°, and 4-*nitro*-3 : 5 : 6-*triphenyl*- (40%), m.p. 130°, -Δ^1-cyclo*hexene*; (II) is accompanied by a *hydrocarbon* (5%), $C_{24}H_{20}$, m.p. 77°. In KOH, but not in neutral solution, (I) gives the 4-*Br*-derivative. Methyleneanthrone gives N oxides, *Bz*-1-phenylbenzanthrone (25%), and its *Bz*-2-NO_2-derivative (3%), m.p. 255° (oxidised to 1-benzoylanthraquinone). Tetracyclone gives C_6HPh_5. Phellandrene, *cyclo*pentadiene, and *cyclo*hexadiene give *adducts*, $C_{18}H_{23}O_2N$ (45%), b.p. 190°/1 mm., $C_{13}H_{13}O_2N$ (95%), b.p. 145°/1 mm., and $C_{14}H_{15}O_2N$, (20%), b.p. 138—142°/1 mm., respectively. R. S. C.

Substitution process. W. Hückel (Österr. Chem.-Ztg., 1939, **42**, 105—109, 121—125).—Comparison of theory (Meer and Polanyi; Ingold and Hughes) with experience is at present possible only with changes of the bimol. type with negative mechanism. All such substitutions are accompanied by Walden inversion. The most important types of change are: replacement of halogen by halogen ion; substitution of halogen by OH; formation of ethers from halides and alkoxides; production of acetates from KOAc and toluene-*p*-sulphonates in EtOH. Study of the interaction of HNO_2 and the amines derived from decahydronaphthalene shows that the steric course of substitution depends greatly on the fine structure of the mol. and is influenced by the steric arrangement of parts of the mol. distant from the asymmetry centre involved in substitution. In those cases in which >50% of hydrocarbon is produced, the formation of alcohol is accompanied by almost complete Walden inversion although a little configuratively-similar alcohol is produced. On the other hand an alcohol formed from an amine almost without hydrocarbon has, in seven out of eight cases, the same configuration as the amine and the stereoisomeric alcohol is not formed in appreciable amount. In the first cases the alcohols exhibit marked steric hindrance whereas in the second case they do not. Ingold's views on substitution are critically discussed. Criticisms of the older and more recent views of the nitration, sulphonation, and halogenation of aromatic compounds lead to the conclusion that a single scheme, applicable to all aromatic substitutions, cannot at present be advanced. H. W.

Rôle of sulphuric acid [in sulphonation, nitration, etc].—See A., 1939, I, 211.

Emulsification and chemical reaction.—See A., 1939, I, 204.

Preparation of *m*-dinitrobenzene. S. V. Shah and D. G. Pishawikar (J. Chem. Educ., 1939, **16**, 35; cf. A., 1937, II, 406).—$NaNO_3$ can replace HNO_3 without loss in yield, and with a considerable reduction in the cost of materials. L. S. T.

Substitution of aromatic hydrocarbons. F. Asinger (J. pr. Chem., 1939, [ii], **152**, 1—8; cf. A., 1934, 878).—Passage of Cl_2 into CH_2PhBr causes rise of temp. to 100° and escape of Br. At 0° in presence of a little I, the total halogen content is that required for $C_6H_4Cl·CH_2Br$ but Br has been partly displaced from the side-chain to the nucleus; at 25° this effect is somewhat less marked. Bromination of CH_2PhCl causes much displacement of Cl by Br; Cl is evolved as HCl and does not enter the nucleus. Passage of Cl_2 through C_6Br_6 + *p*-$C_6H_4Me·NO_2$ at 200° gives unchanged *p*-$C_6H_4Me·NO_2$, *p*-$NO_2·C_6H_4·CH_2Cl$, and *p*-$NO_2·C_6H_4·CH_2Br$; the gaseous products are free from Br. H. W.

Tetra- and penta-chloroethylbenzene.—See B., 1939, 243.

Friedel–Crafts reactions: *n*-octadecylbenzene and diacylations. H. Gilman and J. A. V. Turck, jun. (J. Amer. Chem. Soc., 1939, **61**, 478—479).—Only *n*-$C_{18}H_{37}Ph$ (identified as sulphonamide) is obtained from C_6H_6–*n*-$C_{18}H_{37}Hal$–$AlCl_3$, *n*-$C_{18}H_{37}I$–PhI–Na, or by Clemmensen reduction of stearophenone (I). In the Friedel–Crafts reaction with (I) and *n*-$C_{17}H_{35}·COCl$ in $PhNO_2$, no distearoylbenzene is produced; $CO(C_{17}H_{35})_2$, *o*- and *p*-$C_6H_4Cl·NH_2$ are formed. R. S. C.

Polymethylbenzenes. XXIII. Preparation and physical properties of 3- and 5-ethyl-ψ-cumenes and of ethylmesitylene. L. I. Smith and M. A. Kiess (J. Amer. Chem. Soc., 1939, **61**, 284—288; cf. A., 1939, II, 102).—1 : 2 : 4 : 5-$C_6H_2Me_3·SO_3H$ and Br–aq. HCl give 1 : 2 : 4 : 5-$C_6H_2Me_3Br$ (60%) and 1 : 2 : 4 : 3 : 5-$C_6HMe_3Br·SO_3H$, hydrolysed by 50% H_2SO_4 and steam at 175—180° to ψ-cumene, 1 : 2 : 4 : 3-$C_6H_2Me_3Br$, and other products. The appropriate Grignard reagents (prepared with the aid of EtBr) and Et_2SO_4 in Et_2O give 31—52% of

1 : 3 : 5 : 2-$C_6H_2Me_3Et$ (I), b.p. 210°/725 mm., m.p. −15·56°, 5- (II), b.p. 210°/725 mm., m.p. −13·58°, and 3-*ethyl-ψ-cumene* (III), b.p. 214°/725 mm., m.p. <−50°, with 14—35% of $C_6H_3Me_3$. (I) and (II) are also obtained (Clemmensen) from 1 : 3 : 5 : 2-(74%) and 1 : 2 : 4 : 5-$C_6H_2Me_3$·COMe (77·2%), respectively. With H_2SO_4–HNO_3 (*d* 1·5) in $CHCl_3$ (III) gives the 5 : 6-$(NO_2)_2$-, m.p. 79—80°, and thence by $SnCl_2$–HCl–EtOH the $(NH_2)_2$-derivative (IV), m.p. 84—85°, or by $SnCl_2$–HCl–AcOH 2 : 4 : 6 : 7-*tetramethyl-5-ethylbenziminazole*, m.p. 205·5°. (IV) yields 10 : 12 : 13-*trimethyl-11-ethylphenanthraphenazine*, m.p. 242°. When treated successively with oleum, H_2O, and Br, (III) gives the 5 : 6-Br_2-derivative, m.p. 65—66°. $KMnO_4$–K_2CO_3 converts (III) into 1 : 2 : 3 : 4-$C_6H_2(CO_2H)_4$, but 1 : 2 : 3 : 5-$C_6H_2(CO_2H)_4$ could be obtained from (I) only by long heating with $KMnO_4$–NaOH. R. S. C.

Carotenoids from lucerne silage etc.—See A., 1939, III, 343.

Volatile plant substances. VIII. Synthesis of vetivazulene. A. S. Pfau and P. A. Plattner (Helv. Chim. Acta, 1939, **22**, 202—208).—Gradual addition of 2 : 5 : 1-$C_6H_3Me_2$·CH_2Cl to $CNaPr^{\beta}(CO_2Et)_2$ in xylene followed by protracted boiling of the mixture gives Et_2 2 : 5-dimethylbenzyl*iso*propylmalonate, b.p. 160—165°/3 mm., hydrolysed with difficulty to the corresponding acid, which when distilled in a vac. gives β-2 : 5-*dimethylphenyl*-α-iso*propylpropionic acid*, m.p. 69—70°. The corresponding chloride, b.p. 135°/3 mm., is cyclised by $AlCl_3$ in C_6H_6 to 4 : 7-*dimethyl*-2-iso*propylindan*-1-*one*, b.p. 146°/3 mm., which in consequence of steric hindrance does not give an oxime or a semicarbazone, but is reduced by Na and EtOH to 4 : 7-*dimethyl*-2-iso*propylindan*-1-*ol*, m.p. 98—99°. It is reduced (Clemmensen) to 4 : 7-*dimethyl*-2-iso*propylindane* (I), b.p. 108—110°/3 mm., m.p. 23—24°, oxidised to $C_6H_2(CO_2H)_4$ and nitrated to 5 : 6-*dinitro*-4 : 7-*dimethyl*-2-iso*propylindane*, m.p. 137°. Gradual addition of CHN_2·CO_2Et to (I) at 130° followed by heating the mixture to 160° and distillation yields a product which is hydrolysed, decarboxylated, and dehydrogenated (Pd–C) to vetivazulene [4 : 8-dimethyl-2-*iso*propyl-*dicyclo*[0,3,5]-decapentaene], m.p. 32—33°, identical with the natural product. H. W.

Nitration of naphthalenesulphonic acids. I, II. R. Lantz (Bull. Soc. chim., 1939, [v], **6**, 280—289, 289—302; cf. A., 1936, 62, 197).—2-$C_{10}H_7$·SO_3Na and 100% H_2SO_4 at room temp. for 2 days give 1 : 6-$C_{10}H_6(SO_3H)_2$, purified through 1 : 6-$C_{10}H_6(SO_2Cl)_2$. 2 : 7-, 2 : 6- (I), and 1 : 5-$C_{10}H_6(SO_3Na)_2$ and 100% H_2SO_4 at 100° (1 : 5- at 60°), then 60% oleum, afford 1 : 3 : 6-, 2 : 4 : 6-, and 1 : 3 : 5-$C_{10}H_5(SO_3H)_3$, respectively. (I) and 59% oleum in H_2SO_4,H_2O at 180° for 8 hr. give 1 : 3 : 5 : 7-$C_{10}H_4(SO_3H)_4$ (hygroscopic Na salt). Details of nitration of Na naphthalenesulphonates with H_2SO_4–HNO_3 under varied conditions are recorded; HNO_3 used is estimated by difference before and after nitration. Max. speed of nitration is obtained usually (at room temp.) with ~90% H_2SO_4; in general, under these conditions, the total no. of SO_3H+NO_2 in the final product is 4. With cold 100% H_2SO_4, however, the total no. of substituents is 3, *i.e.*, $C_{10}H_6(SO_3H)_2$ are mononitrated and $C_{10}H_5(SO_3H)_3$ are practically unaffected; under these conditions, NO_2-derivatives of 1 : 5- and 1 : 6-$C_{10}H_6(SO_3H)_2$ are transformed appreciably into products (possibly nitrosonaphtholsulphonic acids) which do not nitrate further, but those of the 2 : 6- and 2 : 7-acids undergo further slow nitration at 60—80° to $(NO_2)_2$-derivatives. 1 : 6-$C_{10}H_6(SO_3H)_2$ thus gives the 3-NO_2- or 3 : 8-$(NO_2)_2$-derivative; 2 : 7-$C_{10}H_6(SO_3H)_2$ affords the 4-NO_2- or 4 : 5-$(NO_2)_2$-compound; the 2 : 6-acid gives the 8-NO_2- or 4 : 8-$(NO_2)_2$- and the 1 : 5-acid a 4(or 3)-NO_2- or 3 : 8-$(NO_2)_2$-derivative. 1 : 3 : 6-, 2 : 4 : 6-, and 1 : 3 : 5-$C_{10}H_5(SO_3H)_3$ all give 8-NO_2-derivatives. Fixation of NO_2 is little altered with variation in time and, within certain limits, with excess of HNO_3. Large excess of HNO_3 and prolonged time give slight dinitration with the 1 : 3 : 5-acid. The 1 : 6- and 2 : 7-di- and the 1 : 3 : 6-tri-sulphonic acids nitrate completely in presence of 90% H_2SO_4 with slight excess of HNO_3 (note final orientation, 1 : 3 : 6 : 8; cf. Vesely *et al.*, A., 1923, i, 911). The 1 : 5-, 2 : 6-, 1 : 3 : 5-, and 2 : 4 : 6-derivatives require a large excess of HNO_3 to give analogous results. The result of Fierz (A., 1921, i, 409) that no NO_2-derivative could be obtained from 1 : 3 : 5 : 7-$C_{10}H_4(SO_3H)_4$ is confirmed. A. T. P.

Free radicals and radical stability. IV. Diphenyl-3-acenaphthylmethyl. S. T. Bowden and W. E. Harris (J.C.S., 1939, 307—310).—Ph 3-acenaphthyl ketone (modified prep.; cf. Graebe *et al.*, A., 1903, i, 408) and MgPhBr give *diphenyl-3-acenaphthylcarbinol* (I), m.p. 196° (corresponding *methane*, m.p. 167°), prepared less readily from 3-bromoacenaphthene, activated Mg, and $COPh_2$. The basicity of (I) compared with that of 1-$C_{10}H_7$·CPh_2·OH (=1) is 1·3, and the halochromic salts of (I) are bluer. (I) and AcCl–C_6H_6 or dry HCl–C_6H_6 (+$CaCl_2$) give the *chloride* (II), m.p. 141°; AcBr–C_6H_6 affords the *bromide*, m.p. 135°. Diphenyl-3-acenaphthylmethyl is isolated from (II) and mol. Ag in C_6H_6, as crystals, m.p. 155° (vac.) (deep bluish-red in C_6H_6; deep bluish-green in liquid SO_2); air oxidation gives the *peroxide*, m.p. 167° (not completely colourless). Radical stability in $PhNO_2$ (bluish-green solutions) is approx. the same as that of diphenyl-α-naphthylmethyl (cf. Schlenk *et al.*, A., 1913, i, 34). Thermal decomp. of diphenyl-α-naphthylmethyl formate at 99° is slow, with formation of CO_2 and the corresponding methane, but the formate of (I) gives no CO_2 and no methane derivative is isolated. A. T. P.

Condensation of benzylidene chloride with *o*-xylene. E. de B. Barnett (J.C.S., 1939, 348).—$CHPhCl_2$ and *o*-xylene, with $AlCl_3$ in $C_2H_2Cl_4$, give a little 9 : 10-*diphenyl*-2 : 3 : 6 : 7-*tetramethylanthracene*, m.p. 312° (cf. Ellison and Hey, A., 1939, II, 14). A. T. P.

Dehydrogenation. II. S. C. Sengupta (J. pr. Chem. 1939, [ii], **152**, 9—19).—Gradual addition of $C_{10}H_8$ and *as*-dimethylsuccinic anhydride (I) to $AlCl_3$ in $PhNO_2$ at 0° and keeping the mixture at room temp. gives *γ-keto-γ-1-naphthyl-αα-dimethylbutyric acid*

(II), m.p. 190—191° (oxidised by NaOBr to α-$C_{10}H_7$·CO_2H), and *γ-keto-γ-2-naphthyl-αα-dimethylbutyric acid* (III), m.p. 170°, oxidised to β-$C_{10}H_7$·CO_2H. (II) is reduced (Clemmensen) to *γ-1-naphthyl-αα-dimethyl-*n*-butyric acid*, m.p. 99—101° (the *Et* ester, b.p. 116—118°/6 mm., could not be condensed with $Et_2C_2O_4$ and KOEt), cyclised by H_2SO_4 at 100° to 1-*keto*-2 : 2-*dimethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 69°; this is reduced (Zn–Hg–HCl) to 2 : 2-*dimethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, b.p. 161—163°/6 mm., dehydrogenated by Se at 250—300° and then at 300—340° to 2-methylphenanthrene, m.p. 55—56° (picrate, m.p. 117—118°). (III) is reduced (Clemmensen) to *γ-2-naphthyl-αα-dimethylbutyric acid*, b.p. 200—205°/5 mm., m.p. 133—135°, cyclised by H_2SO_4 at 100° to 4-*keto*-3 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, b.p. 185—187°/8 mm., whence 3 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, b.p. 155—157°/7 mm., dehydrogenated to impure 3-methylphenanthrene, m.p. 85° after softening at 61°, and other hydrocarbons. 1-$C_{10}H_7$Me and (I) similarly afford *γ-keto-γ-4-methyl-1-naphthyl-αα-dimethylbutyric acid* (IV), m.p. 202—203° [*Me* ester (V), m.p. 77°], oxidised by NaOCl to 4 : 1-$C_{10}H_6$Me·CO_2H. (IV) cannot be reduced (Clemmensen) whereas (V) is transformed (after hydrolysis) into *γ-4-methyl-1-naphthyl-αα-dimethylbutyric acid*, m.p. 105—106°. This is cyclised (H_2SO_4) to 1-*keto*-2 : 2 : 9-*trimethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 123°, reduced to 2 : 2 : 9-*trimethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 90—91°, which is dehydrogenated to 2 : 9-dimethylphenanthrene, m.p. 55—56° (picrate, m.p. 136—137°). H. W.

Polycyclic aromatic hydrocarbons. XX. J. W. Cook and C. G. M. de Worms (J.C.S., 1939, 268—271).—Cyclisation of $CO(C_{10}H_7\text{-}1)_2$ with $AlCl_3$–NaCl at 100° gives 1 : 2 : 5 : 10-dibenz-9-anthrone, oxidised by CrO_3–AcOH to 1 : 2-*benzanthraquinone-5-carboxylic acid*, m.p. 295—296° (*Me* ester, m.p. 163—165°) (oxidised by $KMnO_4$ to anthraquinone-1 : 2 : 5-tricarboxylic acid), which with $SnCl_2$–HCl–AcOH gives 1 : 2-*benz-5-anthroic acid* (I), m.p. 286—287° [the *amide*, m.p. 309—310°, and boiling *o*-$C_6H_4(CO)_2O$ give the *nitrile*, m.p. 190—191°]. The *Et* ester, m.p. 89—90°, of (I) and MgMeI give a carbinol, dehydrated (EtOH–picric acid) to 5-*iso*propenyl-1 : 2-benzanthracene (II) (*picrate*, m.p. 141—142°). A dil. solution in C_6H_6 of its *s*-$C_6H_3(NO_2)_3$ *complex*, m.p. 155°, undergoes fission with activated Al_2O_3 (cf. Fieser *et al.*, A., 1938, II, 356). (II) is hydrogenated (Pt-black; EtOH) to 5-iso*propyl*-1 : 2-*benzanthracene*, m.p 111—112° (*picrate*, m.p. 166·5—167·5°; s-$C_6H_3(NO_2)_3$ *complex*, m.p. 168·5—169·5°), oxidised by $Na_2Cr_2O_7$–AcOH to the *benzanthraquinone*, m.p. 80—82°.

[By J. W. Cook and J. Iball (cf. A., 1938, II, 227)]. Purified 8-methyl-1 : 2-benzanthracene (cryst. form examined) has new m.p. 117—118° (picrate, new m.p. 158—159°; *s*-$C_6H_3(NO_2)_3$ complex, new m.p. 167—168°). A. T. P.

Synthesis of 10-alkyl derivatives of 9-methyl-1 : 2-benzanthracene. B. M. Michailov and N. G. Tschernova (Compt. rend. Acad. Sci. U.R.S.S., 1938, **20**, 579—581).—*o*-(α-1-Naphthylethyl)benzoic acid with $ZnCl_2$ at 180° yields 9-*methyl*-1 : 2-*benzanthrone*-10, m.p. 106·4—107·2°, which, with the appropriate Mg alkyl halide yields 9 : 10-dimethyl- (picrate, m.p. 112·2—113·2°), 9-*methyl*-10-*ethyl*-, m.p. 70—71·5° (*dipicrate*, m.p. 116—116·8°), 9-*methyl*-10-n-*propyl*-, m.p. 99—101° (*dipicrate*, m.p. 95—98°), and 9-*methyl*-10-n-*butyl*-1 : 2-*benzanthracene*, m.p. 71—72° (*dipicrate*, m.p. 104·6—105·8°). J. D. R.

Triterpenes. XLIII. Synthesis of 1 : 10-dimethyl-, 1 : 2 : 8- and 1 : 2 : 10-trimethyl-, and 1 : 2 : 9 : 10-tetramethyl-picene. L. Ruzicka and K. Hofmann [with, in part, E. Hardegger, G. Hoepe, A. Marxer, and J. Frey] (Helv. Chim. Acta, 1939, **22**, 126—134).—1 : 8-Dimethylpicene, the picene derivative obtained by the dehydrogenation of pentacyclic triterpenes, can be certainly distinguished from the homologous picenes which would result by the dehydrogenation of a symmetrically constructed C skeleton. 1-Keto-5-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene (I) is converted by Zn and CH_2Br·CO_2Et in anhyd. C_6H_6 followed by distillation in presence of a little I into Et 5-methyl-3 : 4-dihydro-1-naphthylacetate, b.p. 122—128°/0·1 mm., reduced by Na and abs. EtOH to β-5-methyl-1 : 2 : 3 : 4-tetrahydro-1-naphthylethyl alcohol, b.p. 107—109°/0·1 mm. (3 : 5-*dinitrobenzoate*, m.p. 91—92°). This yields the bromide (II), b.p. 96—97°/0·1 mm., the Mg derivative of which with (I) yields a product dehydrogenated (Pd–C at 320—330°) to αβ-*di*-5-*methyl*-1-*naphthylethane*, m.p. 115—117° after softening, cyclised by $AlCl_3$ in CS_2 at room temp. to 1 : 10-*dimethylpicene*, m.p. 380—381° (corr.). The Mg compound of (II) and 1-keto-5 : 6-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (III) give a product which is distilled and then dehydrogenated (Pd–C at 320—330°) to α-5-*methyl*-1-*naphthyl*-β-5′ : 6′-*dimethyl*-1′-*naphthylethane*, m.p. 128—129°, cyclised ($AlCl_3$–CS_2) to 1 : 2 : 10-*trimethylpicene*, m.p. 380—381° (corr.). Mg β-7-methyl-1 : 2 : 3 : 4-tetrahydro-1-naphthylethyl bromide and (III) give a product which is distilled and dehydrogenated to α-7-*methyl*-1-*naphthyl*-β-5′ : 6′-*dimethyl*-1′-*naphthylethane*, m.p. 107—110° after softening, whence 1 : 2 : 8-trimethylpicene, m.p. 309—310° (corr.). (III) is converted by Zn and CH_2Br·CO_2Et into C_6H_6 into Et 5 : 6-dimethyl-3 : 4-dihydro-1-naphthylacetate, b.p. 105—110°/0·1 mm., reduced to β-5 : 6-*dimethyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthylethyl alcohol*, b.p. 128—132°/0·02 mm. 33% HBr–AcOH at 100° transforms this into the *bromide*, b.p. 130—133°/0·1 mm., the Grignard compound from which with (III) (as above) affords αβ-*di*-5 : 6-*dimethyl*-1-*naphthylethane*, m.p. 163—165°, whence 1 : 2 : 9 : 10-*tetramethylpicene*, m.p. 400—401° (corr.). H. W.

Vinylamines. I. W. Krabbe and K. H. Schmidt [with E. Polzin] (Ber., 1939, **72**, [*B*], 381—390).—Under strictly defined conditions OH·CPh_2·CH_2·NH_2 (I) is transformed by $Et_2C_2O_4$ into *diphenyl-N-ethoxalylamidomethylcarbinol*, m.p. 128—129°, converted by boiling CO_2Et·COCl (II) into *N-ethoxalyl-ββ-diphenylvinylamine* (III), m.p. 128—129°, obtained directly but in poorer yield from (I) and (II). Hydrolysis of (III) with KOH–MeOH affords *ββ-diphenylvinylamine* (IV), m.p. 141·5—142·5° [picrate, m.p. 273° (partial decomp.); unstable hydrochloride].

(IV) is somewhat unstable and is best identified by its red halochromism in conc. H_2SO_4. This effect is also shown by (I) owing to its transformation into (IV), which can thus be effected preparatively. The most characteristic property of (IV) is its sensitiveness to acids. Thus (IV) suspended in MeOH is almost instantaneously converted by HCO_2H into di-ββ-diphenylvinylamine. A solution of (IV) in dioxan can be preserved unchanged for days whereas in ligroin there is gradual formation of $COPh_2$, HCN, and resin. Decomp. is greatly accelerated by the presence of impurities. (IV) does not decolorise Br in $CHCl_3$ and only slowly reduces $KMnO_4$ in aq. Na_2CO_3. Ozonisation of (IV) in *cyclo*hexane and decomp. of the ozonide with H_2O yields $COPh_2$ and $HCO{\cdot}NH_2$. H. W.

Action of dimethylamine on 3 : 4-dibromo-1-methyl*cyclo*hexane. J. Gutman (Compt. rend., 1939, **208**, 524—525; cf. A., 1939, II, 56).—3 : 4-Dibromo-1-methyl*cyclo*hexane with $NHMe_2$ at 120—130° under pressure affords 3-*dimethylamino*-1-*methyl*-Δ^4-cyclo*hexene* (90%), b.p. 65°/25 mm. (*hydrochloride*, m.p. 125—126°; *methiodide*, m.p. 200—201°; *picrate*, m.p. 169—170°), reduced (H_2–Raney Ni) to a mixture, b.p. 85°/50 mm., of *cis*- (*picrate*, m.p. 190—191°) and *trans*-3-dimethylamino-1-methyl*cyclo*hexane (*picrate*, m.p. 178—179°); the respective amines are also obtained by reduction of 3-methyl*cyclo*hexanoneoxime in acid and alkaline solution and subsequent methylation. The *picrates* of *cis*- and *trans*-4-dimethylamino-1-methyl*cyclo*hexane have m.p. 193° and 194°, respectively. J. L. D.

Action of di-(β-hydroxyethyl)amine, methylamine, and ethylamine on halogenonitrobenzenes. K. F. Waldkötter (Rec. trav. chim., 1939, **58**, 132—138).—When boiled with $NH([CH_2]_2{\cdot}OH)_2$ in EtOH, 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$ yields 2 : 4-*dinitro*-, m.p. 99° (*diacetate*, m.p. 77°; *dinitrate*, m.p. 103°), whilst 1 : 2 : 4 : 6-$C_6H_2Cl(NO_2)_3$ gives 2 : 4 : 6-*trinitro*-NN-*di*-β-*hydroxyethylaniline*, m.p. 245° (*mononitrate*, m.p. 198°), together with β-*hydroxyethyl*-β′-2 : 4 : 6-*trinitrophenoxyethylamine*, m.p. 154°, which gives picric acid on nitration. 1 : 3 : 4 : 6-$C_6H_2Cl_2(NO_2)_2$ similarly yields 4 : 6-*dinitro*-1 : 3-*bis*(*di*-β-*hydroxyethylamino*)*benzene*, m.p. 126°. Condensation (sealed tubes) of NH_2Me and NH_2Et with 1 : 4 : 2-$C_6H_3Cl_2{\cdot}NO_2$, 1 : 3 : 4-$C_6H_3Cl(NO_2)_2$, 1 : 3 : 4 : 6- and 1 : 3 : 4 : 5-$C_6H_2Cl_2(NO_2)_2$, 3 : 5 : 1 : 4-$(NO_2)_2C_6H_2Cl{\cdot}OMe$, and the appropriate Br-compounds, followed by acetylation or nitration of some of the products formed, gave the following compounds, having the m.p. given: 4-*chloro*-2-*nitro*-NN-*acetyl-methyl*-, 92°, and -*ethyl-aniline*, 47°, and the 4-*Br*-compounds, 116° and 57°, respectively; 4-chloro-(*Ac* derivative, 134°) and -bromo-2 : 6-dinitro-*N*-methylaniline (*Ac* derivative, 103°); 4-*chloro*-, 101° (*Ac* derivative, 73°), and -*bromo*-2 : 6-*dinitro*-N-*ethylaniline*, 90° (*Ac* derivative, 91°); 5-*chloro*-2-*nitro*-NN-*acetyl-methyl*-, 87°, and -*ethyl-aniline*, 108°, and the 5-*Br*-compounds, 112° and 129°, respectively; 4 : 6-*dinitro*-1 : 3-*di*-(*methylamino*)- (+1EtOH), 160—170° (*Ac*$_2$ derivative, 173°), and -(*ethylamino*)-*benzene* (+1EtOH), 90—110° (*Ac*$_2$ derivative, 108°); 4 : 6-*dichloro*-2-*nitro*-NN-*acetylmethyl*-, 60°, -NN-*nitromethyl*-, 72°, -N-*ethyl*-, 61°, -NN-*nitroethyl-aniline*, 96°, and the corresponding 4 : 6-*Br*$_2$-compounds, 89°, —, 74°, and an oil, respectively. The relation between constitution and m.p., colour, and taste of these compounds is discussed. A. L.

Action of magnesium ethyl bromide on butyrethylanilide. M. Montagne and Y. Isambert (Compt. rend., 1939, **208**, 285—287; cf. A., 1936, 1096).—Butyrethylanilide (I) with MgEtBr affords C_2H_6 and NPhEt·CO·CHEt·MgBr, which reacts with $COEtPr^{\alpha}$ (a by-product) to give, after hydrolysis, β-hydroxy-αβ-diethylhexoethylanilide (II). The alternative view that COPr·CHEt·CO·NPhEt is formed from 2 mols. of (I) and then reacts with MgEtBr is unlikely because (*a*) it is not found in the reaction product, (*b*) it is only partly converted into (II) by a large excess of MgEtBr. J. L. D.

Sulphonation of methylaniline. I. S. Uppal and K. Venkataraman (J.S.C.I., 1938, **57**, 410—412).—Proof of the orientation of the three $NHMe{\cdot}C_6H_4{\cdot}SO_3H$ (*A*) is given. Sulphonation of NHPhMe leads to *p*-$NHMe{\cdot}C_6H_4{\cdot}SO_3H$, decomp. 244—246°, or a mixture of this with the *m*-acid, decomp. 286—290°. The *o*-acid, decomp. 220°, is obtained by the methylation (Me_2SO_4) of orthanilic acid. The three isomerides are oriented by an application of Halberkann's method (A., 1921, i, 779), the *p*-toluenesulphonyl derivative of each being prepared by methylation of *p*-$C_6H_4Me{\cdot}SO_2{\cdot}NH{\cdot}C_6H_4{\cdot}SO_3H$ or from (*A*) and *p*-$C_6H_4Me{\cdot}SO_2Cl$. The *p*-toluenesulphonyl derivatives are characterised as the arylamine salts; the following are described: C_5H_5N, m.p. 255° (very stable to acid hydrolysis), and p-*chloroaniline*, m.p. 230° (decomp.), p-*toluenesulphonylsulphanilate*; *benzidine*, m.p. 255° (decomp.), p-*chloroaniline*, m.p. 202°, and β-$C_{10}H_7{\cdot}NH_2$, m.p. 201°, p-*toluenesulphonyl*-N-*methylsulphanilate*; p-*chloroaniline* p-*toluenesulphonyl-metanilate*, m.p. 202°, p-*toluenesulphonyl*-N-*methyl-metanilate*, m.p. 148°, p-*toluenesulphonylorthanilate*, m.p. 214°, and p-*toluenesulphonyl*-N-*methylorthanilate*, m.p. 195° (β-$C_{10}H_7{\cdot}NH_2$ salt, m.p. 196°).

Phosphorescence of tetraphenylmethane and related substances. D. B. Clapp (J. Amer. Chem. Soc., 1939, **61**, 523—524).—CPh_4 and 14 of its derivatives, 2-triphenylmethylpyrrole, SiX_4 (X = Ph or *p*-C_6H_4Me, but not *p*-C_6H_4Ph), $SnPh_4$, $PbPh_4$ (weak), $(CH_2{\cdot}CO_2H)_2$, *m*-$C_6H_4(OH)_2$, and sucrose fluoresce for various times up to 35 sec. after irradiation with ultra-violet light. Traces of CPh_3-dyes may be responsible for the effect with CPh_4 derivatives. The time of fluorescence increases as the temp. decreases. $CPh_3{\cdot}OH$, NHPhR (or $NPhR_2$), and HCl–AcOH–Ac_2O give 4-*ethyl*-, m.p. 172—173°, 4-n-*butyl*-, m.p. 135—136°, 4-*diethyl*-, m.p. 177·5—178·5°, and 4-*di*-n-*butyl-aminotetraphenylmethane*, m.p. 177—178°. R. S. C.

Mononitration of α- and β-naphthylamines in presence of carbamide. H. H. Hodgson and W. Davey (J.C.S., 1939, 348—349).—$CO(NH_2)_2$ and α-$C_{10}H_7{\cdot}NH_2$, dissolved in this order in conc. H_2SO_4, with KNO_3 (1 mol.) give 8 : 1- (27%) and 5 : 1-$NO_2{\cdot}C_{10}H_6{\cdot}NH_2$ (43%); 2 mols. give 32·5 and 38%

respectively. Similarly, β-$C_{10}H_7$·NH_2 gives 5·4 and 86·7% or a trace and 70·5% of 8 : 2- and 5 : 2-NO_2·$C_{10}H_6$·NH_2, respectively. A. T. P.

Case of simple substitution in the 3-position of a 1 : 2-disubstituted naphthalene. H. H. Hodgson and R. L. Elliott (J.C.S., 1939, 345—346).—1 : 2-NO_2·$C_{10}H_6$·NH_2 and $Hg(OAc)_2$–AcOH give 1-*nitro*-2-*naphthylamine*-3-*mercuriacetate*, converted by I + 10% KI into 3-*iodo*-1-*nitro*-2-*naphthylamine* (I), m.p. 174°, the *Ac* derivative (by Ac_2O), m.p. 196°, of which is reduced (A., 1936, 718) to the *stannichloride* of 2 : 3 : 1-NHAc·$C_{10}H_5$I·NH_2. 4 : 2 : 1-NO_2·$C_{10}H_5$I·NH_2 is not similarly acetylated (cf. *loc. cit.*). (I) is deaminated to 3 : 1-$C_{10}H_6$I·NO_2. 4 : 2 : 1-NO_2·$C_{10}H_5$Cl·NH_2 affords (diazo-reaction) 1 : 2-*dichloro*-4-*nitronaphthalene*, m.p. 119°, but 2 : 4 : 1-NO_2·$C_{10}H_5$Cl·NH_2 similarly gives only an amorphous *product*, m.p. 102°. A. T. P.

Carbodi-imide. F. Zetzsche and A. Fredrich (Ber., 1939, **73**, [*B*], 363—365; cf. A., 1938, II, 470).—Carbodi-imides are determined by weighing the CO_2 evolved when they react with $H_2C_2O_4$ in pure dioxan first at room temp. and finally at >90° (bath). The polymeric β-carboditolylimide reacts similarly to but more slowly than the α- (monomeric) form. H. W.

6 : 6′-Diamino-4 : 4′-di*iso*propylstilbene-2 : 2′-disulphonic acid.—See B., 1939, 243.

Guanyl- and guanido-naphthalenes. Group migration in cyanonaphthalenes. H. King and E. V. Wright (J.C.S., 1939, 253—257; cf. A., 1938, III, 63).—*K* 2-*cyanonaphthalene*-7-*sulphonate* (+2·5H_2O) (prep. from 2 : 7-NH_2·$C_{10}H_6$·SO_3H) or 2 : 7-$C_{10}H_6(SO_3Na)_2$, on dry distillation with KCN in CO_2, gives 2 : 7- (I) and 1 : 7-$C_{10}H_6(CN)_2$ (II) (also obtained similarly from 2 : 8-CN·$C_{10}H_6$·SO_3Na); partial migration of CN thus occurs. Similarly, 2 : 6-CN·$C_{10}H_6$·SO_3Na and KCN give 2 : 6- (III) and 1 : 6-$C_{10}H_6(CN)_2$. (III) and (I) in dioxan–EtOH, saturated with HCl at 0—5°, and kept at 0° for 14 days, afford imino-ether hydrochlorides, converted by EtOH–NH_3 at 40—50° (under pressure) into 2 : 6-, m.p. >300°, and 2 : 7-*naphthylenediamidine dihydrochloride*, m.p. >290° (+H_2O), respectively. 2 : 7-$C_{10}H_6(NH_2)_2$,2HCl refluxed with CN·NH_2 (20 mols.) in EtOH, followed by treatment of the product with aq. NH_4NO_3, gives 7-*guanido*-2-*naphthylamine nitrate*, m.p. 251—252°, and 2 : 7-*diguanidonaphthalene dinitrate*, m.p. 209°. 1 : 5-$C_{10}H_6(NH_2)_2$,2HCl similarly affords 1 : 5-*diguanidonaphthalene dinitrate*, m.p. >300°, but 1 : 8-$C_{10}H_6(NH_2)_2$,2HCl and CN·NH_2–EtOH give aminoperimidine hydrochloride (+H_2O). 1 : 5-$C_{10}H_6(SO_3Na)_2$ and KCN give 1 : 5-$C_{10}H_6(CN)_2$, not convertible into the imino-ether. (II) with HCl–EtOH–dioxan, then NH_3–EtOH, gives 1-*naphthonitrile*-7-*amidine hydrochloride*, m.p. 296—297° (1-$C_{10}H_7$·CN derivatives do not give 1-amidines). 4 : 4′-Diaminoazobenzene dihydrochloride and EtOH–CN·NH_2 (30 mols.) followed by NH_4NO_3 afford 4-*guanido*-4′-*aminoazobenzene nitrate*, m.p. 257° (decomp.). 4 : 4′-Dipiperidyl and SMe·C(NH)·NH_2,HI (IV) in aq. NaOH at 80° give an iodide, converted by moist AgCl into 1 : 1′-*di-guanyl*-4 : 4′-*dipiperidyl dihydrochloride* (+2H_2O), m.p. 361° (decomp.); *monoguanyl*-4 : 4′-*dipiperidyl hydriodide*, m.p. 136—137° (+H_2O), m.p. 166° (dried at 100°), is isolable from the original mother-liquors. 2 : 4′-Dipiperidyl and (IV) at 80° give 1′-*guanyl*-2 : 4′-*dipiperidyl dihydriodide* (+H_2O), m.p. ~123°. Tests for trypanocidal action are given; introduction of the $C_{10}H_8$ nucleus into amidines and guanidines does not impair activity. A. T. P.

Electrochemical oxidation of 5 : 5′-azo-*m*-xylene [3 : 5 : 3′ : 5′-tetramethylazobenzene]. F. Fichter and R. Gunst (Helv. Chim. Acta, 1939, **22**, 267—275).—3 : 5 : 3′ : 5′-Tetramethylazobenzene, m.p. 136—137° (prep. by electrochemical reduction of 1 : 3 : 5-$C_6H_3Me_2$·NO_2 described), is dissolved in 90% H_2SO_4 and oxidised at a Pt anode giving unchanged material, 2 : 6-dimethyl-*p*-benzoquinone, m.p. 71°, and an ill-defined oxidation product (I) transformed by Ac_2O in C_5H_5N into 4 : 4′-*diacetoxy*-3 : 3′ : 5 : 5′-*tetramethylazobenzene* (II), decomp. ~300° (softens at 110—130°). Diazotisation of *vic.*-*m*-xylidine in presence of KNO_3 leads to 4 : 2 : 6 : 1-NO_2·$C_6H_2Me_2$·OH. Electrochemical reduction of the corresponding *acetate*, m.p. 112°, appears to give the corresponding azobenzene but the process is accompanied by some loss of Ac and the product is therefore reduced and then acetylated to 5-*acetamido*-2-*acetoxy*-m-*xylene*, m.p. 157°, more conveniently obtained by treatment of 4 : 2 : 6 : 1-NO·$C_6H_2Me_2$·OH, m.p. 165° (decomp.), with $(NH_4)_2S$ and subsequent acetylation. This is also obtained by reductive fission and subsequent acetylation of (II), whereby the structure of (I) is established. 5-*Benzamido*-m-2-*xylenol*, m.p. 188° [*benzoate*, m.p. 196°, obtained by reductive fission followed by benzoylation of (I)], is described. Chromatographic purification of (I) by Al_2O_3 leads to homogeneous 4 : 4′-*dihydroxy*-3 : 5 : 3′ : 5′-*tetramethylazobenzene*, decomp. >160°. 5-*Nitroso*-m-2-*xylenol Me ether*, m.p. 51°, from the phenol and CH_2N_2, suffers partial loss of Me when reduced; the product is diazotised and coupled with *vic.*-*m*-xylenol to a compound, $C_{17}H_{10}O_2N_2$ or $C_{16}H_{18}O_2N_2$, decomp. 199°, which is converted by Me_2SO_4 and alkali into 4 : 4′-*dimethoxy*-3 : 5 : 3′ : 5′-*tetramethylazobenzene*, m.p. 139°. H. W.

Homologous series of acylated azo-dyes from *o*- and *p*-acylamidophenols and 1 : 7-acylamidonaphthols. H. E. Fierz-David and W. Kuster (Helv. Chim. Acta, 1939, **22**, 82—112).—The most marked influence on the surface tension of aq. solutions of acylated azo-dyes and on alkaline solutions of acylated amino-phenols and -naphthols is exerted by the decoic to palmitic residues. Higher fatty acids with an odd no. of C are usually obtained from the requisite alkyl halide through the corresponding nitriles. Et palmitate is converted by MgPhBr into diphenylpentadecylcarbinol, m.p. 46°, dehydrated at 220—260° to αα-diphenyl-β-tetradecylethylene, m.p. 18—20°, which is oxidised (CrO_3 in AcOH) to pentadecoic acid, m.p. 51°. α-Bromostearic acid is converted by aq. KOH into α-hydroxystearic acid, which at 250—280° passes into margaraldehyde, oxidised ($KMnO_4$ in $COMe_2$) to margaric acid. The

acids are converted into their chlorides by $SOCl_2$. Acylation of *o*- and *p*-aminophenols is effected by treating the base dissolved as salt of the requisite acid in H_2O with the anhydride of the same acid, by the use of the acid chloride [when necessary in presence of an acid-absorbent (C_5H_5N, NaOAc, $CaCO_3$)], or by melting the phenol and acid together. The following are described: *o*-form-, m.p. 130°, -acet-, m.p. 207°, *-propion-*, m.p. 78°, -butyr-, m.p. 81°, -valer-, m.p. 82°, *-hexo-*, m.p. 74°, *-hepto-*, m.p. 83°, *-octo-*, m.p. 71°, *-nono-*, m.p. 86°, *-deco-*, m.p. 72°, -laur-, m.p. 69°, *-myrist-*, m.p. 70°, -palmit-, m.p. 77°, and *-stear-*, m.p. 82°, -amidophenols; *p*-form-, m.p. 139°, -acet-, m.p. 169°, *-propion-*, m.p. 173°, *-butyr-*, m.p. 138°, *-valer-*, m.p. 101°, *-hexo-*, m.p. 112°, *-hepto-*, m.p. 114°, *-octo-*, m.p. 123°, *-nono-*, m.p. 124°, -deco-, m.p. 130·5°, *-laur-*, m.p. 131°, *-myrist-*, m.p. 133·5°, *-palmit-*, m.p. 134·5°, and *-stear-*, m.p. 135·5°, *-amidophenols*; o-ON-*dibutyryl-*, m.p. 76°, *-divaleryl-*, m.p. 71—73°, *-diheptoyl-*, m.p. 47°, *-dioctoyl-*, m.p. 57°, *-dinonoyl-*, m.p. 59°, *-didecoyl-*, m.p. 62°, *-dilauryl-*, m.p. 65°, *-dimyristyl-*, m.p. 65°, and *-distearyl-*, m.p. 62°, *-aminophenols*; p-ON-*divaleryl-*, m.p. 114°, *-dihexoyl-*, m.p. 118—120°, *-diheptoyl-*, m.p. 119·5°, *-dioctoyl-*, m.p. 127—128°, *-dinonoyl-*, m.p. 124°, *-didecoyl-*, m.p. 130°, and *-dilauryl-*, m.p. 119—120°, *-aminophenols*. o-NN-*Distearamidophenol*, m.p. 92°, *pentadecylbenzoxazole*, m.p. 45·5°, and heptadecylbenzoxazole, m.p. 55°, are described incidentally. The following *N*-acyl derivatives of 1 : 7-$NH_2{\cdot}C_{10}H_6{\cdot}OH$ are described: *form-*, m.p. 204°; acet-, m.p. 198° (decomp.); *propion-*, m.p. 138°; *butyr-*, m.p. 161°; *valer-*, m.p. 171°; *hexo-*, m.p. 156°; *hepto-*, m.p. 147°; *octo-*, m.p. 139°; *nono-*, m.p. 137°; *deco-*, m.p. 131°; *undeco-*, m.p. 127°; *laur-*, m.p. 125°; *trideco-*, m.p. 127°; *myrist-*, m.p. 126°; *pentadeco-*, m.p. 128°; *palmit-*, m.p. 129°; *heptadeco-*, m.p. 129°; *stear-*, m.p. 130°; *nonadeco-*, m.p. 129°; *ole-*, m.p. 122°; benz-, m.p. 211°. The following *diacyl* derivatives of 1 : 7-$NH_2{\cdot}C_{10}H_6{\cdot}OH$ are described: *diacetyl-*, m.p. 177°; *dibutyryl-*, m.p. 103°; *divaleryl-*, m.p. 77°; *diheptoyl-*, m.p. 87°; *ditridecoyl-*, m.p. 87°; (?) *distearyl-*, m.p. 102°; *dibenzoyl-*, m.p. 208° (all m.p. are corr.). The coupling of acylated *o*- and *p*-aminophenols with diazotised *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_3H$ proceeds relatively smoothly with the lower homologues only; the *p*-compounds are particularly unsuitable. EtOH, when used as solvent, is partly oxidised to MeCHO. In most cases considerable amounts of unchanged base remain after disappearance of the diazo-reaction. Acylated 1 : 7-aminonaphthols couple readily. The compounds derived from *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_3H$ are usually too sparingly sol. for physiological purposes. The following Na_2 *2'-hydroxy-8'-acylamido-1'-naphthaleneazobenzene-2 : 5-disulphonates* have therefore been prepared, usually retaining a certain proportion of NaCl: *-form-*, *-acet-*, *-propion-*, *-butyr-*, *-valer-*, *-hexo-*, *-hepto-*, *-octo-*, *-nono-*, *-deco-*, *-undeco-*, *-laur-*, *-trideco-*, *-myrist-*, *-pentadeco-*, *-palmit-*, *-heptadeco-*, *-stear-*, *-nonadeco-*, *-ole-*, *-benz-*. H. W.

Reactions and salts of 4 : 4'-dinitrodiazoaminobenzene. F. P. Dwyer (J.S.C.I., 1939, **58**, 110—116).—The dark violet Na, K, and *Ba* salts, BaR_2 (R = $C_{12}H_8O_4N_5$), of 4 : 4'-dinitrodiazoaminobenzene (I) are considered to have the *aci*-structure (*A*) (cf. A., 1938, II, 483); they are readily sol. in EtOH, $COMe_2$, $PhNO_2$, and hot aq. alkali, and are hydrolysed by hot H_2O. Alkali-metal salts of the triazen form appear to be incapable of existence. The yellow C_5H_5N salt, NAr:N·NArH,C_5H_5N (Ar = *p*-$NO_2{\cdot}C_6H_4{\cdot}$), obtained when a solution of either form (*loc. cit.*) of (I) in hot, dry C_5H_5N is cooled, undergoes tautomeric change in presence of H_2O, MeOH, EtOH, or $COMe_2$ (decreasing intensity in the order quoted) to the *aci*-salt (purplish-red; not isolable), which is stabilised by co-ordination, *e.g.*, $\geqslant N\rightarrow H{\cdot}OH$. The NH_4 salt resembles the C_5H_5N salt. (I) (in $COMe_2$) with MeOH–C_5H_5N–$AgNO_3$ + NaOAc gives the yellow *Ag* salt, Ag$\langle$NAr / NAr$\rangle$N, converted by C_5H_5N at 100° into the purple *salt* (II), AgR,C_5H_5N (*A* with M = Ag$\leftarrow C_5H_5N$), which when heated alone or with EtOH or $COMe_2$ regenerates the yellow salt. Meldola's Ag salt (J.C.S., 1887, **50**, 446) is undoubtedly the *ammine*, AgR,NH_3. Treatment of the product obtained from (I) and $Cu(C_5H_5N)_2Cl$ in EtOH–$COMe_2$–3N-NaOAc with C_5H_5N gives the violet *salt*, CuR,C_5H_5N, which is converted by heating to 100° or by warm EtOH or $COMe_2$ into the orange-yellow normal *salt*, CuR. This with dry NH_3 in C_6H_6 affords the *ammine*, CuR,NH_3, and with aq. EtOH–$CS(NH_2)_2$ gives the black *compound*, $CuR,3CS(NH_2)_2$. Since one C_5H_5N or NH_3 is co-ordinated in the above Ag and Cu· salts, it is deduced that (I) (*aci*-form) supplies one co-ordination position. Attempts to prepare a Me derivative of the *aci*-form of (I) from (II) and MeI–moist Ag_2O yielded only the usual yellow, triazen derivative; the Me cannot act as acceptor to the donor azo-N. The *Cu*·· salt, $CuR_2,2C_5H_5N$, blue, and *Hg*·· salt, $HgR_2,2C_5H_5N$, orange-red, are co-ordinated normal salts dissolving in C_5H_5N to orange solutions; removal of C_5H_5N from the former gives the Cu· salts. Attempts to prepare the unco-ordinated Cu·· salt were unsuccessful; a *salt*, probably $CuR(C_{12}H_9O_4N_5)_3$, was obtained with other products from the Na salt of (I) and MeOH–$CuCl_2,2H_2O$. The normal and *aci*-forms of (I) with conc. HCl at 100° (bath) give N_2, *p*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$, and 43 and 62% respectively of *p*-$C_6H_4Cl{\cdot}NO_2$. H. B.

Triaryl phosphates.—See B., 1939, 244.

Detoxication of ingested naphthalene.—See A., 1939, III, 302.

Synthesis of phenanthrenes. A. Schönberg and F. L. Warren (Chem. and Ind., 1939, 199).—Synthesis of 9-hydroxyphenanthrene from *o*-$C_6H_4Ph{\cdot}COCl$ by way of *ω-diazo-o-phenylacetophenone* (prep. by CH_2N_2), m.p. 106°, and *o-diphenylylacetic acid* (prep. by colloidal Ag in H_2O), m.p. 116°, is announced without details. R. S. C.

Oxidation of phenol by hydrogen peroxide in presence of ferrous sulphate. A. Chwala and M. Pailer (J. pr. Chem., 1939, [ii], **152**, 45—48).—

Repetition of the work of Goldhammer (A., 1927, 1181) shows that considerable amounts of quinol (I) and some more highly oxidised material are formed in addition to *o*-$C_6H_4(OH)_2$ (II). Under defined conditions the yield of (I) + (II) is almost 72% of the PhOH taken. It appears essential that PhOH should be in excess with respect to H_2O_2 and also to (I) + (II), and that PhOH and H_2O_2 are in very dil. solution. p_H 3—4 is most suitable. H. W.

Synthesis and bactericidal properties of 5-*n*-alkylresorcinols. C. M. Suter and A. W. Weston (J. Amer. Chem. Soc., 1939, **61**, 232—236).—1 : 3 : 5-$C_6H_3Br_3$ does not give Mg or Li derivatives. Indirect prep. of 3 : 5 : 1-$C_6H_3Br_2Alk$ was not practicable. 3 : 5 : 1-$(OMe)_2C_6H_3$·CO·NH_2 and MgAlkHal give slowly 80—88% of 3 : 5-*dimethoxyphenyl Pr*$^\alpha$, b.p. 157—158°/7 mm., m.p. 33·5—34° (*semicarbazone*, m.p. 188°), Et, b.p. 162—163°/11 mm., m.p. 32·5° (semicarbazone, new m.p. 131·5—132°), Bu$^\alpha$, n-*amyl*, b.p. 175—176°/7 mm., m.p. 53° (*semicarbazone*, m.p. 183—184°), and *n-hexyl ketone*, b.p. 161—161·5°/3 mm., m.p. 30·5—31° (*semicarbazone*, m.p. 133·5—134°). The appropriate hydrazones with KOH at 200—245° give 3 : 5-*dimethoxy*-n-*butyl*-, b.p. 125—128°/6 mm., -*n*-propyl-, b.p. 103—105°/3 mm., -*n*-amyl-, b.p. 133—136°/6 mm., -*n*-heptyl-, b.p. 162—163°/6 mm., and -n-*hexyl-benzene*, b.p. 141—143°/7 mm. [with considerable amounts of azine]. Demethylation then gives 5-*n*-propyl-, b.p. 148—149°/3 mm., new m.p. 86·5—86·7°, and +H_2O, new m.p. 47° (Br_3-derivative, m.p. 97·5—98°), 5-*n*-amyl-, b.p. 162—164°/5 mm. (Br_3-derivative, m.p. 85°), 5-*n*-heptyl-, b.p. 179—181°/6 mm., new m.p. 55—55·5° (Br_3-derivative, m.p. 73·5—74·5°), 5-*n-butyl*-, b.p. 151—152°/3 mm., m.p. 81·5—82·5° (*Br*$_3$-derivative, m.p. 84—84·5°), and 5-n-*hexyl-resorcinol*, b.p. 192—195°/11 mm., m.p. (+H_2O) 49—49·5° (*Br*$_3$-derivative, m.p. 75—76°), which have PhOH coeff. 5, 35, 128, 10, and 49, respectively, against *S. aureus*. Hydrogenation (Pd) of the ketones is very slow. 3 : 5-*Dimethoxybenzdiethylamide*, b.p. 166·5—167°/3·5 mm., with MgAlkHal gives very little ketone. 3 : 5-$(OMe)_2C_6H_3$·COCl with $CdBu^\alpha_2$ gives only 27% of ketone and with $ZnAlk_2$ gives mostly the ester. 3 : 5-*Dimethoxyphenyl Pr*$^\alpha$ *ketazine* has m.p. 96·5—97°. The KBr–$KBrO_3$ titration of resorcinols is improved. R. S. C.

Oxidation processes. XIII. Inhibitory action of sulphite and other compounds in the autoxidation of quinol and its homologues. T. H. James and A. Weissberger (J. Amer. Chem. Soc., 1939, **61**, 442—450; cf. A., 1938, II, 440).—By suitably adjusting p_H and adding sp. inhibitors for the oxidation of Na_2SO_3, and owing to quinones etc. inhibiting the oxidation of Na_2SO_3, the rate of oxidation of quinols in presence of an excess of Na_2SO_3 is measured. The complex results are explained by assuming oxidation of quinols to quinones and H_2O_2, oxidation of Na_2SO_3 by H_2O_2, and interaction of quinones with Na_2SO_3 to form quinolmonosulphonates (followed by oxidation to quinonesulphonates and, if H is still available, further reaction thereof with Na_2SO_3 etc.). Cysteine, SH·CH_2·CO_2H, SH·CH_2·CO·NHPh, and *p*-C_6H_4Me·SH inhibit oxidation of quinol by forming compounds with the catalytic *p*-O:C_6H_4:O formed; these compounds later oxidise faster than does *p*-O:C_6H_4:O. R. S. C.

Mechanism of the autoxidation of ψ-cumoquinol. G. Kornfeld and A. Weissberger (J. Amer. Chem. Soc., 1939, **61**, 360—363).—Previous quant. results (A., 1938, II, 440) are explained on the assumptions that reaction of ψ-cumoquinol (I) with O_2 involves reaction of the intermediate semiquinone with (*a*) O_2 and (*b*) ψ-cumoquinone (II) to yield a complex (analogous to verdoflavin), which then decomposes into (I) and (II). R. S. C.

Condensation of ketones with phenols. M. E. McGreal, V. Niederl, and J. B. Niederl (J. Amer. Chem. Soc., 1939, **61**, 345—348).—PhOH, COR_2, and HCl in AcOH give $CR_2(C_6H_4$·OH-*p*$)_2$ (by way of *p*-OH·C_6H_4·CR_2·OH), converted by distillation/1 atm. into PhOH, *p*-OH·C_6H_4·CHR_2, and tar. Thus are obtained ββ-*di*-p-*hydroxyphenyl*-, m.p. 125° [$(NO_2)_4$-derivative, m.p. 168°], and -*di*-6-*hydroxy*-m-*tolyl*-*butane*, m.p. 146° (*diacetate*, m.p. 71°), ββ-*di*-p-*hydroxyphenyl-pentane*, m.p. 149°, and -δ-*methylpentane*, m.p. 150° [$(NO_2)_4$-derivative, m.p. 154°], ββ-*di*-6-*hydroxy*-m-*tolyl*-δ-*methylpentane*, m.p. 129°, 1 : 1-*di*-p-*hydroxyphenyl*-, m.p. 184° (*diacetate*, m.p. 124°; *bisphenylurethane*, m.p. 148°), and 1 : 1-*di*-6′-*hydroxy*-m-*tolyl*cyclo*hexane*, m.p. 186° (derived *di*-O-*acetic acid*, m.p. 232°; *bisphenylurethane*, m.p. 142°), 1 : 1-*di*-p-*hydroxyphenyl*-3-*methyl*cyclo*hexane*, m.p. 167°, -4-*methyl*cyclo*hexane*, m.p. 180°, and -cyclo*pentane*, m.p. 156°, p-*hydroxyphenyl*-cyclo*hexane*, m.p. 132° (derived *aryloxyacetic acid*, m.p. 145°), -3-*methyl*cyclo*hexane*, m.p. 110° (derived *aryloxyacetic acid*, m.p. 127°), -4-*methyl*-cyclo*hexane*, m.p. 118° (derived *aryloxyacetic acid*, m.p. 136°), and -cyclo*pentane*, m.p. 90° (derived *aryloxyacetic acid*, m.p. 115°), 6′-*hydroxy*-m-*tolyl*cyclo*hexane*, m.p. 126° (derived *aryloxyacetic acid*, m.p. 134°), α-*phenyl*-, m.p. 175° (*diacetate*, m.p. 180°), and α-p-*tolyl*-αα-*di*-p-*hydroxyphenylethane*, m.p. 133° (*diacetate*, m.p. 151°), and α-*phenyl*-αα-*di*-6-*hydroxy*-m-*tolylethane*, m.p. 141° (*diacetate*, m.p. 118°). R. S. C.

Oxidation of 1 : 8-dihydroxynaphthalene and its monomethyl ether with peracetic acid. J. Böeseken and L. G. Smitt (Rec. trav. chim., 1939, **58**, 125—131; cf. A., 1935, 614).—With AcO_2H (1—1·2 mols.) in AcOH, 1 : 8-$C_{10}H_6(OH)_2$ gives only resinous products, but its *Me*$_1$ *ether* (CH_2N_2), m.p. 47°, yields 8-*methoxy*-α-*naphthaquinone*, m.p. 184°, and (?) 7-*methoxyindenone*-2-*carboxylic acid*, m.p. 200°, formed by dehydration of 2-carboxy-3-methoxy*allo*-cinnamic acid. 8 : 1-NHAc·$C_{10}H_6$·OH when distilled at 16 mm. yields 2-*methyl*per*inaphthoxazine*, m.p. 72°, which reverts to the former when cryst. from EtOH. A. Li.

Aromatic fluoro-compounds. M. Seyhan [with N. Esmer] (Ber., 1939, **72**, [*B*], 365—366; cf. Schiemann and Seyhan, A., 1938, II, 52).—Improved methods are described for the conversion of 4 : 2 : 1-NO_2·C_6H_3F·OEt into 4 : 2 : 1-NH_2·C_6H_3F·OEt and thence into 3-fluoro-4-ethoxybenzenediazonium borofluoride, decomp. 82°, and 2 : 4-difluorophenetole, b.p. 72°/18 mm. H. W.

Pyrolysis of *cyclo*hexenyl phenyl ether. J. W. Cornforth, G. K. Hughes, and F. Lions (J. Proc.

Roy. Soc. New South Wales, 1938, **71**, 323—329).—1 : 2-Dibromo*cyclo*hexane is transformed by NaOPh in boiling EtOH into Δ^2-cyclo*hexenyl Ph ether* (I), b.p. 135°/21 mm., *hexahydrodiphenylene oxide* (II), b.p. 157—159°/22 mm., a *product*, b.p. 220—222°/22 mm., and o-cyclo*hexenylphenol* (III), b.p. 153—154°/22 mm.; on one occasion a *product*, $C_{12}H_{14}O$, m.p. 68° with softening, was isolated from the Et_2O extract of the phenols which contained HCl. The structure of (I) is established by its formation from 1-bromo-Δ^2-*cyclo*hexene, PhOH, and anhyd. K_2CO_3 in boiling $COMe_2$. It is oxidised to *α-phenoxyadipic acid*, m.p. 142°. At 215° (I) passes mainly into (II) with a smaller proportion of (III). Dehydrogenation of (II) by Se at 290—300° yields diphenylene oxide, characterised as the 3 : 6-Br_2-derivative. (III) is characterised by conversion into o-cyclo*hexenylphenoxyacetic acid*, m.p. 143—144°, and by methylation (Me_2SO_4–NaOH) to o-cyclo*hexenylanisole*, b.p. 150—151°/22 mm., oxidised to α-o-*anisyladipic acid*, m.p. 179—180°. H. W.

Alkoxyalkyl derivatives of resorcinol. C. D. Hurd and G. W. Fowler (J. Amer. Chem. Soc., 1939, **61**, 249—254).—Resorcinol alkoxyalkyl monoethers are less efficient bactericides than are the corresponding alkyl ethers. OEt·$[CH_2]_2$·Cl and *di*-(β-*ethoxyethyl*) *sulphite* (prep. from the alcohol and $SOCl_2$), b.p. 120°/5 mm., do not react with *m*-OH·C_6H_4·ONa (I), but the appropriate bromides in aq. $COMe_2$ give *resorcinol* β-*ethoxyethyl*, b.p. 146—152°/3 mm., β-*butoxyethyl*, b.p. 153—160°/2 mm., γ-*ethoxypropyl*, b.p. 165—170°/4 mm., m.p. 38—39°, and γ-*butoxypropyl monoether*, b.p. 170—172°/2 mm., with smaller amounts of the *di*(*alkoxyalkyl*) *ethers*, b.p. 170—175°/4 mm., 181—185°/2 mm., 171—180°/4 mm., and 181—189°/2 mm., respectively. *γ-Butoxypropyl bromide* has b.p. 80—83°/21 mm. (CH·$CH_2Br)_2$ (prep. from butadiene described), m.p. 50—52°, and NaOMe give δ-*methoxycrotyl bromide*, b.p. 54·5—56·5°/10 mm., which with (I) in C_6H_6–N_2 gives (?) impure 4-*methoxycrotylresorcinol* (polymerised on " mol." distillation) and thence 2 : 4-*di*(*carboxymethoxy*)-1-δ-*methoxycrotylbenzene*, m.p. 148—150°, and (H_2–Pd) impure (?) 4-δ-*methoxybutylresorcinol*. Most methods of preparing 2 : 4 : 1-$(OH)_2C_6H_3$·CO·CH_2·OAlk failed, but the Hoesch synthesis yields ω-*butoxy-* (II), m.p. 64—65°, and ω-*propoxy-resacetophenone*, m.p. 106—107°; OEt·$[CH_2]_2$·CN similarly gives 2 : 4 : 1-$(OH)_2C_6H_3$·$[CH_2]_2$·CO_2H. Clemmensen reduction converts (II) into 4 : 1 : 3-$C_6H_3Et(OH)_2$ (derived *di*-O-*acetic acid*, m.p. 180—181°), also formed from resacetophenone and H_2–Pd (poor yield). CH_2Cl·OBu and CuCN at 100° give 77·3% of *butoxyacetonitrile*, b.p. 167—171°/738 mm. ω-*Methoxyresacetophenone-oxime* has m.p. 158°. R. S. C.

Polymerisation of ethylchavicol. αζ-Di-*p*-ethoxyphenyl-Δ^a-hexene. J. M. van der Zanden (Rec. trav. chim., 1939, **58**, 181—192; cf. A., 1938, II, 181).—Ethylchavicol heated at 250° for 250 hr. yields αζ-*di*-p-*ethoxyphenyl*-Δ^a-*hexene* (I), m.p. 101—101·5° (*dibromide*, m.p. 96—96·5°), a *trimeride*, m.p. 119·5—120°, and a small amount of *p*-OEt·C_6H_4·CH:CHMe. In presence of Mg a third polymeride is obtained. The constitution of (I) is shown by oxidation ($KMnO_4$ in $COMe_2$) to *p*-OEt·C_6H_4·CO_2H and δ-p-*ethoxyphenyl*-n-*valeric acid* (II), m.p. 104·5—105°, synthesised as follows: γ-p-*ethoxyphenylpropyl alcohol*, m.p. 49·3—49·6° (prep. according to the scheme: *p*-OEt·C_6H_4·CHO + EtOAc → *p*-OEt·C_6H_4·CH:CH·CO_2Et → *p*-OEt·C_6H_4·$[CH_2]_3$·OH), yields a bromide, b.p. 156—158°/14 mm., which with $CH_2(CO_2Et)_2$ and EtOH–NaOEt gives the Et ester, b.p. 190—195°/2 mm., of δ-*p*-ethoxyphenylbutane-αα-dicarboxylic acid, m.p. 113—115°, which yields (II) when heated at 130°/vac. Oxidation (CrO_3) of (II) affords γ-p-*ethoxybenzoylbutyric acid*, m.p. 116·5—117° (p-*nitrophenyl-*, m.p. 168—168·5°, and 2 : 4-*dinitrophenyl-hydrazone*, m.p. 141·8—142·2°) [further oxidised ($KMnO_4$) to *p*-OEt·C_6H_4·CO_2H and *p*-OEt·C_6H_4·CO·CO_2H], the *oxime*, m.p. 115—115·5°, of which with PCl_5 in cold Et_2O yields N-p-*ethoxyphenylglutarimide*, m.p. 156·5—157° (synthesised from *p*-OEt·C_6H_4·NH_2 and CO_2H·$[CH_2]_3$·CO_2H), hydrolysed (aq. EtOH–NaOH) to N-p-*ethoxyphenylglutaramic acid*, m.p. 134·5—135°, and thence (conc. HCl) to CO_2H·$[CH_2]_3$·CO_2H and *p*-OEt·C_6H_4·NH_2. (I) is reduced (Pt) to αζ-*di*-p-*ethoxyphenylhexane*, m.p. 68·5—69°, also prepared from *p*-OEt·C_6H_4·$[CH_2]_3$·Br and Na in Et_2O. A. Li.

Nitration of 2-methoxydiphenyl ether. F. Lions and A. M. Willison (J. Proc. Roy. Soc. New South Wales, 1938, **71**, 435—448).—2-Methoxydiphenyl ether, m.p. 78°, is converted by HNO_3 (*d* 1·42) in AcOH at ≯40° into 5- (I), m.p. 69°, and 4- (II), b.p. 190—191·5°/1·7 mm., 175°/0·8 mm., *-nitro-2-methoxydiphenyl ether*. (I) is slowly hydrolysed by boiling aq. KOH to 5-*nitro*-2-*hydroxydiphenyl ether*, m.p. 63° (*Ac* derivative, m.p. 108°). The synthesis of (I) is recorded from the K salt of 5-nitroguaiacol, boiling PhBr, and Cu powder and from 2-bromo-4-nitroanisole, KOPh, and Cu powder at 180—200°. (II) is obtained synthetically from 2-iodo-5-nitroanisole (III), KOPh, and Cu powder at 180—200°. (III) and boiling piperidine give 4-*nitro*-2-*methoxy*-1-*piperidinobenzene*, m.p. 76°. (I) is reduced by Na_2S in aq. EtOH to 5-*amino*-2-*methoxydiphenyl ether*, m.p. 79° [*hydrochloride*, m.p. 234°; *Ac* (IV), m.p. 115°, *formyl*, m.p. 120°, p-, m.p. 87°, and o-, m.p. 112°, *-nitrobenzylidene* derivatives]. HNO_3 (*d* 1·42) converts (IV) in AcOH at ≯25° into 4-*nitro*-5-*acetamido*-2-*methoxydiphenyl ether*, m.p. 141°; reduced ($SnCl_2$ and Sn in boiling glacial AcOH) to 5-*phenoxy*-6-*methoxy*-2-*methylbenziminazole*, m.p. 149° (also + C_6H_6 of crystallisation), and hydrolysed by acid to 4-*nitro*-5-*amino*-2-*methoxydiphenyl ether* (V), m.p. 167°. Similarly, (II) is reduced to 4-*amino*-2-*methoxydiphenyl ether*, m.p. 119°. The corresponding *Ac* derivative, m.p. 138°, is transformed by HNO_3 (*d* 1·42) in glacial AcOH at room temp. into 5-*nitro*-4-*acetamido*-2-*methoxydiphenyl ether*, m.p. 124°, hydrolysed to 5-*nitro*-4-*amino*-2-*methoxydiphenyl ether* (VI), m.p. 158°. Gradual addition of Zn dust to (V) or (VI) in EtOH containing conc. HCl followed by phenanthraquinone in aq. $NaHSO_3$ gives 3-*phenoxy*-2-*methoxyphenanthraphenazine*, m.p. 270°. *Trinitro*-2-*methoxydiphenyl ether* has m.p. 204°. H. W.

Free radicals and radical stability. III. 3 : 4-Methylenedioxytriphenylmethyl and phenyl-*p*-

anisyldiphenylylmethyl. S. T. Bowden, W. E. Harris, and D. I. Roberts (J.C.S., 1939, 302—307; cf. A., 1939, II, 110).—Me piperonylate and MgPhBr give 3 : 4-*methylenedioxytriphenyl-carbinol*, m.p. 105° (pink solution in liquid SO_2), reduced by Zn–AcOH to the *-methane*, m.p. 65°, or converted by AcCl in Et_2O–light petroleum, in absence of H_2O, into 3 : 4-*methylenedioxytriphenylmethyl chloride* (I), m.p. 105° [1 : 1 *adducts* with $FeCl_3$, m.p. 145—146°, $ZnCl_2$ (hygroscopic), $HgCl_2$, and $SnCl_4$]. The corresponding *bromide* has m.p. 121° ($HgBr_2$ *adduct*, hygroscopic). (I) and excess of Hg in Et_2O in absence of air give an orange-red solution; air oxidation then gives the *peroxide* (II), m.p. 173° (from C_6H_6 in atm. of CO_2), in somewhat greater yield than $(CPh_3{\cdot}O{\cdot})_2$ is obtained (*loc. cit.*). The free radical (III) (from the above halides in PhBr with Ag or Hg) absorbs O_2 (method : *loc. cit.*), with further slow oxidation of (II). (III) [from (I) in C_6H_6–Ag in absence of O_2 and light] absorbs I at room temp. and the thermal stability of the iodide is < that of CPh_3I. Isolation of the radical from C_6H_6 solution (method : *loc. cit.*) gives crystals, m.p. 156° (vac.), which in Et_2O with air give (II). Radical photodecomp. in sunlight is less rapid than with CPh_3 (cf. A., 1928, 747). The thermodynamic stability of 3 : 4-methylenedioxytriphenylmethyl is slightly < that of the 3 : 4-$(OMe)_2$-analogue. *p*-$C_6H_4Ph{\cdot}MgBr$ and *p*-$OMe{\cdot}C_6H_4{\cdot}COPh$ give a product, hydrolysed by H_2SO_4–ice to *phenyl*-p-*anisyldiphenylylcarbinol* (IV), m.p. 78° (solution in liquid SO_2 is reddish-orange; halochromic salts with strong acids; the corresponding *-methane* has m.p. 92°). Its basicity is 9·6 compared with 1·7 for diphenyl-*p*-diphenylylcarbinol, new m.p. 106° (cf. Schlenk *et al.*, A., 1909, i, 791), and 1·0 for $CPh_3{\cdot}OH$. (IV) and AcCl give the *chloride* (not cryst.) (*ferrichloride*; *mercurichloride*), which with mol. Ag in Et_2O in the dark gives a deep wine-red solution of the free radical (not isolated) (*peroxide*, m.p. 166°). It is inferred that radical stability is > that of diphenyldiphenylylmethyl. The rate of decomp. of phenyl-*p*-anisyldiphenylylmethyl formate at 99° is slightly > that of diphenyldiphenylylmethyl formate in early stages of reaction. A. T. P.

Derivatives of 9 : 10-dihydroanthracene. J. N. Graves, G. K. Hughes, and F. Lions (J. Proc. Roy. Soc. New South Wales, 1938, **71**, 318—322).—3 : 4 : 3′ : 4′-Tetramethoxydiphenylmethane (I) could not be condensed with PhCHO in presence of $ZnCl_2$ (under varied conditions) or boiling, conc. HCl; $AlCl_3$ causes demethylation with much charring. (I) does not condense with $CHPhCl_2$ in CS_2 containing $AlCl_3$. Veratrole is transformed by $CHPhCl_2$ and $AlCl_3$ in CS_2 into 3 : 4 : 3′ : 4′-*tetramethoxytriphenylmethane* (II), m.p. 124°, and 2 : 3 : 6 : 7-*tetramethoxy*-9 : 10-*diphenyl*-9 : 10-*dihydroanthracene*, m.p. 308°. HNO_3 (*d* 1·42) in AcOH at 100° converts (II) into a $(NO_2)_2$-derivative, m.p. 204°, which could not be reduced to the corresponding diamine. H. W.

Reaction of sulphur with halogenated derivatives of diphenyl sulphide. J. H. Billman and G. Dougherty (J. Amer. Chem. Soc., 1939, **61**, 387—389).—With S at 240—270° (*p*-$C_6H_4Br)_2S$ (I) gives *p*-$C_6H_4Br_2$ (II), (*p*-$C_6H_4Cl)_2S$ gives *p*-$C_6H_4Cl_2$, *p*-$C_6H_4Br{\cdot}SPh$ gives (II) (trace) and PhBr, *p*-$C_6H_4Cl{\cdot}SPh$ gives PhCl, and *p*-$C_6H_4Cl{\cdot}S{\cdot}C_6H_4Br$-*p* gives (II) and *p*-$C_6H_4ClBr$. In all cases complex sulphides and polysulphides are also formed. The reaction mechanism is : (I) + *x*S → *p*-$C_6H_4Br{\cdot}S{\cdot}C_6H_4{\cdot}[S]_x{\cdot}Br$ (III); (III) + (I) → *p*-$C_6H_4Br{\cdot}S{\cdot}C_6H_4{\cdot}[S]_x{\cdot}SBr(C_6H_4Br\text{-}p)_2$ → (II) + *p*-$C_6H_4Br{\cdot}S{\cdot}C_6H_4{\cdot}[S]_{x+1}{\cdot}C_6H_4Br$-*p*, etc. R. S. C.

Synthesis of *p*-methylbenzyl acetate from toluene. P. P. Schorigin and A. V. Bogdanova (J. Appl. Chem. Russ., 1938, **11**, 1217—1221).—A mixture of PhMe, 35% aq. CH_2O, and $ZnCl_2$ is saturated with HCl (4 hr. at 35°, then 4 hr. at 75°), to give *p*-$C_6H_4Me{\cdot}CH_2Cl$, which with KOH–EtOH yields p-*methylbenzyl Et ether*, b.p. 75°/6 mm., hydrolysed by boiling 6% $NaHCO_3$ to *p*-$C_6H_4Me{\cdot}CH_2{\cdot}OH$. This with Ac_2O–H_3PO_4 or AcOH–H_2SO_4 at room temp. yields the acetate. R. T.

Phenylethyl thioacetate. B. Holmberg (Arkiv Kemi, Min., Geol., 1938, **12**, B, No. 47, 3 pp.).—Interaction of styrene and AcSH yields β-*phenylethyl thioacetate* (I), b.p. 134—135°/13 mm., also formed from $CH_2Ph{\cdot}CH_2{\cdot}SH$ (II) and AcCl in C_5H_5N. With Br in aq. AcOH (I) yields $CH_2Ph{\cdot}CH_2{\cdot}SO_2Br$, with aq. EtOH–NaOH gives (II), and with H_2O_2, di-β-phenylethyl disulphoxide and $CH_2Ph{\cdot}CH_2{\cdot}SO_3H$ are produced. Interaction of CHPhMe·SH and AcCl in C_5H_5N yields *α-phenylethyl thioacetate*, b.p. 123—125°/13 mm. J. D. R.

Walden inversion. XXI. Halogenation of aromatic carbinols. Rotatory dispersion of aromatic carbinols and corresponding bromides. P. A. Levene and A. Rothen (J. Biol. Chem., 1939, **127**, 237—249; cf. A., 1938, II, 360).—In the action of HBr on CHPhR·OH the halide can be formed by at least three different mechanisms, their relative importance depending on the temp. For R = Me, Et, or Pr^{α} the *l*-carbinol reacts chiefly without inversion between −80° and −36° through the formation of an additive compound with HBr. Evidence is recorded to show that the reaction in which the configuration is retained proceeds also by a second mechanism, a third being responsible for the reaction in which, at higher temp., inversion occurs (cf. Hughes *et al.*, A., 1937, II, 363). Racemisation of the bromides does not occur below 0°, and the smallness of the rotations shown by the products of reaction at higher temp. (−20° to 20°) arises from the simultaneous independent formation of *d*- and *l*-isomerides. Details are given for the variation of inversion with temp. for the three carbinols, and rotatory dispersion data are recorded. F. L. U.

Preparation of alkoxy- and arylalkoxy-ethanols and higher homologues. L. Palfray, S. Sabetay, and A. Halasz (Compt. rend., 1939, **208**, 289—291; cf. A., 1934, 990).—$CH_2Ph{\cdot}CH_2{\cdot}OH$ with $(CH_2)_2O$ in acid solution gives β-β′-*phenylethoxyethyl alcohol*, b.p. 140—142°/15 mm. (*acetate*, b.p. 159—160°/18 mm.; *allophanate*, m.p. 150°). CH_2PhCl and $Ph{\cdot}[CH_2]_3{\cdot}Cl$ heated with $OH{\cdot}[CH_2]_2{\cdot}OK$ and excess of $(CH_2{\cdot}OH)_2$ afford β-*benzyloxy*-, b.p. 136—137°/17 mm. (*formate*, b.p. 150°/21 mm.; *acetate*, b.p. 145—146°/15 mm.; *Bu ether*, b.p. 139—140°/15 mm.; *allophanate*, m.p. 156°), and β-γ′-*phenylpropoxy-ethyl*

alcohol, b.p. 154—155°/18 mm. (*acetate*, b.p. 170°/18 mm.; *allophanate*, m.p. 131·5°), respectively; with OH·$[CH_2]_3$·OK γ-benzyloxy-, b.p. 155—157°/20 mm. (*acetate*, b.p. 154—156°/16 mm.; *Bu ether*, b.p. 160—162°/32 mm.; *allophanate*, m.p. 119°), and γ-γ′-*phenylpropoxy-propanol*, b.p. 160°/20 mm. (*acetate*, b.p. 182—184°/20 mm.; *allophanate*, m.p. 113°), respectively, result. Similarly, CH_2PhCl and Ph·$[CH_2]_3$·Cl with OH·CHMe·$[CH_2]_2$·OK afford γ-*hydroxy-α-benzyloxy-*, b.p. 151—152°/18 mm. (*acetate*, b.p. 170°/25 mm.; *allophanate*, m.p. 102°), and -α-γ′-*phenylpropoxy-butane*, b.p. 175°/19 mm. (*acetate*, b.p. 184—185°/18 mm.; *allophanate*, m.p. 165°). Dodecyl iodide with OH·$[CH_2]_2$·OK at 300° (autoclave) affords β-*dodecyloxyethyl alcohol*, m.p. 51°.

J. L. D.

Action of magnesium bromide etherate on 1 : 2-epoxy-1 : 4-dimethylcyclohexane. B. Tchoubar (Compt. rend., 1939, **208**, 355—357).—1 : 2-Epoxy-1 : 4-dimethylcyclohexane with $MgBr_2$ etherate affords trans-2-*bromo*-1 : 4-*dimethylcyclohexanol* (I), b.p. 109—111°/17 mm. (*dinitrobenzoate*, m.p. 134—135°), and *trans*-2-bromo-2 : 5-dimethylcyclohexanol (II) (not isolated). Dehalogenation ($MgBr_2$) of (I) affords only 3-methylcyclopentyl Me ketone (III) (semipinacolic change), whereas a mixture of (I) and (II) gives (III), 2 : 5-dimethylcyclohexanone (migration of H), and 1 : 3-dimethylcyclopentylformaldehyde (semihydrobenzoin change) (corresponding acid *amide*, m.p. 88°). 2-Methylcyclohexanone (A., 1939, II, 61) is thus formed by migration of H during dehalogenation of 2-bromo-2-methylcyclohexanol. J. L. D.

Oxidation of methine and methylene groups [in cyclic hydrocarbons] by ozone. J. R. Durland and H. Adkins (J. Amer. Chem. Soc., 1939, **61**, 429—433).—O_3 in CCl_4 at 0° attacks ≥CH or >CH_2 in saturated cyclic compounds to give ≥C·OH and >CO, respectively. *cyclo*Hexane is most resistant, but gives HCO_2H, adipic acid, and *cyclo*hexanone on prolonged treatment. *cis*-Decahydronaphthalene (30 g.) gives 1-keto- (small amount) and 9-hydroxy-*cis*-decahydronaphthalene (I) (7·4 g.), $\Delta^{9:10}$-octahydronaphthalene (II) (2·2 g.), and mixed acids (10 g.); under similar conditions, *trans*-decahydronaphthalene (34 g.) gives 28% of 9-hydroxy- and 1-keto-*trans*-decahydronaphthalene [or 21% of (II)], and ~10 g. of acids, including *trans-cyclo*hexane-1 : 2-diacetic acid. (I) gives HCO_2H and other acids, (II), and a trace of 9 : 10-dihydroxydecahydronaphthalene, m.p. 86—89°. Mixed dodecahydrophenanthrenes give (1-, 4-, or 10-)*keto*-$\Delta^{11:12}$-*dodecahydrophenanthrene* (III), b.p. 150—155°/8 mm. (2 : 4-*dinitrophenylhydrazone*, *forms*, m.p. 82—84° and 112—115°), and αβ-di-2-ketocyclohexylethane (derived from the $\Delta^{12:13}$-hydrocarbon). Tetradecahydrophenanthrene (IV) gives (III), a *dodecahydrophenanthrene* (V), b.p. 129°/9 mm., and mixed acids, or, in another experiment (III), three *tetradecahydrophenanthr*-11- or -12-*ols*, A, b.p. 130—132°/8 mm., B, b.p. 147—150°/7 mm., and C, b.p. 114—116°/0·4 mm., (?) 1-*ketotetradecahydrophenanthr*-11-*ol* (VI), b.p. 145—148°/0·2 mm., and mixed acids. Hydrogenation (Raney Ni) of *A* or *B* in methylcyclohexane at 200—250° gives (IV). Dehydration of *A* gives (V), and that of *C* gives a similar compound. *A*, being most reactive, is probably a *trans*-isomeride. *A*, *B*, and *C* do not give benzoates and are dehydrated by PhNCO. Hydrogenation of (VI) at 125° gives (?) *tetradecahydrophenanthra*-1 : 11-*diol*, b.p. 190—198°/8 mm. R. S. C.

Free radicals and radical stability. V. Thermal stability of chloroformates and carbonates. S. T. Bowden. **VI. Reactions of triphenylmethoxides.** S. T. Bowden and T. John (J.C.S., 1939, 310—314, 314—317).—V. Attempts to prepare $(CPh_3)_2CO_3$ from CPh_3·OK and $COCl_2$ in PhMe at 0° give an almost quant. yield of CPh_3Cl owing to the thermal instability of the intermediate $ClCO_2CPh_3$. CPh_3·OH and $COCl_2$ in C_6H_6 give CPh_3Cl (76% yield in presence of $CaCl_2$) (mechanism discussed). $CHPh_2$·OH and K in boiling xylene in N_2 give the K derivative, which with $COCl_2$ in PhMe at 0° or at room temp. affords *benzhydryl carbonate*, m.p. 123°, decomp. in N_2 at 260°, with fairly rapid pyrolysis at 270°. $ClCO_2CHPh_2$ could not be isolated, although it is probably formed. CH_2Ph·OK and $COCl_2$–PhMe give benzyl carbonate, m.p. 29°, stable at 350° (in N_2). The greater is the radical stability of the ester group in chloroformates or carbonates, the lower will be the thermal stability of the compound.

VI. Compounds containing the radical CPh_3·O· are compared with those containing CPh_3·. CPh_3·OH and Li in pure N_2 (slow reaction at 280°) or better in xylene (C_6H_6 for 120 hr. is ineffective) give *Li triphenylmethoxide*, decomp. >360°, hydrolysed by moist air to the carbinol and LiOH. An apparatus is described for the prep. on micro-scale of *Rb triphenylmethoxide*, m.p. 235° (decomp.). Ca does not react with CPh_3·OH in boiling xylene (cf. Kraus *et al.*, A., 1924, i, 276), but CPh_3·ONa is prepared in xylene or Ph_2 in N_2 (cf. Blicke, A., 1923, i, 1007). CPh_3·OK and CH_2PhBr or Me_2SO_4 in C_6H_6 give CPh_3·O·CH_2Ph or CPh_3·OMe, respectively; Hg in N_2 has no effect (cf. CPh_3K). CPh_3·OH, or better, $COPh_2$, and MgPhBr, afford CPh_3·O·MgBr (I), which does not give ethers with CH_2PhBr or MeI, but with AcCl–C_6H_6 (through CPh_3·OAc) or $COCl_2$–PhMe (through the unstable chloroformate), it affords CPh_3Cl (37 and 14% conversions, respectively). (I) and CPh_3Br or $CuCl_2$ at room temp. give (after hydrolysis) only CPh_3·OH. PhOH and MgPhBr give MgBr·OPh, which with $COCl_2$–PhMe at 0° affords Ph_2CO_3 (66% yield); this reaction is a possible method for synthesising carbonates when the usual one is not feasible. A. T. P.

Constitution of sterols and steroids. A. Windaus (Chim. et Ind., 1938, **40**, 835—849).—A review.

Colour reactions of sterols. G. Woker and I. Antener (Helv. Chim. Acta, 1939, **22**, 47—59; cf. A., 1937, II, 367; 1938, II, 429).—A description is given of the colour reactions of cholic, deoxycholic, glycocholic, and taurocholic acid, of cholesterol, ergosterol, sitosterol, stigmasterol, œstrone, equilin, equilenin, and œstradiol with furfuraldehyde (I) and conc. H_2SO_4. With ascorbic acid, which slowly yields (I) under these conditions, the appearance of the colours is greatly retarded. H. W.

Sterol group. XXXIX. Structures of ergosterol, lumisterol, pyrocalciferol, and *iso*pyrocalciferol. T. KENNEDY and F. S. SPRING (J.C.S., 1939, 250—253; cf. A., 1938, II, 321).—Pyrocalciferyl acetate, m.p. 81—82°, $[\alpha]_D^{20}$ +407° in $CHCl_3$, and eosin in EtOH in absence of air, irradiated with sunlight (2 weeks), afford *pyrocalciferyl "pinacol" diacetate*, m.p. 196°, $[\alpha]_D^{20}$ −80° in $CHCl_3$, which at 180—190° at 0·1 mm., then 0·0001 mm., gives neoergosteryl acetate, m.p. 121—122°, identical with that prepared similarly from "ergopinacol" diacetate. *iso*Pyrocalciferyl acetate is unaffected by similar long irradiation. Lumisterol is also similarly stable (cf. Dimroth, A., 1936, 840). Since ergosterol, dehydroergosterol (Windaus *et al.*, A., 1928, 425, 1372), and dehydrolumisteryl acetate (Dimroth, *loc. cit.*) yield bimol. "pinacol" derivatives, orientation around $C_{(9)}$ is the determining factor in "pinacol" formation. A positive "pinacol" reaction in the ergosterol series indicates a *trans*-orientation of $C_{(10)}$-Me and $C_{(9)}$-H; with lumisterol, there is *cis*-orientation. Structural formulæ are given.

A. T. P.

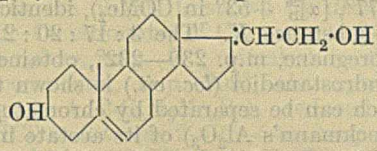
Sex hormones and related substances. XII. Comparison of cinchol with sitosterol and stigmasterol. W. DIRSCHERL (Z. physiol. Chem., 1939, **257**, 239—245; cf. A., 1938, II, 276; Ruzicka *et al.*, A., 1937, II, 497).—Cinchol (I) is probably identical with β-sitosterol and with 22 : 23-dihydrostigmasterol (II). Possibly, however, the terminal C_6H_{13} residue of the side-chain of (I) differs from that of (II). W. McC.

Dihydrotachysterol.—See B., 1939, 325.

Preparation of iodo-compounds of sterols from sterol alcohols. B. HELFERICH and E. GÜNTHER (Ber., 1939, **72**, [*B*], 338—340).—Cholesterol and $MeSO_2Cl$ in cold anhyd. C_5H_5N give *cholesteryl methanesulphonate* (I), m.p. 121—123°, $[\alpha]_D^{23}$ −35·7° in $CHCl_3$, which slowly decomposes at room temp. *Sitosteryl* (II), m.p. 122—123°, $[\alpha]_D^{19}$ +16·4° in $CHCl_3$, and *stigmasteryl* (III), m.p. 140—141°, $[\alpha]_D^{18}$ −47·7° in $CHCl_3$, *methanesulphonates* are obtained similarly. NaI and (I) in $COMe_2$ at 60° afford cholesteryl iodide, m.p. 104—106°, $[\alpha]_D^{23}$ −13·4° in $CHCl_3$, also obtained analogously from cholesteryl *p*-toluenesulphonate. (II) and (III) afford respectively *sitosteryl iodide*, m.p. 100—102°, $[\alpha]_D^{18}$ +34·0° in $CHCl_3$, and *stigmasteryl iodide*, m.p. 86—88°, $[\alpha]_D^{18}$ −26·8° in $CHCl_3$. H. W.

Phytochemical hydrogenation of œstrone to α-œstradiol. A. WETTSTEIN (Helv. Chim. Acta, 1939, **22**, 250—252).—Gradual addition of œstrone in dioxan to a briskly fermenting mixture of glucose and yeast gives α-œstradiol, m.p. 177—179·5°, $[\alpha]_D^{21}$ +83°±2° in abs. EtOH, in ~70% yield. H. W.

Steroid alcohols with semicyclic double linking. K. MIESCHER and C. SCHOLZ (Helv. Chim. Acta, 1939, **22**, 120—125).—Δ^5-17-Vinylandrostene-3*t* : 17-diol is converted by Ac_2O at 100° followed by addition of $CCl_3{\cdot}CO_2H$–AcOH and heating of the mixture at 60° into $\Delta^{5:6\text{-}17:20}$-*pregnadiene*-3*t* : 21-*diol* (I), m.p. 198—199° [Ac_2O and C_5H_5N at room temp. give the *diacetate* (II), m.p. 136·5—137°], and $\Delta^{5:16:20}$-*pregnatrien*-3t-*ol*, m.p. 125·5—126° (*acetate*,



(I.)

m.p. 86·5—87°), after hydrolysis with aq. MeOH–K_2CO_3. The constitution of (I) is established by bromination of (II), fission of the semicyclic double linking with O_3 in AcOH, debromination, reacetylation, and conversion of the product into the semicarbazone of 3*t*-dehydroandrosterone acetate (in very small amount). 17-Vinyltestosterone is converted similarly by Ac_2O and $CCl_3{\cdot}CO_2H$ into $\Delta^{4:5\text{-}17:20}$-*pregnadien*-21-*ol*-3-*one*, m.p. 138—139° (*acetate*, m.p. 107°).

H. W.

Crystalline peroxide of $\Delta^{5:8}$-androstadiene-3 : 17-diol [diacetate]. A. BUTENANDT and J. PALAND (Ber., 1939, **72**, [*B*], 424—425).—Irradiation of $\Delta^{5:7}$-androstadiene-3 : 17-diol diacetate (A., 1938, II, 322) in 96% EtOH containing eosin gives the *peroxide*, $C_{23}H_{32}O_6$, m.p. 221—221·5°, $[\alpha]_D^{23}$ −4·8° in $CHCl_3$. Addition of O to the conjugated system of the diol causes disappearance of the selective absorption in the ultra-violet. H. W.

Steroids and sex hormones. XLIX. 17-Acetylenyl- and 17-vinyl-androstane or -androstene derivatives and their oxidation products. L. RUZICKA and K. HOFMANN (Helv. Chim. Acta, 1939, **22**, 150—155).—17-Acetylenyl-3-*trans* : 17-dihydroxyandrostane diacetate, suspended in EtOH, is hydrogenated (Pd–$CaCO_3$) to 17-*vinyl*-3-trans : 17-*dihydroxyandrostane diacetate*, m.p. 156—158°, $[\alpha]_D$ +20·4° in dioxan, ozonised in well-cooled EtOAc and then converted (H_2–Pd–$CaCO_3$) into 17-*aldehydo*-3-trans : 17-*dihydroxyandrostane diacetate*, m.p. 152—156° (*semicarbazone*). Prolonged treatment of Δ^5-17-vinyl-3-*trans* : 17-dihydroxyandrostene (I) with Ac_2O in C_5H_5N at 100° yields the *diacetate*, m.p. 120—121°, $[\alpha]_D$ −37·4° in dioxan [also obtained by partial reduction (H_2–Pd–$CaCO_3$) of Δ^5-17-acetylenyl-3-*trans* : 17-dihydroxyandrostene diacetate], hydrolysed to (I). Me Δ^5-3-*trans* : 17-dihydroxyætiocholenate and Me Δ^5-17-hydroxy-3-*trans*-acetoxyætiocholenate have $[\alpha]_D$ −62°±2° and −62°±6° in dioxan, respectively. All m.p. are corr. H. W.

Preparation of the principles of the adrenal cortex. A. SERINI, W. LOGEMANN, and W. HILDEBRAND (Ber., 1939, **72**, [*B*], 391—396; cf. A., 1938, II, 322; 1939, II, 112).—Deoxycorticosterone acetate, m.p. 155·5—156·5°, $[\alpha]_D^{20}$ +177° in abs. EtOH, sublimes when Δ^4-pregnene-17 : 20 : 21-triol-3-one 20 : 21-diacetate is heated with Zn dust at 150—200°/10^{-4} mm. 17-Vinyl*iso*androstane-3 : 17-diol (I) is converted by Ac_2O and C_5H_5N at room temp. into its 3-*monoacetate*, m.p. 152—154°, $[\alpha]_D^{20}$ −5·4° in dioxan. (I) is transformed by the successive action of Ac_2O at 100°, $CCl_3{\cdot}CO_2H$ in AcOH at 40—42°, and N-KOH–MeOH into Δ^{17}-allo*pregnene*-3 : 21-*diol*, m.p. 202—204°, $[\alpha]_D^{20}$ +27·2° in dioxan. The *diacetate*, m.p. 156°, $[\alpha]_D^{20}$ +23·7° in dioxan, is transformed by OsO_4 in Et_2O, followed by hydrolysis (aq. EtOH–

Na_2SO_3), into β-allo*pregnane*-3 : 17 : 20 : 21-*tetraol*, m.p. 200°, $[\alpha]_D^{20}$ ±0° in EtOH (3 : 20 : 21-*triacetate*, m.p. 176—177°, $[\alpha]_D^{20}$ +53° in $COMe_2$), identical with Reichstein's substance *K*. The 3 : 17 : 20 : 21-tetrahydroxy*allo*pregnane, m.p. 230—232°, obtained from 17-vinyl*iso*androstanediol (*loc. cit.*) is shown to be a mixture which can be separated by chromatographic analysis (Brockmann's Al_2O_3) of its acetate into two *triacetates*, m.p. 146—148°, $[\alpha]_D^{20}$ ±0° in $COMe_2$, and m.p. 119—120°, $[\alpha]_D^{20}$ −32° in $COMe_2$, which are hydrolysed to the isomeric α-allo*pregnane*-3 : 17 : 20 : 21-*tetraols*, m.p. 210—211°, $[\alpha]_D^{20}$ ±0° in EtOH, and m.p. 236—238°, $[\alpha]_D^{20}$ ±0° in EtOH, respectively. H. W.

Phosphatides. XIV. Inositolmonophosphoric acid from the phosphatide of soya bean. E. Klenk and R. Sakai (Z. physiol. Chem., 1939, **258**, 33—38; cf. A., 1937, III, 56; Cason and Anderson, A., 1939, II, 48).—The isolation from the kephalin fraction of the phosphatide of the Ba salt, $C_6H_{11}O_9PBa_2.2H_2O$, is described. The free acid (I), probably $C_6H_{13}O_9P,3H_2O$ [*brucine* salt, $C_6H_{13}O_9P(C_{23}H_{26}O_4N_2)_2$, m.p. 236°], is very hygroscopic. (I) is accompanied by an acid (II), $[\alpha]_D^{18}$ +31·9° in H_2O, containing ~9% of P, which is probably very closely related to (I). The Ba salt of (II) when freed from PO_4 by boiling with 10% H_2SO_4 yields a substance, m.p. >280°. W. McC.

Preparation of γ-hydroxy-α-*p*-anisylbutyric acid. M. Lapiné (Bull. Soc. chim., 1939, [v], **6**, 390—392; cf. Carré *et al.*, A., 1933, 392).—*p*-OMe·C_6H_4·CH_2Cl (I) in Et_2O with aq. KI gives the corresponding iodide, converted by NaCN in aq. EtOH at 6—8° into the nitrile, b.p. 157°/21 mm., the Na derivative (prep. by $NaNH_2$) of which with $CH_2Cl·CH_2·OH$ in Et_2O gives *γ-hydroxy-α-*p*-anisylbutyronitrile*, b.p. 118—120°/4 mm. Hydrolysis [$Ba(OH)_2$] affords the *-butyric acid*, m.p. 90° (dehydrates readily to form the lactone). (I) and NaCN in aq. EtOH give *p*-OMe·C_6H_4·CH_2·OEt and a resin. A. T. P.

Polycyclic aromatic hydrocarbons. XIX. J. W. Cook, (Mrs.) A. M. Robinson, and (Miss) E. M. F. Roe (J.C.S., 1939, 266—268; cf. A., 1938, II, 227).—9 : 10-Dihydroanthracene (I), $(CH_2·CO)_2O$, and $AlCl_3$ in $PhNO_2$ give β-9-(9 : 10-*dihydro*)*anthroylpropionic acid* (II), m.p. 160—161° [*semicarbazone* (III), m.p. 203—204° (decomp.)], oxidised (CrO_3–AcOH) to anthraquinone. Thus substitution occurs at a saturated C atom, showing great reactivity of CH_2 in (I); direct replacement of H is the most likely mechanism (cf. Nenitzescu *et al.*, A., 1938, II, 494). That (II) was not β-9-anthroylpropionic acid was shown by spectroscopic comparison of allied compounds, and by reduction (Wolff–Kishner) of (III) to γ-9-(9 : 10-*dihydro*)*anthranylbutyric acid*, m.p. 132—133°, dehydrogenated by S at 220—230° to γ-9-*anthranylbutyric acid*, m.p. 187·5—188·5° (CrO_3 gives anthraquinone). CH_2Ph_2 and $(CH_2·CO)_2O$ give [as for (I)] β-*p*-*benzylbenzoylpropionic acid*, m.p. 125—126° (normal nuclear substitution), oxidised (alkaline $KMnO_4$) to *p*-C_6H_4Bz·CO_2H. A. T. P.

Fission of phenylethylthiolacetic acids. B. Holmberg (Arkiv Kemi, Min., Geol., 1938, **12**, A, No. 28, 15 pp.).—$CH_2Cl·CO_2H$ and CHPhMe·S·$CH_2·CO_2H$ (I) in aq. Na_2CO_3 at 100° (bath) yield CHPhMe·OH (II) and $\bar{O}·CO·CH_2·\overset{+}{S}(CH_2·CO_2H)_2$; similarly, $CH_2Ph·CH_2·S·CH_2·CO_2H$ (III) gives $CH_2Ph·CH_2·\overset{+}{S}(CH_2·CO_2H)·CH_2·CO·\bar{O}$, which when heated with NaOH yields CH_2:CHPh and $S(CH_2·CO_2H)_2$. When heated with $HgCl_2$, (I) gives (II) and *chloromercurithiolacetic acid*, ClHgS·$CH_2·CO_2H$, m.p. 202—203° (decomp.), whilst with $HgSO_4$–dil. H_2SO_4, $Hg(S·CH_2·CO_2H)_2$ is formed. With $HgSO_4$–dil. H_2SO_4, (III) yields the *compound*, $(CH_2Ph·CH_2·S)_2Hg_2,HgSO_4$, which when heated with KI gives $CH_2Ph·CH_2·SH$ (IV). CHPhMe·SH or $(CHPhMe·S)_2$ with Br in AcOH gives first CHPhMeBr and then $CHPhBr·CH_2Br$ (V), both of which are formed successively from (I) with Br in AcOH. With SO_2Cl_2, (I) yields CHPhMeCl. Oxidation of (IV) with H_2O_2 affords $CH_2Ph·CH_2·SO_3H$ and *di-*β*-phenylethyl disulphoxide*, m.p. 47·5—48·5°, both of which yield β-*phenylethanesulphonyl bromide*, m.p. 59—60°, with Br in aq. AcOH. Bromination of the sulphoxide of (I) gives a little (V); the sulphone yields α-*phenylethyl dibromomethyl sulphone*, m.p. 96·5—97·5°. J. D. R.

Styrene, iodine, and dithioacetic acid. B. Holmberg (Arkiv Kemi, Min., Geol., 1938, **12**, B, No. 48, 3 pp.).—Styrene and $(S·CH_2·CO_2H)_2$ in Et_2O with a little I yield *styrenedithiolacetic acid*, $CO_2H·CH_2·S·CHPh·CH_2·S·CH_2·CO_2H$, m.p. 84—86°. The reaction fails in absence of I, which is apparently a catalyst. J. D. R.

***dl*-Hexhydrophenylalanine (hydrochloride, m.p. 242—243°); α-acetamido-β-*cyclo*hexylpropionic acid, m.p. 198—199°, $[\alpha]_D^{18}$ −4·23° in 95% EtOH; α-amino-, m.p. 276° (decomp.), and α-acetamido-γ-*cyclo*hexylbutyric acid, m.p. 195—196°, $[\alpha]_D^{21}$ +16·1° in 65% EtOH.**—See A., 1939, III, 174.

Thermal decomposition of the lead salts of α-hydroxycarboxylic acids. J. Kenner and R. L. Wain (Ber., 1939, **72**, [*B*], 456—459).—Pb 9-hydroxyfluorene-9-carboxylate darkens at ~125° and gives fluorenone when distilled. $(OH·CPh_2·CO_2)_2Pb$ affords $CHPh_2·CO_2H$, $C_2H_2Ph_4$, and $COPh_2$. Pb *cyclo*hexan-1-ol-1-carboxylate at 310° yields H_2O, *cyclo*hexene, and an oil transformed by HCO_2H into Δ^1-tetrahydrobenzoic acid (39%), m.p. 33—35° (*chloride*, b.p. 203—204°; amide, new m.p. 129—130·5°; *anilide*, m.p. 110—111°). Pb *cyclo*pentan-1-ol-1-carboxylate gives Δ^1-*cyclo*pentene-1-carboxylic acid (43%), m.p. 119—120° (*chloride*, b.p. 179—180°/758 mm.; *amide*, m.p. 206°; *anilide*, m.p. 125—125·5°). Pb 4-methyl*cyclo*hexan-1-ol-1-carboxylate affords 4-methyl-Δ^1-*cyclo*hexene-1-carboxylic acid (yield ~36%) but no ketone. *cyclo*Heptene (32%) (*nitrosochloride*, m.p. 118°) is obtained from Pb *cyclo*heptan-1-ol-1-carboxylate H. W.

Adduct, m.p. 110°, of dihydro-*o*-tolualdehyde and maleic anhydride. Dihydro-*o*-toluamide, m.p. 88°. *cis*-Δ^5-Tetrahydro-*o*-toluamide, m.p. 104°. Δ^6-Tetrahydro-*o*-toluamide, m.p. 142°.—See A., 1939, III, 175.

Esters of 3 : 5-dihydroxybenzoic acid. C. M. Suter and A. W. Weston (J. Amer. Chem. Soc., 1939, **61**, 531).—Et, m.p. (anhyd.) 128·5°, (+H_2O) ~80° (lit. <100°), *Bu*^{a}, b.p. 209—210°/2 mm., m.p. (anhyd.) 62·5—63·5°, (+0·5H_2O) 39—40°, and n-*heptyl* 3 : 5-*dihydroxybenzoate*, b.p. 235—237°/2 mm., m.p. 74—75°, have PhOH coeff. (*S. aureus*) <10, <10, and 38, respectively. The Me, m.p. 163—165°, *Pr*^{a}, b.p. 215—217°/3 mm., m.p. (+H_2O) 67—68°, n-*amyl*, b.p. 225—227°/4 mm., and n-*hexyl*, b.p. 220—221°/2 mm., m.p. 65—66·5°, esters are also prepared. R. S. C.

***p*-Nitrobenzyl 3 : 5-dinitrosalicylate.**—See A., 1939, III, 218.

Halogen derivatives of the methyl ethers of orcinol, *p*-orsellinic acid, and phloroglucinolcarboxylic acid. C. T. Calam and A. E. Oxford (J.C.S., 1939, 280—284).—Me *p*-orsellinate Me_2 ether and excess of Cl_2 in CCl_4 (Al–Hg couple) at room temp. give *Me* 2 : 6-*dichloro*-3 : 5-*dimethoxy*-p-*toluate* (I), m.p. 86—88°, hydrolysed by 0·5N-NaOH–EtOH to a *substance*, m.p. 235—237° (shrinks at 200°) [probably a polymeride of (II)], which cryst. from boiling H_2O (+ trace of HCl) gives 2 : 6-*dichloro*-3 : 5-*dimethoxy*-p-*toluic acid* (II), m.p. 121—122°. (II) and aq. $KMnO_4$–NaOH give 2 : 6-*dichloro*-3 : 5-*dimethoxyterephthalic acid*, m.p. 235—237°. Crude (II) and 80% H_2SO_4 at 125—130° give 2 : 6-*dichloro*-5-*methoxy*-m-*cresol*, m.p. 129—130°, methylated (CH_2N_2) to 2 : 6-*dichloro*-*orcinol* Me_2 *ether*, m.p. 133—134°, which could not be nitrated (oxidations usually resulted), nor condensed with *o*-$C_6H_4(CO)_2O$ ($AlCl_3$). (I) and H_2SO_4–H_2O (2 : 1) at 125° give 2 : 6-*dichloro*-3-*hydroxy*-5-*methoxy*-p-*toluic acid*, m.p. 202—203° [*Me* ester (HCl method), m.p. 97°]. (II) gives an *amide*, m.p. 167°, converted by P_2O_5 at 180° into 2 : 6-*dichloro*-3 : 5-*dimethoxy*-p-*tolunitrile*, m.p. 124°, but attempts to link it with the orcinol nucleus (Hoesch reaction), or with 1 : 3 : 5-$C_6H_3Me(OMe)_2$ ($AlCl_3$), failed. 2 : 4 : 6 : 1-$(OMe)_3C_6H_2$·CO_2Me and Cl_2 in CCl_4 give *Me* 3-*chloro*-2 : 4 : 6-*trimethoxybenzoate*, m.p. 126—128°. 1 : 2 : 3 : 5-$C_6H_2MeBr(OMe)_2$ and aq. $KMnO_4$–NaOH afford (small yield) 2-*bromo*-3 : 5-*dimethoxybenzoic acid*, m.p. 208—210° [*Me* ester (CH_2N_2), m.p. 59·5—60·5°]. A. T. P.

Action of nitric–sulphuric acids on 5-bromo-3 : 6-dinitro-ψ-cumene. II. I. J. Rinkes (Rec. trav. chim., 1939, **58**, 218—226; cf. A., 1939, II, 111).—*Me* 5-*bromo*-3 : 6-*dinitro*-2 : 4-, m.p. 173—174°, and *Me* 4-*bromo*-2 : 5-*dinitro*-3 : 6-*dimethylbenzoate*, m.p. 142°, are prepared from 2 : 4 : 5 : 1- and 2 : 5 : 4 : 1-$C_6H_2Me_2Br$·CO_2Me, respectively, with HNO_3 (*d* 1·5) and 10% oleum at room temp. —60°. The corresponding *acids*, m.p. 232° (I) and 233° (II), respectively (mixed m.p. 229°), are similarly obtained in poor yield from the $C_6H_2Me_2Br$·CO_2H at 95°. *Me* 2-*bromo*-3 : 6-*dinitro*-4 : 5-*dimethylbenzoate* (III), m.p. 126°, is synthesised according to the scheme : 3 : 4 : 1-$C_6H_3Me_2$·NO_2 → 3 : 4 : 1-$C_6H_3Me_2$·NH_2 → (via the Ac derivatives) 4 : 1 : 2 : 5-NH_2·$C_6H_2Me_2Br$ (IV) → 5-*bromo*-4-*cyano*-o-*xylene*, m.p. 105°, hydrolysed and methylated to Me 2-bromo-4 : 5-dimethylbenzoate, m.p. 29°, nitrated to (III). The constitution of (IV) is proved by conversion into 1 : 2 : 4 : 5-$C_6H_2Me_2Br_2$. The 5-bromo-3 : 6-dinitrodimethylbenzoic acid (V) previously described (*loc. cit.*) is a mixture of (I) and (II). Presence of (II) is shown by decarboxylation (quinoline–Cu chromite) of (V) to some 3-*bromo*-2 : 5-*dinitro*-p-*xylene*, m.p. 97° (nitrated to the 2 : 5 : 6-trinitro-compound, m.p. 209°, also synthesised by nitrating 1 : 4 : 2-$C_6H_3Me_2Br$), reduced ($SnCl_2$ in EtOH–HCl) to 3-*bromo*-2-*nitro*-5-*amino*-p-*xylene*, m.p. 97—98°, which with HNO_2 in EtOH yields 3-*bromo*-2-*nitro*-p-*xylene*, m.p. 64—65°. Reduction (Fe + H_2SO_4) of this yields 3-*bromo*-2-*amino*-, m.p. 58°, brominated (Br in AcOH) to 3 : 5-dibromo-2-amino-*p*-xylene. The Me ester, m.p. 173°, obtainable from (V) is that of (I). A. Li.

Syntheses in the phenanthrene series. I. R. Grewe (Ber., 1939, **72**, [*B*], 426—432).—Condensation of CH_2Ph·$CNa(CO_2Et)_2$ with 2-chloro*cyclo*hexanone gives a mixture of *Et*$_2$ 2-*keto*cyclo*hexylbenzylmalonate* (I), b.p. 180°/0·3 mm., and α-2-*hydroxy*-Δ^{1}-cyclo*hexenyl*-β-*phenylpropiolactone* (II), b.p. 190°/0·3 mm., m.p. 74°, which is separated into its components only with difficulty. Hydrolysis and subsequent decarboxylation of (I) leads to *Et* α-2-*keto*cyclo*hexyl*-β-*phenylpropionate* (III), b.p. 165°/0·3 mm., m.p. 45° (*phenylhydrazone*, m.p. 175°; *semicarbazones*, m.p. 174° and 153°). The non-cryst. free acid (IV) is converted by syrupy H_3PO_4 at 100° into 5 : 6 : 7 : 8 : 9 : 10-*hexahydrophenanthrene*-9-*carboxylic acid*, m.p. 161°, decarboxylated and dehydrogenated by Pd sponge at 260° to phenanthrene. (IV) is converted by dil. H_3PO_4 into (II). Treatment of (III) with Zn and CH_2Br·CO_2Et gives (II); (IV), however, with an excess of the reagents leads to α-2-*hydroxy*-2-*carbethoxymethyl*cyclo*hexyl*-β-*phenylpropiolactone*, b.p. 199—203°/0·3 mm., m.p. 75°. Attempts to open the lactone ring by EtOH were unsuccessful. The corresponding OH-acid could not be obtained by means of alkali, which invariably gives a mixture of the stereoisomeric, unsaturated α-2-*carboxymethylene*-cyclo*hexyl*-β-*phenylpropionic acids*, m.p. 179—184° (V) (*Me*$_2$ ester, m.p. 68°) and m.p. 215—217° (VI) (*Me*$_2$ ester, m.p. 79°). (V) is transformed by syrupy H_3PO_4 into a lactonic *acid*, $C_{17}H_{20}O_4$, m.p. 146°, whereas under allied conditions (VI) gives an unidentified *monocarboxylic acid*, $C_{17}H_{18}O_3$, m.p. 216°. Dry distillation of the Ba salt of (V) or (VI) gives 2-*benzyl*-3 : 4-*tetramethylene*-Δ^{4}-cyclo*pentenone*, b.p. 159°/3 mm. (*semicarbazone*, m.p. 196°; *phenylhydrazone*, m.p. 128°; *oxime*, m.p. 115°). Hydrogenation (Pt in AcOH) of (II) gives β-*cyclo*hexyl-α-2-hydroxy-Δ^{1}-*cyclo*hexenylpropiolactone, b.p. 162°/0·35 mm., converted (MeOH–KOH) into the non-cryst. CO-acid (*Et* ester *semicarbazone*, m.p. 155°). CH_2Ph·$CH(OMe)_2$ is transformed by the successive action of AcCl containing $SOCl_2$ and Et potassio*cyclo*hexanone-2-carboxylate into β-*methoxy*-β-2-*keto*-1-*carbethoxy*cyclo*hexyl*-α-*phenylethane*, b.p. 170°/0·4 mm. H. W.

Synthesis of 6-chloro-10-methyl-1 : 2-benzanthracene and related compounds. M. S. Newman and M. Orchin (J. Amer. Chem. Soc., 1939, **61**, 245—247).—5-Cyano-10-methyl-1 : 2-benzanthracene is as carcinogenic as 10-methyl-1 : 2-benzanthracene, but the 7-CN- and 5- and 7-Cl-derivatives are less active, and the 5-NH_2·CO-, 7-CO_2H, and 7-CO_2Me

derivatives are inactive. 1 : 2-$C_{10}H_6(CO)_2O$ and *m*-$C_6H_4Cl{\cdot}MgBr$ in C_6H_6–Et_2O give 2-m-*chlorobenzoyl*-1-(I), m.p. 189·6—190·2° (31·4%) and 1-m-*chlorobenzoyl*-2-*naphthoic acid*, m.p. 253·0—253·6° (10·3%), and some of the *lactone*, $C_{24}H_{14}O_2Cl_2$, m.p. 157·4—158°. Decarboxylation of the acids gives *m*-$C_6H_4Cl{\cdot}CO{\cdot}C_{10}H_7$-β and -α, respectively, also obtained from *m*-$C_6H_4Cl{\cdot}MgBr$ and $C_{10}H_7{\cdot}CN$. Addition of MgMeBr to (I) in Et_2O–C_6H_6 gives 81% of the *lactone*, m.p. 113·8—114·8°, of 2-α-hydroxy-α-*m*-chlorophenylethyl-1-naphthoic acid, reduced by Zn dust in aq. EtOH to 2-α-m-*chlorophenylethyl*-1-*naphthoic acid*, m.p. 160—160·6°. With H_2SO_4 at 15° this gives an unstable anthrone, reduced by Zn dust in aq. NaOH to 6-*chloro*-10-*methyl*-1 : 2-*benzanthracene* (II), m.p. 157·6—158·2° (*picrate*, m.p. 146·8—147·2°), converted by CuCN–C_5H_5N into 6-*cyano*-10-*methyl*-1 : 2-*benzanthracene*, m.p. 204·4—205·2°, and thence (H_2SO_4–AcOH–H_2O) into 10-*methyl*-1 : 2-*benzanthracene*-6-*carboxylic acid*, m.p. 328—330° (uncorr.; decomp.) (*Me* ester, m.p. 146·2—147°). 2 : 1-$CO_2H{\cdot}C_{10}H_6{\cdot}CO{\cdot}C_6H_4Cl$-*p* (III) with 2% Na–Hg in NaOH–H_2O–EtOH, followed by H_2SO_4 and then Zn–aq. NaOH, yields 6-*chloro*-1 : 2-*benzanthracene* (IV), m.p. 160·6—161·8°, oxidised to the *quinone* (V), m.p. 201—202°, which is also obtained by oxidising (II) and is reduced ($SnCl_2$, AcOH–conc. HCl followed by Zn–NaOH) to (IV). (V) could not be obtained by ring-closure from (III); with $AlCl_3$–NaCl at 160—165°, 7-chloro-1 : 2-benzanthraquinone was formed. M.p. are corr. R. S. C.

Methyl and ethyl esters of the stereoisomeric hexahydro*iso*phthalic acids. A. Skita and R. Rössler (Ber., 1939, 72, [*B*], 265—272).—Variations in the pressure between 1 and 3 atm. and of the temp. between 20° and 66° do not affect the ratio of *cis*- to *trans*-ester formed by the hydrogenation (Pt–$BaSO_4$) of *m*-$C_6H_4(CO_2Me)_2$. With increasing age of the catalyst and consequent decreasing rate of hydrogenation the ratio *cis*- : *trans*-ester becomes displaced in favour of the more stable and energy-poorer *trans*-form. Separation of the ester mixture is effected after hydrolysis by the action of 25% aq. NH_3 on the Ca salts of the acids. Conversion of the *cis*- (I) into the *trans*- (II) -acid by conc. HCl under pressure is inconvenient for considerable amounts but an analogous isomerisation is effected by heating (I) for 24 hr. at 170—180° whereby an equilibrium mixture of 30% of (II) and 70% of (I) results. The Me_2 *cis*- (III), b.p. 148°/21 mm., and Me_2 *trans*- (IV), b.p. 139°/20 mm., Et_2 *cis*- (V), b.p. 151°/15 mm., and Et_2 *trans*- (VI), b.p. 141·5°/15 mm., -esters differ pairwise considerably in b.p., contrary to von Auwers (A., 1924, i, 513). The very slight differences of *d* and *n* in the cases of (III) and (IV) and of *d* in those of (V) and (VI) do not follow the rule of von Auwers, which is followed by *n* of (V) and (VI). The differences, however, are so small as to be valueless for the determination of configuration. The heats of formation of (III) and (V) somewhat exceed those of (IV) and (VI), respectively, but the differences are not very great. The dipole moment of the *cis*- exceeds that of the corresponding *trans*-forms. H. W.

Action of some *endo*succinic acids derived from polycyclic hydrocarbons on the red blood corpuscles of the mouse. F. L. Warren (Biochem. J., 1939, 33, 165—169).—See A., 1939, III, 350. Maleic anhydride additive *compounds* (endo-*succinic acids*) of the following are described: 1 : 2 : 3 : 4-dibenzanthracene, m.p. 250—251°; cholanthrene, m.p. 219—220°; 5 : 6-*cyclo*penteno-, m.p. 245—246°, 3-, m.p. 257—258°, 5-, m.p. 252—253°, and 10-methyl-, m.p. 262—264°, -1 : 2-benzanthracene (all these are *cis*-compounds); also *trans*-1 : 2 : 5 : 6-*dibenzanthracene*-9 : 10-endo-αβ-*succinic acid*, m.p. 255—257°, and its Me_2 ester, m.p. 179—180°. A. L.

Prehnitic (benzene-1 : 2 : 3 : 4-tetracarboxylic) acid. L. I. Smith and E. J. Carlson (J. Amer. Chem. Soc., 1939, 61, 288—291).—No reaction occurs between $(\cdot CH{:}CH{\cdot}CO_2R)_2$ (R = H, Me, or Et) and $(:C{\cdot}CO_2R)_2$ (R = H, Me, or Et), $(\cdot CH{:}CH{\cdot}CO_2Me)_2$ and $(:CH{\cdot}CO)_2O$ or benzoquinone, $(\cdot CH{:}CH{\cdot}CO_2Et)_2$ and dibromofumaric acid. 1 : 4-$C_{10}H_6(CO_2H)_2$ and $KMnO_4$–KOH give 33—40% of 1 : 2 : 3 : 4-$C_6H_2(CO_2H)_4$ [Me_4 ester, m.p. 131—133° (lit. 135°)], which is obtained only in traces by HNO_3; CrO_3–AcOH gives 6% of a yellow substance, m.p. >280°. R. S. C.

Photochemistry of bile acids. III. Ultra-violet irradiation of *apo*cholic, dihydroxycholenic, and *iso*dihydroxycholenic acid. T. S. Sihn (Z. physiol. Chem., 1939, 257, 232—238).—*apo*Cholic acid (I) in $CHCl_3$ in presence or absence of eosin (II) is converted by the light and, when (II) or hæmin is present (solvent EtOH), slowly by sunlight into dihydroxycholenic acid (III). The Me ester of (III) in $CHCl_3$ is converted by ultra-violet light into (I). Me *iso*dihydroxycholenate (from cholic acid and $ZnCl_2$ in boiling AcOH for 90 min. followed by CH_2N_2) in $CHCl_3$ is not converted by HCl or by light into (I) or (III). W. McC.

Configuration of the adrenal hormones at $C_{(17)}$. K. Miescher and A. Wettstein (Helv. Chim. Acta, 1939, 22, 112—117).—Hydrogenation (PtO_2 in EtOH–AcOH) of Me Δ^5-3*t* : 17α-dihydroxy-ætiocholenate (I) (A., 1938, II, 492) gives the very hygroscopic *Me* 3t : 17α-*dihydroxyætio*allo*cholanate* (II), m.p. 213—214°, $[\alpha]_D^{20}$ −1·3±0·3° in MeOH (3t-*Ac* derivative, m.p. 217—217·5°), which does not give a ppt. with digitonin (III) in 60% MeOH. It is hydrolysed (KOH–MeOH) to 3t : 17α-*dihydroxyætio*allo*cholanic acid* (IV) m.p. 260—262° (decomp.) [Ac_2 derivative, m.p. 227·5—228° (decomp.)]. (II) and (IV) are not identical with the analogous compounds derived from substance *P* (Reichstein and Gätzi, *ibid.*, 498) and the sole possible reason for the difference is the configurative reversal at $C_{(17)}$. In the case of such epimeric compounds the behaviour towards (III) is helpful but not decisive. (I) and its 3*t*-Ac derivative have $[\alpha]_D^{20}$ −50·3±1° and $[\alpha]_D^{18}$ −54±4° in dioxan, respectively. All m.p. are corr. H. W.

Isolation of a lactone-like compound from the by-products of the oxidation of cholesterol. K. Miescher and W. H. Fischer (Helv. Chim. Acta, 1939, 22, 155—158).—Hydrolysis of the semicarbazones of the subsidiary ketones obtained during the prep. of dehydroandrosterone from cholesterol and removal of norcholestenolone leaves a product from which CH_2Cl_2 removes a *OH-lactone* (I), probably

$C_{23}H_{34}O_3$, m.p. 252—254°, probably derived from 3*t*-dihydroxynorcholenic acid or 3*t*-dihydroxycholenic acid. Although (I) is found in the ketonic portion, it cannot be caused to react with $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$. The presence of OH is established by the formation of an *acetate*, m.p. 218—219°, and a *benzoate*, m.p. 243—244°. Bromination of (I) followed by oxidation (CrO_3 in AcOH) and debromination gives a *ketone*, $C_{23}H_{32}O_3$, m.p. 206—207° (*semicarbazone*, decomp. 270—290° after becoming brown at >250°), which does not give a colour with $C(NO_2)_4$. H. W.

Saponins. IV. Saponin of the fruits of one of the Chinese gleditsias. K. Fujii and T. Matsukawa (J. Pharm. Soc. Japan, 1935, **55**, 1322—1330).—The fruits of Chinese gleditsia yielded a saponin gledinin, hydrolysed to *gledigenin*, $C_{29}H_{46}(OH){\cdot}CO_2H$ (I), m.p. 310° (decomp.) [*Et* ester, m.p. 203° (*acetate*, m.p. 184°); *acetate*, m.p. 264°; iso-*acetate*, m.p. 190°; *benzoate*, m.p. 217°; *bromolactone*, m.p. 235° (decomp.); *monoacetylbromolactone*, m.p. 200° (decomp.); *acetyl-lactone*, m.p. 279° (decomp.)]. (I) has one double linking αβ or βγ to the CO_2H. Previous work on gleditsia-saponin is reviewed. M.p. are corr. Ch. Abs. (*c*)

"Steric hindrance" in the reactions of aromatic aldehydes. G. Lock (Ber., 1939, **72**, [*B*], 300—304).—$C_6Cl_5{\cdot}CHO$, m.p. 202·5° (corr.), gives a *H sulphite* compound when its solution in C_6H_6 is shaken with aq. $NaHSO_3$; the compound is not obtained from the solid aldehyde probably owing to its sparing solubility in aq. $NaHSO_3$. Under normal conditions $C_6Cl_5{\cdot}CHO$ is transformed into the *anil*, m.p. 187·5° (corr.), *oxime*, m.p. 201° (corr.), and *phenylhydrazone*, m.p. 152·5° (corr.). Boiling 1·5% HCl–EtOH converts $C_6Cl_5{\cdot}CHO$ into *pentachlorobenzaldehyde Et₂ acetal*, m.p. 45° (yield 60% after 96 hr.); similarly 2 : 6 : 1-$C_6H_3Cl_2{\cdot}CHO$ affords 2 : 6-*dichlorobenzaldehyde Et₂ acetal*, b.p. 142—144°/10 mm., m.p. ~ −1° (yield 13·6% after 24 hr. and 43% after 96 hr.). $CHPh(OEt)_2$ is produced in 43% yield after 24 hr. $C_6Cl_5{\cdot}CHO$ is oxidised by alkaline $KMnO_4$ to *pentachlorobenzoic acid*, m.p. 208° (corr.), in 90% yield. With Ac_2O and NaOAc at 170—180° $C_6Cl_5{\cdot}CHO$ affords *pentachlorocinnamic acid*, m.p. 233° (corr.), in 30% yield after 60 hr. With MgMeI and MgPhBr respectively $C_6Cl_5{\cdot}CHO$ yields *pentachlorophenylmethylcarbinol*, m.p. 126°, and 2 : 3 : 4 : 5 : 6-*pentachlorobenzhydrol*, m.p. 117° (oxidised by CrO_3 to 2 : 3 : 4 : 5 : 6-*pentachlorobenzophenone*, m.p. 154°). Hindrance of a reaction of ·CHO in $C_6Cl_5{\cdot}CHO$ is never observed. H. W.

γ-Substitution in the resorcinol nucleus. III. 2 : 6-Dihydroxy-3-ethylbenzaldehyde. H. A. Shah and R. C. Shah (J.C.S., 1939, 300—302).—2 : 4 : 5 : 1-$(OH)_2C_6H_2Et{\cdot}CO_2Me$ and $Zn(CN)_2$–$AlCl_3$–HCl–Et_2O at 0° (method: A., 1939, II, 22) give *Me* 2 : 4-*dihydroxy*-3-*aldehydo*-5-*ethylbenzoate* (I), m.p. 84—86° [2 : 4-*dinitrophenylhydrazone*, m.p. 253—254° (decomp.); *semicarbazone*, m.p. 279—280° (decomp.)], hydrolysed by 15% NaOH at room temp. (72 hr.) to the *acid*, m.p. 192—195° (decomp.), and thence by H_2O at 95—100° (sealed tube) to 2 : 6-*dihydroxy*-3-*ethylbenzaldehyde*, m.p. 117—118°. (I) and $CH_2(CO_2Et)_2$ or $CH_2Ac{\cdot}CO_2Et$ (+ a little piperidine) give *Me* 5-*hydroxy*-3-*carbethoxy*- m.p. 138°, and 5-*hydroxy*-3-*acetyl*-, m.p. 138—140°, -8-*ethylcoumarin*-6-*carboxylate*, respectively, insol. in aq. alkali. (I) (Clemmensen) gives *Me* 2 : 6-*dihydroxy*-5-*ethyl*-m-*toluate*, m.p. 164—166°, hydrolysed by 20% NaOH (50 hr.) to the *acid*, m.p. 244—246° (decomp.). A. T. P.

Condensation of furan compounds. IX. Eutectics of ketone–phenol systems and oxonium complex formation. V. V. Tschelincev and G. Kusnetzov (Bull. Soc. chim., 1939, [v], **6**, 256—265; cf. A., 1924, i, 929; Bennett *et al.*, A., 1936, 1241).—M.p. curves indicate the existence of 2 : 1 mol. compounds of furfurylideneacetone with *p*-$C_6H_4(OH)_2$ and of CHPh:CH·COMe with *o*-, *m*-, and *p*-$C_6H_4(OH)_2$. Similarly, 2 : 1 complexes of difurfurylideneacetone (I) with *m*-$C_6H_4(OH)_2$, 1 : 1 complexes of (I) with *m*- and *p*-$C_6H_4(OH)_2$, and 1 : 2 complexes of (I) with *o*-$C_6H_4(OH)_2$ and of $CO(CH{:}CHPh)_2$ with *o*-, *m*-, and *p*-$C_6H_4(OH)_2$ are indicated. The CO probably undergoes oxonium salt formation. A. T. P.

Derivatives of 2 : 4-dimethylphenylacetic acid. G. Français (Ann. Chim., 1939, [xi], **11**, 212—243).—2 : 4 : 1-$C_6H_3Me_2{\cdot}CH_2{\cdot}CO_2H$ (I) (prep. from pinene described) is transformed by $SOCl_2$ into the chloride, b.p. 132—134°/25 mm.; this is dissolved in PhMe and added to a solution obtained by adding $ZnCl_2$ in Et_2O to an ethereal solution of the requisite Grignard reagent and replacing the Et_2O by PhMe, thus giving a mixture of $C_6H_3Me_2{\cdot}CH_2{\cdot}COR$ and $C_6H_3Me_2{\cdot}CH_2{\cdot}CO_2R$ from which the ester is removed by hydrolysis. The following ketones are described: α-2 : 4-*dimethylphenyl-propan*-β-*one* (II), b.p. 121—123 °/14 mm. [*semicarbazone*, m.p. 164°; *oxime*, m.p. 79° (block)]; -*butan*-β-*one* (III), b.p. 132·5—134°/15 mm. [*semicarbazone*, m.p. 134—135° (block); *oxime* (IV), m.p. 99—100° (block)]; -*pentan*-β-*one*, b.p. 143·9—145·4°/14 mm. (*semicarbazone*, m.p. 174°; *oxime*, m.p. 90—91°); -*hexan*-β-*one* (V), b.p. 152—153·5°/13 mm. (*semicarbazone*, m.p. 160°; *oxime*, m.p. 60—61°); Ph 2 : 4-dimethylbenzyl ketone, m.p. 109° (*semicarbazone*, m.p. 126—127°; oxime, m.p. 113°); α-*phenyl*-γ-2 : 4-*dimethylphenylpropan*-β-*one*, m.p. 85—86° (*oxime*, m.p. 122—123°). Passage of (I) and AcOH over ZrO_2 at 460—480° gives (II), 1 : 2 : 4-$C_6H_3Me_3$, and αγ-*di*-2 : 4-*dimethylphenylpropan*-β-*one*, b.p. 215°/15 mm., m.p. 66—67° (block) [*oxime*, m.p. 90·5—91° (block); *semicarbazone*, m.p. 134°]; (III) is obtained similarly by using $EtCO_2H$. Reduction (Zn–Hg and HCl in H_2O–EtOH) of (V) affords 2 : 4-*dimethylhexylbenzene*, b.p. 131—133°/13 mm. Hydrogenation (Ni) of (IV) gives β-*amino*-α-2 : 4-*dimethylphenylbutane*, b.p. 126—127°/15 mm. (*hydrochloride*, m.p. 170°; *nitrate*, m.p. 142—143°; *picrate*, m.p. 145—146°). Reduction (Ni–Pt in EtOH) of the requisite ketone affords the following carbinols: α-2 : 4-*dimethylphenyl-propan*-β-*ol*, b.p. 126·5—128·5°/14 mm. (*allophanate*, m.p. 183—184°); -*butan*-β-*ol*, b.p. 140·5°/14 mm. (*allophanate*, m.p. 136—137°); -*pentan*-β-*ol*, b.p. 147·2—149·2°/18 mm. (*allophanate*, m.p. 146—147°); -*hexan*-β-*ol*, b.p. 156—157·5°/13 mm. (*allophanate*, m.p. 100—101°); α-*phenyl*-β-2 : 4-*dimethylphenylethan*-α-*ol*, b.p. 191—193°/13 mm. (*allophanate*, m.p. 180—181°), converted by successive

treatment with HBr and KOH–EtOH into 2 : 4-*dimethylstilbene*, m.p. 40—41°. H. W.

Reaction of chlorosulphonic acid with acetophenone. Synthesis of a cyclic keto-sulphone. A. W. Weston and C. M. Suter (J. Amer. Chem. Soc., 1939, **61**, 389—391).—Contrary to Riesz *et al.* (A., 1928, 1009), COPhMe and $ClSO_3H$ in CCl_4, first at 0° and then at 110°, give *acetophenone*-2 : ω-*disulphonyl chloride* (I), m.p. 194—195°, the structure of which is proved by conversion of the corresponding Na_2 salt by KOH at 250—300° into *o*-OH·C_6H_4·CO_2H, and by hot H_2O into 2-keto-1 : 2-dihydrothionaphthen *S*-dioxide and thence (20% NaOH) into *o*-$MeSO_2$·C_6H_4·CO_2H. COPhMe and 45% oleum give a product, converted by KOH into *o*- and *m*-OH·C_6H_4·CO_2H. COPh·CH_2·SO_3Na and $ClSO_3H$ give (I). R. S. C.

Benzoylmesitylacetylene. R. C. Fuson, G. E. Ullyot, and J. L. Hickson (J. Amer. Chem. Soc., 1939, **61**, 410—412).—2 : 4 : 6-$C_6H_2Me_3$·C(OMe):CH·CN and MgPhBr give an amorphous product, converted by boiling AcOH into 2 : 4 : 6-$C_6H_2Me_3$·CO·CH_2·CPh:NH and by boiling 95% EtOH into *benzoylmesitylacetylene* (I), m.p. 72° (*semicarbazone*, m.p. 171—172°) (cf. A., 1938, II, 326). With O_3, (I) in CCl_4 gives an ozonide, converted by H_2O_2 into BzOH, β-*iso*durylic acid, and a little 2 : 4 : 6-$C_6H_2Me_3$·CO·COPh. With H_2–Raney Ni in EtOH at 2·67 atm. (I) gives α-*benzoyl*-β-*mesitylethane* [β-*mesitylpropiophenone*], m.p. 85—85·5°, also obtained from COPh·$[CH_2]_2$·Cl, *s*-$C_6H_3Me_3$, and $AlCl_3$ in CS_2 or, by way of Et α-benzoyl-β-mesitylpropionate, b.p. 225—230° (partial decomp.)/23 mm., from CHNaBz·CO_2Et and 2 : 4 : 6 : 1-$C_6H_2Me_3$·CH_2Cl. With MgPhBr, (I) gives α-*hydroxy*-αα-*diphenyl*-γ-*mesityl*-Δ^{β}-*propinene*, m.p. 97·5—98·5°, which absorbs 3 H_2 (PtO_2). With H_2SO_4 at room temp. (I) gives 2 : 4 : 6-$C_6H_2Me_3$·CO·CH_2·COPh. 2 : 4 : 6-$C_6H_2Me_3$·C:CNa and BzCl in Et_2O, first at −15° and then at 35°, give (I). R. S. C.

Condensation of paraformaldehyde with aromatic ketones. II. Mesityl ketones. R. C. Fuson, W. E. Ross, and C. H. McKeever (J. Amer. Chem. Soc., 1939, **61**, 414—417; cf. A., 1939, II, 68).—2 : 4 : 6 : 1-$C_6H_2Me_3$·COMe, paraformaldehyde, and K_2CO_3 in MeOH give 75% of β-*hydroxypropionylmesitylene* (I), b.p. 132—135°/4 mm., and βδ-*di*-2 : 4 : 6-*trimethylbenzoyl*-$\Delta^{\alpha\gamma}$-*pentadiene* (II), m.p. 107°. (I) reduces Benedict's and Tollens' reagents, with PhNCO gives $CO(NHPh)_2$, and with BzCl gives only BzOH and a resin. With $KMnO_4$ (I) gives 2 : 4 : 6-$C_6H_2Me_3$·CO·CO_2H; with HCl it gives β-*chloropropionylmesitylene*, b.p. 137—139°/3 mm., which readily loses HCl. When 2 : 4 : 6-$C_6H_2Me_3$·COEt and paraformaldehyde are condensed by K_2CO_3 in EtOH, dehydration also occurs to give 70% of *mesityl* iso*propenyl ketone*, b.p. 90—95°/3 mm., reduced by H_2–Raney Ni in EtOH to 2 : 4 : 6-$C_6H_2Me_3$·$COPr^{\beta}$ (III), b.p. 107—110°/5 mm., identified as $(NO_2)_2$-derivative. With paraformaldehyde and K_2CO_3 in EtOH (III) gives 40% of β-*hydroxy*-αα-*dimethylpropionylmesitylene*, b.p. 153°/7 mm. (*phenylurethane*, m.p. 116—116·5°). 2 : 4 : 6-$C_6H_2Me_3$·COMe, 40% CH_2O, and NaOH in MeOH give 35% of (II) and much resin. $[CH_2]_3(CO_2H)_2$ and $SOCl_2$ give the dichloride, which with mesitylene and $AlCl_3$ in CS_2 gives αε-*diketo*-αε-*dimesitylpentane*, m.p. 132—133°, converted by paraformaldehyde and K_2CO_3 in hot EtOH into (II). In presence of Raney Ni in EtOH (II) absorbs 2 H_2 to give βδ-*di*-2 : 4 : 6-*trimethylbenzoylpentane*, b.p. 228—230°/4 mm., and other products. In CCl_4 (II) absorbs only 2 Br, giving only a *dibromide*, m.p. 108·5—109·5°, from which NaI in $COMe_2$ regenerates (II). In presence of $ZnCl_2$ (II) absorbs 2 AcCl, giving a *compound*, $C_{29}H_{34}O_4Cl_2$, m.p. 177—178°. HNO_3–H_2SO_4 converts (II) into a *substance*, $C_{25}H_{24}O_2(NO_2)_4$, m.p. 258—259°. (2 : 4 : 6-$C_6H_2Me_3$·CO·CH_2·CH_2·)$_2$, paraformaldehyde, and K_2CO_3 in EtOH give βε-*di*-2 : 4 : 6-*trimethylbenzoyl*-(?)$\Delta^{\beta\delta}$-*hexadiene*, m.p. 122—123°. R. S. C.

Synthesis of mixed benzoins. III. R. C. Fuson, W. S. Emerson, and H. H. Weinstock, jun. (J. Amer. Chem. Soc., 1939, **61**, 412—413; cf. A., 1936, 1110).—2 : 4 : 6-$C_6H_2Me_3$·CO·CHO, the appropriate hydrocarbon, and $AlCl_3$ in CS_2 give 2 : 4 : 6-$C_6H_2Me_3$·CO·CHPh·OH (57%), new m.p. 103·5—104·5°, 2 : 4 : 6 : 4′-*tetra*- (24%), m.p. 95—95·5°, 2 : 4 : 6 : 2′ : 4′-*penta*- (17%), m.p. 120—120·5°, and 2 : 4 : 6 : 2′ : 4′ : 6′-hexa-methylbenzoin (40%), m.p. 130·5—131° (lit. 59—60°). The time of heating is very important. *m*-Xylene in CS_2 gives also 34% of 2 : 4 : 6-*trimethylbenzoyldi*-m-4-*xylylmethane*, m.p. 146·5—147°, which is the only product if excess of *m*-xylene is used as solvent. 1 : 3 : 5-$C_6H_3Me_2$·OMe and -$C_6H_3Me_2$·OEt give only 2 : 4 : 6-*trimethylbenzoyldi*-(6-*methoxy*-2 : 4-*dimethylphenyl*)*methane*, m.p. 155·5—156·5° [with (?) *mesityldi*-(6-*methoxy*-2 : 4-*dimethylphenyl*)*carbinol*, m.p. 185·5—186·5°], and 2 : 4 : 6-*trimethylbenzoyldi*-(6-*ethoxy*-2 : 4-*dimethylphenyl*)*methane*, m.p. 168—169°, respectively. *s*-$C_6H_3Et_3$, durene, and *iso*durene either do not react or give tars. 2 : 4 : 6 : 4′-*Tetra*-, m.p. 102·5—103°, and 2 : 4 : 6 : 2′ : 4′-*penta*-*methylbenzil*, m.p. 84·5—85°, are prepared. R. S. C.

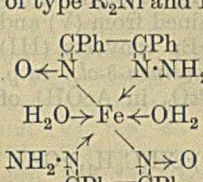
Arylglyoxals and steric hindrance. R. C. Fuson, W. S. Emerson, and H. W. Gray (J. Amer. Chem. Soc., 1939, **61**, 480—482).—With *o*-$C_6H_4(NH_2)_2$ in AcOH α-naphthyl- (prep. from α-$C_{10}H_7$·COMe and SeO_2 in hot, moist dioxan), b.p. 142—145°/6 mm. (hydrate, m.p. 89—91°; 2 : 4-*dinitrophenylhydrazone*, m.p. 246·5—247·5°), and *m*-4-xylyl-glyoxal (similarly prepared), b.p. 118—123°/13 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 180—181°), give 2-α-*naphthyl*-, m.p. 116—116·5° (corr.), and 2-m-4′-*xylyl*-*quinoxaline*, m.p. 56—57° (corr.), respectively, but 2 : 4 : 6-$C_6H_2Me_3$·CO·CHO (I) and 2 : 4 : 6-*triethylphenylglyoxal* (II) (prep. as above), b.p. 125—130°/10 mm., stable (*oxime*, m.p. 107—107·5°), give NN′-*dimesityl*-, m.p. 183—184° (corr.), and NN′-*di*-2′ : 4′ : 6′-*triethylphenylglyoxylidene*-*o*-*phenylenediamine*, m.p. 136—136·5° (corr.), respectively. With HCl–aq. EtOH (I) gives the *Et hemiacetal* (III), m.p. 55—55·5°, which reduces Tollens' reagent, decomposes in hot C_6H_6, with NH_2OH gives the oxime of (I), and with NaOMe–MeOH and a little I gives 2 : 4 : 6-$C_6H_2Me_3$·CH(OH)·CO_2Me. *Et mesitylglycollate*, m.p. 53·5—54°, prepared for comparison from the acid by HCl–EtOH, depresses the m.p. of (III). With $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ (I) gives

Pr$^{\beta}$ *mesitylglycollate*, b.p. 122—124°/2 mm., m.p. 62·5—63·5°, readily hydrolysed to the acid. Hot NaOEt–EtOH converts (II) into 2 : 4 : 6-*triethylphenylglycollic acid*, m.p. 91—92°. R. S. C.

Kinetic study of Friedel–Crafts benzophenone synthesis.—See A., 1939, I, 205.

Secondary reactions in the condensation of organo-magnesium compounds with phenylhydrazones. P. Grammaticakis (Compt. rend., 1939, **208**, 287—289; cf. A., 1936, 837; 1938, II, 283).—MgPhBr with CHPh:N·NHPh (I) affords NH_2Ph and NH:CPh_2 as the main secondary reaction products. Similarly, the phenylhydrazones of *p*-C_6H_4Me·CHO and *p*-OMe·C_6H_4·CHO afford *p*-C_6H_4Me·CPh:NH (II) and *p*-OMe·C_6H_4·CPh:NH (III) respectively, and NH_2Ph. (II) and (III) are also obtained from (I) and *p*-C_6H_4Me·MgBr and *p*-OMe·C_6H_4·MgBr, respectively. The above phenylhydrazones with MgEtBr similarly afford NH_2Ph and NH:CPhEt, *p*-C_6H_4Me·CEt:NH, and *p*-OMe·C_6H_4·CEt:NH, respectively, also obtained from CHEt:N·NHPh and MgArBr. (I) with MgMeI affords NH_2Ph and NH:CPhMe. Small amounts of anils may be formed by reaction of the ketimines with NH_2Ph. J. L. D.

Metallic derivatives of hydrazones and of the oxime-hydrazones of benzil. T. W. J. Taylor, (Mrs.) N. H. Callow, and C. R. W. Francis (J.C.S., 1939, 257—263).—Benzilmonohydrazone (I) and $Ni(OAc)_2$ in EtOH or $COMe_2$ give a *Ni complex*, decomp. ~200—230°, probably $(C_{14}H_{11}ON_2)_2Ni$ (% Ni very variable), not formed in presence of AcOH. It is decomposed by HNO_3, giving either benzil or (COPh·CPh:N·)$_2$. It is almost certainly not a salt and Ni is probably held by two covalencies and two co-ordinate linkings. (I) also forms a Pd complex, but no complex with Cu, Co^{II}, or Co^{III} salts. Benzilmonophenylhydrazone and $Ni(OAc)_2$ in C_5H_5N give only a dark red colour (not in EtOH) destroyed by H_2O; the -monophenylmethylhydrazone or -semicarbazone does not give a colour in EtOH or C_5H_5N. No complex formation is noted with deoxybenzoin- or benzoin-hydrazone. Benzildihydrazone in EtOH affords a Ni complex (Ni, 19·3%), decomposed by H_2O. No solid Ni complex was isolated from β-camphorquinonehydrazone (II), which gives (in EtOH) a red colour not observed with the α-isomeride. $COMeBu^{\gamma}$ and SeO_2 at 110—120° give tert.-*butylglyoxal hemihydrate*, m.p. 85°. Its *monohydrazone* (III), m.p. 81°, and $Ni(OAc)_2$ in EtOH (+ aq. NH_3) yield a *complex* (21·5% Ni; R_3Ni_2), decomposed by H_2O. This suggests that the stereochemical configurations of (I) and (III) are the same as that of (II), *i.e.*, complex formation involves formation of a 6-membered ring, Ni being attached to O by a co-ordinate linking and to N by a covalent linking, replacing H. Benzil and CMe_2:N·NH_2 in EtOH, or (I) and $COMe_2$ [+ a little $Ni(OAc)_2$ (essential)] give *benzil acetone azine* (IV), COPh·CPh:N·N:CMe_2, m.p. 86°, which does not undergo complex formation with Fe, Ni, or Co. (IV), $Ni(OAc)_2$, and (I) in EtOH, or better, (I)–$Ni(OAc)_2$–EtOH–$COMe_2$ afford an *azine Ni complex*, $C_{31}H_{26}O_2N_4Ni$, containing the ·N·CMe_2·N· group (alternative structures discussed); no similar Pd complex is formed. (I) and PhCHO–EtOH yield *benzil benzaldehyde azine*, COPh·CPh:N·N:CHPh, m.p. 151°, which does not give a Ni complex analogous to the above. Salicylidenehydrazone forms complexes of type R_2Ni and R_2Cu, decomposed by mineral acids, AcOH, or NH_3. α-*Benzilmono-oxime-hydrazone* (V), m.p. 216°, forms metallic complexes (Ni, Co, Cu) in C_5H_5N or dioxan, but the β-isomeride does not (configurations discussed). Aq. $FeSO_4$ or $Co(OAc)_2$ and (V) give a *Fe*^{II} (*A*), $C_{28}H_{24}O_2N_6Fe,2H_2O$, and a Co^{II} complex, m.p. 119° (formed more slowly from chloropentamminocobaltic chloride). The above hydrazone complexes are amorphous (except azine complex), whereas metallic derivatives of the oximes crystallise well. A. T. P.


(*A*.)

Non-incidence of furan ring-closure in the dehydration of αδ-diketones. H. Kleinfeller and H. Trommsdorff (Ber., 1939, **72**, [*B*], 256—262).—COPh·CO·CHPhBr (I) is transformed by $CHNaBz_2$ in $COMe_2$ at 0° into αβε-*triketo*-δ-*benzoyl*-αγε-*triphenyl*-n-*pentane*, m.p. 138°, which is unchanged when its solution in boiling AcOH or Ac_2O containing $ZnCl_2$ is treated with HCl, or by warm conc. H_2SO_4; with *o*-$C_6H_4(NH_2)_2$ it gives 2-*phenyl*-3-ββ-*dibenzoyl*-α-*phenylethylquinoxaline*, m.p. 176°, hydrolysed by $Ba(OH)_2$ in boiling MeOH to 2-*phenyl*-3-β-*benzoyl*-α-*phenylethylquinoxaline*, m.p. 148°. *o*-$C_6H_4(NH_2)_2$ and (I) in EtOH afford 2-*phenyl*-3-α-*bromobenzylquinoxaline*, m.p. 109—110°. CH_2Ph·CO·CHPhBr and $CHNaBz_2$ in $COMe_2$ afford βε-*diketo*-δ-*benzoyl*-αγε-*triphenyl*-n-*pentane*, m.p. 138°, accompanied by more or less 4-*benzoyl*-2 : 3 : 5-*triphenyl*-Δ^2-cyclo*pentenone* (II), m.p. 192°, which is formed by the action of HCl on the triketone in boiling AcOH; it does not give a hydrazone or phenylhydrazone and is not attacked by Br even when irradiated. The successive action of $NaNH_2$ and I on $CO(CH_2Ph)_2$ in abs. Et_2O leads to βε-*diketo*-αγδζ-*tetraphenyl*-Δ^{γ}-*hexene*, m.p. 196—197°, and 2 : 4 : 5-*triphenyl*-3-*benzyl*-Δ^2-cyclo*pentenone*, m.p. 147—148°. The last substance is also obtained from $CO(CH_2Ph)_2$, NaOMe, and CH_2Ph·CO·CHPhBr in MeOH. It does not give a phenylhydrazone or a hydrazone and with Br in warm $CHCl_3$ gives much HBr and resin. $CO(CH_2Ph)_2$ is converted by NaOEt in boiling EtOH into BzOH, $OH·CH(CH_2Ph)_2$, and β-*keto*-δ-*benzyl*-αγε-*triphenyl*-Δ^{γ}-*pentene*, a colophony-like mass, b.p. 220—240°/0·2 mm. Warm conc. HNO_3 converts (II) into γδ-*dinitro*-αβε-*triketo*-δ-*benzoyl*-αγε-*triphenylpentane*, complete decomp. 120° after softening at 80—85°. Oxidation of (II) by $KMnO_4$ in $COMe_2$ yields BzOH and a product which with EtOH–N_2H_4,H_2O gives (mainly) 6-*benzoyl*-3 : 5-*diphenyldihydropyridazine hydrazone*, decomp. 160—170°. H. W.

Dehydration of acetylenic glycols. H. Kleinfeller (Ber., 1939, **72**, [*B*], 249—256; cf. A., 1929, 929).—αζ-Diketo-αβεζ-tetraphenyl-Δ^{γ}-hexinene-βε-diol (I) is converted by Br in $CHCl_3$ into αββζ-tetraphenyl-Δ^{γ}-hexinene-αεζ-trione (II) [*monosemicarbazone*, m.p. 242° (decomp.)] and benzil. Conc. H_2SO_4 at 80° transforms (I) into *αzγ-tribenzoyl-*

α-phenyl-Δ$^{\beta}$-propinene (III), colourless needles or leaflets, m.p. 264°, with smaller amounts of isomeric *substances*, m.p. 228° (IV) and 178° (V). Under similar conditions (II) is converted by conc. H_2SO_4 into a *compound*, $C_{30}H_{20}O_3$, m.p. 230°. (II) is oxidised by $KMnO_4$ in $COMe_2$ to (III), also obtained from (V) and NH_2OH in boiling EtOH. MgMeBr converts (III) into *αα-dibenzoyl-αδ-diphenyl-Δ$^{\beta}$-pentinen-δ-ol*, m.p. 218°. Catalytic hydrogenation (PtO_2 in AcOH) of (III) affords the *compound*,

$$C_6H_{11}\cdot CH<\begin{matrix}O\cdot CH(C_6H_{11})\\ CH_2\text{——}CH_2\end{matrix}>C(C_6H_{11})\cdot CH(C_6H_{11})\cdot OAc,$$

a resin which softens at 30° and could not be induced to crystallise. 3 : 4-Diphenylfuran-2-carboxylic acid is converted by PCl_5 in C_6H_6 into the corresponding *chloride*, m.p. 155—156°, which with $AlCl_3$ and C_6H_6 yields *2-benzoyl-3 : 4-diphenylfuran*, m.p. 128°; Bz can be removed from this product by hydrolysis whereas this reaction is not possible if Bz is attached to $C_{(3)}$ or $C_{(4)}$. Addition of 4 : 4′-dibromobenzil in $CHCl_3$ to well-cooled $(:C\cdot MgBr)_2$ (VI) in the same solvent yields *αζ-diketo-αβεζ-tetra-p-bromophenyl-Δ$^{\gamma}$-hexinene-βε-diol* (VII), m.p. 232°, which is stable towards HCl–EtOH but isomerised and not dehydrated by conc. H_2SO_4 to a *substance*, $C_{30}H_{18}O_4Br_4$, m.p. 206°. Boiling aq. NaOH transforms (VII) into *αδ-di-p-bromophenyl-Δ$^{\beta}$-butinene-αδ-diol*, m.p. 181°, and *p*-$C_6H_4Br\cdot CO_2H$. *α-Keto-αβ-di-p-bromophenyl-Δ$^{\gamma}$-butinen-β-ol*, m.p. 208°, is obtained as by-product in the prep. of (VII). Ac_2 and (VI) in $CHCl_3$ give *β-keto-γ-methyl-Δ$^{\delta}$-pentinen-γ-ol*, b.p. 95°/18 mm., and *β-keto-ζ-acetyl-γ-methylhept-Δ$^{\delta}$-en-Δ$^{\delta}$-inen-γ-ol*, m.p. 179°. (VI) and $(CH_2Ac)_2$ afford *β-keto-ε-methyl-Δ$^{\zeta}$-heptinen-ε-ol*, b.p. 75°/15 mm. *β-Keto-δ-methyl-γγ-diethyl-Δ$^{\epsilon}$-hexinen-δ-ol*, b.p. 135°/760 mm., is derived from (VI) and diethylacetylacetone. H. W.

Constitution of the so-called "phenoldiphenein." E. H. Huntress and G. E. Moos (J. Amer. Chem. Soc., 1939, **61**, 526—527).—Bachmann's 2 : 2′-di-*p*-anisoyldiphenyl (A., 1932, 745) is identical with Underwood's "phenoldiphenein lactone Me_2 ether." All the "dipheneins" of the latter author (A., 1924, i, 176, 1197; 1930, 1580; 1936, 723) are thus 2 : 2′-diaroyldiphenyls (cf. Bell *et al.*, A., 1938, II, 495). R. S. C.

2-Alkylidene- and 2-alkyl-*cyclo*pentanone.—See B., 1939, 244.

Stereochemistry of cyclanes. VII. Stereoisomeric diar[alk]ylcyclanones and spatial structure of their oximes. R. Cornubert, M. André, M. de Demo, R. Joly, and A. Strébel. **VIII. 2 : 6-Dibenzyl- and -dihexahydrobenzyl-*cyclo*hexanones.** R. Cornubert, M. André, and M. de Demo. **IX. 2 : 5-Dibenzyl- and -dihexahydrobenzyl-*cyclo*pentanones.** R. Cornubert, M. de Demo, R. Joly, and A. Strébel (Bull. Soc. chim., 1939, [v], **6**, 103—113, 113—132, 132—143; cf. A., 1939, II, 70).—VII. Parts VIII, IX (below), and X (following abstract) are summarised.

VIII. Reduction (H_2, Ni, EtOH) of 2 : 6-dibenzylidene*cyclo*hexanone yields the 2 : 6-dibenzyl-ketones, m.p. 122° (I) and 55° (II) (Borsche, A., 1912, i, 194; Cornubert *et al*, A., 1929, 560; 1934, 297), either of which with NaOH, NaOEt, or HCl gives an equilibrium mixture of the two [~78% of (I)], and when heated at >80° gives a mixture (composition varies with temp.). (I) and (II) give mixtures of the same two oximes in proportions varying with conditions; both oximes are hydrolysed to mixtures of (I) and (II), the proportions of which show that the oxime of (I) has m.p. 92° (another form, stable at room temp., m.p. 114°), and that of (II), 183°. (I) and (II) yield the same semicarbazone, m.p. 197—198°, *tetrahydropyrone* derivative (using excess of PhCHO), m.p. 177—178°, and (Na + EtOH) sec.-*alcohol*, m.p. 123° (*phenylurethane*, m.p. 142—143°); catalytic reduction in neutral or acid solution causes hydrogenation of the Ph groups. Reduction (Pt-black in Et_2O) of (I) yields a 2 : 6-*dihexahydrobenzyl*cyclo*hexanone* (III), m.p. 78° (*oxime*, m.p. 94—95°; *semicarbazone*, m.p. 157°), also prepared by condensing (NaOH) *cyclo*hexanone with hexahydrobenzaldehyde, and reducing the product (Ni). Further reduction (Pt-black) of (III) yields two 2 : 6-*dihexahydrobenzyl*cyclo*hexanols*, m.p. 73° and 92° [also formed (above) from (I)] (*phenylurethanes*, m.p. 149° and 137°, respectively), oxidised (CrO_3) to (III). Reduction of (II) yields a third 2 : 6-*dihexahydrobenzyl*cyclo*hexanol*, m.p. 56—58° (*phenylurethane*, m.p. 104°), oxidised (CrO_3) to an oily *ketone* (IV), giving the same oxime and semicarbazone as (III), and converted into (III) by boiling with EtOH–HCl. (II) yields with MgMeI a tert.-*alcohol*, m.p. 88—89° [dehydrated (excess of MgMeI) to an impure *hydrocarbon*, ? $C_{21}H_{24}$], and with MgPhBr a tert.-*alcohol*, m.p. 110°. (I) with MgPhBr gives a tert.-*alcohol*, m.p. 110—111° (differing from the above), unaffected by CrO_3; with MgMeI, (I) gives only liquid products. The oxime, m.p. 114°, of (I) is reduced (Na, *iso*amyl alcohol) to an *amine*, $C_{20}H_{25}N$ (*acetate*, m.p. 163°); with H_2–Pt–AcOH an isomeric *amine* (*acetate*, m.p. 170°) results. The oxime, m.p. 183°, of (I) with Na + *iso*amyl alcohol yields a third *isomeride* (*acetate*, m.p. 144°), but H_2–Pt–AcOH causes hydrogenation of the Ph groups. It is concluded that (I) and (III) are *cis*- and (II) and (IV) *trans*-isomerides. The results of reducing the oximes confirm the theory that the :N·OH is in the plane of the ring.

IX. Reduction (Ni or Na–Hg) of 2 : 5-dibenzylidene*cyclo*pentanone yields 2 : 5-dibenzyl-ketones (cf. A., 1930, 474), m.p. 39° (V) and 58° (VI), either of which with NaOH, NaOEt, or HCl, or by distillation under reduced pressure, gives an equilibrium mixture of the two, the proportions varying with the reagent. Both yield the same oxime, m.p. 140°, semicarbazone, m.p. 166°, tetrahydropyrone derivative, and sec.-*alcohols*, m.p. 60° and 127°. Reduction (Pt-black under pressure) of (V) and (VI) yields the corresponding 2 : 5-*dihexahydrobenzyl*cyclo*pentanones*, m.p. 81° (VII) (*oxime*, m.p. 90°) and 73° (VIII) (*oxime*, m.p. 126°), respectively. 2 : 5-*Dihexahydrobenzylidene*cyclo*pentanone*, m.p. 123° (from *cyclo*pentanone, hexahydrobenzaldehyde, and MeOH–NaOMe), is reduced (H_2, Ni, EtOH) to (VII) or to a *compound* (IX), m.p. 63—64°, also obtained from (VII) and Na + EtOH. (IX) is an approx. 45 : 55 solid solution of (VII) and (VIII). With MgMeI, (V) yields a tert.-*alcohol*, m.p. 121—122°, but (VI) yields an oil. 2-Benzyl*cyclo*pentanone, b.p. 151·5°/16 mm., obtained from *α-benzyladipic acid*, m.p. 118°

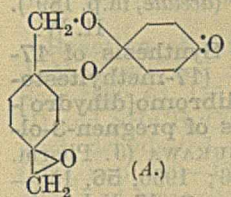
(? prep. from *Et* 2-*benzyl*cyclo*pentanone*-2-*carboxylate*), and Ac_2O at 155°, when benzylated, gives a product similar to that formed by benzylation of *cyclo*hexanone. A. Li.

Stereochemistry of cyclanes. X. Di-*p*-methylbenzyl*cyclo*-pentanones, -hexanones, and -heptanones. R. Cornubert, M. André, and R. Joly. **XI.** R. Cornubert, C. Borrel, and A. Maurel (Bull. Soc. chim., 1939, [v], **6**, 265—270, 270—273).—X. 2 : 5-Di-*p*-tolylidene*cyclo*pentanone, m.p. 235—236°, is hydrogenated (Ni formate) to 2 : 5-*di*-p-*methylbenzyl*cyclo*pentanone* (I), m.p. 67—68°, converted by 0·2N-NaOH in EtOH at room temp. into (mainly) a *stereoisomeride* (II), m.p. 75—76°. Either form with 0·2N-NaOH in EtOH for 36 hr., or with NaOEt for 3 days at room temp., or with HCl–EtOH for 1 week, affords an approx. 9 : 1 equilibrium mixture of (II) and (I); heating at ~ b.p./15—20 mm., however, gives a 1 : 4 mixture of (II) and (I). Hydrogenation of 2 : 6-di-*p*-tolylidene*cyclo*hexanone gives 2 : 6-*di*-p-*methylbenzyl*cyclo*hexanone* (70%), m.p. 114° (III), and a *stereoisomeride* (5%), m.p. 85—87° (IV). Either form, by refluxing with NaOEt–EtOH for 2 hr., or by heating at 263—265°/17 mm. for 2 hr., or by refluxing with HCl–EtOH for 4 hr., affords equilibrium mixtures of (III) : (IV) of 70 : 25, 55 : 45, and 71 : 27 (all approx.), respectively. *cyclo*Heptanone and *p*-C_6H_4Me·CHO in MeOH–NaOMe give 2 : 7-*di*-p-*tolylidene*cyclo*heptanone*, m.p. 131°, hydrogenated (Ni formate) to 2 : 7-*di*-p-*methylbenzyl*cyclo*heptanone*, m.p. 55—56° (V), converted by 0·2N-NaOH in EtOH at room temp. into a *stereoisomeride*, m.p. 66—67° (VI). Equilibrium mixtures of (VI) : (V) are obtained by 0·2N-NaOH at room temp. (4 : 1), by NaOEt–EtOH at room temp. (4 : 1) and HCl–EtOH (1 week) (3 : 1), or at ~ b.p./vac. (1 : 3).

XI. α-Benzyl-α′-methyladipic acid (cf. A., 1930, 776) is separated into two *stereoisomerides*, m.p. 101—105° and 133—135°; either is cyclised by Ac_2O to the same 5-benzyl-2-methyl*cyclo*pentanone (I) [tetrahydropyrone derivative, m.p. 156·5° (*loc. cit.*); *semicarbazone*, m.p. 190°, also obtained from (I) prepared by hydrogenation of 5-benzylidene-2-methyl*cyclo*pentanone (*loc. cit.*)]. Et 2 : 5-dimethyl*cyclo*pentanone-5-carboxylate (modified prep.) is converted by NaOEt at 140—150° for 9 hr. into *Et αα′-dimethyladipate*, b.p. 127°/10 mm., hydrolysed (EtOH–KOH) mainly to the acid, m.p. 143·5°, which is cyclised by Ac_2O to 2 : 5-dimethyl*cyclo*pentanone (semicarbazone, new m.p. 176—177°). A. T. P.

Reactions of αβ-unsaturated cyclic aldehydes and ketones. IV. *d*-Cryptone and *trans-d*-cryptol. A. K. Macbeth and F. L. Winzor (J.C.S., 1939, 264—266; cf. A., 1937, II, 426; 1939, II, 17).—*d*-Cryptone, α_D +75·1° (homogeneous), from water-fennel oil, is reduced by $Al(OPr^\beta)_3$–$Pr^\beta OH$ to *d*-cryptol (I), b.p. 72°/2 mm., $[\alpha]_D^{25}$ +146·4° in EtOH, purified through the p-*nitrobenzoate*, m.p. 84°, $[\alpha]_D^{25}$ +174° in $CHCl_3$; the *α-naphthylurethane* has m.p. 118·5°, $[\alpha]_D^{21}$ +136·2° in EtOH. (I) is a *trans*-epimeride, as hydrogenation (Pd–C; EtOH) gives *trans*-dihydrocryptol. (I) and $K_2Cr_2O_7$–aq. H_2SO_4 give *d*-cryptone, b.p. 78°/3 mm., $[\alpha]_D^{25}$ +102° in EtOH (*semicarbazone*, m.p. 187—188°, $[\alpha]_D^{20}$ +33° in $CHCl_3$; 2 : 4-dinitrophenylhydrazone, m.p. 135—136°), but is not claimed to be stereochemically pure (cf. Galloway *et al.*, A., 1937, II, 26). A. T. P.

Action of diazomethane on *cyclo*hexane-1 : 4-dione. J. R. Vincent, A. F. Thompson, jun., and L. T. Smith (J. Org. Chem., 1939, **3**, 603—610).—*cyclo*Hexane-1 : 4-dione (I) is converted by CH_2N_2 in Et_2O–MeOH into 1 : 4-*dimethylene*cyclo*hexane dioxide* (II), m.p. 106—108°, and *substances* (III), (IV), and (V), b.p. 65—66°/2 mm., 81—88°/2 mm., and 101—113°/3 mm., respectively. (II) does not react with NH_2·CO·NH·NH_2,HCl, Fehling's solution, or decolorised fuchsin. It does not give a :CHPh derivative. Active H or CO is not present. With HCl it gives the *compound*, $C_8H_{14}O_2Cl_2$, m.p. 142·5—143°. It is transformed by piperidine into the *substance*, $C_{18}H_{34}O_2N_2$, m.p. 128·5—130° [*picrate*, m.p. 222—223·5° (decomp.)], and by very dil. AcOH at 100° into the *compound*, $C_8H_{16}O_4$, m.p. 199·5—201·5°. It appears to yield an aldehyde when heated with fused $ZnCl_2$. (III) is $C_{13}H_{18}O_2$. It gives a *semicarbazone*, m.p. 202° (decomp.), an unstable phenylhydrazone, m.p. 121—127°, and a non-cryst. compound with piperidine [unstable picrate, m.p. 200—205° (decomp.) after darkening at ~190°]. When boiled with very dil. HCl it yields an org. solid, m.p. >325°, and a viscous oil which does not react with NH_2·CO·NH·NH_2 or 1-$C_{10}H_7$·NCO. (IV) is $C_{14}H_{20}O_2$. It is converted by NH_2·CO·NH·NH_2 into the disemicarbazone of (I). Further (I) separates when (IV) in Et_2O is exposed to moist air. The presence of (I) as an impurity is excluded and hence (IV) must be regarded as a compound easily cleaved by moisture to (I).



(*A.*)

CO and active H are present in (IV). Non-cryst. products are obtained from (IV) and MgPhBr, Ag_2O or CrO_3, H_2 in presence of Raney Ni, or $Al(OPr^\beta)_3$, PhCHO–HCl, $CH_2(CO_2H)_2$–C_5H_5N, or $BuNO_2$–NaOEt. Tars result with NH_2OH, NHPh·NH_2, or HCl–Et_2O. Hydration of (IV), with or without acid catalysts, gives only oils. (IV) gives an oily product with *o*-$C_6H_4(CO)_2O$ and does not react with 1-$C_{10}H_7$·NCO. With piperidine it yields the *adduct*, $C_{24}H_{42}O_2N_2$, m.p. 100—101° (non-cryst. picrate). (IV) is probably (*A*). (V) is too unstable to permit investigation. H. W.

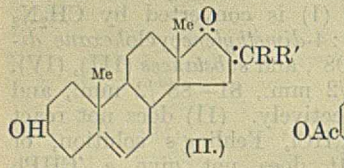
Aldehyde, $C_{20}H_{34}O$ (semicarbazone, m.p. 229—230°, $[\alpha]_D^{20}$ +132·8° in $CHCl_3$), and ketone, $C_{18}H_{32}O$ (semicarbazone, m.p. 216°, $[\alpha]_D^{20}$ +55·6° in $CHCl_3$), from vitamin-D_3.—See A., 1939, III, 292.

$\Delta^{4:5}$-Unsaturated 3-ketones of the *cyclo*pentanopolyhydrophenanthrene series.—See B., 1939, 326.

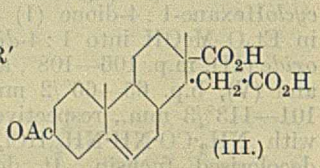
Partial reduction of androstenedione to testosterone. K. Miescher and W. H. Fischer (Helv. Chim. Acta, 1939, **22**, 158—160).—Reduction of androstenedione by $Al(OBu^\gamma)_3$ in abs. $Bu^\beta OH$ gives testerosterone in 70% yield. H. W.

16-Hydroxytestosterone. A. Butenandt, J. Schmidt-Thomé, and T. Weiss [with, in part, D. von Dresler and U. Meinerts] (Ber., 1939, **72**, [*B*],

417—424).—Dehydroandrosterone (I) or its acetate in Et_2O is condensed with COMeEt by Na or $NaNH_2$ to the *substance* (II) (R = Me, R′ = Et), m.p. 176°. The corresponding *acetate*, leaflets, m.p. 148°, or needles, m.p. 156°, is brominated and then ozonised in $CHCl_3$; the ozonide is transformed by Zn dust and



(II.)



(III.)

AcOH into the *carboxylic acid* (III), m.p. 251° (decomp.) (softens 235°) (*anhydride*, m.p. 186°), and 3-*acetoxyandrostenolone* (IV) (+1H_2O), m.p. 192° [*oxime*, m.p. 244° (decomp.)], hydrolysed to 3-hydroxyandrostenolone, m.p. 197° (*diacetate*, m.p. 123°). (IV) is hydrogenated to 3-*acetoxyandrostene*-16 : 17-*diol*, m.p. 179°, transformed by cold AcOH–C_5H_5N into the *triacetate*, m.p. 224—226°, and hydrolysed by 4% KOH–MeOH to *androstene*-3 : 16 : 17-*triol* (V), m.p. 273—275°. $COMe_2$ containing 1% of HCl transforms (V) at room temp. into the :CMe_2 ether, m.p. 163—164°, oxidised by $Al(OPr^{\beta})_3$ in *cyclo*hexanone and PhMe to 16-*hydroxytestosterone* :CMe_2 *ether*, m.p. 183—184°, which is hydrolysed by aq. AcOH in boiling dioxan to 16-*hydroxytestosterone* (VI), m.p. 172—173° (*diacetate*, m.p. 199°). The physiological action of (V) shows that the introduction of OH at $C_{(16)}$ causes a marked weakening of the male hormone action whereas that of (VI) proves that the introduction produces enhanced œstrogenic activity. $COMe_2$ and (I) condense to the iso*propylidene* derivative [cf. (II), R = R′ = Me], m.p. 223° (*acetate*, m.p. 189°). H. W.

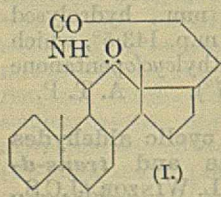
Saponins and sterols. V. Synthesis of 17-methylandrosten-17-ol-3-one (17-methyltestosterone). VI. Oxidation of dibromo[dihydro]-cholesteryl acetate. Synthesis of pregnen-3-ol-20-one. K. Fujii and T. Matsukawa (J. Pharm. Soc. Japan, 1935, **55**, 1333—1336; 1936, **56**, 158—161).—V. 17-*Methyl*-$\Delta^{5:6}$-*androstene*-3 : 17-*diol*, m.p. 195—196° [from *trans*-dehydroandrosterone (I) and MeMgI], was brominated, oxidised (CrO_3–AcOH), and debrominated (Zn) to yield 17-*methyltestosterone* (17-*methyl*-$\Delta^{4:5}$-*androsten*-17-*ol*-3-*one*), m.p. 155—156° (corr.).

VI. On repeating the prep. of (I) from dibromodihydrocholesteryl acetate by oxidation, pregnen-3-ol-20-one acetate, m.p. 147—148° (corr.) [semicarbazone, m.p. ? 265° (corr.)], was isolated, hydrolysis yielding pregnen-3-ol-20-one (II), m.p. 186°. The synthesis of (II) from 3-hydroxycholenic acid is proposed. Ch. Abs. (*c*)

Supposed androgenic action of *epiallo*pregnan-3-ol-20-one. A. Butenandt and A. Heusner (Z. physiol. Chem., 1938, **256**, 236—242; cf. Marker *et al.*, A., 1937, II, 250).—Pregnenolone (A., 1934, 1268) in AcOH with Pt–H_2 to saturation gives a mixture of *allo*pregnane-3 : 20-diols which with CrO_3–AcOH at room temp. yields *allo*pregnanedione, reduced (Ni–H_2, EtOH) to a mixture of *allo*pregnanolone (separated by pptn. with digitonin) together with 5—10% of *epiallo*pregnan-3-ol-20-one (I), m.p. 173—174° (acetate, m.p. 139—140°), which is purified by adsorption on Al_2O_3. (I) is devoid of androgenic activity. W. McC.

Preparation of progesterone and neoprogesterone from dehydroandrosterone. K. Miescher and H. Kägi (Helv. Chim. Acta, 1939, **22**, 184—195).—Addition of $CMeCl_2$·CO_2Et in Et_2O to a mixture of *t*-dehydroandrosterone acetate and Mg–Hg in Et_2O, removal of secondary volatile products by steam distillation, and treatment of the resultant product (*A*), with MeOH–NaOH give *Et* Δ^5-3t-*acetoxy*-17 : 20-*oxidobisnorcholenate*, m.p. 150—151°. Alkaline hydrolysis of (*A*) gives a mixture (I) of acids from which 3-t-*hydroxy*-17 : 20-*oxidobisnorcholenic acid* (II), m.p. 186—187° (*Me* ester, m.p. 150—151°, $[\alpha]_D^{24}$ −123° in EtOH, and its *acetate*, m.p. 172—174°, $[\alpha]_D^{24}$ −121° in EtOH), is separated. The mother-liquors from (II) contain an isomeric *acid* B (III), $C_{22}H_{32}O_4$, m.p. 248° (decomp.) [*Me* ester (+1H_2O), m.p. 73—74°, $[\alpha]_D^{24}$ −160° in EtOH, and its *acetate*, m.p. 175—176°, $[\alpha]_D^{24}$ −146° in EtOH]. Direct methylation of (I) followed by acetylation and chromatography with floridin leads to the isolation of the *acetates* of the *Me esters* of *acids* C and D, $C_{25}H_{36}O_5$, m.p. 153—154°, $[\alpha]_D^{20}$ −81° in EtOH, and m.p. 189°, $[\alpha]_D^{20}$ −49° in EtOH. In quinoline at 200° (I) gives (III) (which is decarboxylated with great difficulty) (unexamined), non-ketonic material, and a mixture of ketones (as acetates). This is separated chromatographically (Al_2O_3 or floridin) into pregnenolone acetate, m.p. 148·5—149·5°, $[\alpha]_D$ +18° in EtOH, and *neopregnenolone acetate*, m.p. 178—179°, $[\alpha]_D^{20}$ −114° in EtOH, hydrolysed to *neopregnenolone* (IV), m.p. 223—224°, $[\alpha]_D^{20}$ −124° in EtOH. Bromination oxidation, and debromination of crude (IV) leads to *neoprogesterone*, m.p. 217—218°, $[\alpha]_D^{20}$ +48° in $CHCl_3$, and progesterone. H. W.

Cholanic acid derivatives with substituents in the 11- and 12-position. II. J. Barnett and T. Reichstein (Helv. Chim. Acta, 1939, **22**, 75—82; cf. A., 1938, II, 497).—Further experiments indicate that the lactam, m.p. 320° (corr.) (*loc. cit.*), is probably (I). It is converted by prolonged heating with red P and HI at 165—200° essentially into 11(12)-amino-12(11)-ketocholanic acid, isolated as the *hydriodide* (+H_2O) (II), m.p. ~285° (corr.; decomp.). Reductive removal of O vicinal to NH_2 could not be effected. (II) is converted by CH_2N_2 into Me 11(12)-amino-12(11)-ketocholanate (III) characterised as the *hydrochloride*, m.p. 235° (decomp.) after softening ~230°, or the *Ac* derivative, m.p. 214—216°. The proof that (I) is merely hydrolysed by HI is afforded by the observation that (III) is transformed into (I) in good yield by the protracted action of MeOH at 130°. In harmony with the present formulation (I) is unchanged by the protracted action of CrO_3 in AcOH at room temp. Me 12-keto-$\Delta^{9:11}$-cholenate is unaffected by H_2 at room temp. in presence of PtO_2–MeOH–AcOH. With Raney Ni and H_2 at 100°/140 atm. it gives a non-cryst. product, oxidised



(I.)

essentially to Me 12-ketocholanate. All m.p. are corr. H. W.

Catalytic hydrogenation of organic compounds with carbon monoxide. O. Neunhoeffer and W. Pelz (Ber., 1939, **72**, [*B*], 433—439).—The catalyst is prepared by pptg. Pd from aq. $PdCl_2$ by H_2 on a suitable carrier, preferably active C ($BaSO_4$ and sugar C can also be used). During the action the gases are circulated through a system containing conc. aq. KOH to remove the CO_2 produced, small traces of which very appreciably restrict hydrogenation. In H_2O the hydrogenation is slow and succeeds best with 3—10% HCl. Usually there is a distinct induction period. Hydrogenation with CO cannot be applied to all substances which absorb H_2. *p*-NO_2·C_6H_4·CO_2H is very slowly reduced to *p*-NH_2·C_6H_4·CO_2H but reduction of $PhNO_2$ or *cyclo*hexene does not occur. Quinones are very suitable acceptors. *p*-Benzoquinone (I) acts most rapidly and is followed in order of decreasing velocity by toluquinone (II), thymoquinone (III), phenanthraquinone (IV), and 2 : 5-dihydroxy-*p*-benzoquinone (V). Anthraquinone (VI) does not give a certain result, whilst 2-hydroxynaphthaquinone is not attacked. Pd does not cause reduction of (I) by H_2. This change proceeds rapidly in the presence of a Pt catalyst; there is no distinct pause at the quinol stage and reaction proceeds to the formation of *cyclo*hexanol. Toluquinol is not formed from (II) in presence of Pd and H_2; (III) reacts very slowly and incompletely whereas the change occurs better with (IV), (V), and (VI). The mechanism of hydrogenation by CO is discussed. H. W.

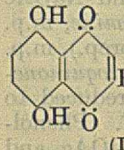
Oxidation–reduction potentials of substituted quinoneanils and indoanilines. L. F. Fieser and H. T. Thompson (J. Amer. Chem. Soc., 1939, **61**, 376—383).—Studies with 3-substituted 1 : 4-quinoneanils show that substituents exert their effect on both oxidant and reductant. 1 : 4-Naphthaquinoneanil (E_0 0·532 v.), m.p. 102°, with Zn dust and NaOAc in Ac_2O gives *phenyl-4-acetoxy-1-naphthylamine*, m.p. 135°. *p*-OH·C_6H_4·NH·$C_{10}H_7$-α (modified prep.), m.p. 85° (lit. 91°), and HgO in C_6H_6 give p-*benzoquinone-2′ : 3′-benzanil* (E_0 0·678 v.), m.p. 138°, reduced to p-*acetoxyphenyl-α-naphthylamine*, m.p. 135°. Phenol-blue (E_0 0·650 v.), prepared from PhOH, NaOAc, and NaOH by NaOCl and *p*-NH_2·C_6H_4·NMe_2,HCl at 0° to −5°, and reduced to 4-dimethylamino-4′-hydroxydiphenylamine hydrochloride, is considered to be *p*-O:C_6H_4:N·C_6H_4·NMe_2-*p* over the whole p_H range studied. 2-Methyl-*NN*-dimethylindoaniline [2-methyl-1 : 4-benzoquinone-4-*p*-dimethylaminoanil] (similarly prepared) (E_0 0·6081 v.), new m.p. 127°, gives *4′-dimethylamino-4-hydroxy-3-methyldiphenylamine hydrochloride*. 3-Methyl-*NN*-dimethylindoaniline (E_0 0·6343 v.), new m.p. 121°, gives *4′-dimethylamino-4-hydroxy-2-methyldiphenylamine*, m.p. 121—122° (decomp.) (*hydrochloride*). 2 : 1 : 5-NH_2·C_6H_3Me·NMe_2 gives *2′-methyl-NN-dimethylindoaniline* (E_0 0·6425 v.), m.p. 113—114°, reduced to *4-dimethylamino-4′-hydroxy-2-methyldiphenylamine hydrochloride*. 2 : 4 : 1-NO_2·$C_6H_3(SO_3H)$·N_2Cl and *o*-C_6H_4Me·NMe_2 give a dye (*Na* salt), reduction of which gives only a triazole, but the dye, *p*-NO_2·C_6H_4·N_2·C_6H_4Me·NMe_2-1 : 3 : 4, m.p. 122°, with $SnCl_2$ gives 2 : 1 : 5-NMe_2·C_6H_3Me·NH_2, b.p. 253—255°/762 mm., new m.p. 45—46° (*dihydrochloride*; *Ac* derivative, m.p. 96°), which, however, gives no indoaniline. *m*-OH·C_6H_4·OMe gives crude 3-methoxy-*NN*-dimethylindoaniline (E_0 0·5905 v.) and thence *4′-dimethylamino-4-hydroxy-2-methoxydiphenylamine*, m.p. 137°. The *hydrochloride* of *4-nitroso-NN-dimethyl-m-anisidine* (prep. by HNO_2), m.p. 131°, gives ($SnCl_2$) the 4-NH_2-derivative, b.p. 130—131°/4 mm. (*dihydrochloride*), which affords 2′-methoxy-*NN*-dimethylindoaniline (E_0 0·6355 v.) and thence *4′-dimethylamino-4-hydroxy-2′-methoxydiphenylamine hydrochloride*. *m*-C_6H_4Cl·OH (prep. from *m*-C_6H_4Cl·NH_2) affords (crude) 3-chloro-*NN*-dimethylindoaniline (E_0 0·6888 v.) and thence *2-chloro-4′-dimethylamino-4-hydroxydiphenylamine hydrochloride*. *m*-C_6H_4Cl·NMe_2, b.p. 239—240° (*picrate*, m.p. 145°), prepared from $NPhMe_2$ by way of the NO_2-, m.p. 60°, and NH_2-derivative, b.p. 128—129°/7 mm., gives the NO-derivative, m.p. 136° (decomp.), and thence 2-chloro-4-dimethylaminoaniline, b.p. 124—125°/3 mm., m.p. 40—41° (*hydrochloride*; *Ac* derivative, m.p. 117°), which yields (crude) 2′-chloro-*NN*-dimethylindoaniline (E_0 0·6683 v.) and thence *2-chloro-4-dimethylamino-4′-hydroxydiphenylamine hydrochloride*. *ar*-Tetrahydro-α-naphthol gives (crude) 2 : 3-tetramethylene-*NN*-dimethylindoaniline (E_0 0·5828 v.) and thence p-*dimethylaminophenyl-4′-hydroxy-5′* : 6′ : 7′ : 8′-*tetrahydro-1′-naphthylamine*, m.p. 158°. α-$C_{10}H_7$·NMe_2 is reduced by Na–C_5H_{11}·OH to the H_4-derivative, which with *p*-SO_3H·C_6H_4·N_2Cl gives a dye, reduced to 4-dimethylamino-5 : 6 : 7 : 8-tetrahydro-1-naphthylamine, b.p. 312° (*dihydrochloride*; *Ac* derivative, m.p. 172·5°), which, however, yields no indoaniline. R. S. C.

Reaction of thiol compounds with quinones. J. M. Snell and A. Weissberger (J. Amer. Chem. Soc., 1939, **61**, 450—453).—1 mol. each of *p*-O:C_6H_4:O (I) and SH·CH_2·CO_2H (II) in aq. EtOH give a product, dehydrated at 150° to *quinol-2-thiolacetolactone* (III), m.p. 169—171°; (I) (2 mols.) and (II) (1 mol.) give 1 : 4-*benzoquinone-2-thiolacetic acid*, m.p. 157—158° (decomp.) (and 1 mol. of quinol), reduced (Zn–AcOH) to (III). SH·CH_2·CO·NHPh and (I) (2 mols.) give 1 : 4-benzoquinone-2-thiolacetanilide, m.p. 175—176° (lit. 165—166°), and PhSH gives *2-phenylthiol-1 : 4-benzoquinone*, m.p. 110—112°, reduced by Zn dust in AcOH to a syrup, which with Ac_2O and a little H_2SO_4 yields *2-phenylthiolquinol diacetate*, m.p. 84—85°. EtSH and (I) at 100° give 2 : 5-diethylthiol-1 : 4-benzoquinone, m.p. 158—159°; Récsei's so-called 1 : 1-diethanesulphonyl-$\Delta^{2:5}$-hexadien-4-one (A., 1927, 1079) has not the composition stated. SH·$[CH_2]_2$·CO_2H and (I) in EtOH give 1 : 4-*benzoquinone-2* : *5-di(thiolpropionic acid)*, m.p. ~240° (decomp.), and *-2-thiolpropionic acid*, m.p. 165—166° (reduced by Zn–AcOH to β-2 : 5-dihydroxyphenylthiolpropionic acid, m.p. 121—123°). ψ-Cumoquinone (IV) and (II) in EtOH give 2 : 5-*dihydroxy-3* : 4 : 6-*trimethylphenylthiolacetic acid*, double m.p. 142° (decomp.) and ~190°, oxidised by $FeCl_3$–HCl to 3 : 5 : 6-*trimethyl-1* : 4-*benzoquinone-2-thiolacetic acid*, softens at 123°, m.p. 126—127°. *n*-$C_{18}H_{37}$·S(NH_2):NH, m.p. 83—85°, gives *n*-$C_{18}H_{37}$·SH, b.p. 165—170°/1 mm., which with (IV) gives 3 : 5 : 6-

trimethyl-2-n-*octadecylthiol*-1 : 4-*benzoquinone*, m.p. 71—73°, reduced to 3 : 5 : 6-*trimethyl*-2-n-*octadecylthiol*-*quinol*, m.p. 76—77°. In 80% EtOH duroquinone and (II) give duroquinol if the reaction mixture is slightly alkaline (Na_2CO_3); otherwise no reaction occurs. PhSH and *p*-xyloquinone give 2-*phenylthiol*-3 : 5-*dimethyl*-1 : 4-*benzoquinone*, m.p. 106—107°. Addition of RSH to quinones thus gives quinol derivatives, which may be oxidised to the quinone derivatives with simultaneous reduction of part of the original quinone to quinol. R. S. C.

4-Alkyl derivatives of 1 : 2-naphthaquinone. L. F. Fieser and C. K. Bradsher (J. Amer. Chem. Soc., 1939, **61**, 417—423).—4-Alkyl-1 : 2-naphthaquinones react generally as true quinones. 1 : 4-$C_{10}H_6Me{\cdot}SO_3K$ (modified prep. in 58% yield from 1-$C_{10}H_7Me$) gives 1 : 4-$C_{10}H_6Me{\cdot}OH$, which, by coupling with *p*-$SO_3H{\cdot}C_6H_4{\cdot}N_2Cl$, followed by reduction, affords 52% of 2-*amino*-4-*methyl*-1-*naphthol hydrochloride*, oxidised by $FeCl_3$–HCl to 4-*methyl*-1 : 2-*naphthaquinone* (I) (89%), m.p. 109° (decomp.). (I) is unstable in air and in hot MeOH, has E_0 0·531 v. in EtOH, and with Zn dust in Ac_2O–AcOH gives 3 : 4-*diacetoxy*-1-*methylnaphthalene*, m.p. 124·5—125·5°; it is insol. in alkali and bears no relation to the compound of Dean *et al.* (A., 1916, i, 555), which was believed to be the enolic form, but is probably a multimol. condensation product. With Cl_2 in AcOH (I) gives the 3-*Cl*-derivative, decomp. 150—160° [oxidised by $KMnO_4$ to *o*-$C_6H_4(CO_2H)_2$], the Cl of which does not react with AgOAc or $CHNa(CO_2Et)_2$. 1 : 4-$OMe{\cdot}C_{10}H_6{\cdot}COPh$ (improved prep.), m.p. 81—82°, with H_2 + Cu–Ba chromite at 175°/167 atm. (not Zn–Hg–HCl) gives 1 : 4-$OMe{\cdot}C_{10}H_6{\cdot}CH_2Ph$ (84—86%), m.p. 83—84°, converted by HBr–AcOH into 1 : 4-$OH{\cdot}C_{10}H_6{\cdot}CH_2Ph$, m.p. 122·5—123·5°, and thence (*p*-$SO_3H{\cdot}C_6H_4{\cdot}N_2Cl$, $Na_2S_2O_4$) into the 2-NH_2-derivative, which with $K_2Cr_2O_7$–H_2SO_4 gives 4-*benzyl*-1 : 2-*naphthaquinone* (II), softens at ~130°, m.p. 148° (decomp.). (II) is stable, gives a *phenazine* derivative, m.p. 195·5—196° (corr.), has E_0 0·562 v., and yields 3 : 4-*diacetoxy*-1-*benzylnaphthalene*, m.p. 96—96·5° (corr.). Et_2 naphtha-1 : 2-quinone-4-malonate (III) [modified prep.; cf. Sachs *et al.*, A., 1905, i, 909)], m.p. 105—106°, with Ac_2O–NaOAc or Ac_2O–H_2SO_4 gives the *acetate*, m.p. 93—94°, of the isomeric 2-hydroxy-1 : 4-quinone-4-methide, but normally exists, and in other reactions behaves, as (III). Thus with $Na_2S_2O_4$ it gives Et_2 3 : 4-*dihydroxy*-1-*naphthylmalonate*, m.p. 132° (decomp.), the Ac_2 derivative [prep. from (III) by Ac_2O–AcOH–Zn dust], m.p. 95—96°, of which with HCl–AcOH, followed by Ac_2O and a trace of H_2SO_4, gives 3 : 4-*diacetoxy*-1-*naphthylacetic acid*, m.p. 158—159° (could not be decarboxylated; decomp. with Cu). (III) gives a *phenazine* derivative, m.p. 164—165°, converted by hot 10% KOH into 3-carboxymethyl-1 : 2-benzphenazine, m.p. 168—172°, converted by Cu-bronze in quinoline at 140—190° into CO_2 and 3-*methyl*-1 : 2-*benzphenazine*, m.p. 174°, which is also obtained from (I) and *o*-$C_6H_4(NH_2)_2$. With $(CH_2{:}CMe)_2$ in EtOH at 100° (II) and (III) give poor yields of 12-*benzyl*-2 : 3-*dimethyl*-, m.p. 179—179·5° (corr.), and 2 : 3-*dimethyl*-12-*dicarbethoxymethyl*-, m.p. 127—128° (corr.), -1 : 4 : 11 : 12-*tetrahydrophenanthra*-9 : 10-*quinone*, respectively. With NH_2Ph in EtOH at 100° (I), (II), and (III) lose the 4-substituent, giving 2-anilino-1 : 4-naphthaquinone-4-anil. With Ac_2O and a drop of conc. H_2SO_4 (I) gives an abnormal *triacetate*, $C_{17}H_{16}O_6$, m.p. 101—102°, hydrolysed by cold, aq. alkali and oxidised by $KMnO_4$ to *o*-$C_6H_4(CO_2H)_2$; (II) gives similarly or with Ac_2O–NaOAc a *triacetate*, $C_{23}H_{30}O_6$, m.p. 139·5—140°. 3-Chloro-1 : 2-naphthaquinone with Ac_2O–H_2SO_4 gives 3-*chloro*-1 : 2 : 4-*triacetoxynaphthalene*, m.p. 172—173°, but the 4-chloroquinone is unchanged. R. S. C.

Constitution of shikonin. II. Synthesis of alkyl derivatives of naphthazarin, naphthapurpurin, and related compounds. C. Kuroda and M. Wada (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1938, **34**, 1740—1761; cf. A., 1937, II, 66, 344).—Naphthazarin is prepared from 1 : 5-$C_{10}H_6(NO_2)_2$, 18% oleum, and S at 60°, or from quinol, maleic anhydride, and $AlCl_3$–NaCl at 300°. *p*-$OMe{\cdot}C_6H_4{\cdot}OAcyl$ with $AlCl_3$–NaCl at 200° give 2-acylquinols (Ac, m.p. 202°, *propionyl*, m.p. 97°, *n*-butyryl, m.p. 175°), reduced (Clemmensen) to the 2-alkylquinols (*Et*, m.p. 112°, *Pr*^{a}, m.p. 88°, *iso*amyl, m.p. 101°), which with maleic anhydride and $AlCl_3$–NaCl yield 2-alkylnaphthazarins (*Pr*^{a}, m.p. 97°). 1 : 2 : 4-$C_6H_3(OH)_3$ with maleic anhydride and $AlCl_3$–NaCl gives naphthapurpurin. Similarly 3-methoxy-2-methylquinol (prepared thus: *o*-cresol → 3 : 2 : 1-$NO_2{\cdot}C_6H_3Me{\cdot}OH$ → $NO_2{\cdot}C_6H_3Me{\cdot}OMe$ → $NH_2{\cdot}C_6H_3Me{\cdot}OMe$ → 3-methoxy-2-methyl-benzoquinone and -quinol) yields 5 : 7 : 8-trihydroxy-6-methyl-1 : 4-naphthaquinone, m.p. 193°, identical with the known compound. 1 : 2 : 4-$C_6H_3(OH)_3$ with citraconic anhydride and $AlCl_3$–NaCl yields 5 : 6(or 7) : 8-trihydroxy-2-methyl-1 : 4-naphthaquinone, m.p. 202°, identical with that obtained from methylnaphthazarin [m.p. 202°, wrongly reported as 192° (A., 1937, II, 344)]. Hence the compounds previously reported (*loc. cit.*) as 3 : 5 : 8-trihydroxy-2-*iso*hexyl- and -ethyl-naphthaquinone are really 5 : 6(or 7) : 8-trihydroxy-2-alkyl-compounds. Since shikonin is lævorotatory, being enantiomeric with alkannin, and resembles in properties the alkyl-naphthazarins rather than -purpurins, it is given the formula (I) [R = $CH(OH){\cdot}CH_2{\cdot}CH{:}CMe_2$]. Further details and analyses of previous work (*loc. cit.*) are given. A. Li.



(I.)

Oxidation of alkylanthracenes, alkylanthraquinones, and their derivatives. I. Oxidation with chromic anhydride of 2-methylanthraquinone to anthraquinone-2-carboxylic acid. II. Influence of water on the oxidation of 2-methylanthraquinone to anthraquinone-2-carboxylic acid by chromic anhydride. M. A. Iljinski, L. G. Gindin, and V. A. Kasakova (Compt. rend. Acad. Sci. U.R.S.S., 1938, **20**, 555—558, 559—560).—I. Oxidation of 2-methylanthraquinone (I) with CrO_3 in glacial AcOH at 70° gives anthraquinone-2-carboxylic acid (II) in 96% yield.

II. The presence of small quantities of H_2O in the AcOH drastically reduces the yield of (II) from the oxidation of (I) with AcOH–CrO_3. J. D. R.

Constitution and synthesis of phœnicin, the pigment of *Penicillium phœniceum*. T. Posternak (Arch. Sci. phys. nat., 1938, [v], **20**, Suppl., 63—65).—Phœnicin (Friedheim, Compt. rend. Soc. Biol., 1933, **112**, 1030), $C_{14}H_{10}O_6$, m.p. 231°, is shown to be 2 : 2′-*dihydroxy*-4 : 4′-*dimethyldiphenyl*-3 : 6 : 3′ : 6′-*diquinone*. It is dibasic, gives yellowish-red solutions at p_H 1·6—3·5 and reddish-violet solutions at p_H 4·9—6·0, liberates 4 I from HI, gives a *diquinol*, m.p. 247° [*hexa-acetate* (I), m.p. 202—203°], with CrO_3 yields 2 AcOH, with dehydrating agents loses H_2O to give a dibenzfuran derivative, and with 2 mols. of *cyclo*pentadiene gives an *adduct*, $C_{24}H_{22}O_6$, m.p. 181°. 4 : 4′-Dimethyldiphenyl-3 : 6 : 3′ : 6′-diquinone (ditoluquinone) and Ac_2O–H_2SO_4 yield (I) and a small amount of an *isomeride*, m.p. 181—182°. R. S. C.

Catalytic hydrogenation of α- and β-ionone. J. Kandel (Ann. Chim., 1939, [xi], **11**, 73—142).—Mainly an account of work already reported (A., 1937, II, 108, 415; 1938, II, 96). Tetrahydroionol with $K_2Cr_2O_7$–H_2SO_4 gives tetrahydroionone [*semicarbazone*, m.p. 194—195° (corr.; block), 182° (corr.; tube)]. α- and β-Ionol, respectively, and SiO_2 gel at 300° give 2 : 4 : 4-*trimethyl*-3-(α-*ionene*) and 1 : 3 : 3-*trimethyl*-2-$\Delta^{\alpha\gamma}$-*butadienyl*-Δ^1-cyclo*hexene* (β-*ionene*), previously (*loc. cit.*, 1938) erroneously named 3-βδδ- and 2-ααγ-trimethylbutadienyl*cyclo*hexene, respectively. *Tetrahydroionyl* 3 : 5-*dinitrobenzoate* melts at 75° (block). R. S. C.

Bitter constituents of navel and Valencia oranges.—See A., 1939, III, 343.

Citronellal-terpene. II. Structure of the new terpene "menogene." H. Otsuki (J. Chem. Soc. Japan, 1936, **57**, 415—423; cf. A., 1937, II, 200).—*Menogene* (I), which occurs together with isomeric α-terpinene in the distillate from citronellal and H_2SO_4, is structurally related to $\Delta^{2:4(8)}$-*p*-menthadiene. It gives with Na orange-red colour reactions and on distillation (but not with KOH in EtOH) $COMe_2$ and two fractions, b.p. 100—130° and 184—186°. (I) and maleic anhydride in C_6H_6 or Et_2O and then with MeOH gives an unsaturated *adduct*, $C_{14}H_{18}O_3$,$5H_2O$, m.p. 205—208°, softening at 195° (additive *product* with Br, m.p. 282—285°). Hydrogenation of (I) (PdO) gives *p*-menthane. Ch. Abs. (*c*)

Spatial isomerism in the fenchol series. H. Schmidt and L. Schulz (Schimmel & Co., Ann. Rep., 1935, 93—95).—β-Fenchol (I), m.p. 3—4°, b.p. 200·5°/750 mm. (phenylurethane, m.p. 90—90·5°; H phthalate, m.p. 153—153·5°), bears the same relation to fenchol (II) as *iso*borneol to borneol; (I) and (II) differ markedly in odour but yield the same fenchone on oxidation. Properties of all the isomeric fenchols are summarised. Ch. Abs. (*c*)

Monochlorinated derivatives of pinane. G. Bonnet (Bull. Inst. Pin, 1938, 217—232, 241—256; 1939, 1—12).—*d*-Pinane (I), b.p. 166°, $[\alpha]_j$ +24·97°, $[\alpha]_v$ + 28·50°, is obtained by hydrogenation (Adams) of *d*-pinene in EtOH, and purified from any unchanged material by conc. H_2SO_4 or by a second hydrogenation; the use of $KMnO_4$ is unsuccessful. *l*-Pinane (II) is obtained similarly from a mixture of pinene and nopinene (III) or from (III). (I) and (II) are scarcely attacked by Cl_2 in diffused light in the absence of catalyst but the action occurs readily in bright light. Under these conditions (I) yields l-2-*chloropinane* (IV), b.p. 57°/2·5 mm., $[\alpha]_j$ −5·46°, $[\alpha]_v$ −5·95°, d-7-*chloropinane* (V), b.p. 66°/2·5 mm. $[\alpha]_j$ +9·77°, $[\alpha]_v$ +10·75°, and *dichloropinane*, b.p. 102°/2·5 mm., $[\alpha]_j$ −11·07°, $[\alpha]_v$ −12·54°, the Raman spectra of which are recorded. (IV) is unaffected by Na and abs. EtOH or by Al–Hg and Et_2O or 96% EtOH, but is converted by Zn–Cu into (I). Replacement of Cl by OH in (IV) cannot be effected by alkali, alkaline-earth, or Ag hydroxides since these reagents essentially cause withdrawal of HCl, as does AgOAc. Treatment of (IV) in Et_2O by Mg followed by O_2 and H_2O leads to *cis-l*-pinocampheol, m.p. 58—59° (*H phthalate*, m.p. 109—110°), oxidised by CrO_3 in AcOH to *d*-pinocamphone, b.p. 59°/3 mm., 211—212°/760 mm., $[\alpha]_j$ +20·28°, $[\alpha]_v$ +24·11°. dl-2-*Chloropinane* (obtained by mixing equal wts. of the optical isomerides) is similarly transformed into *dl*-pinocampheol, m.p. 41—43°, and *dl*-pinocamphone, b.p. 59—60°/3 mm., 210—212°/770 mm. (semicarbazone, m.p. 207°), oxidised by $KMnO_4$ to *dl*-pinonic acid. Boiling KOH–EtOH is without action on (IV), from which HCl is very incompletely removed by NaOMe. (IV) is converted by KOPh at 150° into α-pinene, probably containing a little δ-pinene. (V) is not reduced satisfactorily by Na–EtOH or by Al–Hg but is converted by Zn–Cu into (I). The successive action of Mg in Et_2O, O_2, and H_2O on (V) leads to *cis*-myrtanol, b.p. 81—82°/3 mm., $[\alpha]_j$ +12·67°, $[\alpha]_v$ +14·70° (*H phthalate*, m.p. 120°), oxidised to *cis*-myrtanal. Withdrawal of HCl from (V) gives principally (III), with smaller amounts of α- and probably δ-pinene, identified by the Raman spectrum and by conversion into nopinone (semicarbazone, m.p. 187°). Chlorination of (I) in daylight at 50° occurs very slowly. At 75° more (I) remains unattacked and less (IV) is produced whereas the proportions of (V) and polychloro-derivatives are essentially the same as when chlorination is effected at room temp. in bright light. At 100°, 44% of the material is unchanged, 23% of Cl_1- and 33% of polychloro-derivatives are formed. With the boiling material the proportion of polychloro- is somewhat increased at the expense of the Cl_1-derivative but there is evidence of decomp. The course of chlorination of (I) in presence of PCl_5 is very similar to that under the influence of intense light or higher temp. With S_2Cl_2, I, or $FeCl_3$ the proportion of unchanged material and polychloro-compounds is greatly increased and that of Cl_1-derivatives is diminished. At room temp., in daylight and in presence of I the Cl_1-compounds consist mainly of bornyl chloride (VI) with some (IV) and possibly (V). The proportion of (VI) appears somewhat increased if action takes place in the dark or at raised temp. (VI) is identified by conversion into camphene, *iso*bornyl formate, and *iso*borneol. H. W.

Action of acetic acid on α-pinene in presence of boron trioxide. M. Imoto (J. Soc. Chem. Ind. Japan, 1938, **41**, 375—376B).—α-Pinene and AcOH of various grades in presence of B_2O_3 at 100—120° gives 45% of an ester hydrolysed to borneol, *iso*-

borneol, and fenchyl alcohol. Other terpenes are also formed. E. W. W.

Acidic oxidation products of lupenyl esters: addition of hydrogen chloride to lupeol. A. Duerden, I. M. Heilbron, W. McMeeking, and F. S. Spring (J.C.S., 1939, 322—324).—Ozonolysis of lupenyl acetate (cf. A., 1938, II, 195) gives the *acetate-acid A* ($C_{32}H_{52}O_4$ or $C_{31}H_{50}O_4$), m.p. 272° (*Me* ester, m.p. 232—234°), hydrolysed to the *OH-acid A*, m.p. 262—264°, also obtained by ozonolysis of lupenyl benzoate. Oxidation of lupenyl acetate with CrO_3 affords the acetate-acid B, m.p. 296° (cf. Ruzicka *et al.*, *ibid.*) (*acetate-anhydride*, m.p. 195—197°, remelts 277—284°), and similar oxidation of the benzoate yields the benzoate-acid, m.p. 320—322°. Lupeol and HCl form *lupeol hydrochloride* (I) m.p. 195—196° $[\alpha]_D^{20}$ −10·3° in $CHCl_3$, which with AgOAc gives lupenyl acetate and with $NPhMe_2$ affords *isolupenyl acetate*, m.p. 269—270°, $[\alpha]_D^{20}$ +25·26° in $CHCl_3$. The mother-liquors from the prep. of (I) with Ac_2O yield an *acetate*, m.p. 231—232°, not identical with β-amyrenyl acetate. F. R. S.

Structure of origanene. I. A. J. Birch (J. Proc. Roy. Soc. New South Wales, 1938, **71**, 330—335).—Careful fractionation of technical α-phellandrene (from *Eucalyptus dives*) and treatment of the product with maleic anhydride gives what appears to be a reasonably pure origanene (I), b.p. 155—160°, α_D^{24} +12·5°, the physical consts. of which differ somewhat from those recorded by Pickles (J.C.S., 1908, **93**, 862) so that it is improbable that (I) is a monocyclic terpene as postulated by him. Titration with Br in glacial AcOH indicates the presence of one double linking so that, considered along with the analytical results, it is very probable that (I) is a dicyclic terpene; this supposition agrees well with the observed physical consts. Pickles' observation of the formation of terpin hydrate or *p*-cymene from (I) could not be confirmed. The nitrosochloride (II) and the nitrolpiperidide are optically inactive in $CHCl_3$. Oxidation of (I) with H_2O_2 gives only liquid products from which $(CH_2{\cdot}CO_2H)_2$ could not be extracted whilst dil. aq. $KMnO_4$ affords a small amount of neutral ketonic material with $H_2C_2O_4$ and liquid acids which do not react with 2 : 4-$(NO_2)_2C_6H_3{\cdot}NH{\cdot}NH_2$. With EtOH–KOH (II) gives only liquid products whereas C_5H_5N yields a small amount of cryst. material, m.p. 151°, possibly a previously unknown oxime. The following derivatives are described: *nitrolmorpholide*, m.p. 190°; nitrolpiperidide, m.p. 198°; nitrolbenzylamide, m.p. 106°; *nitroldiethylamide*, m.p. 140°; *nitroldimethylamide*, m.p. 178°; *nitrodiisobutylamide*, m.p. 120°; *nitrol-α-phenylethylamide*, m.p. 161°. H. W.

Constitution of gmelinol. I. A. J. Birch and F. Lions (J. Proc. Roy. Soc. New South Wales, 1938, **71**, 391—405; cf. Smith, A., 1913, i, 1057).—Extraction of the wood of *Gmelina Leichhardtii* ("colonial beech") with boiling H_2O gives gmelinol (I), m.p. 124° after softening at 122°, which is now shown by analyses and determinations of mol. wt. in freezing C_6H_6 to be $C_{21}H_{24}O_7$. It contains 4 OMe and, with some difficulty, yields a *phenylurethane*, m.p. 189°, reconverted by boiling KOH–EtOH into (I). Since (I) does not give any ketonic compound when oxidised, the OH is probably *tert.* (I) distils almost unchanged at about 330°/20 mm. but under atm. pressure it breaks down into veratric acid (II), veratraldehyde (III), and, mainly, homoveratrole. (I) is readily converted by mineral acids into a dark brown resin whereas boiling 20% HCO_2H transforms it into *isogmelinol* (IV), m.p. 147°, which is dextrorotatory in $CHCl_3$. The yield of homogeneous (II) obtained by oxidation of (I) with $KMnO_4$ strongly suggests the presence of two veratryl residues whilst a somewhat lower yield is obtained by the similar oxidation of (IV). (I) is oxidised by HNO_3 to 4 : 5-dinitroveratrole in amount somewhat < that required for one veratryl residue. Further support of the hypothesis that (I) contains two veratryl residues is found in the observation that (II) is the sole isolable product of the oxidation with $KMnO_4$. Oxidation of (I) in glacial AcOH with a deficiency of CrO_3 gives (III) and unchanged (I). Fuming HNO_3 converts (I) in glacial AcOH at room temp. into *dinitrogmelinol*, $C_{21}H_{12}O_7(NO_2)_2$, m.p. 190°, which is optically active, insensitive to the action of aq. or alcoholic acids, and resistant to oxidation by $KMnO_4$. Prolonged treatment of it with PhNCO results in a tar. It is indifferent towards 2 : 4-$(NO_2)_2C_6H_3{\cdot}NH{\cdot}NH_2$. Controlled oxidation by CrO_3 in AcOH leads almost certainly to 6-nitroveratraldehyde [2 : 4-*dinitrophenylhydrazone*, m.p. 260° (decomp.)]. *Dinitroisogmelinol*, m.p. 235°, is obtained similarly from (IV). Bromination of (I) in C_6H_6 containing C_5H_5N (to absorb the liberated HBr) leads to *dibromogmelinol* (V), m.p. 145°, whilst (IV) in glacial AcOH is transformed by Br into *dibromoisogmelinol* (VI), m.p. 196°. A mixture of (V) and (VI) is obtained when (I) is brominated in AcOH. (V) is isomerised to (VI) when boiled with EtOH and conc. HCl. (V) and (VI) are unchanged by boiling aq. or alcoholic alkali or boiling C_5H_5N, showing that Br is probably a substituent on an aromatic nucleus. Both substances resist oxidation by $KMnO_4$. 4-Bromo-5-nitroveratrole is the sole isolable product of their oxidation with conc. HNO_3, thus again emphasising the probability of the presence of two veratryl residues in (V) and (VI), each of which is substituted during bromination. The saturated nature of (I) is evidenced by the non-absorption of H_2 in presence of Pd–norit. It is reduced by Na and boiling EtOH or amyl alcohol to a pale yellow, viscous liquid which is not phenolic, indicating the absence of a coumarone or catechin type of mol. The available evidence suggests the structure $(C_3H_3O_2)(OH)[>CH{\cdot}C_6H_3(OMe)_2]_2$ for (I). H. W.

Triterpenes. XLIV. Transformation of glycyrrhetic acid into β-amyrin. L. Ruzicka and A. Marxer (Helv. Chim. Acta, 1939, **22**, 195—201).—Deoxyglycyrrhetic acid (A., 1937, II, 510) is transformed by Ac_2O in abs. C_5H_5N at 100° into *acetyldeoxyglycyrrhetic acid* (I), m.p. 309—310° after softening at 304°, $[\alpha]_D$ +115·8° in $CHCl_3$, converted by $SOCl_2$ at 100° into *acetyldeoxyglycyrrhetyl chloride*, m.p. 248—251°, which is reduced (Pd–$BaSO_4$ in xylene at 155°) to *acetyldeoxyglycyrrhetaldehyde*, m.p. 243—246° after softening at 238° [*oxime*, m.p. 252—255° (decomp.)]. The corresponding *semicarbazone*, m.p. 342° when placed in bath at >230° or m.p. ~340° after

re-solidification if placed in bath at a higher temp., is transformed by NaOEt–EtOH at 200° into β-amyrin, m.p. 190—102° after slight softening, $[\alpha]_D$ +90·0° in $CHCl_3$ (Ac, m.p. 241—242°, $[\alpha]_D$ +81·2° in $CHCl_3$, and Bz, m.p. 232—234°, derivatives), and *hydroxy-β-amyrin*, $C_{30}H_{50}O_2$, m.p. 241—243°, $[\alpha]_D$ +87·2° in $CHCl_3$ (*diacetate*, m.p. 198° after softening at 182°, $[\alpha]_D$ +96·19° in $CHCl_3$), which greatly depresses the m.p. of erythrodiol and soyasapogenol *C*. With CrO_3 in AcOH, (I) gives the modification of acetylglycyrrhetic acid, m.p. 322—325°, $[\alpha]_D$ +141·2° in $CHCl_3$, and an *acetylketolactone*, $C_{32}H_{48}O_{53}$, m.p. 319—322° after softening at 308°, $[\alpha]_D$ +134·5° in $CHCl_3$. All m.p. are corr. H. W.

Constituents of pyrethrum flowers. XIV. Structures of the enols of pyrethrolone. H. L. Haller and F. B. La Forge (J. Org. Chem., 1939, **3**, 543—549; cf. A., 1938, II, 372; Staudinger and Ruzicka, A., 1924, i, 522, 523).—Tetrahydropyrethrolone is converted by boiling KOH–EtOH containing Zn dust into some optically inactive tetrahydropyrethrolone and *tetrahydroisopyrethrolone enol* (I), b.p. 150°/0·25 mm., identical with the compound obtained by hydrogenating *iso*pyrethrolone enol (II), b.p. 105—160°/0·7 mm. [*acetate* (III), b.p. 118—120°/4 mm.], obtained by Staudinger *et al.* (*loc. cit.*) together with pyrethrolone enol by the action of NaOMe on pyrethrolone. (I) is converted by Ac_2O at 100° into its *acetate* (IV), b.p. 115—120°/0·35 mm., which is rapidly hydrogenated (PtO_2 in EtOAc) to a product (V), b.p. 67—70°/2 mm.; this is transformed by $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$,HCl–$C_5H_5N$–$H_2O$–EtOH into two isomeric *semicarbazones*, m.p. 206° and 140—142° respectively. (II) gives an acetate which absorbs 4 H_2 giving two *iso*hexahydropyrethrones, isolated as semicarbazones identical with those derived from (V). Partial hydrogenation of (III), involving only the double linkings in the side-chain, is effected by PtO_2 in denatured EtOAc, thus giving (IV). (II) is therefore regarded as 2-*hydroxy*-4-*methyl*-3-*pentadienyl*-Δ^2-cyclo*penten*-1-*one* and the *iso*hexahydropyrethrones as 4-*methyl*-3-*amyl*cyclo*pentan*-1-*ones*. H. W.

Xanthoxylin *S*, a constituent of *Xanthoxylum carolinianum*. II. H. Dieterle and K. Schwengler (Arch. Pharm., 1939, **277**, 33—44; cf. A., 1931, 1199).—Xanthoxylin *S* (I) contains two methylenedioxyresorcinol nuclei and probably has a formula of the type suggested by Erdtmann (A., 1937, II, 28, 69). (I), new formula, $C_{20}H_{18}O_6$, m.p. 121°, $[\alpha]_D^{23}$ —122°, with HNO_3–AcOH gives 68% of a $(NO_2)_2$-derivative (II), m.p. 221°, and 60% of 1 : 2 : 4-CH_2O_2:$C_6H_3{\cdot}NO_2$. With H_2–Pd–C (I) absorbs 2 H_2 with ring fission to give a *diol* (2 active H; *dibenzoate*; *diacetate*). H_2–Pd–C converts (II) into a *diaminoalcohol*, m.p. 129—132° (2 CH_2O_2:), but Sn–HCl–AcOH gives *diaminoxanthoxylin* S and thence a *diol*, oxidised by H_2O_2 to an *acid*, $C_8H_{10}O_6$, m.p. 187°. *l*-Asarinin (Huang-Minlon, A., 1937, II, 298) is identical with (I). Myristic acid, vanillin, a coumarin (Me ether, m.p. 107°), and the sterol, $C_{27}H_{46}O$, m.p. 141°, were isolated from *X. carolinianum*. R. S. C.

***m*-Dinitrobenzene reaction of ouabain and its application to the examination of East African arrow poison.** W. D. Raymond (Analyst, 1939, **64**, 113—115).—The reaction (cf. A., 1938, II, 344) is not sp. to ouabain (I) but is also given by members of the digitoxin group. A colorimetric method of determination based on the reaction is described, and the % of (I) in some arrow poisons so determined was checked by determining the lethal dose when injected into frogs. The botanical source of the principles present in some arrow poisons is discussed. E. C. S.

Secretin picrolonate, m.p. 234—235° (decomp.).—See A., 1939, III, 270.

Sulphite cooking process. II. Reaction between thioglycollic acid and spruce lignin. C. E. Ahlm and F. E. Brauns (J. Amer. Chem. Soc., 1939, **61**, 277—280; cf. B., 1938, 1025).—Spruce lignin and $SH{\cdot}CH_2{\cdot}CO_2H$ in 2N-HCl at 100° give the *acid* (I), $C_{42}H_{32}O_6(OMe)_5(OH)_5(SH{\cdot}CH_2{\cdot}CO_2H)_4$, converted by CH_2N_2 into the *ether ester*, $C_{42}H_{32}O_6(OMe)_6(OH)_4(SH{\cdot}CH_2{\cdot}CO_2Me)_4$ (*tetra-acetate*), which with Me_2SO_4–NaOH is partly methylated to give the *ether*, $C_{42}H_{32}O_6(OMe)_{10}(SH{\cdot}CH_2{\cdot}CO_2Me)$ and is partly decomposed and hydrolysed to the *acid*, $C_{42}H_{32}O_6(OMe)_6(OH)_4(SH{\cdot}CH_2{\cdot}CO_2H)_2$. PhOH replaces 2 $SH{\cdot}CH_2{\cdot}CO_2H$ of (I). At most one $SH{\cdot}CH_2{\cdot}CO_2H$ of (I) is linked to a phenolic group. R. S. C.

Lignin. XX. Union of formaldehyde in lignin. K. Freudenberg, F. Klinck, E. Flickinger, and A. Sobek (Ber., 1939, **72**, [*B*], 217—226).—Distillation with mineral acids cannot lead to a decision with respect to the mode of formation of CH_2O from lignin (I). A more suitable reagent is NH_2Ph containing some HCl which gives (readily isolated) acridane (II) with aromatic CH_2O_2-compounds and polyoxymethylenes but not with $CHPh{:}CH{\cdot}CH_2{\cdot}OH$ and its ether, coniferin, or fructose. Intact (I) and pine wood afford (II), which is not obtained from Tornesch lignin. The presence of CH_2O_2 groups in (I) is established by the formation of CH_2O under the action of acids and of NH_2Ph and by the observation that the ratio between the amounts of CH_2O found by the two processes is the same for (I) as for piperonylic acid (III). CH_2O is not obtained from 28% H_2SO_4 and $CH_2Ph{\cdot}OH$, $(CH_2Ph)_2O$, $CH_2Ph{\cdot}CH_2{\cdot}OH$, $CHPh{:}CH{\cdot}CHO$, geraniol, $CH_2Bz{\cdot}OH$ (IV) and its $(OMe)_2$-derivative, and veratroylcarbinol. (IV) yields PhCHO but CH_2O could not be detected. Phenylglycol gives PhCHO and an unidentified compound, m.p. 161°. CH_2O can no longer be detected in (I) which has been repptd. from a solution of K in liquid NH_3. Under these conditions (III) is transformed into *m*-$OH{\cdot}C_6H_4{\cdot}CO_2H$ and dihydrosafrole into *p*-$C_6H_4Pr{\cdot}OH$. It is therefore beyond doubt that CH_2O in lignin is present entirely or predominatingly in aromatic CH_2O_2 groups. The relationships of pine and beech (I) are discussed. Unsuccessful attempts are described to isolate from (I) fragments containing CH_2O_2. It is concluded that there are no such terminal groups but that the aromatic CH_2O_2 complexes are built into the interior of the mol. of (I). H. W.

Sulphuric esters of the components of pine wood. K. Freudenberg and R. Keller (Ber., 1939, **72**, [*B*], 331—334).—Pine wood is transformed

by C_5H_5N–H_2SO_4 into a pale-coloured product, the amount and composition of which suggest that each polysaccharide unit has combined with three and each lignin (I) unit with one $SO_3{\cdot}C_5H_5N$ group. It is divided by hot and cold H_2O into several fractions and further purification is effected by taking advantage of the insolubility of the K salts of polysaccharide ester in an excess of KOH. Portions containing (I) are to some extent sol. in excess of alkali and are salted out when the solution is neutralised. Thus are obtained (*a*) salts of polysaccharide sulphuric esters (II) free from OMe, (*b*) salts of lignin sulphuric esters free from sugar and corresponding with a sulphuric ester salt derived from cuproxam lignin, and (*c*) mixtures of (II) with salts of sulphuric esters derived from compounds of carbohydrates and (I). In (*b*) and (*c*) all the OMe of the wood is found. H. W.

Lignin and related compounds. XXXV. Ethanolysis of spruce wood. A. B. Cramer, M. J. Hunter, and H. Hibbert. **XXXVI. Ethanolysis of maple wood.** M. J. Hunter, A. B. Cramer, and H. Hibbert (J. Amer. Chem. Soc., 1939, **61**, 509—516, 516—520; cf. A., 1938, II, 238).—XXXV. The extract obtained from spruce wood-meal by 1 : 1 EtOH–C_6H_6 is heated with 3% HCl–abs. EtOH. The phenols, b.p. 130—150°/0·01 mm., of the H_2O-sol. portion of the product give, when treated with CH_2N_2, 4-α-*ethoxypropioveratrone* (I), m.p. 81—82° (2: 4-*dinitrophenylhydrazone*, m.p. 140—141°), stable to NaOI, oxidised by $KMnO_4$–NaOH to 3 : 4-$(OMe)_2C_6H_3{\cdot}CO_2H$. OEt·$[CH_2]_2$·CN (prep. from the bromide and KCN), b.p. 75—77°/23 mm., with HCl gives OEt·$[CH_2]_2{\cdot}CO_2H$, b.p. 121°/20 mm., the chloride, b.p. 64—67°/30 mm., of which with $AlCl_3$ and veratrole (II) in CS_2 at +20° gives 4-β-*ethoxypropioveratrone*, m.p. 50—51° (2 : 4-*dinitrophenylhydrazone*, m.p. 167—168°), better obtained from 3 : 4-$(OMe)_2C_6H_3{\cdot}CO{\cdot}[CH_2]_2{\cdot}Cl$, NaI, and EtOH. OMe·CHMe·COCl, (II), and $AlCl_3$ in CS_2 give a *compound* [not (I)], $C_9H_7O(OMe)_2{\cdot}OEt$, m.p. 81—82°. Propioveratrone and Br–$CHCl_3$ give the α-*Br*-derivative, m.p. 89°, which with KOAc in abs. EtOH gives the α-*OAc*-compound, m.p. 65—66°, converted by 2% HCl–abs. EtOH into (I) or by $BaCO_3$ in hot H_2O into 4-α-*hydroxypropioveratrone* (III), b.p. 140°/0·01 mm. 1% HCl–abs. EtOH decomposes (III) at 0°, but hot 0·5% HCl–abs. EtOH converts it into (I). It is probable that 4-α-hydroxypropiovanillone, its dienol, 4 : 3-OH·C_6H_3(OMe)·CHAc·OH, or some precursor readily transformed into one of these isomerides occurs in spruce lignin as precursor of the various substances obtained therefrom.

XXXVI. Maple wood yields, by similar methods, phenols, which with CH_2N_2 give (I) and with *p*-$NO_2{\cdot}C_6H_4{\cdot}COCl$–$C_5H_5N$ give 5-α-*ethoxypropiosyringone* p-*nitrobenzoate* (IV), m.p. 140—142°. 3 : 4 : 5-$(OMe)_3C_6H_2{\cdot}COEt$ (improved prep.) and Br give α-*bromo*-3 : 4 : 5-*trimethoxypropiophenone*, m.p. 83—84°, converted by H_2SO_4 at 45—47° into 5-α-*bromopropiosyringone*, m.p. 89—90°, and thence by NaOAc–AcOH (not KOAc–EtOH) into the α-*OAc*-compound, m.p. 172—173°, which with 2% HCl–abs. EtOH yields 5-α-*hydroxypropiosyringone*, b.p. 160—180°/0·007 mm. [gives (IV)]. *Pyrogallol* 1 : 3-Me_2 *ether* 2-*propionate*, b.p. 125—127°/0·5 mm., and $AlCl_3$ in $PhNO_2$ give *propiosyringone*, m.p. 109—110°, also obtained from 3 : 4 : 5-$(OMe)_3C_6H_2{\cdot}COEt$ and conc. H_2SO_4. The presence of α-hydroxypropio-veratrone and -syringone in maple lignin is thus indicated. R. S. C.

Aldehydic constituents from the ethanolysis of spruce and maple woods. L. Brickman, J. J. Pyle, and H. Hibbert (J. Amer. Chem. Soc., 1939, **61**, 523).—The products obtained from spruce and maple woods by HCl–EtOH include an *aldehyde*, $C_{11}H_{12-14}O_5$ (*semicarbazone*, m.p. 210—210·5°), probably α- or β-keto-β-4-hydroxy-3 : 5-dimethoxypropaldehyde. R. S. C.

Reconversion of an "extracted" lignin into its primary building units. Q. P. Peniston, J. L. McCarthy, and H. Hibbert (J. Amer. Chem. Soc., 1939, **61**, 530).—Acetylated oak lignin (OMe 8·7, Ac 35%) and hot 2% HCl–EtOH give a mixture closely resembling that obtained directly by HCl–EtOH from maple wood. R. S. C.

Pantothenic acid. III. Analysis and determination of constituent groups. R. J. Williams, H. H. Weinstock, jun., E. Rohrmann, J. H. Truesdail, H. K. Mitchell, and C. E. Meyer (J. Amer. Chem. Soc., 1939, **61**, 454—457; cf. A., 1939, III, 100).—Quant. oxidation, analysis, and loss, retention, or recovery of biological activity under the influence of reagents show pantothenic acid to be $C_8H_{15}O_5N$, containing CO_2H, 2 OH, and (?)·CO·NH·, but not other simple groups. It is not an α-OH-acid and contains no aromatic ring (absorption spectrum). R. S. C.

Composition of the so-called pyroabietic acid prepared without a catalyst. E. E. Fleck and S. Palkin (J. Amer. Chem. Soc., 1939, **61**, 247—249).—Pyroabietic, prepared by heating at 340° *l*-abietic acid, $[\alpha]_D^{20}$ −104° in EtOH, contains dehydroabietic acid, m.p. 172—173°, $[\alpha]_D^{20}$ +62° in EtOH, and the H_2-lactone, m.p. 130—131°, $[\alpha]_D^{20}$ −4° in EtOH, but not the H_4- or H_2-acid, $[\alpha]_D^{20}$ +108°. The lactone gives the hydroxytetrahydro-acid, m.p. 164—165°, $[\alpha]_D^{20}$ +35° in EtOH. R. S. C.

αδ-Di-iodobutane from tetrahydrofuran. G. B. Heisig (J. Amer. Chem. Soc., 1939, **61**, 525—526).—Tetrahydrofuran (prep. in 91% yield from furan by H_2–Raney Ni at 80°) and red P–I give 51% of $(\cdot CH_2{\cdot}CH_2I)_2$, b.p. 105—110°. R. S. C.

3-Chloro-2-alkoxy-2-methyltetrahydrofurans.—See B., 1939, 245.

Orientation in the furan series. XI. Cleavage-rearrangements in Friedel–Crafts reactions. H. Gilman and J. A. V. Turck, jun. (J. Amer. Chem. Soc., 1939, **61**, 473—478; cf. A., 1938, II, 866).—Et 5-bromo-4-*tert.*-butyl-2-furoate (I) is obtained as sole cyclic product from Et 5-bromo-2-furoate, $AlCl_3$, and $Bu^{\alpha}Cl$, $Bu^{\gamma}Br$, *n*-$C_5H_{11}Cl$, *iso*-$C_5H_{11}Br$, CMe_2EtCl, *n*-$C_5H_{11}I$, *n*-$C_6H_{13}Cl$, *n*-$C_6H_{13}Br$, *n*-$C_{12}H_{25}Br$, *n*-$C_{16}H_{33}Br$, or *n*-$C_{18}H_{37}Br$ (46% yield) in CS_2. $CMe_2Et{\cdot}OH$ leads to 5-bromo-4-*tert.*-butylfuroic acid, but CHEt:CH_2, di*iso*butylene, *n*-Δ^{β}-pentene, and *cyclo*hexene do not react. *n*-$C_5H_{11}Br$ gives (I) or Et 5-*tert.*-butyl-2-furoate (II) or mixtures of the two according to the conditions, but Et 5-chloro-2-furoate

gives only the 4-Bu$^{\gamma}$ derivative (hydrolysed by KOH to 5-*chloro*-4-tert.-*butyl*-2-*furoic acid*, m.p. 172—173°). Et 4-bromo-2-furoate and *n*-$C_5H_{11}Cl$ give only (II), the Br being lost after condensation. No reaction occurs with Et 4 : 5-dibromo-2-furoate and *n*-$C_5H_{11}Br$ or 5-bromofurfuraldehyde and *n*-$C_5H_{11}Cl$. $FeCl_3$ alone does not induce alkylation of furoates, but presence of traces thereof in $AlCl_3$ slightly increases the yields and increases the amount of (II) formed at the expense of the (I). <1 mol. of $AlCl_3$ is required for reaction of alkyl halides, probably owing to complex formation with the CO_2Et. The reaction mechanism is discussed. When *n*-$C_5H_{11}Cl$ is used, *n*- and *iso*-C_4H_{10} are formed with smaller amounts of products of lower mol. wt.; if no solvent is used, C_4H_{10}, C_5H_{12}, and resins are formed. With *n*-$C_{18}H_{37}Br$ in $(CHCl_2)_2$, C_4H_{10}, C_5H_{12}, C_6H_{14}, and higher products are obtained. Details of the effect of concn. and reaction time are given. Et 5-bromo-2-furoate, *tert.*-$C_5H_{11}Ph$, and $AlCl_3$ give small amounts of an *acid*, $C_{11}H_{16}O_2$, m.p. 187—187·5°. R. S. C.

Raney nickel applied to the hydrogenation of furancarboxylic acids. R. Paul and G. Hilly (Compt. rend., 1939, **208**, 359—361; cf. A., 1937, II, 298; 1938, II, 346).—Pyromucic acid, furylacrylic acid (I), and furfurylidenemalonic acid dissolved in the theoretical quantity of NaOH with H_2–Raney Ni at 100—110° under pressure afford *tetrahydro-furan*-2-*carboxylic acid*, b.p. 128—129°/13 mm., and -*furyl-propionic acid*, b.p. 156—157°/15 mm. Pyromucamide in EtOAc similarly affords *tetrahydrofuran*-2-*carboxylamide*, m.p. 78—79°. Et pyromucate, furylacrylate, furfurylidene-malonate and -acetoacetate with Raney Ni–H_2 at 100—110° under pressure afford *Et tetrahydrofuran*-2-*carboxylate*, b.p. 80°/11 mm., β-*tetrahydrofurylpropionate*, b.p. 110°/15 mm., *tetrahydrofurfurylmalonate*, b.p. 166—167°/17 mm., and β-*hydroxy*-α-*tetrahydrofurfurylbutyrate*, b.p. 152—153°/10 mm., respectively. (I) gives some γ-propylbutyrolactone when reduced. J. L. D.

Side-chain derivatives of pyromucic acid. E. Votoček and A. Krošlák (Coll. Czech. Chem. Comm., 1939, **11**, 47—53).—2-Aldehydofuran-5-carboxylic acid (I) (*Me* ester *phenylhydrazone*, m.p. 183°) when heated with $CH_2(CO_2H)_2$ in C_5H_5N, and the product hydrolysed (dil. H_2SO_4), yields β-(2-*carboxyfuryl*)-*acrylic acid* (II), m.p. 273—274° [*Me* ester {from the Me ester of (I)}, m.p. 206—208°], together with a compound, m.p. >300°. Distillation of (II) gives a substance, m.p. 132—134°, containing C 56·6, H 4·7%. (II) is reduced (Na–Hg) to the -5-*propionic acid*, m.p. 180°. The Me ester of (I), when treated with N_2H_4,H_2O in Et_2O, and the product heated with EtOH–NaOEt at 150—160°, yields 2-methylfuran-5-carboxylic acid, when boiled with H_2O–EtOH–KCN yields 2-*carbomethoxyfuran*-5-*glycollic acid*, m.p. 238—239°, and with CH_2N_2 yields *Me* 5-*acetylfuran*-2-*carboxylate*, m.p. 103°. A. Li.

Properties of some isomeric 1 : 4- and 1 : 5-epoxides. R. Paul (Bull. Soc. chim., 1939, [v], **6**, 331—335; cf. A., 1938, II, 289).—Physical consts., *e.g.*, b.p., n, η, mol. vol., and parachor, of isomeric 2-alkyltetrahydro-furans (I) and -pyrans (II) are compared. Although generally, b.p. of (I) are 6—7° > those of (II), an exception is the case of 2-benzyltetrahydrofuran, b.p. 109—110°/10 mm., compared with 2-phenyltetrahydropyran, b.p. 111—112°/10 mm. A. T. P.

Synthesis of bis-(5-hydroxymethylfurfuryl-acrylic acid) ether. K. Aso (J. Agric. Chem. Soc. Japan, 1939, **15**, 56).—The *substance*, m.p. 203—204° (decomp.), is obtained from ω-hydroxymethylfurfuraldehyde ether by Perkin's reaction. J. N. A.

Decomposition products of substances containing uronic acid by heating in autoclave. II. Reduction of dimethylalginetin. K. Aso (J. Agric. Chem. Soc. Japan, 1939, **15**, 57—58; cf. A., 1935, 753).—*Dimethyltetrahydroalginetin* [4-*hydroxy*-3 : 8-*dimethoxy*-2-*methylchroman*], m.p. 182° (*acetate*, m.p. 117°), is formed by catalytic reduction of dimethylalginetin [3 : 8-dimethoxy-2-methylchroman]. J. N. A.

6-Hydroxy-2 : 5 : 7 : 8-tetramethyl-2-δθ-dimethylnonylchroman (allophanate, m.p. 170°).—See A., 1939, III, 169.

Synthesis of 6-hydroxy-8-methoxycoumarin. F. Mauthner (J. pr. Chem., 1939, [ii], **152**, 23—26).—8-Methoxycoumarin [prep. from *o*-vanillin (I), anhyd. NaOAc, and Ac_2O at 170—175° described] is oxidised by $K_2S_2O_8$ in alkaline solution containing $FeSO_4$ at 16—18° to 6-*hydroxy*-8-*methoxycoumarin*, m.p. 239—240°. Hippuric acid, anhyd. NaOAc, Ac_2O, and (I) at 115—120° afford α-3-*methoxy*-2-*acetoxybenzimido-cinnamic anhydride*, m.p. 158—159°, and 3-*benzamido*-8-*methoxycoumarin*, m.p. 207—208°. H. W.

Heterocyclic compounds. IX. Coumarins from substituted resacetophenones and aceto-acetic ester. R. D. Desai and M. Ekhlas (Proc. Indian Acad. Sci., 1938, **8**, A, 567—577; cf. A., 1938, II, 152, 373).—$CH_2Ac{\cdot}CO_2Et$, 2 : 4-$(OH)_2C_6H_3{\cdot}COMe$, and $POCl_3$–C_6H_6 at 100° (bath) (general method *A*) give 7- (I), m.p. 212° (*carbethoxy*-derivative, m.p. 141°) and a little 5-hydroxy-6-acetyl-4-methylcoumarin, m.p. 164—165°. (I) is reduced (Clemmensen) to 7-hydroxy-4-methyl-6-ethylcoumarin. 2 : 4-Dihydroxy-5-ethylacetophenone gives (method *A*) 5-hydroxy-6-acetyl-4-methyl-8-ethylcoumarin (II), m.p. 169° (*Me ether*, m.p. 173°; *Ac* derivative, m.p. 149°; semicarbazone, m.p. >285°), reduced by Zn–Hg to 5-hydroxy-4-methyl-6 : 8-diethylcoumarin. (II) and Ac_2O–NaOAc at 170—180° (oil-bath) give 5-*acetyl*-4′ : 6-*dimethyl*-8′-*ethylcoumarino*-5′ : 6′-2 : 3-γ-*pyrone*, m.p. 173°. Me 2 : 4-dihydroxy-5-ethylbenzoate, $CH_2Ac{\cdot}CO_2Et$, and 73% H_2SO_4 at 0° afford *Me* 5-*hydroxy*-4-*methyl*-8-*ethylcoumarin*-6-*carboxylate*, m.p. 185—186°, converted by 10% aq. NaOH at room temp. (3 days) into the 6-*carboxylic acid*, m.p. 240° (decomp.), decarboxylated at 250° to 5-hydroxy-4-methyl-6-ethylcoumarin, m.p. 211—212°, the *Ac* derivative, m.p. 112—113°, of which is transformed (Fries) by $AlCl_3$ at 140—145° (oil-bath) into (II). 2 : 4-Dihydroxy-6-methylacetophenone [*A*] affords 5-*hydroxy*-6-*acetyl*-4 : 7-*dimethylcoumarin* (III), m.p. 178° (*Ac* derivative, m.p. 160°; semicarbazone, m.p. >280°), and some 5-hydroxy-4 : 7-dimethylcoumarin, m.p. 258—259° [*Ac* derivative, m.p. 202°, is transformed into (III) (Fries)], also obtained from orcinol and $CH_2Ac{\cdot}CO_2Et$. Gallacetophenone [*A*] gives 7 : 8-

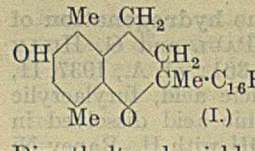
dihydroxy-6-*acetyl*-4-*methylcoumarin*, m.p. 148° [not obtained from 7 : 8-diacetoxy-4-methylcoumarin (Fries)], and 2 : 4-dihydroxypropiophenone [*A*] affords 7-hydroxy-6-propionyl-4-methylcoumarin, m.p. 227—228° (cf. Limaye *et al.*, Rasáyanam, 1937, **1**, 96) (Ac derivative, m.p. 132°; semicarbazone, m.p. >285°; *carbethoxy*-derivative, m.p. 132°; 3-*Br*-derivative, m.p. 140°), converted by Ac_2O–NaOAc at 170—180° into 4 : 2′ : 3′-*trimethylcoumarino*-7 : 6-*γ*-*pyrone*, m.p. >270°. 7-*Hydroxy*-6-*butyryl*-4-*methylcoumarin*, m.p. 151° (*Ac* derivative, m.p. 156°), is converted into 4 : 2′-*dimethyl*-3′-*ethylcoumarino*-7 : 6-*γ*-*pyrone*, m.p. 244—245°. *m*-$C_6H_4(OH)_2$ and BzCl–$AlCl_3$–$PhNO_2$ at room temp. (48 hr.) give 4-benzoylresorcinol, m.p. 145°, in 70% yield (cf. A., 1936, 1245), which [*A*] affords 7-hydroxy-6-benzoyl-4-methylcoumarin, m.p. 180° (semicarbazone, m.p. 240°), converted into 4-methyl-4′-phenylcoumarino-7 : 6-α-pyrone, m.p. 255°. Resacetophenone and Br–AcOH at room temp. (24 hr.) give the 5- or 3-Br-derivative (V), m.p. 167° (*Me*$_2$ *ether*, m.p. 146°; *Ac*$_2$ derivative, m.p. 161—162°), and a little Br_2-compound, m.p. 173—174°. (V), β-Me resacetophenonecarboxylate, 2 : 4- or 4 : 6-diacetylresorcinol, and quinacetophenone (indefinite) do not react [*A*]. 4-Acetyl-, -propionyl, or -butyryl-α-naphthol with $CH_2Ac{\cdot}CO_2Et$ and H_2SO_4 or $POCl_3$ gives only 4-methyl-1 : 2-α-naphthapyrone. Thus substituents as Br, CO_2Me, and acyl hinder the coumarin condensation, this effect in the case of COR groups being in the order R = Ph>Me>Et>Pr. An electronic conception of the effect of substituents is discussed.

A. T. P.

Esters of α-tocopherol. V. Demole, O. Isler, B. H. Ringler, H. Salomon, and P. Karrer (Helv. Chim. Acta, 1939, **22**, 65—68).—dl-α-*Tocopheryl acetate* (I), b.p. 184°/0·01 mm., is obtained from *dl*-α-tocopherol (II), anhyd. C_5H_5N, and Ac_2O at room temp. and then at 60° or by condensing trimethylquinol with phytyl bromide by $ZnCl_2$ in light petroleum and treating the product with Ac_2O containing H_2SO_4 at 40°. (I) is not autoxidisable and is not attacked by $AgNO_3$ or $AuCl_3$. The corresponding *propionate* and *butyrate*, b.p. 230°/0·25 mm., are described. The *hexoate*, *succinate*, *benzoate*, and *stearate* have been prepared; the last of these is cryst. The esters are not inferior to (II) in vitamin-*E* activity. H. W.

Potentiometric determination of the tocopherols. Behaviour of *dl*-α-tocopherol when irradiated. P. Karrer and H. Keller (Helv. Chim. Acta, 1939, **22**, 253—259).—The following method is recommended for the elimination of the "carotenoid" error in the potentiometric determination of tocopherols (I) by titration with $AuCl_3$ (A., 1938, II, 450). The total reducing matter is determined in one sample of the unsaponifiable matter. A second sample is fully acetylated by treatment with Ac_2O in C_5H_5N at 100 for 2 hr. The mixture is diluted with light petroleum and the solution is washed with dil. HCl and then with H_2O until neutral. After removal of the light petroleum the residue is determined potentiometrically. Since (I) are thereby converted into their non-reducing acetates, the reducing power of the acetylated sample is ascribed entirely to the carotenoids. The difference between the two titrations is ∞ (I). Solutions of *dl*-α-tocopherol in EtOH gradually lose their reducing power when exposed to ultra-violet light in presence or absence of air; the product has not been identified. H. W.

Lower homologues of α-tocopherol. β-Tocopherol. Constitution-specificity of vitamin-*E* action. P. Karrer and H. Fritzsche (Helv. Chim. Acta, 1939, **22**, 260—263; cf. A., 1938, II, 450).—For the production of max. vitamin-*E* activity the presence of 3 Me groups in the aromatic nucleus of tocol is necessary (α-tocopherol). Substances with 2 Me in any positions are active but the therapeutic dose is 3—4 times that of the Me_3 compound. A single Me in the aromatic nucleus is not causative of -*E* activity. Since it does not appear possible to replace the phytol residue by another group without loss of -*E* activity, the conditions necessary for an active product appear very narrow. *m*-OH·C_6H_4·OMe, phytol, HCO_2H, and C_6H_6 at 100° give a *methyltocol*, devoid of physiological activity. 5 : 7-Dimethyltocol (*loc. cit.*) is characterised by a cryst. p-*nitrophenylurethane*, m.p. 90°, and *allophanate*, m.p. 150°. *dl*-5 : 8-Dimethyltocol yields a p-*nitrophenylurethane*, m.p. ~91°, and an *allophanate*, m.p. 154—155°, which do not depress the m.p. of the corresponding compounds from β-tocopherol, which is therefore (I). H. W.



(I.)

Constitution of the compound obtained from trimethylquinol and crotyl bromide. P. Karrer and R. Escher (Helv. Chim. Acta, 1939, **22**, 264).—The formation of $COMe_2$ when the compound is oxidised (Oppenauer) and then degraded with CrO_3 shows that it is 6-hydroxy-2 : 5 : 7 : 8-tetramethylchroman as previously assumed (A., 1938, II, 450).

H. W.

Specificity of vitamin-*E* action. F. von Werder, T. Moll, and F. Jung (Z. physiol. Chem., 1939, **257**, 129—139; cf. A., 1938, II, 359; 1939, II, 82).—The following were active in the doses mentioned: 3 mg., *dl*-α-tocopherol; 50 mg., 6-acetoxy-2 : 5 : 7 : 8-tetramethylchromone; 100 mg., 2 : 5-dimethylquinol, duroquinol (I) and its n-*nonadecyl ether*, m.p. 105—106° [from the mother-liquors from (II)], *ψ*-cumoquinol (IV) and its *benzoate*, m.p. 150—151° [from trimethylquinol (III) in C_5H_5N in a stream of H_2 and BzCl], and chroman. The following were inactive in the doses given: 20 mg., α-tocopherylquinone; 30 mg., 2 : 5 : 7 : 8-*tetramethylchroman*, m.p. 48° [obtained by reduction (Pt–H_2) of the corresponding chromone in 96% AcOH], and 5-hydroxy-2 : 4 : 6 : 7-tetramethylcoumarone; 50 mg., the ε-(1′ : 1′ : 3′-*trimethyl*-2′-cyclo*hexyl*)-*γ*-*methylamyl ether* (*allophanate*, m.p. 173—174°) of (I) [from (I), and ε-(1′ : 1′ : 3′-trimethyl-2′-*cyclo*hexyl-*γ*-methyl)amyl bromide (V) in EtOH at 80° in a stream of H_2 with KOH in EtOH, the product being adsorbed on Al_2O_3 and eluted with light petroleum], 1 : 2 : 4 : 5 : 3 : 6-$C_6Me_3Ac(OH)_2$ and -$C_6Me_3Et(OH)_2$; 100 mg., 2 : 6-dimethylquinol, the *bis*-n-*nonadecyl ether* (II), m.p. 97—98° of (I) [from (I) and *n*-nonadecyl bromide in EtOH in a stream of H_2 at 85° with KOH in EtOH], the *bis*-β-*iodopropionate*,

m.p. 126—127°, of (IV) [from (III) and $CH_2I{\cdot}CH_2{\cdot}COCl$ in $PhNO_2$ under N_2 with $AlCl_3$], 2 : 3-dimethylnaphthoquinone, coumaran, 6-*hydroxy*-2 : 5 : 7 : 8-*tetramethylchroman*, m.p. 145° (from the corresponding chromone in 96% AcOH and Pt–H_2), 5-hydroxy-2 : 4 : 6 : 7-tetramethylcoumaran, and 6-*deoxy*-dl-α-*tocopherol*, b.p. 180—182°/0·1 mm. [from 1 : 2 : 3 : 6-$C_6H_2Me_3{\cdot}OH$ in light petroleum with *o*-$C_6H_4(COBr)_2$ and $ZnCl_2$, impurities being removed from the product by adsorption on Al_2O_3]. The high toxicity of naphthoquinone in doses of 50 and 100 mg. prevents its activity from being determined with rats. The prep. of the following is described: the 4-β-*methylamyl ether* (*allophanate*, m.p. 206°) of (I) [from (I) and $CHMeBu^{\beta}Br$ in EtOH in a current of H_2 at 85° and N-KOH in EtOH], n-*nonadecyl bromide*, m.p. 38—39° [from the Et ester of the corresponding acid by reduction (EtOH–Na) and treatment of the resulting *n*-nonadecyl alcohol with PBr_3], an *allyl ether*, m.p. 83—84° (probably 2 : 3 : 6-trimethyl-1-allylquinol), of (III) [from (IV) at 60° in N_2 and $CH_2{:}CH{\cdot}CH_2Br$ with KOH in EtOH followed by adsorption of the product on Al_2O_3 and elution with C_6H_6–light petroleum], the n-*octyl*, m.p. 72—73° [from (IV) and $C_8H_{17}I$ in EtOH at 80° in H_2 with N-KOH in EtOH followed by distillation of the product and crystallisation and adsorption on Al_2O_3 of the portion of b.p. 180—185°/1·5 mm.], and the ε-(1′ : 1′ : 3′-*trimethyl*-2′-cyclo*hexyl*)-γ-*methylamyl ether* (*allophanate*, m.p. 128°) of (IV) [from (III) and (V) in EtOH with KOH in EtOH at 85° followed by distillation of the product, the fraction of b.p. 200°/0·8 mm. being converted into allophanate] and 2 : 5 : 7 : 8-*tetramethyl*- (VI), m.p. 116° (from 1 : 2 : 4 : 6-$C_6H_2Me_3{\cdot}OH$ in EtOAc and P_2O_5), and 5 : 7 : 8-*trimethyl*-2-*styryl-chromone*, m.p. 152° [from (VI), NaOH in EtOH, and PhCHO]. The absorption max. of the coumarans are at slightly longer λ than are those of the chromans. Possibly the simple chromans are inactive because of their stability which prevents them playing a part in a species of oxidation–reduction mechanism (quinol–quinone transformation). W. McC.

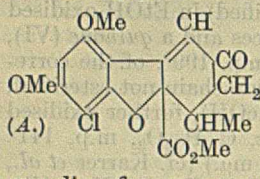
Antisterility factors (vitamin-*E*). VI. Oxidation products of tocopherols and of simple analogous models. W. John, E. Dietzel, and W. Emte (Z. physiol. Chem., 1939, **257**, 173—189; cf. A., 1938, II, 241, 359).—Details of the prep. of α-tocopherylquinone (I) are given; when $AgNO_3$ is the oxidising agent red substances are produced as a result of further oxidation. Such substances are also produced in greater yield during the prep. of β-tocopherylquinone (II) from β-tocopherol by oxidation with $AgNO_3$; this oxidation is also achieved with $FeCl_3$. (I) in light petroleum is reduced to α-tocopherylquinol (III) (absorption curve almost identical with that of duroquinol) [*triacetate*, m.p. 75°, obtained by boiling (I) with Ac_2O, NaOAc, and Zn] by Pd–H_2 and by Zn–AcOH. (III) is very readily re-oxidised to (I) by atm. O_2. α-Tocopherol (IV) is obtained from (I) by boiling in AcOH with Zn and HBr or by heating with Zn and HCl in EtOH and from (III) by heating with strong acid. Reductive esterification of (I) in Et_2O with *p*-$C_6H_4Br{\cdot}COCl$ and $Na_2S_2O_4$ gives a *di*-p-*bromobenzoate*, m.p. 114°, and treatment in MeOH with Me_2SO_4, NaOH, and $Na_2S_2O_4$ gives the *Me*$_2$ *ether* (*dinitrobenzoate*, m.p. 57°) of (III). Similarly (II) gives the *Me*$_2$ *ether* of β-tocopherylquinol. 6-Hydroxy-2 : 5 : 7 : 8-tetramethylchroman (V) (*acetate*, m.p. 102°; 6-OH not esterified) in EtOH oxidised with $AgNO_3$ gives red substances and a *quinone* (VI), m.p. 79° (*di*-p-*bromobenzoate*, m.p. 199°, of the corresponding quinol; OH of the side-chain not esterified, readily attacked by CrO_3 in AcOH), further oxidised by $AgNO_3$ to a red *substance*, $C_{12}H_{14}O_3$, m.p. 141° (absorption max. 275 and 365 mμ.) (cf. Karrer *et al.*, *ibid.*, 450), reconverted into (V) by Zn–AcOH. (VI), which is also obtained without production of red substances by oxidation of (V) with $FeCl_3$, yields the *triacetate*, m.p. 104°, of 2 : 4 : 5-trimethyl-1-γ-hydroxybutylquinol when boiled with Ac_2O, NaOAc, and Zn. 6-Hydroxy-2 : 2 : 5 : 7 : 8-pentamethylchroman (VII) in EtOH oxidised with $FeCl_3$ gives a *quinone* (VIII), m.p. 62° (*di*-p-*bromobenzoate*, m.p. 202°, of the corresponding quinol, resistant to oxidation by CrO_3), also obtained together with red substances when $AgNO_3$ replaces $FeCl_3$. (VIII), which is further oxidised by $AgNO_3$ to a red *substance*, m.p. 109°, is reduced by Zn–AcOH to the corresponding quinol, little or no (VII) being produced, and is converted into the *triacetate*, m.p. 113°, of 2 : 4 : 5-trimethyl-1-γ-hydroxy-*iso*amylquinol by Ac_2O, NaOAc, and Zn. 6-Hydroxy-5 : 7 : 8-trimethyl-3 : 4-dihydrocoumarin is quantitatively oxidised by $AgNO_3$ to *Et* β-2 : 4 : 5-*trimethylbenzoquinonylpropionate*, m.p. 59·6°, when the solvent is boiling EtOH and to the corresponding *Me* ester, m.p. 33°, when it is boiling MeOH. (I) has no vitamin-*E* activity. The monocetyl ether of duroquinol (IX) in $COMe_2$ boiled for 2 hr. with $AgNO_3$ is converted quantitatively into (IX) and cetyl alcohol. Other mono-ethers of (IX) and of ψ-cumoquinol are also hydrolysed in the same way by $AgNO_3$ and by $FeCl_3$ (cf. Karrer *et al.*, *ibid.*, 197). The light absorption max. of coumarans are higher and at shorter λ than are those of similarly substituted chromans. In (IV) the O bridge is probably united to *tert.* C. The tocopherols are probably chroman derivatives. W. McC.

Synthesis of 3 : 8-dimethoxyflavone. K. Aso (J. Agric. Chem. Soc. Japan, 1939, **15**, 59—60).—The *substance*, m.p. 156—157°, is obtained by condensation of 2-hydroxy-3 : ω-dimethoxyacetophenone with Bz_2O and NaOBz. The absorption spectrum has max. at 332 and 392 mμ. J. N. A.

Simultaneous multiple alkylation of phenols. Synthesis of a phenolic coumarone involving the condensation of diethyl ketone with resorcinol. J. B. Niederl and V. Niederl (J. Amer. Chem. Soc., 1939, **61**, 348—350).—*m*-$C_3H_4(OH)_2$ (1 mol.), $COEt_2$ (2 mols.), and HCl in AcOH at room temp. give 5-*hydroxy*-1-*methyl*-2-*ethyl*-4-α-*ethylpropenyl*-1 : 2-*dihydrobenzfuran*, m.p. 134—135° [*acetate*, m.p. 42°, b.p. 158°/4 mm. (*dibromide*, m.p. 168—170°); *phenylurethane*, m.p. 155—156°; *Br*-derivative *dibromide*, m.p. 165°]. R. S. C.

Biochemistry of micro-organisms. LX. Griseofulvin, a metabolic product of *Penicillium griseo-fulvum*, Dierckx. A. E. Oxford, H. Raistrick, and P. Simonart (Biochem. J., 1939, **33**,

240—248; cf. A., 1935, 786).—The dry micro-organism, propagated at 30° for 65—85 days on a medium containing glucose, $NaNO_3$, KH_2PO_4, KCl, $MgSO_4$, and $FeSO_4$, yields ~ 1·5% of *griseofulvin* (I), probably



(*A*), m.p. 218—219°, $[\alpha]^{19}_{5461}$ +417° in $COMe_2$ (*oxime*, m.p. 226—227°; sinters 120°, melts with loss of gas 120—140°, resolidifies at >140°). (I) in EtOH, hydrolysed with boiling 2N-H_2SO_4, gives the corresponding free monocarboxylic acid, *griseofulvic acid* (II), $C_{16}H_{15}O_6Cl$, m.p. 256—260°, $[\alpha]^{19}_{5461}$ +508° as Na salt in aq. $COMe_2$, further hydrolysed by boiling 0·5N-NaOH to *decarboxyfulvic acid* (III), $C_{15}H_{15}O_4Cl$, m.p. 138—140°, $[\alpha]^{18}_{5461}$ −31° in $COMe_2$, and *norgriseofulvic* acid (IV), $C_{15}H_{13}O_6Cl$, m.p. 260° (decomp.), $[\alpha]^{18}_{5461}$ +609° as Na salt in H_2O. (III) and (IV) are also obtained directly from (I) by boiling with dil. aq. NaOH. (II) and (IV) in Et_2O with CH_2N_2 give (I) together with iso*griseofulvin*, $C_{17}H_{17}O_6Cl$, m.p. 198—200°, $[\alpha]^{19}_{5461}$ +265° in $COMe_2$. Catalytic reduction (Pd–norit–H_2) of (I) in EtOAc gives *dihydrogriseofulvin*, m.p. 194—196°, $[\alpha]^{18}_{5461}$ −33° in $COMe_2$ (*compound*, m.p. 264—266°, probably 2 : 4-dinitrophenylhydrazone, with Brady's reagent), and *tetrahydrogriseofulvin*, $C_{17}H_{21}O_5Cl$, m.p. 180°, not hydrolysed when boiled for 4 hr. with aq.-alcoholic N-H_2SO_4 or for 7 hr. with 0·5N-NaOH. (I), (II), and (III) in $COMe_2$ with $KMnO_4$ give 3-*chloro*-2-*hydroxy*-4 : 6-*dimethoxybenzoic acid*, m.p. 224° (decomp.) (with CH_2N_2 this gives Me 3-chloro-2 : 4 : 6-trimethoxybenzoate), and a monobasic *dimethoxy-acid*, $C_{14}H_{15}O_7Cl$, m.p. 200° (decomp.), $[\alpha]^{18}_{5790}$ −24° as Na salt in 20% aq. MeOH, from which Ac_2O in C_5H_5N at 37° for several days eliminates H_2O, producing the neutral *substance*, $C_{14}H_{13}O_6Cl$, m.p. 220°. (I) with KOH at 225—250° for 1 hr. gives orcinol. When the KCl of the medium is replaced by KBr no metabolic product containing Br is obtained although growth of the micro-organism occurs. When the medium for the isolation of fulvic acid is used no (I) is obtained.

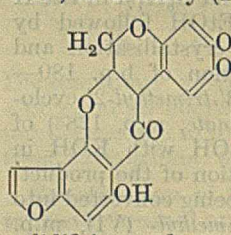
W. McC.

Condensation product of 5-methylcoumaranone. W. Baker and R. Banks (J.C.S., 1939, 279—280).—5-Methylcoumaranone and Na give a bimol. compound, isolated as 3-*acetoxy*-5 : 5′-*dimethyl*-2 : 3′-*dicoumaronyl*, m.p. 127°, which with AcOH–HCl affords s-*tris*-5-*methyl*-2 : 3-*coumaronobenzene*, m.p. >440° (mol. wt. determination). F. R. S.

Syntheses of furanochromones and furanoflavones. B. L. Manjunath and E. Seetharamiah (Ber., 1939, **72**, [*B*], 97—100).—3-Hydroxy-4-methoxyacetylbenzfuran (I) is converted by Ac_2O and NaOAc at 165—170° into 3-*methoxy*-2-*methyl*-2′ : 3′-7 : 8-*furanochromone*, m.p. 154·5°, converted by HI (*d* 1·7) in Ac_2O at 140° into 2-*methyl*-2′ : 3′-7 : 8-*furanochromonol*, m.p. 240—242°. Similarly (I), $(CHPh{:}CH{\cdot}CO)_2O$, and $CHPh{:}CH{\cdot}CO_2Na$ at 180—190° yield 3-*methoxy*-2-*styryl*-2′ : 3′-7 : 8-*furanochromone*, m.p. 173°, whence 2-β-*phenylethyl*-2′ : 3′-7 : 8-*furanochromonol*, m.p. 154—156°. (I), anisic anhydride, and Na anisate afford 3 : 4″-*dimethoxy*-2′ : 3′-7 : 8-*furanoflavone*, m.p. 166—168°, reduced to 4″-*hydroxy*-2′ : 3′-7 : 8-*furanoflavanol*, gradual decomp. 271—282° after softening at 271°, converted by boiling Ac_2O containing a trace of C_5H_5N into the *diacetate*, m.p. 164—166°. Similarly, veratric anhydride gives 3 : 3″ : 4″-*trimethoxy*-2′ : 3′-7 : 8-*furanoflavone*, m.p. 184°, and 3″ : 4″-*dihydroxy*-2′ : 3′-7 : 8-*furanoflavonol*, decomp. 282—299° after softening at 282° in a sealed capillary (*Ac* derivative, m.p. 176—178°), and trimethylgallic anhydride affords 3 : 3″ : 4″ : 5″-*tetramethoxy*-2′ : 3′-7 : 8-*furanoflavone*, m.p. 158—159°, whence 3″ : 4″ : 5″-*trihydroxy*-2′ : 3′-7 : 8-*furanoflavonol*, decomp. 315° [*Ac* derivative, m.p. 234—236° (decomp.)]. H. W.

Crystalline solvates of inactive deguelin. L. D. Goodhue and H. L. Haller (J. Amer. Chem. Soc., 1939, **61**, 486—488).—Deguelin (modified prep. from "cubé") forms *solvates* with 1 mol. of $CHBr_3$, CCl_4, $CHCl_3$, or $(CH_2Br)_2$ and with 0·5 mol. of PhCHO, PhBr, or PhCl. R. S. C.

Constituents of derris root. I. T. M. Meyer and D. R. Koolhaas (Rec. trav. chim., 1939, **58**, 207—217).—A *ketone* ("*derride*"), $C_{18}H_{10}O_4(OMe)_2$, m.p. 162—163°, $[\alpha]$ −19° in C_6H_6, +13·7° in $COMe_2$ (*oxime*, m.p. 240°), isomeric with the compound, m.p. 183°, of Buckley (B., 1936, 1117), has been isolated



from the Et_2O extract of derris root. Derride gives no colour with $FeCl_3$, is not dehydrated by AcOH–H_2SO_4, and when boiled with NaOAc and I in EtOH gives the same dehydrocompound as that of Buckley's product, together with a substance, m.p. 176°, resolidifying and remelting at 252°. Derride probably has the structure of *iso*rotenone, but without the Pr^{β}. The Et_2O extract of Sumatra derris root contains sumatrol, *l*-α-toxicarol, and a *substance*, $C_{20}H_{16}O_7$, m.p. 244°, $[\alpha]_D$ +107° in C_6H_6, +189·1° in $COMe_2$, resembling toxicarol; the appended structure is suggested.

A. Li.

Self-condensation of ethyl methylenebisthioacetate. New method for the preparation of derivatives of 1 : 3-dithian. F. Challenger and S. A. Miller (J.C.S., 1939, 347—348).—Self-condensation of Et methylenebisthioacetate gives *Et* 1 : 3-*dithian*-5-*one*-4-*carboxylate*, m.p. 62° (2 : 4-*dinitrophenylhydrazone*, m.p. 147°), hydrolysed to methylenebisthioacetic acid (*Fe*^{III} salt). F. R. S.

Piperidine derivatives.—See B., 1939, 243.

Dimorphism of dipyridine cobaltous chloride. D. P. Mellor and B. S. Morris (J. Proc. Roy. Soc. New South Wales, 1938, **71**, 536—539).—The mol. wt. of the violet (I) and blue (II) form of dipyridine Co^{II} chloride is identical in $CHBr_3$ and in this solvent both forms have the same absorption spectrum and neither is a conductor at room temp. or during heating of the solution to 135°. In MeOH and H_2O (I) and (II) form pink solutions. The mol. conductivity of 0·0002N. solutions of (I) and (II) in EtOH is $320\Omega^{-1}$. This and the instantaneous and complete pptn. of AgCl on treating alcoholic solutions with $AgNO_3$ indicate that the substances can function as salts as well as non-electrolytes. The evidence favours the view that (I) and (II) are dimorphous and that it is unnecessary to

postulate *cis–trans* isomerism of square co-ordinated Co^{II} to explain their occurrence. H. W.

Pyridinium salts.—See B., 1939, 245, 247.

Pyridine-3-carboxdiethylamide [nicotindiethylamide]. Its detection in "Cormed." G. Baumgarten (Arch. Pharm., 1939, **277**, 86—91).—This amide is identified in the prep. "Cormed" by its *derivatives*, $C_{22}H_{28}O_2N_6S_2Cu$ [prep. from $Cu(CNS)_2$], softens at 165—170°, decomp. 180°, and $3[Cu(CNS)_2],4(C_{10}H_{14}ON_2)$. R. S. C.

Oxidative degradation of adermin. R. Kuhn and G. Wendt (Ber., 1939, **72**, [*B*], 305—309; cf. A., 1938, II, 373).—Adermin Me ether (I) is unchanged by $Pb(OAc)_4$ in AcOH at 60°; it is therefore not an α-glycol. Oxidation of vitamin-B_6 hydrochloride by 5N-CrO_3 in H_2SO_4 gives 0·86 mol. of AcOH. $KMnO_4$ (O ≡ 2) oxidises (I) in neutral aq. solution at 20° to a *lactone* (II), $C_9H_9O_3N$, m.p. 108°. With $KMnO_4$ (O ≡ 7) in alkaline solution (I) gives 3-methoxypyridine-4 : 5 : 6- or -2 : 4 : 5-tricarboxylic acid, anhydrised with loss of CO_2 to 3-*methoxypyridine*-4 : 5-*dicarboxylic anhydride*, m.p. 158° (Berl). The absorption spectrum of adermin (III) in 0·1N-HCl or 0·1N-NaOH is very similar to that of 3-hydroxypyridine and differs considerably from that of the 2- and 4-OH-compounds. A reversible displacement of the absorption spectrum by alkali is not observed. With the Folin–Denis reagent (III) gives a dark blue colour whereas (I) does not react. 3-Hydroxy- and 3-hydroxy-5-methyl-pyridine and 3-hydroxypyridine-5-carboxylic acid show the reaction, which is not given by 2-hydroxy-, 2-hydroxy-4 : 6-dimethyl-, 2 : 4-dihydroxy-6-methyl-3-ethyl-, 4-hydroxy-2 : 6-dimethyl-pyridine, or by 2-hydroxypyridine-5-carboxylic acid. The production of (II) proves that the CH_2·OH of (III) are vicinal to one another. (III) is therefore 3-hydroxy-2-methyl-4 : 5-dihydroxymethyl-, -6-methyl-4 : 5-dihydroxymethyl-, or -4-methyl-5 : 6-dihydroxymethyl-pyridine. H. W.

Vitamin-B_6, a derivative of 3-hydroxypyridine. R. Kuhn, H. Andersag, K. Westphal, and G. Wendt (Ber., 1939, **72**, [*B*], 309—310).—The synthesis of 3-methoxypyridine-4 : 5-dicarboxylic anhydride, m.p. 158°, identical with that derived from adermin (I), is announced but not described. Partial oxidation of adermin Me ether gives a methyl-3-methoxypyridinedicarboxylic acid which gives an anhydride which does not yield a colour with $FeSO_4$. CH_2·OH cannot therefore be attributed to $C_{(2)}$ or $C_{(6)}$ and (I) is therefore 3-hydroxy-2-methyl-4 : 5-dihydroxymethyl- or -6-methyl-4 : 5-dihydroxymethyl-pyridine. H. W.

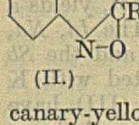
Constitution of adermin. R. Kuhn, G. Wendt, and K. Westphal (Ber., 1939, **72**, [*B*], 310—311).—Oxidation of adermin Me ether with $Ba(MnO_4)_2$ gives a methoxymethylpyridinedicarboxylic acid (+1·5H_2O) which does not contain CO_2H at $C_{(2)}$ or $C_{(6)}$ since it does not give a colour with $FeSO_4$. It is converted by hot Ac_2O into an anhydride, m.p. 64°, identified by comparison with synthetic 3-*methoxy*-2-*methylpyridine*-4 : 5-*dicarboxylic anhydride*. Adermin is therefore 3-hydroxy-2-methyl-4 : 5-dihydroxymethylpyridine. H. W.

Re-conversion of adermin methyl ether into adermin. R. Kuhn and G. Wendt (Ber., 1939, **72**, [*B*], 311—312).—Adermin Me ether is transformed by boiling 66% HBr into 3-*hydroxy*-2-*methyl*-4 : 5-*dibromomethylpyridine hydrobromide*, m.p. 217° (decomp.), which gives a dark blue colour with the Folin–Denis reagent and couples with diazotised *p*-NH_2·C_6H_4·SO_3H to an orange dye. It is converted by AgOAc in boiling H_2O followed by HCl into adermin hydrochloride, m.p. 200—201°, whence the free base, m.p. 159°. *Adermin hydrobromide* has m.p. 193° (decomp.). H. W.

Indolines.—See B., 1939, 248.

6 : 8-Dichlorobenzoylenecarbamide and the interaction of 5 : 7-dihalogenoisatoic anhydrides with ammonia. New reagent for sodium. F. E. Sheibley (J. Org. Chem., 1938, **3**, 414—423; cf. A., 1934, 307).—2 : 3 : 5 : 1-NH_2·$C_6H_2Cl_2$·CO_2H (I) is transformed by $CO(NH_2)_2$ at 140° into 6 : 8-*dichlorobenzoylenecarbamide* [6 : 8-*dibromo*-2 : 4-*diketo*-1 : 2 : 3 : 4-*tetrahydroquinazoline*] (II), m.p. 296° (corr.) after softening and undergoing an apparent change of cryst. form ~280°, and [3 : 5-*dichloro*-2-*aminobenzamide*, m.p. 182·5° (corr.), which is possibly an intermediate since it yields (II) when heated with $CO(NH_2)_2$ at 160—165°. (II) dissolved in KOH is a useful reagent for Na, with which it gives a *ppt.*, $C_6H_3O_2N_2Cl_2Na$,1·5H_2O. Boiling $ClCO_2Et$ and (I) give a *substance*, m.p. ~220°, and 5 : 7-*dichloroisatoic anhydride* (III), m.p. 261° (corr.; decomp.), also obtained by oxidation of tetrachloroindigotin by CrO_3 in AcOH. 5 : 7-*Dibromoisatoic anhydride* (IV), m.p. 263·5° (corr.; decomp.), is obtained analogously from tetrabromoindigotin. 28% NH_3 at 100° transforms (III) into (II) and (I). (IV) behaves similarly. H. W.

Heterocyclic compounds containing nitrogen. XXXVI. Preparation from *oo'*-dinitrotolan of a vat dye containing chlorine. P. Ruggli and H. Zaeslin (Helv. Chim. Acta, 1939, **22**, 134—139; cf. A., 1938, II, 460).—Chlorination of 2 : 2'-dinitrostilbene in AcOH in the light of an arc lamp gives mainly the normal dichloride with some red 2-(3' : 5'-*dichloro*-2'-*nitrophenyl*)*isatogen*, $C_6H_4<^{CO}_{NO}>CR$ (R = 3 : 5 : 2-$C_6H_2Cl_2$·NO_2) (I), m.p. 185—186°. The yellow substance, m.p. 177° (Ruggli *et al.*, A., 1938, II, 437), obtained by the action of NaI in $COMe_2$ on ββ-dichloro-α-keto-α-2-nitrosophenyl-β-3' : 5'-dichloro-6'-nitrophenylethane is identified as 2-(3' : 5'-*dichloro*-2'-*nitrophenyl*)iso*isatogen* (II); it is also obtained by isomerisation of (I) by EtOH–conc. HCl. It is stable towards halogen and only slowly attacked by $KMnO_4$–Na_2CO_3. *o*-NO_2·C_6H_4·CO_2H and an acid, m.p. 225°, in small amount are the sole cryst. products of its oxidation. Reduction of (II) with $SnCl_2$ in AcOH–HCl gives a canary-yellow *compound*, $C_{14}H_6O_2N_2Cl_2$, m.p. 224—225°, and a red-brown *substance*, $C_{14}H_8ON_2Cl_2$, m.p. 236°, which possibly belong to the di-indole series. Complete reduction of (II) (H_2–Ni; NHPh·NH_2; Zn dust and AcOH) affords a vat which on exposure to air after addition of NH_3 deposits 3 : 5'-*dichloro*-2'-



(II.)

aminophenylindolone, $C_6H_4<^{CO}_{N=}>C{\cdot}C_6H_6Cl_2{\cdot}NH_2$, m.p. 203—204° (slight decomp.) (*semicarbazone*), best obtained by direct catalytic hydrogenation of (II). H. W.

Heterocyclic compounds containing nitrogen. XXXVIII. *iso*Isatogens. P. Ruggli, E. Caspar, and B. Hegedüs (Helv. Chim. Acta, 1939, **22**, 140—146).—The best reagent for the isomerisation of 6-carbethoxy-2-phenylisatogen (A., 1919, *i*, 221) to 6-carbethoxy-2-phenyl*iso*isatogen (I), m.p. 100·5°, is H_2SO_4–EtOH, which also slowly transforms 2-phenylisatogen (II) into 2-*phenyl*iso*isatogen* (III), m.p. 94°. (I) is reduced by Zn dust and warm AcOH to 6-carbethoxy-2-phenylindoxyl and does not appear to react with CH_2N_2. (III) dissolves in CH_2N_2–Et_2O without evolution of gas and is recovered mixed with some resin when the solution is evaporated. Reduction of (II) with Zn dust and AcOH gives the additive product of phenylindoxyl and phenylindolone whilst catalytic reduction (Raney Ni in Ac_2O at room temp.) leads to acetyl-2-phenylindoxyl. Oximation of (II) gives 15% of the *C*-oxime and 37% of the *N*-oxime (IV). Similar treatment of (III) gives a small amount of 2-phenylindoloneoxime obviously due to a reducing action of the NH_2OH salt. The sole main product of the change appears to be (IV). PhNCO does not appear to react with (II) or (III). H. W.

Heterocyclic compounds containing nitrogen. XXXIX. Reduction of *o*-nitrobenzil and a further synthesis of 2-phenylisatogen. P. Ruggli and B. Hegedüs (Helv. Chim. Acta, 1939, **22**, 147—150).—Oxidation of *o*-nitrotolan with a considerable excess of CrO_3 in AcOH gives *o*-nitrobenzil (I), m.p. 100°. Interruption of the catalytic hydrogenation (Raney Ni in moist EtOAc) after absorption of 3 H gives 2-phenylisatogen in 34% yield which diminishes to 10% after absorption of 6 H. Hydrogenation in Ac_2O permits the isolation of the intermediately formed *o*-hydroxylaminobenzil as its Ac_1 derivative, *o*-COBz·C_6H_4·NAc·OH, m.p. 169—171° (decomp.) after incipient reddening at 165°. Reduction of (I) with Zn dust and AcOH affords exclusively the substance, $\left(C_6H_4<^{CO\text{-}}_{NH}>CPh\right)_2O$. H. W.

Isatindiresorcinol (tetrahydroxydiphenyloxindole) and some derivatives. E. Bureš and J. Hrabová (Coll. Czech. Chem. Comm., 1939, **11**, 39—46).—Isatin and resorcinol with $ZnCl_2$ at 115°, or when treated in H_2O with conc. H_2SO_4, yield tetrahydroxydiphenyloxindole (I), which gives with Br in AcOH, Br_2- and Br_4-compounds, with I in aq. KI–KOH, a I_2-, and with Cl_2 in AcOH, a Cl_8-compound (II). Condensation (conc. H_2SO_4) of isatin with resorcinol, and bromination of the product, yields a *tetrabromodisulphonic acid* (III) of (I). The *Li*, *Na*, and *K* derivatives of all these phenols, and the *Sb* derivatives (solution in aq. NaOH treated with K antimonyl tartrate) of all except (II) and (III), have been prepared. A. Li.

Indoles. IV. Utilisation of the Japp–Klingemann reaction for the preparation of substituted indolecarboxylic acids. G. K. Hughes and F. Lions [with, in part, J. G. McKean, A. J. Murray, V. Callanan, D. H. Freeman, C. S. Ralph, R. Rassack, J. Dombroski, F. Finch, R. Andrews, R. C. Betty, R. H. Scott, C. W. Vernon, A. Flack, and C. H. Laurence] (J. Proc. Roy. Soc. New South Wales, 1938, **71**, 475—485; cf. A., 1933, 835).—The substituted phenylhydrazones of Et α-acetylpropionate, α-acetylbutyrate, α-acetylhexoate, and α-acetyl-β-phenylpropionate are obtained by use of the requisite diazonium chloride. These are cyclised by dry HCl in abs. EtOH and the indole esters are hydrolysed by KOH. The following compounds are described: (from α-$C_{10}H_7{\cdot}NH_2$) *Et pyruvate*-1-*naphthylhydrazone*, m.p. 125°; *Et* 6 : 7-*benzindole*-8-*carboxylate*, m.p. 170° (*acid*, m.p. 204—205°); *Et* 7-*methyl*-6 : 7-*benzindole*-8-*carboxylate*, m.p. 176°; *Et* 7-n-*propyl*-5 : 6-*benzindole*-8-*carboxylate*, m.p. 185—186° (*acid*, m.p. 182—183°); *Et* 7-*phenyl*-5 : 6-*benzindole*-8-*carboxylate*, m.p. 187°: (from β-$C_{10}H_7{\cdot}NH_2$) *Et* 4 : 5-*benzindole*-2-*carboxylate*, m.p. 161° (*acid*, m.p. 160°); *Et* 1-*methyl*-4 : 5-*benzindole*-2-*carboxylate*, m.p. 176° (*acid*, m.p. 176°); *Et* 1-*phenyl*-4 : 5-*benzindole*-2-*carboxylate*, m.p. 179° (*acid*, m.p. 201°); (from *o*-OEt·$C_6H_4{\cdot}NH_2$) *Et* 7-*ethoxyindole*-2-*carboxylate*, b.p. 170—175°/2 mm., m.p. 160°; Et 7-*ethoxy*-3-n-*propylindole*-2-*carboxylate*, b.p. 177°/2 mm. (*acid*, m.p. 162°); *Et* 7-*ethoxy*-3-*phenylindole*-2-*carboxylate*, b.p. 216—224°/2 mm., m.p. 93° (*acid*, m.p. 206—207°); (from *p*-OEt·$C_6H_4{\cdot}NH_2$) *Et* 5-*ethoxyindole*-2-*carboxylate*, m.p. 155—156°; *Et* 5-*ethoxy*-3-*methylindole*-2-*carboxylate*, m.p. 167° (*acid*, m.p. 178°); *Et* 5-*ethoxy*-3-n-*propylindole*-2-*carboxylate*, m.p. 142° (*acid*, m.p. 178°); *Et* 5-*ethoxy*-3-*phenylindole*-2-*carboxylate*, m.p. 148—149° (*acid*, m.p. 183—185°); (from *p*-OMe·$C_6H_4{\cdot}NH_2$) *Et* 5-*methoxyindole*-2-*carboxylate*, m.p. 152—153°; *Et* 5-*methoxy*-3-*methyl*-, m.p. 146—147°, -3-n-*propyl*-, m.p. 106°, -2-*phenyl*-, m.p. 121—122°, -*indole*-2-*carboxylate*; (from *p*-$C_6H_4Br{\cdot}NH_2$) *Et* 5-*bromoindole*-2-*carboxylate*, m.p. 153° [*acid*, m.p. 188° (decomp.)]; *Et* 5-*bromo*-3-*methylindole*-2-*carboxylate*, m.p. 163° (*acid*, m.p. 217—218°); *Et* 5-*bromo*-3-n-*propylindole*-2-*carboxylate*, m.p. 149° (*acid*, m.p. 160°); *Et* 5-*bromo*-3-*phenylindole*-2-*carboxylate*, m.p. 185° (*acid*, m.p. 216°); (from *p*-$NH_2{\cdot}C_6H_4{\cdot}CO_2Et$) *Et pyruvate*-p-*carbethoxyphenylhydrazone*, m.p. 137°, unaffected by HCl or by boiling AcOH; *Et* α-*ketobutyrate*-p-*carbethoxyphenylhydrazone*, m.p. 141°; *Et* 5-*carbethoxy*-3-*methylindole*-2-*carboxylate*, m.p. 181°, and 3-*methylindole*-2 : 5-*dicarboxylic acid*, m.p. 298°; Et_2 3-n-*propylindole*-2 : 5-*dicarboxylate*, m.p. 133—134° (dibasic *acid*, m.p. 282°); Et_2 3-*phenylindole*-2 : 5-*dicarboxylate*, m.p. 196—197° (dibasic *acid*, m.p. 290° after softening at 270°). H. W.

Indoles. VI. Application of the Fischer synthesis to some *cyclo*hexyl ketones. G. K. Hughes and F. Lions (J. Proc. Roy. Soc. New South Wales, 1938, **71**, 494—502).—*cyclo*Hexyl Me ketone (*dinitrophenylhydrazone*, m.p. 128°) and NHPh·NH_2 give a non-cryst. phenylhydrazone, transformed by boiling AcOH into 1-cyclo*hexane*-3-2-*methylindoleninespiran* $N<^{C_6H_4}_{CMe}>C<^{CH_2{\cdot}CH_2}_{CH_2{\cdot}CH_2}>CH_2$, b.p. 131—134°/2 mm. [*picrate*, m.p. 188°; *methiodide* (I), m.p. 248°; *ethiodide*, m.p. 252°]. (I), $CH(OEt)_2$, and anhyd. C_5H_5N at 100° yield 3 : 3′-*di*(cyclo*hexanespiran*)-1 : 1′-*dimethylindocarbocyanine*, m.p. 265°; the corresponding

1 : 1′-Et_2 compound has m.p. 265°. (I) and *p*-NMe_2·C_6H_4·CHO in boiling MeOH afford 1-cyclo*hexane*-3-2-p-*dimethylaminostyrylindoleninespiran methiodide*, m.p. 241°, whereas p-*dimethylaminobenzylidenedi*-2 *methyl*-3-cyclo*hexanespiranindolenine methiodide*, m.p. 248°, is obtained from the same reactants in other proportions. Anisole, *cyclo*hexanecarboxyl chloride, and $AlCl_3$ in CS_2 give cyclo*hexyl* p-*anisyl ketone*, b.p. 206—208°/26 mm., m.p. 66° (*dinitrophenylhydrazone*, m.p. 123°), the *phenylhydrazone*, m.p. 120°, of which passes in boiling glacial AcOH into 1-cyclo*hexane*-3 : 2-p-*anisylindoleninespiran*, b.p. 205—210°/1·2 mm., m.p. 107° (*picrate*, m.p. 211°; *methiodide*, m.p. 156°). Similarly the non-cryst. *phenylhydrazone* of *cyclo*hexyl Ph ketone is converted into 1-cyclo*hexane*-3-2-*phenylindoleninespiran*, b.p. 195—200°/1·5 mm., m.p. 86° (*picrate*, m.p. 170°; *methiodide*, m.p. 204°). cyclo*Hexyl Ph ketone dinitrophenylhydrazone* has m.p. 192°. cyclo*Hexyl veratryl ketone*, b.p. 221—223°/20 mm., m.p. 51° (*dinitrophenylhydrazone*, m.p. 147°), yields a *phenylhydrazone*, m.p. 190°, transformed by AcOH into 1-cyclo*hexane*-3-2-*veratrylindoleninespiran*, m.p. 152° (*picrate*, m.p. 217°; *methiodide*, m.p. 207°). H. W.

Syntheses in the series of chemotherapeutically active derivatives of sulphanilamide. B. Bobrański (Arch. Pharm., 1939, **277**, 75—86).—2- and 4-Chloroquinoline and *p*-NH_2·C_6H_4·SO_2·NH_2 at 170—180° give p-2-, m.p. 251° (*hydrochloride*, m.p. 264°), and p-4-*quinolylaminobenzenesulphonamide*, m.p. 262—263° [*hydrochloride*, m.p. 311° (decomp.; sinters at 300°)]. *p*-NHAc·C_6H_4·SO_2Cl and the appropriate aminoquinoline in hot C_5H_5N give 5-, m.p. 258° (decomp.), 6-, m.p. 282° (decomp.), 7-, m.p. 238°, and 8-p-*acetamidobenzenesulphonamidoquinoline*, m.p. 193°, hydrolysed by 15% HCl to the p-*aminobenzenesulphonamidoquinolines*, m.p. 230°, 201°, 206°, and 193·5°, respectively. R. S. C.

Quinoline derivatives [trypanocides].—See B., 1939, 326.

Antimalarials. I. Derivatives of 4-acetoacetyl-6-methoxyquinoline. W. H. Linnell and W. Rigby (Quart. J. Pharm., 1938, **11**, 722—728).—Et quininate with $COMe_2$–NaOEt affords 4-*acetoacetyl*-6-*methoxyquinoline* (I) [two cryst. forms (?), m.p. 90° and 99°] [*oxime*, m.p. 182° (corr.), converted by HCl–Et_2O into 5-(7′-*methoxy*-4′-*quinolyl*)-3-*methyl*isooxazole, m.p. 92—93° (corr.) (*phenylhydrazone*, m.p. 171—172°), converted by dil. HCl into 1-*phenyl*-5-(7′-*methoxy*-4′-*quinolyl*)-3-*methylpyrazole*, m.p. 94° (corr.)]. (I) with NH_3 yields 6-*methoxy*-4-(Δ$^{\beta}$-α-*keto*-γ-*aminobutenyl*)*quinoline*, m.p. 253—255°, and with bornylamine, 6-*methoxy*-4-(Δ$^{\beta}$-α-*keto*-γ-*bornylaminobutenyl*)-*quinoline*, m.p. 110° (corr.). F. O. H.

Abrin naphthalene-2-sulphonate, m.p. 192—194°, flavianate, decomp. 195°, picrolonate, decomp. 285—286°, and phosphotungstate.—See A., 1939, III, 296.

***aci*-Nitrobetaines.** F. Kröhnke and H. Schmeiss (Ber., 1939, **72**, [*B*], 440—445; cf. A., 1937, II, 208).—2 : 4-$(NO_2)C_6H_3$·CH_2Cl is converted by C_5H_5N in EtOH at 100° into 2 : 4-*dinitrobenzylpyridinum chloride* (I), decomp. >190° (corresponding *perchlorate*, m.p. 160—161°), also obtained less advantageously by the prolonged hydrolysis of ω-2 : 4-dinitrophenylphenacylpyridinium enol betaine. N-NaOH transforms (I) into the corresponding *nitrobetaine*, m.p. 124—126°, which is regarded, on account of its dark colour and its ability to condense with *p*-NO·C_6H_4·NMe_2 in EtOH containing piperidine to 2 : 4-dinitrophenyl-*N*-4′-dimethylaminophenylnitrone, m.p. 198° (decomp.), as a mesomeric equilibrium mixture of the *aci*- and the carbeniate zwitterion forms. 2 : 4-*Dinitrobenzyl*iso*quinolinium chloride*, m.p. 180°, is converted by alkali into a very unstable, blue, amorphous product. 2 : 4 : 6-*Trinitrobenzylpyridinium chloride*, m.p. 140—141° (decomp.) (corresponding *perchlorate*, decomp. >210°), obtained by the action of hot, conc. HCl on ω-trinitrophenylphenacylpyridinium enol betaine, is converted by 0·1N-NaOH or aq. $NHEt_2$ into the aci*nitrobetaine*, decomp. ~140° according to the rate of heating. 5-*Chloro*-2 : 4-*dinitrobenzylpyridinium chloride*, decomp. ~190° (corresponding *perchlorate*, m.p. 174—175°), yields a moderately stable *betaine* $C_{12}H_8O_4N_3Cl$, slow decomp. ~150°. 1 : 3 : 5-$C_6H_3Me(NO_2)_2$ and Br at 110° give 3 : 5-*dinitrobenzyl bromide*, b.p. 177°/0·3 mm., m.p. 65—66°, converted by C_5H_5N in EtOH at 100° into 3 : 5-*dinitrobenzylpyridinium bromide*, m.p. 273—274° (corresponding *perchlorate*, m.p. 191—192°), whence is derived 3 : 5-*dinitrophenyl*-N-4′-*dimethylaminophenylnitrone*, m.p. 239° (decomp.) (or, in an individual case, a *substance*, m.p. 191°), hydrolysed by 5N-H_2SO_4 to 3 : 5-$(NO_2)_2C_6H_3$·CHO, p-*Nitrodiphenylmethylpyridinium perchlorate*, m.p. 133°, yields the corresponding *dimethylaminophenylnitrone*, decomp. ~155°, hydrolysed to *p*-$C_6H_4Br_3$·NO_2. H. W.

Heterocyclic compounds derived from pyrocatechol ethers. I. Derivatives of 6 : 7-dimethoxyquinoline. F. Lions (J. Proc. Roy. Soc. New South Wales, 1938, **71**, 242—250).—4-Aminoveratrole (I) is converted by paracetaldehyde in presence of conc. HCl and $ZnCl_2$ into 6 : 7-dimethoxy-2-methylquinoline, b.p. 195—200°/4 mm., m.p. 103° (*methiodide*, m.p. 241°; ethiodide). CH_2Ac·CO_2Et and (I) in presence of a little 5N-HCl afford *Et* β-3 : 4-*dimethoxyanilinocrotonate*, m.p. 61°, readily cyclised in paraffin oil at 270° to 4-*hydroxy*-6 : 7-*dimethoxy*-2-*methylquinoline*, m.p. 280°. Similarly 3 : 4 : 1-$(OEt)_2C_6H_3$·NH_2, CH_2Ac·CO_2Et, and a little HCl yield non-cryst. *Et* β-3 : 4-*diethoxyanilinocrotonate*, cyclised at 280° to 4-*hydroxy*-6 : 7-*diethoxy*-2-*methylquinoline*, m.p. 211°. CH_2Ac·CO_2Et and (I) at 160° give 4-*acetoacetamidoveratrole*, m.p. 59°, transformed by cold, conc. H_2SO_4 into 2-*hydroxy*-6 : 7-*dimethoxy*-4-*methylquinoline*, m.p. 235°. Et *cyclo*hexanone-2-carboxylate and (I) in presence of 5N-HCl afford *Et* 2-3′ : 4′-*dimethoxyanilino*-Δ^1-cyclo*hexene*-1-*carboxylate*, m.p. 72° (yield 90—95%), which passes in paraffin at 270° into 5-*hydroxy*-7 : 8-*dimethoxy*-1 : 2 : 3 : 4-*tetrahydroacridine*, m.p. >300° (*hydrochloride*, m.p. 244°). Similarly, 3 : 4 : 1-$(OEt)_2C_6H_3$·NH_2 gives successively *Et* 2-3′ : 4′-*diethoxyanilino*-Δ^1-cyclo*hexene*-1-*carboxylate*, m.p. 44°, and 5-*hydroxy*-7 : 8-*diethoxy*-1 : 2 : 3 : 4-*tetrahydroacridine*, m.p. 281°. CH_2AcBz and (I) in presence of a little 5N-HCl yield *Ph* β-3 : 4-*dimethoxyanilino*-Δ$^{\alpha}$-

propenyl ketone, m.p. 100°, in nearly quant. yield; it is converted by cold, conc. H_2SO_4 into 6 : 7-*dimethoxy*-4-*phenyl*-2-*methylquinoline*, m.p. 142°. H. W.

Heterocyclic compounds derived from pyrocatechol ethers. II. 7 : 8-Dimethoxy- and 5 : 6 : 7-trimethoxy-quinolines. J. N. GRAVES, G. K. HUGHES, and F. LIONS (J. Proc. Roy. Soc. New South Wales, 1938, **71**, 251—254).—3-Aminoveratrole (I), $CH_2Ac{\cdot}CO_2Et$, and 5N-HCl at room temp. yield the non-cryst. *Et* β-2 : 3-*dimethoxyanilinocrotonate*, which passes in paraffin at 280° into 4-*hydroxy*-7 : 8-*dimethoxy*-2-*methylquinoline*, m.p. 212° (*picrate*, m.p. 230°). (I) is transformed by the successive action of $CH_2Ac{\cdot}CO_2Et$ at 145° and conc. H_2SO_4 at 0° into 2-*hydroxy*-7 : 8-*dimethoxy*-4-*methylquinoline*, m.p. 175°. Et *cyclo*hexanone-2-carboxylate (II), (I), and 5N-HCl at room temp. give a non-cryst. product which passes at 280° into 5-*hydroxy*-8 : 9-*dimethoxy*-1 : 2 : 3 : 4-*tetrahydroacridine*, m.p. 212° (decomp.) (*picrate*, m.p. 158°). 5-Aminopyrogallol Me_3 ether (III), $CH_2Ac{\cdot}CO_2Et$, and 5N-HCl yield an oil which passes at 280° into 4-*hydroxy*-5 : 6 : 7-*trimethoxy*-2-*methylquinoline*, m.p. 198°. 2-*Hydroxy*-5 : 6 : 7-*trimethoxy*-4-*methylquinoline*, m.p. 218° (*picrate*, m.p. 180°), is obtained by treating (III) with $CH_2Ac{\cdot}CO_2Et$ at 140° and then with conc. H_2SO_4 at 0°. 5-*Hydroxy*-6 : 7 : 8-*trimethoxy*-1 : 2 : 3 : 4-*tetrahydroacridine*, m.p. 200°, is obtained by treating (II) and (III) with 5N-HCl and heating the product at 280°. Attempts to prepare 1-carboxy-2 : 3-dimethoxyphenylthiolacetic acid by diazotising 2-aminoveratric acid (IV) and adding $SH{\cdot}CH_2{\cdot}CO_2H$ to the solution gave only unchanged (IV). H. W.

***iso*Quinoline compounds. I.** P. K. PAUL (Science & Culture, 1936, **1**, 781).—Gallic acid Me_3 ether and CH_2O yield a chloromethylphthalide which with KCN affords the *cyanomethylphthalide* derivative, m.p. 146°, hydrolysed (10% NaOH) to a $CH_2Ph{\cdot}CO_2H$ *derivative*, m.p. 212°, the chloride of which with β-veratrylethylamine gives the substituted *amide*, m.p. 154°; the last is cyclised with $POCl_3$ to an *iso*quinoline derivative, m.p. 183° (*hydrochloride*, m.p. 208°), with the emetine skeleton. CH. ABS. (*c*)

Heterocyclic compounds derived from pyrocatechol ethers. V. Synthesis of 2 : 3 : 6 : 7-tetramethoxycarbazole and some dimethoxycarbazoles. G. K. HUGHES, F. LIONS, J. J. MAUNSELL, and L. E. A. WRIGHT (J. Proc. Roy. Soc. New South Wales, 1938, **71**, 428—434).—Gradual addition of Cu powder to 4-bromo-5-nitroveratrole (I) at 210—225° and subsequent heating of the mixture at 240° gives 2 : 2′-*dinitro*-4 : 5 : 4′ : 5′-*tetramethoxydiphenyl*, m.p. 218°, reduced by Zn dust and AcOH at 70° to 2 : 2′-*diamino*-4 : 5 : 4′ : 5′-*tetramethoxydiphenyl*, m.p. 180° [*picrate*, m.p. 226° (decomp.)], which is demethylated and extensively decomposed by hot dil. acids but is transformed by tetrazotisation and treatment with K_2S into 2 : 3 : 6 : 7-*tetramethoxycarbazole*, m.p. 212°. NH_2Ph (I) and anhyd. NaOAc at 200—210° afford 2-*nitro*-4 : 5-*dimethoxydiphenylamine*, m.p. 91°, little affected by Zn dust and AcOH or by $SnCl_2$ but reduced by Sn–conc.HCl–EtOH to 2-amino-4 : 5-dimethoxydiphenylamine, m.p. 152°. This is transformed by HNO_2 at 0° into 5 : 6-*dimethoxy*-1-*phenylbenztriazole*, m.p. 128°, which passes at 300°/partial vac. into 2 : 3-*dimethoxycarbazole*, b.p. 255—260°/25 mm., m.p. 125°. Addition of 2-chloro-*cyclo*hexanone to a mixture of 4-aminoveratrole and anhyd. NaOAc which is then heated to 170° yields 2 : 3-dimethoxy-5 : 6 : 7 : 8-tetrahydrocarbazole, b.p. 255—260°/25 mm., m.p. 98°, slowly converted by boiling Ac_2O into 9-*acetyl*-2 : 3-*dimethoxy*-5 : 6 : 7 : 8-*tetrahydrocarbazole*, b.p. 220°/2 mm., m.p. 136°. H. W.

Structural problems in the indole group. III. Halogen compounds. S. G. P. PLANT and (MISS) A. E. J. WILSON (J.C.S., 1939, 237—239).—4 : 2-$CO_2H{\cdot}C_6H_3Cl{\cdot}NH{\cdot}NH_2$,HCl and *cyclo*hexanone give (H_2SO_4) 5-*chlorotetrahydrocarbazole*-8-*carboxylic acid*, m.p. 245° (decomp.), which, after acetylation and treatment with quinoline and Cu chromite, affords 5-chloro-9-acetyltetrahydrocarbazole. *cyclo*Hexanone and *m*-$C_6H_4Br{\cdot}NH{\cdot}NH_2$ with H_2SO_4 yield a mixture of 7-, m.p. 183° (decomp.) [9-*Ac* derivative (I), m.p. 123°], and 5-*bromotetrahydrocarbazole* (9-*Ac* derivative, m.p. 137—139°). HNO_3 converts (I) into 7-*bromo*-10 : 11-*dihydroxy*-9-*acetylhexahydrocarbazole*, m.p. 217° (decomp.), which with Ac_2O loses H_2O to form 8-*bromo*-6-*acetyl*-ψ-*indoxyl*spirocyclo*pentane*, m.p. 107—108°. After removal of Ac, this compound is nitrated to 8-*bromo*-7 : 9-*dinitro*-ψ-*indoxyl*spirocyclo*pentane*, m.p. 202°, which with NH_2Ph gives the 7 : 9-*dinitro*-8-*anilino*-compound (II), m.p. 235°. 7-Chloro-9-acetyltetrahydrocarbazole and HNO_3 yield 7-*chloro*-10 : 11-*dihydroxy*-9-*acetylhexahydrocarbazole*, m.p. 205—206°, which is converted by a similar series of reactions into (II). Treatment of 5-bromo-9-acetyltetrahydrocarbazole gives only 5-*bromo*-7-*nitro*-9-*acetyltetrahydrocarbazole*, m.p. 217°. F. R. S.

Heterocyclic compounds derived from pyrocatechol ethers. III. Synthesis of 1 : 2-dimethoxyacridine. J. N. GRAVES, G. K. HUGHES, and F. LIONS (J. Proc. Roy. Soc. New South Wales, 1938, **71**, 255—258).—3-Aminoveratrole, *o*-$C_6H_4Br{\cdot}CO_2H$, Cu powder, and anhyd. K_2CO_3 in boiling amyl alcohol give 2 : 3-*dimethoxydiphenylamine*-2′-*carboxylic acid* (I), m.p. 162°. Gradual addition of Cu-bronze and anhyd. K_2CO_3 to 2-aminoveratric acid in boiling PhBr affords 2 : 3-*dimethoxydiphenylamine*-6-*carboxylic acid* (II), m.p. 155°. PCl_5 in boiling CS_2 cyclises (I) and (II) to 1 : 2-*dimethoxyacridone*, m.p. 225°, reduced by Na and abs. EtOH to 1 : 2-*dimethoxydihydroacridine*, m.p. 218°, which shows a vivid blue fluorescence in EtOH and is oxidised ($K_2Cr_2O_7$–dil. H_2SO_4) to 1 : 2-*dimethoxyacridine*, m.p. 189° [*picrate*, m.p. 220° (decomp.)]. H. W.

Heterocyclic compounds derived from pyrocatechol ethers. IV. Syntheses of dimethoxybenzacridines. G. K. HUGHES, F. LIONS, F. H. MONAGHAN, and T. WILKINSON (J. Proc. Roy. Soc. New South Wales, 1938, **71**, 421—429).—4-Aminoveratrole (I) is converted by PhCHO at 100° into 4-*benzylideneaminoveratrole* (II), m.p. 71°, and by piperonal into 4-*piperonylideneaminoveratrole* (III), m.p. 107°. β-$C_{10}H_7{\cdot}OH$ and (II) at 210° give 7 : 8-*dimethoxy*-5-*phenyl*-3 : 4-*benzacridine*, m.p. 205° (*hydrochloride*; *picrate*, m.p. 289°; *methiodide*, m.p. 223°), and 7 : 8-*dimethoxy*-5-*phenyl*-5 : 10-*dihydro*-1 : 2-

benzacridine, m.p. 198° (*Ac* derivative, m.p. 228°). Similarly, (III) and β-$C_{10}H_7$·OH yield 6 : 7-*dimethoxy*-5-*piperonyl*-3 : 4-*benzacridine*, m.p. 245° (*hydrochloride*, m.p. 228°; *picrate*, decomp. 269°), and 6 : 7-*dimethoxy*-5-*piperonyl*-5 : 10-*dihydro*-1 : 2-*benzacridine*, m.p. 242° (*Ac* derivative, m.p. 258°). (I), its hydrochloride, and 40% CH_2O yield 2 : 2′-*diamino*-4 : 5 : 4′ : 5′-*tetramethoxydiphenylmethane*, m.p. 140° [*dihydrochloride*, m.p. 220°; *picrate*, m.p. 190—195° (decomp.); Ac_2 derivative], which can be diazotised and coupled with β-$C_{10}H_7$·OH to a red dye; attempts to transform it into an acridine derivative were unsuccessful.

H. W.

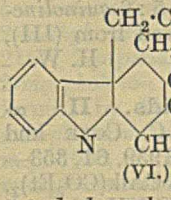
Derivatives of 4-hydroxyquinoline. G. K. Hughes and F. Lions (J. Proc. Roy. Soc. New South Wales, 1938, **71**, 458—461).—Equimol. quantities of amine and β-keto-ester are mixed and in some cases gently heated on the water-bath. If the intermediate arylamino-ester crystallises it is filtered and purified. If not cryst. it is dissolved in Et_2O and the solvent is removed. The intermediates are cyclised by first warming at 100° and then adding them to liquid paraffin at 280°. The following *Et arylamino*-Δ^1-cyclo*hexene*-2-*carboxylates* are derived from Et *cyclo*hexanone-2-carboxylate; o-*toluidino*-, m.p. 84°; p-*bromoanilino*-, m.p. 78°; p-*xenylamino*-, m.p. 107°; o-*anisidino*-, m.p. 80°; p-*anisidino*-, m.p. 71°; p-*phenetidino*-, m.p. 87°; p-*carboxyanilino*-, m.p. 166°; 3-*acenaphtheneamino*-, m.p. 122°. The following substituted *tetrahydroacridines* are described: 1-, m.p. >300°, and 3-*methyl*-, m.p. >300°; 1-, m.p. 278°, and 3-*methoxy*-, m.p. 284°; 1-, m.p. 237°, and 3-*ethoxy*-, m.p. >300°; 2 : 3-, m.p. >300°, and 3 : 4-*benzo*-, m.p. >300°; 1-, m.p. 200°, and 3-*phenyl*-, m.p. >300°; 3-*nitro*-, m.p. >300°; 3-*bromo*-, m.p. >300°; 1-, m.p. 260°, and 3-*chloro*-, m.p. >300°; 1 : 3-*dichloro*-, m.p. 296°; 3-*carboxy*-, m.p. >300°; 3-*carbethoxy*-, m.p. >300°; 3-*acetamido*-, m.p. >300°; *compounds* $C_{19}H_{17}ON$, m.p. >300°, and $C_{15}H_{17}ON$, m.p. 255°, from 3-aminoacenaphthene and *p*-xylidine respectively. The following 4-*hydroxy*-2-*methylquinolines* are described. 6-, m.p. >300°, and 7-*bromo*-, m.p. >300°; 8-*phenyl*-, m.p. 280°; 6-*acetamido*-, m.p. >300°; 8-*chloro*-, m.p. 220°; 6 : 8-*dichloro*-, m.p. 290°.

H. W.

Synthesis of pharmacologically important amines. XII. Di- and tetra-hydrobenz*iso*quinolines as protozoa-poisons. K. Kindler, W. Peschke, and G. Plüddemann (Arch. Pharm., 1939, **277**, 25—32; cf. A., 1936, 200).—Hydrogenation (Pd–C) of β-$C_{10}H_7$·CH_2·CN (prep. from 2-$C_{10}H_7Me$ by way of 2-$C_{10}H_7$·CH_2Br) in H_2SO_4–AcOH at room temp./1 atm. gives 60% of 2-$C_{10}H_7$·$[CH_2]_2$·NH_2, b.p. 168—169°/19 mm., the Bz derivative, new m.p. 142—143°, of which with $POCl_3$ in boiling xylene gives 56% of 1-*phenyl*-3 : 4-*dihydro*-6 : 7-*benzisoquinoline* (I), m.p. 127—128°. The 3 : 4-*diethoxybenzoyl* derivative, m.p. 144—146°, gives similarly 1-3′ : 4′-*diethoxyphenyl*-3 : 4-*dihydro*-6 : 7-*benzisoquinoline* (II), m.p. 148—149°. 1-$C_{10}H_7$·CH_2·CN gives similarly 1-$C_{10}H_7$·$[CH_2]_2$·NH_2, b.p. 178—181°/20 mm. (Bz derivative, new m.p. 96°), and 1-*phenyl*-3 : 4-*dihydro*-5 : 6-*benzisoquinoline* (III), m.p. 78—80° (*picrate*, m.p. 200—202°). Hydrogenation (Pd–$BaSO_4$) of (I) and (III) gives 1-*phenyl*-1 : 2 : 3 : 4-*tetrahydro*-6 : 7-(IV), m.p. 124—125° (and a by-*product*, m.p. 229—230°), and -5 : 6-*benzisoquinoline* (V), m.p. 103—104°, respectively. (I), (II), (III), (IV), and (V) are 2·4, 1·6, 2·0, 11·0, and 7·5 times, respectively, as effective as quinine against protozoa.

L (A., II.) R. S. C.

Synthetic substances allied to strychnine. F. Lions (J. Proc. Roy. Soc. New South Wales, 1938, **71**, 192—208).—Et_2 α-acetyl-α-methylglutarate is hydrolysed by conc. HCl to γ-acetyl-*n*-valeric acid (I), b.p. 148—151°/11 mm. [semicarbazone, m.p. 159—162° (decomp.)]. This is converted by *o*-NH_2·C_6H_4·CHO and NaOH in EtOH into γ-2-*quinolyl*-n-*valeric acid*, m.p. 133°, transformed by successive treatments with Na–Hg and boiling HCl into γ-2-1 : 2 : 3 : 4-*tetrahydroquinolyl*-n-*valeric anhydride* (II), $CH_2<\begin{matrix}CH_2—CH\cdot CHMe\cdot CH_2\\ C_6H_4\cdot N\cdot CO——CH_2\end{matrix}$, m.p. 80°, which in 60% H_2SO_4 gives a transient, deep purple coloration on addition of a little aq. $K_2Cr_2O_7$. Similarly isatin and (I) yield 4-*carboxyquinolyl*-2-γ-*valeric acid*, m.p. 248—249°, which loses CO_2 when heated above its m.p., giving an oil from which (II) cannot be isolated. Successive additions of Et *cyclo*hexanone-2-carboxylate and CH_2Cl·CH_2·CO_2Et to KOEt–EtOH give *Et* 2-*carbethoxy*cyclo*hexanone*-2-β-*propionate*, b.p. 156—158°/2 mm., hydrolysed by HCl to cyclo*hexanone*-2-β-*propionic acid* (III), b.p. 183—184°/12 mm., m.p. 62° (*semicarbazone*, m.p. 194° (decomp.)]; *Et* (IV), b.p. 140—143°/12 mm., and *Me*, b.p. 133—134°/12 mm., esters]. cyclo*Hexanone*-2-β-*propionamide*, m.p. 162—163°, passes above its m.p. into 2-*keto*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydroquinoline*, m.p. 142°. Isatin, (III), and KOH in H_2O at 100° afford 5-*carboxy*-1 : 2 : 3 : 4-*tetrahydroacridyl*-1-β-*propionic acid*, m.p. 307—308° (decomp.), decarboxylated at 310° to a brown oil containing a little 1 : 2 : 3 : 4-*tetrahydroacridyl*-1-β-*propionic acid* (V), m.p. 164—165°. *Et* 5-*carboxy*-1 : 2 : 3 : 4-*tetrahydroacridyl*-1-β-*propionate*, m.p. 174° (*monohydrate*, m.p. 100°), is described. (IV) is condensed with *o*-NH_2·C_6H_4·CHO and the product is hydrolysed to (V) in 75% yield. NHPh·NH_2 and (IV) give *Et* 1 : 2 : 3 : 4-*tetrahydrocarbazolenine*-11-β-*propionate* (VI), b.p. 225—228°/15 mm. (*methiodide*, m.p. 165°), hydrolysed to 1 : 2 : 3 : 4-*tetrahydrocarbazolenine*-11-β-*propionic acid*, m.p. 226°. Condensation of 2-ethyl*cyclo*hexanone and NHPh·NH_2 gives 1-*ethyl*-1 : 2 : 3 : 4-*tetrahydrocarbazole*, b.p. 200—205°/16 mm., and 11-*ethyl*-1 : 2 : 3 : 4-*tetrahydrocarbazolenine*, b.p. 160—161°/16 mm. (*picrate*, m.p. 147°; yellow and red *methiodides*, m.p. 153° and 94° respectively; almost colourless *ethiodide*, m.p. 192°).



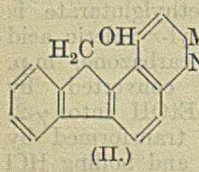
(VI.)

H. W.

Anthraquinone group. I. 1-Amino-2-anilomethylanthraquinone. G. B. Crippa and R. Caracci (Gazzetta, 1938, **68**, 820—825).—1-Amino-2-anilomethylanthraquinone, m.p. 213° (G.P. 343,064; 346,188; cf. A., 1922, i, 942), in boiling PhCHO gives 4-*anilo*-5-*phenylanthraquinono*-1′ : 2′ : 2 : 3-*pyrrole*, m.p. 260°, also obtained from the *CHPh*: derivative, m.p.

321—325°, of 1-aminoanthraquinone-2-aldehyde (*loc. cit.*) and NH_2Ph at 185°. E. W. W.

Derivatives of 2′ : 3′-indeno-5 : 6-quinoline. G. K. Hughes, F. Lions, and L. E. A. Wright (J. Proc. Roy. Soc. New South Wales, 1938, **71**, 449—457).—2-Aminofluorene (I) and $CH_2Ac{\cdot}CO_2Et$ in presence of a little HCl at 100° give *Et* β-2-*fluorenylaminocrotonate*, m.p. 96°, cyclised in paraffin oil at 280° to 4-*hydroxy*-2-*methyl*-2′ : 3′-*indeno*-5 : 6-*quinoline* (II), m.p. >290°, which gives a blue fluorescence in EtOH; the *picrate* has m.p. 231° (decomp.). Addition of (I) to $CH_2Ac{\cdot}CO_2Et$ at 160° gives 2-*acetoacetamidofluorene*, m.p. 145—146°, transformed by cold, conc. H_2SO_4 into 2-*hydroxy*-4-*methylindeno*-2′ : 3′-5 : 6-*quinoline*, m.p. 265° (decomp.). Et *cyclo*hexanone-2-carboxylate and (I) in presence of acid at 100° afford *Et* 1-2′-*fluorenylamino*-β′-cyclo*hexene*-2-*carboxylate*, m.p. 110°, cyclised at 290° to 5-*hydroxyindeno*-2′ : 3′-1 : 2 : 3 : 4-*tetrahydro*-6 : 7-*acridine*, m.p. >300°. Paracetaldehyde, (I), HCl (*d* 1·19), and $ZnCl_2$ at 100°, followed by boiling the product with 2·5N-HCl and treatment of it with $NaNO_2$, give 2-*methylindeno*-2′ : 3′-5 : 6-*quinoline*, m.p. (indef.) 145—159° [*methiodide*, m.p. 243° (decomp.]. Gradual addition of (I) in boiling EtOH to $AcCO_2H$ and PhCHO in boiling EtOH yields 2-*phenylindeno*-2′ : 3′-5 : 6-*quinoline*-4-*carboxylic acid*, m.p. 272° after darkening at 250°. Similar processes lead to 3-*piperonyl*-, decomp. about 245° after darkening at 220°, and 2-p-*anisyl*-, decomp. about 255°, -*indeno*-2′ : 3′-5 : 6-*quinoline*-4-*carboxylic acid*. 2-Aminofluorenone (III) (*dinitrophenylhydrazone*, m.p. 287° after darkening at 265°) and CH_2Ac_2 in presence of a trace of HCl at 100° afford *Me* β-2-*fluorenonylaminopropenyl ketone*, m.p. 145—146°, converted by conc. H_2SO_4 at 0° into 2 : 4-*dimethyl*-1′-*keto*-2′ : 3′-*indeno*-5 : 6-*quinoline*, m.p. 126°. $AcCO_2H$ and PhCHO transform (III) into 2-*phenyl*-1′-*ketoindeno*-2′ : 3′-5 : 6-*quinoline*-4-*carboxylic acid*, m.p. 205° (decomp.) after darkening at 185°, whilst 2-*piperonyl*-1′-*ketoindeno*-2′ : 3′-5 : 6-*quinoline*-4-*carboxylic acid*, m.p. >290°, is derived from (III), $AcCO_2H$, and piperonal. H. W.


(II.)

Substituted vinylbarbituric acids. II. α-Methylpropenyl derivatives. A. C. Cope and E. M. Hancock (J. Amer. Chem. Soc., 1939, **61**, 353—354; cf. A., 1939, II, 127).—$CHMe{:}CR{\cdot}CAlk(CO_2Et)_2$, $CO(NH_2)_2$ [or $NHMe{\cdot}CO{\cdot}NH_2$ or $CS(NH_2)_2$], and NaOEt–EtOH give 5-*methyl*-, m.p. 189·5—190·5°, 5-*ethyl*- (I), m.p. 154—155°, 1-*methyl*-5-*ethyl*-, m.p. 103—104°, 5-*propyl*-, m.p. 157—159°, 5-*allyl*- (II), m.p. 126—127°, and 5-*butyl*- (III), m.p. 166—167°, -5-α-*methylpropenylbarbituric acid* and 5-*propyl*-5-α-*methylpropenylthiobarbituric acid*, m.p. 163—165°, which are mixtures of *cis*- and *trans*-isomerides, since with O_3 they give only traces of CH_2O (derived from the cyclic portion of the mol.) but require many recrystallisations to reach const. m.p. $CN{\cdot}CR(CMe{:}CHMe){\cdot}CO_2Et$ gives, by way of the imine, (I) and (III) (with a little nitrile), which are sterically purer. Of these products (II) is the most effective anæsthetic. R. S. C.

Piperazine derivatives from amino-alcohols. J. P. Bain and C. B. Pollard (J. Amer. Chem. Soc., 1939, **61**, 532).—$OH{\cdot}CH_2{\cdot}CHMe{\cdot}NH_2$, $NH(CH_2{\cdot}CH_2{\cdot}OH)_2$, and $NHPh{\cdot}[CH_2]_2{\cdot}OH$ with H_2–Cu–Cr_2O_3 at 250—275° give 20—50% of *trans*-2 : 5-dimethyl-, 1 : 4-di-(β-hydroxyethyl)-, m.p. 134—135°, and 1 : 4-diphenyl-piperazine, respectively. R. S. C.

Homologues of alloxandimethylaminoanil [dimethylaminobarbiturylideneaniline] and (barbiturylideniminodimethylaminophenyl)dialuric acids. H. Rudy and K. E. Cramer (Ber., 1939, **72**, [*B*], 227—248; cf. A., 1938, II, 336).—If the condensation of o-$NH_2{\cdot}C_6H_4{\cdot}NMe_2$,HCl and alloxan (I) is effected in presence of a large excess of (I), the formation of alloxan-2-dimethylaminoanil (II) is almost entirely suppressed and two substances result, one of which, distinguished by its solubility in anhyd. C_5H_5N, is 5-4-*dimethylamino*-3′-*barbiturylideneiminophenyldialuric acid* (III),

$$CO\langle{}^{NH{\cdot}CO}_{NH{\cdot}CO}\rangle C(OH){\cdot}C_6H_3(NMe_2){\cdot}N{:}C\langle{}^{CO{\cdot}NH}_{CO{\cdot}NH}\rangle CO.$$

(III) forms a *tetrahydrate*, m.p. 265—270° (decomp.) when rapidly heated in a bath preheated to 235—240°, and a *monohydrate*, m.p. 260—270° when rapidly heated in a bath preheated to 235—240°, either of which is converted by boiling H_2O or dil. AcOH into a sparingly sol. γ-form. The three forms are closely similar to one another, give a weakly acidic solution in H_2O, dissolve slowly in aq. $NaHCO_3$, and evolve NH_3 copiously when boiled with 30% NaOH. The sol. but not the insol. form of (III) is converted by CH_2N_2 into the hygroscopic Me_4 derivative, m.p. 228°, insol. in dil. NaOH at room temp. (III) is transformed by Ac_2O in boiling C_5H_5N into an *Ac* derivative, which melts initiallly at 180—230° but becomes progressively less sol. as purification proceeds and finally has m.p. >430°. (III) is obtained by the condensation of (II) and (I) in presence of HCl. CH_2N_2 in $COMe_2$ transforms (II) into *dimethylalloxan*-2-*dimethylaminoanil*, m.p. 186° and m.p. 250° (decomp.) after re-solidification and softening at 230°; it is insol. in cold 15% NaOH, freely sol. in cold 2N-HCl. It does not yield a picrate. Similarly 5 : 4′-dimethylaminophenyldialuric acid is converted by CH_2N_2 in MeOH–$COMe_2$ into 5-4-*dimethylaminophenyldimethyldialuric acid*, m.p. 168—169°, transformed by Ac_2O in boiling C_5H_5N into the Ac_1 derivative, m.p. 149—150°. 4 : 5-Dinitro-*o*-xylene is converted by $NHMe_2$ in EtOH at 100° into 4-*nitro*-5-*dimethylamino*-*o*-*xylene*, b.p. 174°/15 mm., m.p. 49—50° (*picrate*, m.p. 141—142°; *hydrochloride*, m.p. 149°), reduced (Pd–$CaCO_3$ in MeOH at 40—50°) to 4-*amino*-5-*dimethylamino*-*o*-*xylene* (II), b.p. 133°/15 mm., m.p. 15—20° [*picrate*, m.p. 163° after softening at 153°; *hydrochloride*, m.p. 148—153° (decomp.); *Ac* derivative, m.p. 124°, and its *hydrochloride*]. (IV) condenses with (I) in acid medium to *alloxan*-5-2′-*dimethylamino*-4′ : 5′-*dimethylanil*, m.p. 248° when rapidly heated or decomp. >300° when slowly heated. It reduces $AgNO_3$ and Fehling's solution and gives a sparingly sol. Na salt, and is not produced when the condensation of (IV) and (I) is attempted in EtOH in absence of acid. Also the amount of crude condensation product formed from (IV) and <2 equivs. of (I)

is ⊁ is produced with an equiv. amount of (I). Since this is not the case with other similar diamines it follows that a dialuric acid is not formed in the present instance. CH_2N_2 converts (IV) suspended in $COMe_2$ into *dimethylalloxan-5-2′-dimethylamino-4′ : 5′-dimethylanil*, m.p. 175° and m.p. 268° (slight decomp.) after re-solidification. (IV) is degraded by boiling 20% NaOH to *2-dimethylamino-4 : 5-dimethylphenyliminomalonimide*, m.p. 250° (decomp.). 3 : 1 : 4-$NH_2{\cdot}C_6H_3Me{\cdot}NMe_2$ and (I) in presence of HCl yield *alloxan-5-2′-dimethylamino-5′-methylanil*, m.p. 248° when rapidly heated, whence (CH_2N_2) *dimethylalloxan-5-2′-dimethylamino-5′-methylanil*, m.p. 174—175° and m.p. 246° (slight decomp.) after re-solidification and softening at 220°. In presence of a large excess of (I), 3 : 1 : 4-$NH_2{\cdot}C_6H_3Me{\cdot}NMe_2$ affords *5-4′-barbiturylideneimino-5′-dimethylamino-2′-methylphenyldialuric acid*, m.p. 257° (decomp.) (*Me* derivative, m.p. 221°). 4 : 1 : 3-$NO_2{\cdot}C_6H_3Me{\cdot}OH$ is converted by NaOH and Me_2SO_4 into the Me ether, b.p. 166°/17 mm., m.p. 62°, whence 4 : 1 : 3-$NO_2{\cdot}C_6H_3Me{\cdot}NHMe$, which is transformed by Me_2SO_4 and NaOH into *4-nitro-3-dimethylaminotoluene*, b.p. 128°/3 mm., m.p. 41° (*picrate*, m.p. 127°). This is reduced (Pd–$CaCO_3$–MeOH) to *4-amino-3-dimethylaminotoluene*, b.p. 86°/3 mm. [*picrate*, m.p. 143°; *hydrochloride*, m.p. 204° (decomp.); *Ac* derivative, m.p. 109—110°], which condenses with (I) to *alloxan-5-2′-dimethylamino-4′-methylanil*, m.p. 248° when placed on a block preheated to this temp., otherwise a slow transformation without melting; *dimethylalloxan-5-2′-dimethylamino-4′-methylanil* has m.p. 173—174° and, after re-solidification, m.p. ~270° (decomp.). *5-3′-Barbiturylideneimino-4′-dimethylamino-6′-methylphenyldialuric acid* has m.p. 235—240° (decomp.). *o*-$C_6H_4(NMe_2)_2$ reduces (I) to alloxantin. H. W.

Pyrimidines.—See B., 1939, 326.

Quinazolines and pyrimidines.—See B., 1939, 246.

Oxidising action of selenium dioxide. (SIGNA.) L. MONTI (R.C. Atti Accad. Lincei., 1938, [vi], **28**, 96—99).—4-Hydroxy-2-methylquinazoline (I) is oxidised by SeO_2 in AcOH, at 50—60°, to *4-hydroxyquinazoline-2-aldehyde*, decomp. from 210°, which with $MeNO_2$ in EtOH ($NHMe_2$) gives *β-nitro-α-(4-hydroxy-2-quinazolyl)ethyl alcohol*, m.p. 216—218°. The prep. of (I), or of 4-hydroxyquinazoline, is improved by heating *o*-$NH_2{\cdot}C_6H_4{\cdot}CO_2H$ with NH_2Ac or HCO_2NH_4 respectively in heavy petroleum at 240° for 15—20 min. E. W. W.

Chemiluminescence of 3-aminophthalhydrazide. F. H. STROSS and G. E. K. BRANCH (J. Org. Chem., 1938, **3**, 385—404).—In solutions containing an excess of $Fe(CN)_6'''$ and H_2O_2 the glow of 3-aminophthalhydrazide [luminol (I)] ceases because of the removal of (I) by a two-unit oxidation. In acid solution the product can be reconverted into (I) by $Fe(CN)_6''''$ and hence the loss of N during the oxidation of (I) is a slower reaction following two units of oxidation which probably leads to the substance $NH_2{\cdot}C_6H_3{<}^{CO{\cdot}N}_{CO{\cdot}N}$. Although this oxidation is the fastest change decreasing the luminescence, the reaction $2Fe(CN)_6''' + 2OH' + H_2O_2 \rightarrow 2Fe(CN)_6'''' +$ $2H_2O + O_2$ is sufficiently rapid to decrease the $[Fe(CN)_6''']$ sufficiently to diminish the glow and to introduce sufficient $Fe(CN)_6''''$ into the mixture to affect markedly the brightness during the glowing period. The decomp. of H_2O_2 is not sufficiently rapid to affect the luminescence. The subsequent changes in which N_2 is evolved and further oxidations occur are immaterial to the study of luminescence as they occur chiefly after the glow has ceased. The rate of decay of the luminescence is measured by use of a flow method and a photo-electric cell. From these measurements it appears probable that a more and a less luminescent reaction are competing for a product of a preliminary change. The more luminescent oxidation is by H_2O_2, the less by $Fe(CN)_6'''$. OH′ either hinders the more luminescent oxidation or helps the less. The more rapid preliminary reaction is a reversible oxidation by $Fe(CN)_6''''$ helped by OH′. The intermediate is a one-unit oxidation product $C_8H_6O_2N_3$ of (I); the final product is a two-unit oxidation product of (I). The most probable scheme is: $NH_2{\cdot}C_6H_3{<}^{CO{\cdot}N-}_{CO{\cdot}NH} \rightarrow NH_2{\cdot}C_6H_3{<}^{CO{\cdot}N}_{CO{\cdot}NH}$ (II) $\rightarrow$ $NH_2{\cdot}C_6H_3{<}^{CO-C_6H_3{\cdot}NH_2}_{CO-NH}{>}N{\cdot}N{<}^{CO-C_6H_3{\cdot}NH_2}_{NH{\cdot}CO}$ (III). (II) + $H_2O_2 \rightarrow NH_2{\cdot}C_6H_3{<}^{CO{\cdot}N{\cdot}OH}_{CO{\cdot}NH}$ + OH. OH + (III) $\rightarrow$ $NH_2{\cdot}C_6H_3{<}^{CO{\cdot}N{\cdot}OH}_{CO{\cdot}NH} + NH_2{\cdot}C_6H_3{<}^{CO{\cdot}NH}_{CO{\cdot}N}$. The efficiency of luminescence and the effect of variation of temp. are discussed. H. W.

Synthesis of 2-aminomethylbenziminazole and related substances. G. K. HUGHES and F. LIONS (J. Proc. Roy. Soc. New South Wales, 1938, **71**, 209—222).—*o*-$C_6H_4(NH_2)_2$ is converted by $CH_2Cl{\cdot}CO_2H$ in boiling 4N-HCl into *2-chloromethylbenziminazole* (I), m.p. 160—161°, better obtained by the action of $SOCl_2$ on 2-hydroxymethylbenziminazole (II) in $CHCl_3$; attempts to replace Cl in (I) by NH_2 were not successful. (I) is transformed by *o*-$NH_2{\cdot}C_6H_4{\cdot}CO_2Me$ or the requisite *sec.* base into the following *-methylbenziminazoles*; *2-o-carbomethoxyanilino-*, m.p. 216°; *2-methylanilino-*, m.p. 202°; *2-diphenylamino-*, m.p. 215°; *2-piperidino-*, m.p. 193—194° (softens at 180°); *2-morpholino-*, m.p. 211°. (II) in MeOH is transformed by Me_2SO_4–NaOH into *1-methyl-2-hydroxymethylbenziminazole*, m.p. 143—144°, or (hydrated) m.p. 105°, converted by $SOCl_2$ into *1-methyl-2-chloromethylbenziminazole*, m.p. 94°, which appears to undergo a complex reaction with NH_3. It gives *1-methyl-2-anilinomethyl-*, m.p. 118°, and *-2-methylanilinomethyl-*, m.p. 145°, *-benziminazole*. $NHPh{\cdot}CH_2{\cdot}CO_2H$ and *o*-$C_6H_4(NH_2)_2$ yield *2-anilinomethylbenziminazole*, m.p. 162°, when cautiously melted together. *o*-$C_6H_4(NH_2)_2$ and *o*-$C_6H_4(CO)_2N{\cdot}CH_2{\cdot}CO_2H$ yield a substance free from O. *2-Benzamidomethylbenziminazole* (anhyd. or hydrated), m.p. 231°, obtained in excellent yield from *o*-$C_6H_4(NH_2)_2$ and hippuric acid, is hydrolysed by boiling conc. HCl to *2-aminomethylbenziminazole dihydrochloride*, m.p. 263° (also hydrated); the corresponding *trihydrated base*, m.p. 53°, gives a gum when dried in vac. over conc. H_2SO_4. *2-Acetamidomethylbenziminazole* has m.p. 200°. $SH{\cdot}CH_2{\cdot}CO_2H$ and

o-$C_6H_4(NH_2)_2$ in boiling N-HCl give 2-*thiolmethyl-benziminazole*, m.p. 158°, with (?) the corresponding *disulphoxide*, $C_{16}H_{14}O_2N_4S_2$, m.p. 182°. The following *-benziminazoles* are prepared from *o*-$C_6H_4(NH_2)_2$ and the requisite acid: 2-*phenoxymethyl-*, m.p. 162°; 2-*methoxymethyl-*, m.p. 136°; 2-*benzyl-*, m.p. 187°; 2-β-*phenylethyl-*, m.p. 186°; 2-p-*nitrobenzyl-*, m.p. 215°; 2-o-*nitrobenzyl-*, m.p. 217°; 2-p-*aminobenzyl-*, m.p. 213°. H. W.

Heterocyclic compounds derived from 5- and 8-aminoquinoline. S. J. Hazlewood, G. K. Hughes, and F. Lions (J. Proc. Roy. Sci. New South Wales, 1938, **71**, 462—474).—8-Aminoquinoline (I), b.p. 174°/26 mm., 164°/19 mm., is reduced by Na and boiling abs. EtOH to 8-*amino*-1 : 2 : 3 : 4-*tetrahydroquinoline* (II), b.p. 145°/2 mm. (*picrate*, m.p. 178°), which darkens rapidly on exposure to air. It passes in boiling HCO_2H into 1 : 7-*trimethylenebenziminazole* [5 : 6-*dihydroquinolino*-1 : 3-*diazole*], m.p. 148°. With boiling Ac_2O (II) yields 2-*methyl*-1 : 7-*trimethylenebenziminazole*, m.p. 128°, whilst with boiling $EtCO_2H$ and $CH_2Ph{\cdot}CO_2H$ it affords 2-*ethyl-* (III), b.p. 195°/20 mm., m.p. 86°, and 2-*benzyl-*, m.p. 109°, -1 : 7-*trimethylenebenziminazole*. (II) and $OH{\cdot}CH_2{\cdot}CO_2H$ or (I) and $OH{\cdot}CH_2{\cdot}CO_2H$ in presence of boiling 4N-HCl give 2-*hydroxymethyl*-1 : 7-*trimethylenebenziminazole*, m.p. 183°, whilst with $OH{\cdot}CHMe{\cdot}CO_2H$ and *dl*-$OH{\cdot}CHPh{\cdot}CO_2H$ respectively there are obtained 2-α-*hydroxyethyl-*, m.p. 142°, and 2-α-*hydroxybenzyl-*, m.p. 205°, -1 : 7-*trimethylenebenziminazole*. $OH{\cdot}CPh_2{\cdot}CO_2H$ and (I) yield 2-α-*hydroxybenzhydryl*-1 : 7-*trimethylenebenziminazole*, m.p. 275°. With an excess of $AcCO_2H$ (II) affords 3-*keto*-2-*methyl*-6 : 7-*dihydroquinolino*-1 : 4-*diazine*, m.p. 113°. $CH_2Ac{\cdot}CO_2Et$ containing dil. HCl converts (II) at room temp. into *Et* β-8-*tetrahydroquinolylaminocrotonate*, m.p. 56—57°, cyclised in paraffin at 280° to (III). Benzoin and (II) do not appear to react in EtOH but if fused together they yield dl-2 : 3-*diphenyl*-6 : 7-*dihydroquinolo*-1 : 4-*diazine*, m.p. 146°. With Ac_2 in EtOH at 0° (II) gives a *compound*, $C_{22}H_{26}N_4$, m.p. 123°, which appears to be an anil from 2 mols. of the base and 1 mol. of Ac_2. Anhyd. alloxan and (II) in warm EtOH give a *compound*, $C_{13}H_{10}O_2N_4$, m.p. 255°, whereas in AcOH containing H_3BO_3 at 20° they yield a *substance*, (?) $C_{13}H_{10}O_2N_4$, m.p. >320°. Treatment of (I) with $CH_2Ac{\cdot}CO_2Et$ and dil. HCl at 100° and heating of the product at 270° affords 4-*hydroxy*-2-*methyl*-1 : 10-*phenanthroline*, m.p. 196° after softening at 193°. Gradual addition of (I) to $CH_2Ac{\cdot}CO_2Et$ at 140—160° leads to 8-*acetoacetamidoquinoline*, m.p. 93°, which could not be cyclised by conc. H_2SO_4. Similarly the cyclisation of *Me* β-8-*quinolylaminopropenyl ketone*, m.p. 95°, obtained from (I) and CH_2Ac_2 at 100°, could not be achieved by conc. H_2SO_4, P_4O_{10}, or $POCl_3$. Treatment of 5-aminoquinoline (IV) with $CH_2Ac{\cdot}CO_2Et$ and dil. HCl at 100° and heating of the product to 270° yields 7-*hydroxy*-9-*methyl*-4 : 10-*phenanthroline*, m.p. >345°. Similar treatment of (IV) with Et *cyclo*hexanone-2-carboxylate appears to yield the expected *acridine* derivative, incipient decomp. 250°, but an analogous product could not be obtained similarly from (I). Gradual addition of $CH_2Cl{\cdot}COCl$ in $CHCl_3$ to (I) in $CHCl_3$ at 0° leads to 8-*chloroacetamidoquinoline*, m.p. 132°, which passes at 200° into *anhydroglycollylaminoquinolinium chloride*, the aq. solution of which gives an immediate ppt. of AgCl when treated with $AgNO_3$–HNO_3. H. W.

Binuclear isomerism of diphenyl type. III. G. K. Hughes, F. Lions, J. J. Maunsell, and T. Wilkinson (J. Proc. Roy. Soc. New South Wales, 1938, **71**, 406—420; cf. A., 1934, 82).—γ-*o*-Carboxyphenylpentane-ββδ-dione (I) condenses with N_2H_4,H_2O in boiling EtOH to 4-o-*carboxyphenyl*-3 : 5-*dimethylpyrazole*, m.p. 250°, and with $NHPh{\cdot}NH_2$ to 1-*phenyl*-4-o-*carboxyphenyl*-3 : 5-*dimethylpyrazole*, m.p. 247°, which could not be resolved into its optical antipodes because of its weakness as an acid and its inability to form satisfactory alkaloidal salts. CH_2Ac_2 and *p*-carboxyphenylhydrazine afford 1-p-*carboxyphenyl*-3 : 5-*dimethylpyrazole*, m.p. 158°, whilst (I) similarly gives 1-p-*carboxyphenyl*-4-o-*carboxyphenyl*-3 : 5-*dimethylpyrazole*, m.p. 133°; this gives a strychnine salt, m.p. 187°, which has not been completely examined. *p*-Carbethoxyphenylhydrazine is converted by CH_2Ac_2 into 1-p-*carbethoxyphenyl*-3 : 5-*dimethylpyrazole*, m.p. 65°, and by (I) into 4-o-*carboxyphenyl*-1-p-*carbethoxyphenyl*-3 : 5-*dimethylpyrazole*, m.p. 139°. With $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$, (I) yields 4-o-*carboxyphenyl*-3 : 5-*dimethylpyrazole*-1-*carboxylamide*, m.p. 189°. Homophthalic acid and 1-*o*-aminophenylpiperidine (II) at 180° afford 1 : 3-*diketo*-2-o-*piperidinophenyl*-1 : 2 : 3 : 4-*tetrahydroisoquinoline*, m.p. 143° (*CHPh* derivative, m.p. 160—161°), which does not appear to give quaternary NH_4 salts. 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$ and (II) at 100° yield 2 : 4-*dinitro*-2′-*piperidinodiphenylamine*, m.p. 174°, reduced ($SnCl_2$–HCl–Sn in boiling EtOH) to 2 : 4-*diamino*-2′-*piperidinodiphenylamine*, m.p. 157°. Et phenacylacetoacetate (III) is converted by 4-aminoveratrole in boiling EtOH containing AcOH into *Et* 5-*phenyl*-1-3′ : 4′-*dimethoxyphenyl*-2-*methylpyrrole*-3-*carboxylate*, m.p. 115°, by *o*-$NH_2{\cdot}C_6H_4{\cdot}CO_2H$ into *Et* 5-*phenyl*-1-o-*carboxyphenyl*-2-*methylpyrrole*-3-*carboxylate*, m.p. 110°, and by *o*-$C_6H_4Ph{\cdot}NH_2$ into *Et* 5-*phenyl*-1-o-*xenyl*-2-*methylpyrrole*-3-*carboxylate*, m.p. 150—151°. $(CH_2Ac)_2$ and (II) afford 1-o-*piperidinophenyl*-2 : 5-*dimethylpyrrole*, m.p. 72°, which does not appear to form a methiodide or a methosulphate. With phenacyl-lævulic acid (II) yields 2-*phenyl*-1-o-*piperidinophenylpyrrole*-5-β-*propionic acid*, m.p. 151°, the acidic properties of which are not sufficiently pronounced to enable it to form alkaloidal salts. (II) and (III) give *Et* 5-*phenyl*-1-o-*piperidinophenyl*-2-*methylpyrrole*-3-*carboxylate*, m.p. 102—103°. *o*-$C_6H_4(CO)_2O$ and (II) in boiling AcOH afford o-*piperidinophenylphthalimide*, m.p. 119—120°, which does not appear to form a methiodide or a methosulphate. (II) is acetylated and converted by MeI into 1-o-*acetamidophenylpiperidine methiodide*, m.p. 217—218°. Successive additions of $CH_2Ac{\cdot}CO_2Et$ and $CH_2Cl{\cdot}COEt$ to Na in Et_2O lead to *Et* α-*acetyl*-β-*propionylpropionate*, b.p. 140°/26 mm., 251°/760 mm., converted by K_2CO_3 in boiling H_2O into *heptane*-βε-*dione* (IV), b.p. 90°/21 mm., about 194°/760 mm. (*semicarbazone*, m.p. 231°), which is transformed by β-$C_{10}H_7{\cdot}NH_2$ in boiling EtOH containing AcOH into 1-β-*naphthyl*-2-*methyl*-5-*ethylpyrrole*, m.p. 102°. H. W.

Naphthiminazoles.—See B., 1939, 256.

***m*- and *p*-Bis-(5′-keto-2′ : 3′-dimethyl-1′-pyrazolyl)benzene** (" ***m*- and *p*-diantipyrine "). J. Böeseken and J. B. Roos (Rec. trav. chim., 1939, 58, 58—62).—The *m*-phenylenedihydrazone of $CH_2Ac{\cdot}CO_2Et$ (A., 1933, 1285; cf. also A., 1934, 67) and the corresponding *p*-compound with AcOH in boiling xylene give m-, m.p. 185—187°, and p-*bis*-(5′-*keto*-3′-*methyl*-1′-*pyrazolyl*)*benzene*, which with MeI–MeOH at 110° give m-, m.p. 177—179°, and p-*bis*-(5′-*keto*-2′ : 3′-*dimethyl*-1′-*pyrazolyl*)*benzene*, m.p. 300°, respectively (" m- and p-*diantipyrine* ").

E. W. W.

Salts of 6 : 8-diamino-2-hydroxypurine. J. R. Spies and T. H. Harris, jun. (J. Amer. Chem. Soc., 1939, **61**, 351—352).—Addition of 2 : 4-$C_6H_3Cl_2{\cdot}N_2Cl$ to 6-amino-2-hydroxypurine sulphate in NaOH at 0—10° gives the diazo-compound, reduced by $Na_2S_2O_4$ to 6 : 8-diamino-2-hydroxypurine [sulphate, $+3H_2O$ ($1H_2O$ retained at 139°/vac.); hydrochloride, anhyd. and $+1{\cdot}5H_2O$; *acetate*, anhyd. and $+3{\cdot}5H_2O$; *carbonate*, anhyd. and $+H_2O$; *picrate*, anhyd. and $+0{\cdot}5H_2O$].

R. S. C.

Phthalocyanines.—See B., 1939, 249.

Porphyrins. XLIII. Chemistry of pyrrole. H. Fischer and E. Elhardt (Z. physiol. Chem., 1939, **257**, 61—105; cf. A., 1937, II, 168, 169).—Attempts to synthesise pyrrole-3-acetic-5-propionic acid with a view to the synthesis of uroporphyrin I and octachloroporphin as a means of improving the synthesis of porphin are described. 5-Carbethoxy-2-methyl-4-cyanomethylpyrrole (I) in Et_2O gives, with 4·5 mols. of SO_2Cl_2, *Et* 3-*chloro*-2-*trichloromethyl*-4-*cyanomethylpyrrole*-5-*carboxylate*, m.p. 211—212° (decomp.), which yields a *substance*, m.p. 128° (possibly Et_2 3-chloro-4-cyanomethylpyrrole-2 : 5-dicarboxylate), when boiled with aq. EtOH. With 4 mols. of SO_2Cl_2 (I) in Et_2O gives a product which, when boiled with H_2O for 48 hr., yields a *substance*, $C_8H_6O_4N_2$, m.p. 234° (probably 4-cyanomethylpyrrole-2 : 5-dicarboxylic acid). Me 2-methylpyrrole-4-acetate in EtOH with HCN and HCl gas gives an iminochloride, decomposed by NH_3 to *Me* 5-*aldehydo*-2-*methylpyrrole*-4-*acetate*, m.p. 181—182° (*oxime*, m.p. 217°), which condenses with $CN{\cdot}CH_2{\cdot}CO_2Et$ in presence of NH_2Me,HCl and Na_2CO_3 to the *substance*, $C_{14}H_{16}O_4N_2$, m.p. 142°. 5-Aldehydo-2 : 4-dimethylpyrrole with $CN{\cdot}CH_2{\cdot}CO_2Et$ in presence of NH_2Ph gives 2 : 4-*dimethyl*-5-ω-*cyano*-ω-*carbethoxyvinylpyrrole*, m.p. 126—129°, which in $CHCl_3$ with excess of HCN gives the corresponding 3-*aldehydo*-compound, m.p. 184° converted into 3 : 5-*dialdehydo*-2 : 4-*dimethylpyrrole*, m.p. 165°, by conc. aq. KOH. 2-Carboxy-5-carbethoxy-4-methylpyrrole-3-propionic acid in Et_2O–MeOH gives, with CH_2N_2, *Me* 2-*carbomethoxy*-5-*carbethoxy*-4-*methylpyrrole*-3-*propionate*, m.p. 66—68°. This substance, in Et_2O, yields with SO_2Cl_2 a compound which, when boiled with H_2O, gives a Cl-free *substance*, m.p. 136°. 5-Carbethoxy-2-methylpyrrole in Et_2O treated twice with 3 mols. of SO_2Cl_2 affords *Et* 3 : 4-*dichloro*-2-*chloromethylpyrrole*-5-*carboxylate* (II), m.p. 160—161° (brown colour) (*OMe*-, m.p. 115°, *OEt*-, m.p. 105°, and *NHPh*-, m.p. 145°, derivatives), which, boiled with H_2O, gives H_2O-insol. 3 : 3′ : 4 : 4′-*tetrachloro*-5 : 5′-*dicarbethoxypyrromethane* (III), m.p. 210—211° (yield almost quant. if H_2O vol. small and duration of boiling brief) (free dicarboxylic *acid*, darkens 205°, m.p. ≠350°), and the H_2O-sol. *compound* (IV), m.p. 145°, resulting from replacement of CH_2Cl by $CH_2{\cdot}OH$. (III) is also obtained together with the *formate*, m.p. 168°, of (IV) by boiling (II) with HCO_2H. 5-Carbethoxy-2-methylpyrrole in Et_2O with >4 mols. of SO_2Cl_2 gives *Et* 3 : 4-*dichloro*-2-*dichloromethylpyrrole*-5-*carboxylate* (XI), m.p. 94°; with ~6 mols. of SO_2Cl_2 it gives the *chloride* (V), m.p. 142—144°, of *Et* 3 : 5-*dichloro*-2-*carboxypyrrole*-5-*carboxylate* (VI), m.p. 275° (decomp.; darkens). With boiling aq. EtOH (V) gives Et_2 3 : 4-*dichloropyrrole*-2 : 5-*dicarboxylate* (X), m.p. 116°, hydrolysed to the *acid*, decomp. 260—300° [corresponding *anilide*, m.p. 174°, *hydrazide* (VII), m.p. 224°, *amide* (VIII), m.p. 270°, *hydroxamic acid*, decomp. 191°]; with 2 mols. of MgMeI the corresponding tert. *alcohol*, m.p. 107—108°; in C_6H_6 with Na (VI) and 3 : 3′ : 4 : 4′-*tetrachloro*-5 : 5′-*dicarbethoxydipyrryl diketone*, m.p. 219—220°, and with NaN_3 a good yield of the corresponding *azide* (IX), m.p. 143° (explodes), also obtained in poor yield from (VII) in 50% aq. AcOH at 0° with $NaNO_2$. (VI) at 290° gives *Et* 3 : 4-*dichloropyrrole*-5-*carboxylate*, m.p. 110—112°. (VIII) boiled for 45 min. with NaOAc and Ac_2O gives the *substance*, (?) $C_{13}H_{10}O_5N_2Cl_2$, m.p. 123°, and (IX) boiled with MeOH for 1 hr. gives the corresponding *methylurethane*, m.p. 174—176°. (X) boiled for 5 min. with $N_2H_4{\cdot}H_2O$ gives the corresponding *dihydrazide*, colours 280°, decomp. 312°, which with $COMe_2$ gives the *compound*, $C_{12}H_{15}O_2N_5Cl_2$, m.p. 276° (decomp.), and, in 80% aq. AcOH with $NaNO_2$ at −7° to −2° the corresponding *diazide*, explodes 144°. (II) in AcOH with CrO_3 in H_2O at 60° gives *Et* 3 : 4-*dichloro*-2-*aldehydopyrrole*-5-*carboxylate*, m.p. 150° (*oxime*, m.p. 185°) [also obtained in better yield from (XI) and boiling 50% aq. EtOH], hydrolysed to the *acid*, m.p. 240° (decomp.), also obtained by boiling (XI) with EtOH, adding aq. NaOH, and again boiling. Et_2 2 : 5-dimethylpyrrole-3 : 4-dicarboxylate (XII) in EtOH gives, with 2 mols. of SO_2Cl_2, 2 : 5-*di*(*chloromethyl*)-, m.p. 158°, and with 4 mols. of SO_2Cl_2, *Et* 2 : 5-*di*(*dichloromethyl*)-*pyrrole*-3 : 5-*dicarboxylate*, m.p. 117—119°, which, boiled for 6 hr. with H_2O with frequent addition of a few drops of aq. Na_2CO_3, gives a *substance*, m.p. 255°, possibly Et_2 2 : 5-dialdehydopyrrole-3 : 4-dicarboxylate (*diphenylhydrazone*, m.p. 160—162°), and boiled for 2 days with 50% aq. EtOH gives a *substance*, m.p. 218°, of high N content. (XII) in Et_2O with 8 mols. of SO_2Cl_2 gives a *substance*, $C_{12}H_{12}O_4NCl_5$, m.p. 127°, with 10 mols. of SO_2Cl_2 followed by boiling for 2 days with EtOH a *substance*, m.p. 79° (possibly Et_2 2 : 5-di(trichloromethyl)pyrrole-3 : 4-dicarboxylate], and with 4 Br a Br-compound (probably a perbromide) which reacts with EtOH and with $COMe_2$ to give a *substance*, $C_{10}H_{13}O_4N$, m.p. 239—241°, probably 3-carboxy-4-carbethoxy-2 : 5-dimethylpyrrole. The Br-compound with NH_2Ph gives (XII). Et 3-cyano-2 : 4-dimethylpyrrole-5-carboxylate boiled with $N_2H_4{\cdot}H_2O$ gives the corresponding *hydrazide*, m.p. 268°, converted, in 80% aq. AcOH, by $NaNO_2$ into the corresponding *azide*, decomp. 138°, which yields the corresponding *methyl-*

urethane, m.p. 192°, when boiled with MeOH. Similarly Et 2 : 3 : 4-trimethylpyrrole-5-carboxylate gives the corresponding *hydrazide*, m.p. 236°, and *azide*, decomp. 145°. This azide, boiled with MeOH for 2 days, yields a *substance*, $C_9H_{14}O_3N_2$, decomp. 187°; treated in Et_2O with 1 mol. of SO_2Cl_2 it yields the unstable light-sensitive *azide*, becomes red-brown at 130°, decomp. 141°, of 3 : 4-dimethyl-2-chloromethylpyrrole-5-carboxylic acid and treated with 2 mols. of SO_2Cl_2 it yields the unstable, light-sensitive *azide* (XIII), decomp. 129°, of 3 : 4-dimethyl-2-dichloromethylpyrrole-5-carboxylic acid. (XIII) boiled for 2 hr. with aq. EtOH gives the *hydrochloride*, decomp. slowly >250°, of the 5 : 5′-diethylurethane of 3 : 3′ : 4 : 4′-tetramethylpyrromethene. The oxime of Et 5-aldehydo-2-methylpyrrole-3-carboxylate, boiled with NaOAc and Ac_2O for 30 min., gives *Et 5-cyano-2-methylpyrrole-3-carboxylate*, m.p. 129°, but the attempt to introduce a 4-CHO into this compound fails. Et 3-aldehydo-2-methylpyrrole-5-carboxylate in AcOH gives with Br the corresponding 4-*Br*-derivative, m.p. 188° (excess of Br does not attack Me), and with NH_2OH the 3-*oxime*, m.p. 197°, which is converted by NaOAc and Ac_2O into the corresponding 3-*CN*-compound (XIV), m.p. 125°, a *substance*, m.p. 306° (decomp.), being produced simultaneously. (XIV) is hydrolysed to 3-*cyano*-2-*methylpyrrole*-5-*carboxylic acid*, m.p. 273° (decomp.), by aq. NaOH, and in AcOH with Br it gives *Et* 4-*bromo*-3-*cyano*-2-*methylpyrrole*-5-*carboxylate*, m.p. 196°, the Br of which does not react with NH_2Ph. With 2—4·5 mols. of SO_2Cl_2 under various conditions (XIV) yields *Et* 4-*chloro*-3-*cyano*-2-*methylpyrrole*-5-*carboxylate*, m.p. 191°, and *Et* 4-*chloro*-3-*cyano*-2-*chloromethylpyrrole*-5-*carboxylate*, m.p. 138—140° (boiled for 1 hr. with H_2O this yields the corresponding 2-*OH·CH*$_2$ compound, m.p. 180°). When treatment with SO_2Cl_2 is followed by boiling for 2 hr. with 50% aq. MeOH 2-*Me* 5-*Et* 4-*chloro*-3-*cyanopyrrole*-2 : 5-*dicarboxylate*, m.p. 187°, and when it is followed by boiling for 2 hr. with aq. EtOH *Et*$_2$ 4-*chloro*-3-*cyanopyrrole*-2 : 5-*dicarboxylate* (XV), m.p. 166°, are obtained, a *Cl*-compound, m.p. 114°, being also produced in the second case. If this compound is boiled with H_2O *Et* 4-*chloro*-3-*cyano*-2-*carboxypyrrole*-5-*carboxylate*, m.p. (rapid heating) 252—254° (slow heating, decomp. 245—248°), is obtained. (XV) in conc. aq. NH_3 at 130° for 10 hr. gives 4-*chloro*-3-*cyano*-2 : 5-*dicarbamylpyrrole*, m.p. 344° (decomp.; blackens 335°). Et 3-aldehydo-2-methyl-4-ethylpyrrole-5-carboxylate yields the *oxime*, m.p. 167°, which gives the corresponding 3-*CN*-compound, m.p. 138°. This in Et_2O with SO_2Cl_2 gives *Et* 2-*dichloromethyl*-3-*cyano*-4-*ethylpyrrole*-5-*carboxylate*, m.p. 110°; when treatment with SO_2Cl_2 is followed by boiling with H_2O the 2-*OH·CH*$_2$, m.p. 128° and the 2-*CHO*-, m.p. 148°, derivatives of Et 3-cyano-4-ethylpyrrole-5-carboxylate are obtained. Et 3-cyano-2 : 4-dimethylpyrrole-5-carboxylate in Et_2O boiled for several hr. with SO_2Cl_2 gives *Et* 3-*cyano*-4-*methyl*-2-*dichloromethylpyrrole*-5-*carboxylate*, m.p. 123°, converted into *Et* 2-*aldehydo*-3-*cyano*-4-*methylpyrrole*-5-*carboxylate*, m.p. 158° (*oxime*, m.p. 198°, obtained in the cold; when heat is used, a *substance*, m.p. 259°, is also obtained), by boiling with 50% aq. EtOH. The oxime is converted in the usual way into *Et* 2 : 3-*dicyano*-4-*methylpyrrole*-5-*carboxylate*, m.p. 135°. The effects of substituents on the acidity of derivatives of pyrrole have been determined by titration and it is shown that some of the derivatives act as acids although containing no true acid group. 4-Cl and 4-Br confer acidity. W. McC.

Protochlorophyll and vinylphæoporphyrin-a_5. H. Fischer, H. Mittenzwei, and A. Oestreicher (Z. physiol. Chem., 1939, **257**, IV—VII; cf. A. 1936, 1393; Noack and Kiessling, A., 1931, 247).—Methylphæophorbide-*a* (I) in HCO_2H boiled for 3·5 min. with Fe powder yields a complex Fe salt, converted by 20% HCl or, better, by leaving overnight in Et_2O, followed by treatment with CH_2N_2, into vinylphæoporphyrin-a_5 (II), m.p. >320°, which gives a cryst. *compound* when heated for 12 hr. at 100° with $CHN_2·CO_2Et$ followed by treatment with CH_2N_2 and is identical with the product obtained from protochlorophyll by removal of Mg with $H_2C_2O_4$. The chief component of the chlorophyll of the skins of gourd seeds is the Mg salt of (II). (II) is also obtained from 10-acetoxyvinylphæoporphyrin-a_5 by hydrolysis with conc. H_2SO_4 (which gives 10-*hydroxyvinylphæoporphyrin*-a_5) followed by long treatment with HCO_2H at 50—60°. When the treatment given to (I) is applied to pyrophæophorbide-*a*, *vinylphylloerythrin*, m.p. >33°, spectroscopically identical with (II), is obtained. (II) with dil. KOH in MeOH gives vinylchloroporphyrin-e_6, reconverted into (II) by C_5H_5N and Na_2CO_3. W. McC.

Bile pigments. XXI. Aminohydroxypyrromethenes. Pentduopent reaction. H. Fischer, H. Reinecke, and H. Lichtenwald (Z. physiol. Chem., 1939, **257**, 190—200; cf. A., 1935, 994; 1938, II, 509).—The azo-dye from the Me ester of neoxanthobilirubinic acid gives, with hot AcOH and Zn powder, *Me* 5′-*amino*-5-*hydroxy*-3′ : 4-*dimethyl*-3-*ethylpyrromethene*-4′-*propionate*, m.p. 202° (*Ac*$_1$ derivative, m.p. 216°). In the same way the azo-dye from the Me ester of *iso*neoxanthobilirubinic acid (I) gives *Me* 5′-*amino*-5-*hydroxy*-3 : 3′-*dimethyl*-4-*ethylpyrromethene*-4′-*propionate*, m.p. 181° (*Ac*$_1$ derivative, m.p. 216°), also obtained from the azo-dye of the Me ester of (I) by catalytic reduction (PtO_2–H_2–AcOH); that from the Me ester of *iso*coproneoxanthobilirubinic acid gives *Me*$_2$ 5′-*amino*-5-*hydroxy*-3 : 3′-*dimethylpyrromethene*-4 : 4′-*dipropionate*, m.p. 171°, and that from the Me ester of coproneoxanthobilirubinic acid (II) gives *Me*$_2$ 5′-*amino*-5-*hydroxy*-4 : 3′-*dimethylpyrromethene*-3 : 4′-*dipropionate*, m.p. 180° (*Ac*$_1$ derivative, m.p. 185°). The no. of H in the Ac derivatives is 2 < the calc. no. but catalytic reduction does not introduce 2 H. The aminohydroxypyrromethenes when warmed with strong alkali or treated successively with $NaNO_2$ and NaOH give the pentduopent reaction. If the solution is diluted the reaction is negative but becomes positive after warming with $Na_2S_2O_4$. Opsopyrrole (III) in MeOH couples with PhN_2Cl to give a bisazo-*dye* (IV), m.p. 222° [*dihydrochloride*, m.p. 185°; complex *Cu* salt, $C_{26}H_{26}N_6Cu$, m.p. 234° (decomp.), 2 pyrrole rings to 1 Cu, stable to alkali, acid eliminates Cu], and with diazotised *p*-$C_6H_4Me·NH_2$ the corresponding bisazo-*dye*. On catalytic hydrogenation

(IV) takes up first 8 H and then, after separation of the rings, 2 H. The carboxylic acid of (III) in $CHCl_3$ with MeOH and PhN_2Cl followed by treatment with HBr gives the *hydrobromide*, m.p. 203°, of the azo-dye (V), $C_{28}H_{28}O_4N_6$, and in the same way the aldehyde of the carboxylic acid gives the azo-*dye* (VI), $C_{15}H_{15}O_3N_3$, m.p. 145° (*oxime*, m.p. 158°). The carboxylic acid of (III) treated with H_2O_2 in C_5H_5N gives 5-hydroxy-3-methylpyrrole-4-propionic acid (VII), m.p. 187°, and a *substance*, $C_8H_{11}O_3N$, m.p. 169° (cf. A., 1937, II, 215). (VI) and the carboxylic acid boiled for 8 hr. in MeOH containing HBr followed by treatment with conc. HCl give the hydrochloride of Me_2 5-hydroxy-5′-azobenzene-4 : 3′-dimethylpyrromethene-3 : 4′-dipropionate and, similarly, (VI) and (VII) give the hydrochloride of Me_2 5-hydroxy-5′-azobenzene-3 : 3′-dimethylpyrromethene-4 : 4′-dipropionate. W. McC.

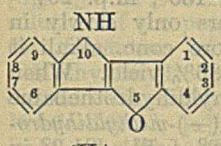
Adsorption values of porphyrins.—See A., 1939, I, 195.

[**Tautomerism of oximes.**] A. H. Blatt (J. Org. Chem., 1938, **3**, 506—507; cf. A., 1939, II, 38). —Many corrections of formulæ are made. H. W.

Benzoylformyloxindolephenylhydrazones.—See A., 1939, I, 178.

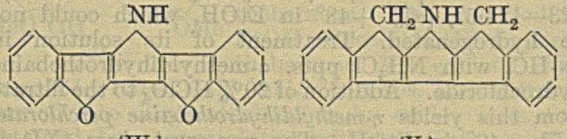
Oxazines.—See B., 1939, 297.

Indoles. V. Coumarono(3, 2-*b*)indole and derivatives. J. W. Cornforth, G. K. Hughes, F. Lions, and R. H. Harradence (J. Proc. Roy. Sci. New South Wales, 1938, **71**, 486—493).—Coumaranone (I) and $NHPh{\cdot}NH_2$ at 100° give a gummy phenylhydrazone, which passes in boiling glacial AcOH into



(II.)

coumarono-(3, 2-b)-*indole* (II), m.p. 198°. The 7-*methyl*-, m.p. 183°, 7-*bromo*-, m.p. 159°, 6 : 7-*benz*-, m.p. 166°, and 10-*methyl*-, m.p. 240°, -derivatives are obtained analogously from (I) and p-$C_6H_4Me{\cdot}NH{\cdot}NH_2$, p-$C_6H_4Br{\cdot}NH{\cdot}NH_2$, β-$C_{10}H_7{\cdot}NH{\cdot}NH_2$, and $NPhMe{\cdot}NH_2$, respectively. (I), N_2H_4,H_2SO_4, and NaOAc in boiling EtOH–H_2O yield *coumaranoneazine* (III), m.p. 207—208°, which is not hydrolysed by HCl–MeOH but is readily affected by aq. HCl. Boiling glacial AcOH transforms (III) into *dicoumaronopyrrole* (IV), m.p. 330°. 2-*Hydrindoneazine*, m.p. 195—196°, is very readily cyclised to 2 : 1 : 2′ : 1′-*di-indeno*-2 : 3 : 4 : 5-*pyrrole* (V), m.p. >360°, by treatment with cold, 5% HCl–MeOH or HCl–EtOH, by passing dry HCl into its suspension in Et_2O, or by boiling it for a few min. with glacial



(IV.) (V.)

AcOH, whereas 3-*hydrindoneazine* affords only 1 : 2 : 1′ : 2′-*di-indeno*-2 : 3 : 4 : 5-*pyrrole*, m.p. >360°, when dry HCl is passed over the fused material at about 170°. H. W.

Cyanine dyes.—See B., 1939, 328.

Thi- and selen-azoles.—See B., 1939, 245, 248.

Rhodanine dyes [photosensitisers].—See B., 1939, 328.

***Cactus* alkaloids. XX. *O*-Methyl-*d*-anhalonidine.** E. Späth and J. Bruck (Ber., 1939, **72**, [*B*], 334—338; cf. A., 1938, II, 71).—Repeated fractional extraction of the mother-liquors from the non-phenolic bases of mezcal buttons gives portions from which, after treatment with tartaric acid in MeOH, *N*-methylmescaline and d-O-*methylanhalonidine* (I) [d-6 : 7 : 8-*trimethoxy*-1-*methyl*-1 : 2 : 3 : 4-*tetrahydroisoquinoline*], b.p. 140° (bath)/0·05 mm., $[\alpha]_D^{16}$ +20·7° in MeOH [2 : 4 : 6-*trinitrobenzoyl* derivative (II), m.p. 259—260° (vac.), $[\alpha]_D^{13}$ +39·7° in $CHCl_3$], are isolated. The constitution of (I) follows from the identity of (I) and (II) with the compounds obtained by the resolution of synthetic *r*-6 : 7 : 8-trimethoxy-1-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline with *d*-tartaric acid in H_2O. The 1-*base* has $[\alpha]_D^{16}$ −20·1° in MeOH [2 : 4 : 6-*trinitrobenzoyl* derivative, m.p. 259—260° (vac.), $[\alpha]_D^{13}$ −43·7° in $CHCl_3$]. H. W.

Carnosine and anserine. V. du Vigneaud and O. Behrens (Ergebn. Physiol., 1939, **41**, 917—973).—A review.

Cinchona alkaloids. XXX. Syntheses in the series of the cinchona alkaloids. P. Rabe and K. Kindler (Ber., 1939, **72**, [*B*], 263—264).—*epi*Quinine *epi*quinidine sulphate, $C_{20}H_{24}O_2N_2,C_{20}H_{24}O_2N_2,H_2SO_4,6H_2O$, has been isolated from the residue left after removal of quinine and quinidine from the products of the reduction of quininone by Al powder and NaOEt in EtOH (cf. A., 1918, I, 303). Normal epi*quinine hydrobromide*, m.p. 71—77°, decomp. 108°, and normal epi*quinidine thiocyanate*, m.p. 193°, are described. H. W.

Modified cinchona alkaloids. VI. Niquidine. E. M. Gibbs and T. A. Henry (J.C.S., 1939, 240—246).—Quinidine with HI–P gives α-iododihydroquinidine, m.p. 202° (decomp.), $[\alpha]_D^{18}$ +259° in 0·1N-HCl [*dihydrochloride* (+5·5H_2O), m.p. 202° (decomp.), $[\alpha]_D^{18}$ +224·4° in 0·1N-HCl; *acid sulphate* (+4H_2O), m.p. 172° (decomp.), $[\alpha]_D^{18}$ +212·3° in 0·1N-HCl], and with HBr affords a mixture of α-, decomp. 235°, $[\alpha]_D^{18}$ +271·2° in 0·1N-HCl [*acid sulphate* (+4H_2O), m.p. 180°, $[\alpha]_D^{18}$ +217·2° in 0·1N-HCl], and α′-*bromodihydroquinidine* (+3H_2O), m.p. 210° (decomp.), $[\alpha]_D^{18}$ +231·7° in 0·1N-HCl [*nitrate*, m.p. 225° (decomp.); *dihydrobromide* (+3H_2O), m.p. 235° (decomp.), $[\alpha]_D^{18}$ +166° in H_2O; *sulphate* (+3H_2O), m.p. 207°, $[\alpha]_D^{18}$ +206·1° in 0·1N-HCl]. Debromination of crude bromodihydroquinidine with $AgNO_3$ gives CH_2O and "niquidine" (cf. Domanski and Suszko, A., 1936, 490), which can be separated into *niquidine* (I), probably $CHMe{:}CH{\cdot}CH<\begin{matrix}CH_2\\CH_2{\cdot}CH_2{\cdot}NH\end{matrix}>CH{\cdot}CHQ{\cdot}OH$ (Q = quinolyl or 6-methoxyquinolyl), $C_{19}H_{24}O_2N_2$, m.p. 172°, $[\alpha]_D^{18}$ +301·5° in 0·1N-H_2SO_4 [*dihydrobromide* (+2H_2O), m.p. 230° (decomp.), $[\alpha]_D^{18}$ +198·7° in H_2O], and iso*quinidine* (II), $C_{19}H_{24}O_2N_2$, m.p. 163°, $[\alpha]_D^{18}$ +222·0° in 0·1N-H_2SO_4. Hydrogenation (H_2–PtO_2) of either (I) or (II) yields *dihydroniquidine*, m.p. 165°, $[\alpha]_D^{18}$ +231·6° in 0·1N-H_2SO_4 [*sulphate* (+2H_2O), m.p. 180°, $[\alpha]_D^{18}$ +200·4° in 0·1N-H_2SO_4; *NO*-derivative,

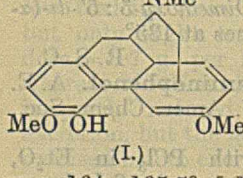
m.p. 170°; N-*Me* derivative, m.p. 212°, $[\alpha]_D^{18}$ +234° in 0·1N-H_2SO_4; *phenylthiocarbamide*, m.p. 112°], indicating that (I) and (III) are geometrical isomerides. The H_2-base in AcOH is converted by boiling into *epi*-C_9-dihydroniquidine, $[\alpha]_D^{18}$ −140·8° in 0·1N-H_2SO_4 [*sesquihydrobromide* (+H_2O), m.p. 240° (decomp.), $[\alpha]_D^{18}$ −102·8° in 0·1N-H_2SO_4; *sesquinitrate* (+2H_2O), m.p. 196° (decomp.), $[\alpha]_D^{18}$ −110·3° in 0·1N-H_2SO_4], also obtained from *epi*-C_9-quinidine through *iododihydro*epi-C_9-*quinidine*, m.p. 150—155° (decomp.).

F. R. S.

Addition of Grignard's reagent to ψ-codeine types. III. Methyldihydrothebaines. L. Small and E. M. Fry (J. Org. Chem., 1939, **3**, 509—540; cf. A., 1936, 490, 1277).—Gradual addition of thebaine to a solution of MgMeI in boiling Et_2O gives mainly α-*methyldihydrothebaine* (I), m.p. 87·5—89·5°, $[\alpha]_D^{25}$ +140° in EtOH (*perchlorate*, $[\alpha]_D^{25}$ +84° in EtOH; *methiodide*, m.p. 219—221°, $[\alpha]_D^{20}$ +76° in EtOH), which could not be hydrogenated (Adams' catalyst in EtOH or PtO_2–PdO_2) and is not affected by short boiling with conc. HCl. The *acetate* (*perchlorate*, $[\alpha]_D^{25}$ +78° in EtOH, and *methiodide hemihydrate*, m.p. 193—195°, $[\alpha]_D^{25}$ +55° in EtOH) is described. MeI and NaOH convert (I) into α-*methyldihydrothebaine Me ether methiodide*, m.p. 177—178°, $[\alpha]_D^{21}$ +43·3° in EtOH, with an unidentified by-product, m.p. about 60° and >230° after resolidification at about 100°, $[\alpha]_D$ ±0°. Boiling 40% NaOH transforms (I) into α-*methyldihydrothebaine*isomethine (II) (*Na* salt), isolated as the *salicylate* (III), m.p. 163—164·5°, $[\alpha]_D^{20}$ −90° in EtOH, and *methiodide* (IV), m.p. 227—230°, $[\alpha]_D^{25}$ −80° in EtOH. Reduction (Adams) of (II) affords non-cryst. *dihydro*-α-*methyldihydrothebaine*isomethine, isolated as the *salicylate*, m.p. 165—167°, $[\alpha]_D^{25}$ −47·7° in EtOH. (IV) is extremely resistant to the ordinary Hofmann degradation but is converted by TlOH followed by boiling 50% NaOH into the optically inactive, non-cryst. *vinyldihydro*-x-*methylthebaol* (V) (*Na* salt); the corresponding *Ac* derivative, m.p. 103—105·5°, $[\alpha]_D^{25}$ ±0° in EtOH, absorbs 2 H_2 forming a non-cryst. substance hydrolysed to a non-cryst. compound. Successive treatment of (II) with boiling conc. HCl, NH_3, MeI, and 40% NaOH gives a mixture of (+)-6-*methoxy*-x-*methylthebentriene* (VI), m.p. 99—101°, $[\alpha]_D^{22}$ +9° in EtOH, and r-6-*methoxy*-x-*methylthebentriene*, m.p. 91·5—93·5°, obtained also by admixture of equal amounts of the corresponding optical antipodes and by the action of boiling, conc. HCl on (V). (VI) is not racemised or hydrolysed by conc. HCl but is reduced (PtO_2 in EtOH) to 6-*methoxy*-x-*methylthebendiene*, m.p. 56—59·5°, $[\alpha]_D^{20}$ −5° in EtOH. Boiling AcCl transforms (III) into an alkali-sol., non-cryst. base (*salicylate*; *benzoate*; *phthalate*, m.p. 150—160°; *fumarate*; *picrate*, m.p. 172—180°) and an alkali-insol. α-9-*dimethylamino*-6-*methoxy*-x-*methylthebendiene*, m.p. 76·5—78°, $[\alpha]_D^{22}$ −82° in EtOH, which is indifferent towards catalytic hydrogenation; the corresponding *methiodide*, m.p. 115—117°, $[\alpha]_D^{25}$ −51° in EtOH, is degraded (Hofmann) to (VI). Passage of (I) over Zn dust–pumice at a dull red heat gives a small proportion of phenanthrene, also obtained at a lower temp. with an unidentified *compound*, m.p. 116—120° (*picrate*, 133—134°). Non-cryst. δ-*methyldihydrothebaine* (VII) [*perchlorate*, $[\alpha]_D^{25}$ +50° in EtOH; non-cryst. *Ac* derivative (*perchlorate*, $[\alpha]_D^{25}$ +67·5° in EtOH; *methiodide* (+H_2O), softens at 109° and m.p. 198° after becoming dehydrated, $[\alpha]_D^{25}$ +56° in EtOH)] is obtained as a by-product of the prep. of (I) or by treating the perchlorate of (I) with boiling EtOH. The base and its hydrochloride are not hydrogenated (Adams) in EtOH. Treatment of the amorphous methiodide of (VII) with boiling 40% NaOH yields the non-cryst. δ-*methyldihydrothebaine*-isomethine (VIII) (*salicylate*, m.p. 209—211° after softening slightly at 190°, $[\alpha]_D^{20}$ −16° in EtOH; *methiodide monohydrate*, m.p. 176·5—178·5° and 233° after resolidification at 180°, $[\alpha]_D^{23}$ −30° in EtOH). δ-*Methyldihydrothebaine*isomethine *Me ether methiodide*, m.p. 172·5—174°, $[\alpha]_D^{22}$ −25° in EtOH, is converted by the successive action of 40% NaOH and picric acid into δ-*methyldihydrothebaine*isomethine *Me ether picrate*, m.p. 172—174°. Hydrogenation (PtO_2 in EtOH) of (VIII) gives the non-cryst., phenolic *dihydro*-δ-*methyldihydrothebaine*isomethine [*salicylate* (IX), m.p. 182·5—185·5°, $[\alpha]_D^{20}$ +12·8° in EtOH], the methiodide of which is degraded to (V). AcCl, pretreated with a little H_2O, transforms (VIII) into a compound hydrolysed by NaOH to *hydroxydihydro*-δ-*methyldihydrothebaine*isomethine, m.p. 163—165°, $[\alpha]_D^{30}$ +25° in EtOH, transformed by AcCl–HCl into δ-9-*dimethylamino*-6-*methoxy*-x-*methylthebendiene*, m.p. 101·5—103°, $[\alpha]_D^{23}$ +33° in EtOH, which is indifferent towards catalytic hydrogenation. The closure of the thebenane ring is accomplished in a single operation when (IX) is boiled with AcCl. Degradation of δ-9-*dimethylamino*-6-*methoxy*-x-*methylthebendiene methiodide* (+0·5H_2O), softens at 155°, m.p. 207—208°, $[\alpha]_D^{25}$ −13° in EtOH, occurs only slowly in boiling 40% NaOH but with more conc. alkali it proceeds smoothly, giving (VI) in 86% yield. When heated at 98°/vac. acetyl-δ-methyldihydrothebaine methohydroxide passes into (−)-*methyldihydrothebainemethine* (X), m.p. 106—108°, $[\alpha]_D^{23}$ −21·3° in EtOH (*tartrate*, m.p. 135—140°, $[\alpha]_D^{25}$ −7° in EtOH; corresponding *Me ether methiodide*, m.p. 190—192°, $[\alpha]_D^{23}$ +20° in EtOH), whereas at 128°/vac. it gives r-*methyldihydrothebainemethine*, m.p. 139·5—141·5°, $[\alpha]_D^{25}$ ±0° in EtOH. (−)-Methyldihydrothebaine-9 : 10-dihydromethine Me ether (*tartrate*, m.p. 106—110°, $[\alpha]_D^{22}$ +32·3° in EtOH; *methiodide*, m.p. 182—183° after softening at about 170°, $[\alpha]_D^{29}$ +29·1° in EtOH) is unchanged by boiling conc. HCl. (X) yields a *methiodide*, m.p. >230°, degraded by 40% NaOH to (V) and its (+)-isomeride. When heated at 125° in vac. for 4 days (I) is mainly transformed into the mol. compound, *αη-methyldihydrothebaine*, m.p. 123—124·5°, $[\alpha]_D^{23}$ +48° in EtOH, which could not be hydrogenated. Treatment of its solution in 6N-HCl with NH_4Cl ppts. α-methyldihydrothebaine hydrochloride. Addition of 20% $HClO_4$ to the filtrate from this yields η-*methyldihydrothebaine perchlorate*, $[\alpha]_D^{25}$ −49° in EtOH. The non-cryst. *base* (XI) is indifferent towards catalytic hydrogenation. δη-*Methyldihydrothebaine perchlorate* $[\alpha]_D$ ±0°, gives a *base*, m.p. 79—83°. Degradation of (XI) is exactly analogous to that of (VII), giving at every step derivatives having the same composition as, but rotatory power opposite to, those of the δ-series with which

compounds having the properties of racemates were formed. *η-Methyldihydrothebaineisomethine salicylate*, prepared as described for the δ-compound, has m.p. 209—211°, $[\alpha]_D^{20}$ +14° in EtOH; it gives the corresponding *δη-compound*, m.p. 190—195° (decomp.), $[\alpha]_D^{25}$ ±0° in EtOH. The non-cryst. η-methyldihydrothebaine*iso*methine is transformed by partly hydrolysed AcCl into *hydroxydihydro-η-methyldihydrothebaineisomethine*, m.p. 163·5—165·5°, $[\alpha]_D^{25}$ −23° in EtOH (corresponding *δη-compound*, m.p. 167—168·5°, $[\alpha]_D^{25}$ ±0° in EtOH), and *9-dimethylamino-6-methoxy-η-methylthebendiene* (XII), m.p. 101—103°, $[\alpha]_D^{25}$ −34° in EtOH (*δη-substance*, m.p. 110—112°, $[\alpha]_D$ ±0° in EtOH). Boiling 80% NaOH degrades (XII) to (−)-*6-methoxy-x-methylthebentriene*, m.p. 99—101·5°, $[\alpha]_D^{25}$ −7·2° in EtOH (r-*compound*, m.p. 91·5—94°, $[\alpha]_D$ ±0° in EtOH). (XI) is converted by MeI and 3N-alkali into the Me ether methiodide, degraded by boiling 40% NaOH into (+)-*methyldihydrothebainemethine Me ether methiodide*, m.p. 190·5—192°, $[\alpha]_D^{25}$ −20° in EtOH (corresponding r-*compound*, m.p. 207·5—209·5°, $[\alpha]_D$ ±0° in EtOH), and *η-methyldihydrothebaineisomethine Me ether methiodide*, m.p. 172·5—178°, $[\alpha]_D^{25}$ +26·4° in EtOH. At 155°/vac. for 10 hr. (VII) passes into the bimol. *δω-methyldihydrothebaine* (XIII), m.p. 123—124·5°, $[\alpha]_D^{25}$ −48° in EtOH. This is dissolved in 6N-HCl and treated with saturated aq. NH_4Cl, whereby *ω-methyldihydrothebaine hydrochloride* is pptd. The free *base* (XIV) has m.p. 86·5—89·5°, $[\alpha]_D^{25}$ −140° in EtOH (*perchlorate*, $[\alpha]_D^{25}$ −81° in EtOH). Equal wts. of it and the δ-base afford (XIII). Equal wts. of it and (I) afford the racemic *αω-methyldihydrothebaine*, m.p. 179—182°, $[\alpha]_D$ ±0° in EtOH. Protracted ebullition of a conc. solution of the perchlorate of (XI) in EtOH leads to the formation of a small proportion of (XIV). ω-Methyldihydrothebaine methiodide is degraded to ω-methyldihydrothebaine*iso*methine (*salicylate*, m.p. 161·5—165·5°, $[\alpha]_D^{25}$ +85° in EtOH; *αω-methyldihydrothebaineisomethine salicylate* has m.p. 201—204°, $[\alpha]_D^{25}$ ±0° in EtOH). Speculations on the structure of the series are offered. H. W.

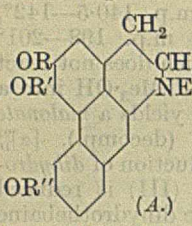
Reduction studies in the morphine series. VII. Thebaine. L. Small and G. L. Browning, jun. (J. Org. Chem., 1939, **3**, 618—637).—Codeine Me ether is converted by NaOEt–EtOH at 100° into *thebainone Me enolate* (I), m.p. 154—156° after slight softening at 148°, $[\alpha]_D^{22}$ +9·6° in 95% EtOH, which is too readily hydrolysed to permit the isolation of salts. It is converted by warm 3N-HCl into thebainone. Na and boiling EtOH reduce (I) to Δ⁵:⁶-dihydrothebainone Me enolate (II), m.p. 164—165·5°, $[\alpha]_D^{25}$ −115·7° in abs. EtOH, transformed into dihydrothebainone by acids; it is also obtained by the catalytic reduction (PtO_2 in abs. EtOH) of (I). iso*Codeine Me ether*, m.p. 80—82° (*salicylate*, m.p. 158—159°, $[\alpha]_D^{24}$ −122·4° in H_2O), codeine, *iso*codeine, and tetrahydrothebaine are recovered nearly quantitatively from the attempted rearrangement with NaOEt and at higher temp. only decomp. products result. Hydrogenation (Pd–$BaSO_4$ in 95% EtOH containing $NaHCO_3$) of thebaine (III) gives *dihydrothebainol 6-Me ether*, m.p. 140·5—142°, $[\alpha]_D^{21}$ −23·4° in EtOH [*fumarate*, m.p. 198—201° (decomp.), $[\alpha]_D^{22}$ −28·1° in H_2O], which does not react with CH_2N_2 but is converted by $NPhMe_3$·OH into a non-cryst. Me ether and (II), which yields a *malonate* and a *fumarate*, m.p. 215—217° (decomp.), $[\alpha]_D^{23}$ −64·4° to −39·0° in H_2O, with production of *dihydrothebainone fumarate*, m.p. >220°. (III) is reduced by Na and boiling EtOH to phenolic dihydrothebaine (IV), m.p. 152—154°, $[\alpha]_D^{27}$ +25·5° in EtOH, hydrogenated (PtO_2 in EtOH) to Δ⁶:⁷-*dihydrothebainone Me enolate*, m.p. 127—128°, $[\alpha]_D^{27}$ −8·0° in EtOH, readily hydrolysed to dihydrothebainone. (IV) is converted by H_2O saturated with SO_2 at 25° into *α-thebainone*, $C_{18}H_4O_3N$, m.p. 184—185°, $[\alpha]_D^{27}$ +158·5° in $CHCl_3$. An excess of dil. aq. $KHSO_4$ transforms (IV) at 25° into *β-thebainone*, $C_{18}H_{21}O_3N,H_2O$, m.p. 98—99° after softening at 92°, $[\alpha]_D^{27}$ +114·9° in $CHCl_3$ [*perchlorate* (+$2H_2O$) (V), m.p. 149—157°, $[\alpha]_D^{27}$ +67·3° in EtOH; *hydrobromide*, m.p. 168—169° (vac.; decomp.), $[\alpha]_D^{27}$ +61·1° in H_2O; *hydriodide*, m.p. 150—155° (vac.; decomp.), $[\alpha]_D^{27}$ +55·3° in H_2O; *picrate*, m.p. 172—183° (decomp.), $[\alpha]_D^{27}$ +43·8° in $COMe_2$; non-cryst. *oxime* and its *fumarate*, m.p. 220·5° (vac.), $[\alpha]_D^{27}$ +46·0° in H_2O; non-cryst. *semicarbazone* and its *picrate*, m.p. 203—204° (vac.; decomp.)]. Hydrogenation (PtO_2 in EtOH) of (V) and treatment of the product with NH_3 affords *β-dihydrothebainone*, a non-cryst. liquid, $[\alpha]_D^{27}$ −48·1° in EtOH [*hydrochloride*, m.p. 245—248° (vac.) after partial melting at 183—190° followed by resolidification, $[\alpha]_D^{27}$ −34·4° in H_2O; *hydrobromide*, m.p. 182—185° and, after re-solidification, m.p. 225·5—227·5° (vac.), $[\alpha]_D^{27}$ −31·5° in H_2O; *perchlorate*, m.p. 254—255° (vac.), $[\alpha]_D^{24}$ −32·5° in H_2O; *picrate*, m.p. 202—215° (vac.; decomp.), $[\alpha]_D^{27}$ −16·5° in $COMe_2$; *methiodide*, (+$2H_2O$) (VI), m.p. 149—154° (vac.); *oxime*, m.p. 225—226°, $[\alpha]_D^{21}$ −100·4° in EtOH]. Boiling 40% NaOH transforms (VI) into *β-dihydrothebainonemethine* (VII) [*de*-N-*methyl*-β-*dihydrothebainone*], m.p. 183—184°, $[\alpha]_D^{28}$ −257·9° in EtOH (*perchlorate*, m.p. 225·5—226° (vac.); *picrate*, m.p. 164—165° (vac.), $[\alpha]_D^{27}$ −181·1° in $COMe_2$; *oxime*, m.p. 160—162° (vac.)]. Hydrogenation (PtO_2 in dil. AcOH) of (VII) yields *β-dihydrothebainone dihydromethine* [*dihydrode*-N-*methyl*-β-*dihydrothebainone*] (VIII), m.p. 177—178° (vac.), $[\alpha]_D^{27}$ +63·8° in $CHCl_3$ [*hydrobromide*, m.p. 260—260·5° (vac.), $[\alpha]_D^{28}$ +24·0° in H_2O; *perchlorate*, m.p. 232·5—233·5° (vac.), $[\alpha]_D^{28}$ +23·8° in MeOH; *picrate*, m.p. 203—207° (vac.; decomp.), $[\alpha]_D^{27}$ +18·2° in $COMe_2$]; its oxime is non-cryst. and does not yield cryst. salts. Successive treatment of (VIII) with MeI in C_6H_6 and boiling 40% NaOH affords *β-thebenone*, m.p. 189—190°, $[\alpha]_D^{23}$ +113·6° in EtOH (*oxime*, m.p. 176—177°, $[\alpha]_D^{28}$ +30·6° in EtOH). H. W.



(I.)

Constitution of tuduranine. K. Goto and H. Shishido (Proc. Imp. Acad. Tokyo, 1939, **15**, 8—9; cf. A., 1936, 88; 1937, II, 435).—Tuduranine (I) is 1-3-*hydroxy*-5 : 6-*dimethoxy*-N-*noraporphine*. Notice is given of the synthesis of the *substance A* (R = R″ = Me, R′ = Et), which is shown by the products obtained from it by the Hofmann degradation not to be identical with the Et derivative of natural (I).

The compound *A* (R = Et; R′ = R″ = Me) could be obtained in only very small yield. r-5 : 6-*Dimethoxy-3-ethoxy-N-ethylnoraporphine ethiodide*, m.p. 186—187°, is converted into de-*N*-diethyltuduranine Et ether ethiodide, new m.p. 194°, and thence into 5 : 6-dimethoxy-3-ethoxy-8-vinylphenanthrene, m.p. 108°, identical with the substances derived from the natural alkaloid. H. W.



(*A.*)

Delphinine. W. A. Jacobs and L. C. Craig (J. Biol. Chem., 1939, **127**, 361—366).—The seeds of *Delphinium staphisagria*, L., yield to light petroleum delphinine (I), new formula, $C_{33}H_{45}O_9N$, m.p. 198—200°, $[\alpha]_D^{25}$ +25° in abs. EtOH (*hydrochloride*, m.p. variable, 208—210°). With NaOH–aq. MeOH (I) gives 1 mol. each of BzOH and AcOH, with H_2–PtO_2 at 3 atm. in EtOH containing a little AcOH gives a H_6-derivative, m.p. 192—193° (hydrolysed to hexahydrobenzoic acid instead of BzOH), with KOH at 260° gives NH_2Me, and with $KMnO_4$–$COMe_2$ yields the neutral substance, " X 214° " (II) (Keller, A., 1925, i, 831), m.p. 218—220° or 225°. (II) retains the OBz and OAc, but has lost the *N*-Me. An OH is present in (I). R. S. C.

Alkaloids of fumariaceous plants. XVIII. *Fumaria officinalis*, L. R. H. F. Manske (Canad. J. Res., 1938, **16**, **B**, 438—444).—The following alkaloids have been isolated: protopine, *dl*-tetrahydrocoptisine, cryptocavine, aurotensine, and possibly sinactine, m.p. 177°, $[\alpha]_D^{23}$ −78·9° in $CHCl_3$. Two new *alkaloids* have also been obtained: $C_{21}H_{23}O_5N$, m.p. 177°, non-phenolic, containing 2 OMe, and $C_{20}H_{19}O_6N$, m.p. 256°, phenolic and probably a phthalide *iso*quinoline alkaloid. A neutral *substance*, $C_{11}H_{10}O_3$, m.p. 152°, has been isolated. The significance of alkaloid structure in an evolutionary series of plants is discussed. F. R. S.

Lobinaline, an alkaloid from *Lobelia cardinalis*, L. R. H. F. Manske (Canad. J. Res., 1938, **16**, **B**, 445—448).—Only one alkaloid, *lobinaline*, $C_{28}H_{38}ON_2$, m.p. 94—95°, $[\alpha]_D^{24}$ +22·3° in $CHCl_3$ [*monohydrochloride* (+1·5H_2O), m.p. 220°], has been isolated. Oxidation with $KMnO_4$ yields BzOH in amount insufficient for the presence of two mono-substituted C_6H_6 nuclei. F. R. S.

Calycanthine. III. Degradation experiments. L. Marion and R. H. F. Manske (Canad. J. Res., 1938, **16**, **B**, 432—437).—Dehydrogenation of calycanthine (I) by either Se or Zn gives a base, $C_{16}H_{10}N_2$ (?), m.p. 307°, and 4-carboline; this supports the structure for (I) previously suggested (A., 1931, 855). Reduction (P–HI) of (I) affords quinoline and oxidation [$Hg(OAc)_2$] results in the formation of a base with loss of 2 H. *o*-$C_6H_4(CO)_2O$ and (I) yield 12 : 13-*benzcanthin*-11-*one* (?), m.p. 227°, also obtained from tryptamine and *o*-$C_6H_4(CO)_2O$. Tryptamine and $(CH_2{\cdot}CO)_2O$ give 3 : 4 : 5 : 6 : 12 : 13-*hexahydro*-3-*hydroxycanthin*-11-*one* (?), m.p. 172°. The *phenylcarbamyl* derivative of (I) has m.p. 252°. Methylation of (I) with MeI gives products containing 1, 2, and 3 O, which are not homogeneous; the N is eliminated as NH_2Me. F. R. S.

Alkaloids of *Salsola richteri*. IV. Salsolidine. N. Proskurnina and A. Orekhov (Bull. Soc. chim., 1939, [v], **6**, 144—146; cf. A., 1937, II, 265, 394; 1938, II, 117).—*d*- and *l*-Salsolidine each exist in two forms, m.p. 47—48° and 71—73°, produced respectively by distilling in vac. and by crystallising from H_2O; they give the same salts and have the same [α]. The free racemic base is said to absorb CO_2 far more rapidly than the active isomerides, and the base, m.p. 117—119°, previously reported was the carbonate. A. Li.

Behaviour of alkaloids to filtered ultra-violet light.—See A., 1939, I, 178.

Arsenic derivatives of phenylmethylcarbinol. C. K. Banks and C. S. Hamilton (J. Amer. Chem. Soc., 1939, **61**, 357—360).—3 : 4 : 1-$NO_2{\cdot}C_6H_3(OH){\cdot}COMe$ (modified prep.) and Raney Ni–H_2 give 3-*amino*-4-*hydroxyacetophenone*, m.p. 98° [*hydrochloride*, m.p. >250° (decomp.)], which yields (Bart) 4-*hydroxy*-3-*arsinoacetophenone*, m.p. 225°, and thence (SO_2) 2-*hydroxy*-5-*acetylphenylarsenious oxide*, m.p. 104°, and 2 : 2′-*dihydroxy*-5 : 5′-*diacetylarsenobenzene*, m.p. 193—198° (decomp.), but attempts to reduce the CO to CH·OH lead to removal of AsO_3H_2. 3-*Amino*-4-*methoxyacetophenone*, m.p. 85° [*hydrochloride*, m.p. 170° (decomp.)], similarly prepared, gives similarly 4-*methoxy*-3-*arsinoacetophenone* (I), m.p. 212°, 2-*methoxy*-5-*acetylphenylarsenious oxide*, m.p. 294° (decomp.), and 2 : 2′-*dimethoxy*-5 : 5′-*diacetylarsenobenzene*, m.p. 168° (decomp.). H_2–Raney Ni reduces (I) in aq. NaOH at 80°/2·67 atm. to *Na H* 5-*methoxy*-2-α-*hydroxyethylphenylarsinate* (II), m.p. >300° (decomp.); decomp. of (II) by acid leads to loss of H_2O and formation of a *polymeride*, m.p. 295—320°, of 4-*aminostyrene*-3-*arsinic acid*, but Ac_2O yields α-4-*methoxy*-3-*arsinophenylethyl acetate*, m.p. ~320° (decomp.), and reduction affords 2 : 2′-*dimethoxy*-5 : 5′-*di*-(α-*hydroxyethyl*)*arsenobenzene*, m.p. 245—250° (decomp.) [*diacetate*, m.p. 268° (decomp.)]. The *oxime*, m.p. 200°, of (I) with H_2–Raney Ni in N-NaOH at 80°/3 atm. gives much (I) and a *polymeride*, m.p. >300°, of 2 : 2′-*dimethoxy*-5 : 5′-*divinylarsenobenzene* with small amounts of α-4-*methoxyphenylethylamine*-3-*arsinic acid*, m.p. 248° (decomp.) (*Ac* derivative, m.p. >300°), *di*- [*Ac* derivative, m.p. 278° (decomp.)] and *tri*-α-4-*methoxy*-3-*arsinophenylethylamine*, m.p. 205°. 2 : 2′-*Dimethoxy*-5 : 5′-*di*-(α-*oximinoethyl*)*arsenobenzene* sublimes at 135°. R. S. C.

Arsenicals derived from *m*-aminophenol. A. E. Beguin and C. S. Hamilton (J. Amer. Chem. Soc., 1939, **61**, 355—357).—4 : 2 : 1-$CO_2Et{\cdot}NH{\cdot}C_6H_3(OH){\cdot}AsO_3H_2$ with PCl_3 in Et_2O, followed by H_2O, gives 4-*carbethoxyamino*-2-*hydroxyphenylarsenious oxide*, m.p. 159° (*Na* salt), which with $(CH_2)_2O$ and KOH in EtOH gives β-3-*carbethoxyamino*-6-*arsinophenoxyethyl alcohol* (I), m.p. 233°, reduced to 4 : 4′-*di*(*carbethoxyamino*)-2 : 2′-*di*-(β-*hydroxyethoxy*)*arsenobenzene*, m.p. 222°. 4 : 2 : 1-$NH_2{\cdot}C_6H_3(OH){\cdot}AsO_3H_2$ with Ac_2O–AcOH gives 4-*acetamido*-2-*hydroxyphenylarsinic acid*, decomp. 266°, and with $ClCO_2Pr^{\alpha}$ and 2N-NaOH gives 4-*carbo-*

n-*propoxyamino*-2-*hydroxyphenylarsinic acid*, decomp. 220°, and thence the derived *arsenious oxide*, m.p. 198°. 4-*Carbobenzyloxyamino*-2-*hydroxyphenylarsinic acid* (II), decomp. 223°, is similarly prepared and yields the derived *arsenious oxide*, m.p. 217°, β-3-*carbobenzyloxyamino*-, m.p. 235°, and thence (0·5N-NaOH) β-3-*amino*-6-*arsinophenoxyethyl alcohol*, m.p. 164°. With propylene oxide and KOH–EtOH (II) gives β-3-*carbobenzyloxyamino*-, m.p. 176°, and thence β-3-*amino*-6-*arsinophenoxyisopropyl alcohol*, softens at 159°, which with $ClCO_2Et$ gives β-3-*carbethoxyamino*-6-*arsinophenoxyisopropyl alcohol* (III), m.p. 185°. m-NO_2·C_6H_4·$[CH_2]_2$·OH and Raney Ni–H_2 at 2·67 atm. yield β-m-*aminophenoxyethyl alcohol*, an oil (N-*Ac*, m.p. 106°, and N-CO_2Et-derivative, m.p. 56°), also obtained from (I) by Raney Ni–H_2 in $COMe_2$ at 2·67 atm. β-m-*Carbethoxyaminophenoxyisopropyl alcohol*, b.p. 225°/11 mm., is similarly prepared from the NO_2-compound or (III). R. S. C.

Relation between the constitution of 4-*p*-arsinoanilinonaphtha-1 : 2-quinone-8-sulphonic acid (2654N) and its therapeutic action. E. A. H. Friedheim (Arch. Sci. phys. nat., 1938, [v], **20**, Suppl., 73—78).—The trypanocidal action of 2654N depends on its 1 : 2-quinone structure. Thus, the leuco-derivative is slightly more toxic, but about as trypanocidal; the 2-Bz and 2-CO_2Et-derivatives (which are 1 : 4-quinone-imines) are slightly more toxic and considerably less trypanocidal; the dibenzoate of the leuco-derivative is not trypanocidal, being excreted unchanged, but the $(CO_2Et)_2$-derivative has some effect, being partly hydrolysed in the body; the *azine* [obtained by condensation with o-$C_6H_4(NH_2)_2$] and the *sulpho*- and *arsino-azines* (obtained by condensing with *o*-phenylenediamine-3-sulphonic and -3-arsinic acid, respectively) are not trypanocidal, but are very toxic, particularly the first-named (max. dose tolerated = 0·1 g. per kg.). The isomeric red 1 : 4-*quinone* (2-*p*-arsinoanilinonaphtha-1 : 4-quinone-8-sulphonic acid, obtained from arsanilic acid and naphtha-1 : 2-quinone-4 : 8-disulphonic acid in HCl, from naphtha-1 : 4-quinone-8-sulphonic acid, or from 2654N by dil. HCl) has no trypanocidal action and is very toxic (max. dose tolerated = 0·05 g. per kg.). 4-2′-*Hydroxy*-5′-*arsinoanilinonaphtha*-1 : 2-*quinone*-8-*sulphonic acid* (obtained from naphtha-1 : 2-quinone-4 : 8-disulphonic acid and 3-amino-4-hydroxyphenylarsinic acid) has low toxicity (max. dose tolerated = 3 g. per kg.), but only slight trypanocidal action (min. curative dose = 0·7 g. per kg.); it is excreted in the bile, whereas 2654N is eliminated by the kidneys. 2654N is partly reduced to the leuco-derivative before excretion, but the latter, when administered, is partly oxidised before excretion. R. S. C.

Decomposition of unsymmetrical organomercuric compounds. Method of establishing the relative electronegativities of organic radicals. M. S. Kharasch, R. R. LeGault, and W. R. Sprowls (J. Org. Chem., 1938, **3**, 409—413).—Cleavage experiments with HCl and Hg compounds show that the 2 : 4-$C_6H_3Cl_2$ radical is less electronegative than m-C_6H_4Cl and more electronegative than CH_2Ph. 2 : 5-$C_6H_3Cl_2$ is less electronegative than m-C_6H_4Cl and more so than Me. Direct substitution decreases the electronegativity of Ph. Introduction of a second Cl in the aromatic nucleus decreases still more the electronegativity of the C_6H_4Cl radicals. All substituted aromatic radicals thus far observed are more electronegative than any of the aliphatic radicals. *Compounds*, HgRCl, are described in which R = 2 : 4-$C_6H_3Cl_2$, m.p. 196°, 2 : 5-$C_6H_3Cl_2$, m.p. 205°, 2 : 4 : 6-$C_6H_2Cl_3$, m.p. 184°, CH_2Ph, m.p. 104°, Ph, m.p. 250—251°, o-C_6H_4Cl, m.p. 147°, m-C_6H_4Cl, m.p. 208°, and Me, m.p. 170°. Also *substances* HgRR′, in which the pairs of radicals are: Ph, 2 : 4-$C_6H_3Cl_2$; o-C_6H_4Cl, 2 : 4-$C_6H_3Cl_2$, m.p. 152—162°; m-C_6H_4Cl, 2 : 4-$C_6H_3Cl_2$, m.p. 136—142°; CH_2Ph, 2 : 4-$C_6H_3Cl_2$, m.p. 100—147°; Ph, 2 : 5-$C_6H_3Cl_2$, m.p. 120° after softening at 95°; m-C_6H_4Cl, 2 : 5-$C_6H_3Cl_2$, m.p. 134—138°; 2 : 5-$C_6H_3Cl_2$, Me, m.p. 75—80°; CH_2Ph, m-C_6H_4Cl, an oil. H. W.

Reactivity of organo-lithium compounds. E. Müller and T. Töpel (Ber., 1939, **72**, [*B*], 273—290).—LiBu and O_2 give Bu^sOH in 75% yield. An intermediate peroxide is probably formed since the Li salt of 1 : 2 : 3 : 4-tetrahydronaphthalene peroxide and LiPh give LiOPh and Li 1 : 2 : 3 : 4-tetrahydronaphth-1-oxide. LiPh and O_2 give about 65% of Ph_2, 18% of PhOH, and 6% of CHPhMe·OH formed by intervention of the solid. Only 4% of Ph_2 is formed during the prep. of the reagent. Analogously p-LiC_6H_4Ph, readily obtained from p-C_6H_4PhCl, gives >85% of quaterphenyl, about 3% of p-C_6H_4Ph·OH, and about 7% of Ph_2. p-LiC_6H_4Me and O_2 afford *p*-cresol (37%), *pp*′-ditolyl (35%), PhMe (8%), and *p*-tolylmethylcarbinol (corresponding *phenylurethane*, m.p. 92°) (yield 11%). From m-LiC_6H_4Me the yields of mm′-*ditolyl*, b.p. 280—284°, *m*-cresol, *m*-tolylmethylcarbinol (*phenylurethane*), and PhMe are respectively 17%, 31%, 22%, and 12% whilst from o-LiC_6H_4Me the yields of *oo*′-ditolyl, *o*-cresol, *o*-tolylmethylcarbinol (*phenylurethane*, m.p. 79—80°), and PhMe are 5%, 54%, 28%, and 60% respectively. p-LiC_6H_4·OMe and O_2 give about 26% of *pp*′-dianisyl, about 35% of p-OH·C_6H_4·OMe, and about 36% of PhOMe. Under mild conditions the formation of p-LiC_6H_4·OMe proceeds normally since the product is transformed by $COPh_2$ into diphenylanisylcarbinol, whence diphenylanisylcarbinyl chloride, m.p. 122°. Under more drastic conditions reaction occurs between p-LiC_6H_4·OMe and unchanged p-C_6H_4Br·OMe with formation of 2 : 4 : 1-LiC_6H_3Br·OMe. 2 : 1 : 4-$LiC_6H_3(OMe)_2$ and O_2 give 60% of the initial material and 40% of 2 : 1 : 4-OH·$C_6H_3(OMe)_2$; the formation of a dimeric compound could not be detected. $LiC_{10}H_7$-1 and O_2 yield exclusively α-$C_{10}H_7$·OH, the small amount of $(C_{10}H_7)_2$ found being formed during the prep. of the reagent. Similarly Li *ar*-α-bromotetrahydronaphthalene gives solely *ar*-α-tetrahydronaphthol. Li styryl affords a polymeric compound containing O which has not been identified but no diphenylbutadiene. $LiCH_2Ph$ gives mainly CH_2Ph·OH. An explanation of the unique behaviour of LiPh and p-LiC_6H_4Ph is advanced. NaPh could not be caused to react with O_2 in Et_2O. 9-Bromoanthracene and Li rapidly give *Li*$_2$ 9 : 10-*dihydro*-

anthracene (the isolation of the intermediate Li 9-anthryl appearing impossible). With NHPhEt it yields 9 : 10-dihydroanthracene and with CO_2 9 : 10-dihydroanthracenedicarboxylic acid. An additive compound is also formed from Li and 9 : 10-dibromoanthracene. 9-Bromo-1—8-octahydroanthracene and Li rapidly give 1—8-octahydroanthracene but the reaction cannot be stopped at the intermediate stage. 9-Bromophenanthrene reacts very slowly with Li; the Li compound immediately decomposes the Et_2O and the phenanthrene so formed adds to metal atoms at $C_{(9)}$ and $C_{(10)}$. During the prep. of $LiC_{10}H_7$-1 and *p*-LiC_6H_4Ph considerable amounts of hydrocarbon are formed by intervention of Et_2O; these add metallic Li with production of H_2-compounds. The incidence of the change is indicated by a change in colour and the action must be immediately interrupted at this stage if good yields of organo-Li compounds are to be obtained. Determination of yield by titration with acid is untrustworthy and should be replaced by reaction with ketones or BuBr. The applicability of Li compounds is restricted by their great activity towards Et_2O and $(CH_2{\cdot}OMe)_2$. *cyclo*Hexane-1 : 4-dione and *p*-LiC_6H_4Ph give the corresponding carbinol, which loses 2 H_2O during the reaction, yielding dihydroquinquephenyl; this becomes partly oxidised during manipulation so that ultimately the *quinhydrone*, m.p. 362—363°, from quinquephenyldihydroquinquephenyl results, and is dehydrogenated (Se) to quinquephenyl, m.p. 388—389°. Bis-βγ-dimethylbutadienebenzoquinone and LiPh afford *bis*-(2 : 3-*dimethylbutadiene*)*benzo*-9 : 10-*diphenylquinol*, m.p. 223—224°, dehydrogenated by Se at 270° to 9 : 10-*diphenyl*-2 : 3 : 6 : 7-*tetramethylanthracene*, m.p. 284—285°. H. W.

Arylated chlorostibiates and chlorostibanates. P. PFEIFFER and P. SCHMIDT (J. pr. Chem., 1939, [ii], 152, 27—44).—*m*-Chlorophenylstibinic acid (prep. from *m*-$C_6H_4Cl{\cdot}NH_2$ described) is dissolved in conc. HCl–MeOH–H_2O containing a trace of KI and reduced by SO_2 to *Sb* m-*chlorophenyl oxide*, which with C_5H_5N in AcOH–conc. HCl gives *pyridinium* m-*chlorophenylotrichlorostibiate*, m.p. 117—118°, and with quinoline yields the corresponding *quinolinium* compound, m.p. 118—119° (slight decomp.). *α-Naphthyldiazonium tetrachlorostibiate* is converted by 10% NaOH at room temp. into *α-naphthylstibinic acid*, whence *Sb α-naphthyl chloride*, m.p. 105°, and *pyridinium α-naphthylotrichlorostibiate*, m.p. (indef.) 90°. Analogously, β-$C_{10}H_7{\cdot}NH_2$ affords successively *β-naphthyldiazonium tetrachlorostibiate*, decomp. 100—120°, *β-naphthylstibinic acid*, *Sb β-naphthyl oxide*, m.p. (indef.) 135—140°, and *pyridinium β-naphthylotrichlorostibiate*. The following *-pentachlorostibanates* are obtained by treating a solution of the requisite stibinic acid with the requisite base dissolved in conc. HCl: *pyridinium phenylo-*, m.p. 105° (decomp.); NH_4 *m-chlorophenylo-*, m.p. >240°; *pyridinium* m-*chlorophenylo-*; *quinolinium* m-*chlorophenylo-*; NH_4 *α-naphthylo-*, m.p. >240°, sublimes at 200°; *pyridinium α-naphthylo-*, m.p. 187—189°; *pyridinium β-naphthylo-*, m.p. 200—202° (decomp.); *quinolinium β-naphthylo-*, m.p. 174—176° (decomp.), after softening at 110° and darkening at ~140°. *Pyridinium β-naphthylopentabromostibanate*, m.p. 193—195°, and *pyridinium diphenylotetrachlorostibanate*, decomp. ~265°, are described. H. W.

Organo-silicon synthesis. II. Reactions of aryl Grignard reagents with silicon halides. W. C. SCHUMB and C. M. SAFFER, jun. (J. Amer. Chem. Soc., 1939, **61**, 363—366; cf. A., 1938, II, 476).—The reactions with $SiCl_4$, Si_2Cl_6, Si_3Cl_8, Si_2OCl_6, $SiBr_4$, Si_2Br_6, Si_2OBr_6, and $Si_3O_2Br_8$ in the conventional way yield only partly substituted silanes, but by the high-temp. modification of the Grignard reaction hexa-aryl-disilanes and -disiloxanes may be prepared in fairly good yields. The reaction cannot be extended to the prep. of compounds containing the Si·Si·Si or Si·O·Si·O structures, or of tetra-*o*-substituted phenylsilanes. The prep. of *hexa*-p-*tolyldisilane*, m.p. 345°, and *hexa*-n-*propyldisilane*, b.p. 114°/3 mm., is described. E. S. H.

Formation of organo-metalloidal and similar compounds by micro-organisms. VII. Dimethyl telluride. M. L. BIRD and F. CHALLENGER (J.C.S., 1939, 163—168; cf. A., 1939, II, 12).—Air aspirated through cultures of *Scopulariopsis brevicaulis*, Saccardo (strain Washington 2), on bread or a 2% glucose Czapek–Dox solution containing K_2TeO_3 and passed through aq. $HgCl_2$–HCl gives $Me_2Te,HgCl_2$. Similarly, $TeMe_2$ is obtained with other strains of *S. brevicaulis* and with *Penicillium notatum*, Westling, and identified by absorption in EtOH–CH_2PhCl followed by treatment with Na picrate, when *benzyldimethyltelluronium picrate*, m.p. 121°, is obtained. Similarly, *P. notatum* and *P. chrysogenum* with Na_2SeO_3 or Na_2SeO_4 on aq. bread culture yield Me_2Se. Interaction of Me_2Te with $CH_2Br{\cdot}CO_2Et$ and with CH_2BzBr in Et_2O or EtOH yields respectively *dimethylcarbethoxymethyl-*, m.p. 137·5, and *phenacyldimethyl-telluronium bromide*, m.p. 90—91°. J. D. R.

Elastoidin. R. ENGELAND and A. BASTIAN (Compt. rend., 1938, **207**, 945—947).—Elastoidin (from *Carcharias glaucus*) with boiling 25% H_2SO_4 affords a hydrolysate from which the Cu salts of NH_2-acids are isolated by Brazier's method. Extraction of these salts with MeOH, followed by treatment with H_2S, gives glycine, alanine, serine, hydroxyproline, a compound, $C_7H_{15}O_5N$, and a diaminodihydroxyvaleric acid (?). From the phosphotungstic acid ppt. of the hydrolysate, the betaine of dihydroxyornithine is isolated. J. L. D.

Nature of the cyclol bond. I. LANGMUIR and D. WRINCH (Nature, 1939, **143**, 49—52).—The nature of the cyclol bond, the making and breaking of which is a prototropic tautomerism, is discussed in relation to the properties of globular proteins and to the cyclol theory. L. S. T.

Organic chemistry of proteins. J. OVERHOFF (Chem. Weekblad, 1939, **36**, 115—122).—A review. S. C.

Use of semi-micro-technique in organic chemistry. N. D. CHERONIS (J. Chem. Educ., 1939, **16**, 28—34).—A simple micro-condenser, distillation tubes, simple arrangements for fractionating, refluxing, distilling, extraction, separation, filtration, and

measuring are described, and their use is illustrated by the prep. of $PhNO_2$, PhEt, *cyclo*hexene, BzOH, etc. L. S. T.

Determination of carbon in organic compounds. A. K. Parpart and A. J. Dziemian (Ind. Eng. Chem. [Anal.], 1939, **11**, 107).—The combustion vessel employed in the method of Van Slyke *et al.* (A., 1933, 1314) is modified to obviate the possibility of leaks. F. N. W.

Micro-titrimetric dry combustion method for carbon. II. Modified titration vessel. R. H. Nagel (Mikrochem., 1939, **26**, 22—24).—A modified absorption and titration vessel is described suitable for use with the micro-method described by Schmitt and Niederl (A., 1938, II, 209). Provision is made for alternate washing of the cell after use with H_2O and EtOH, thereby eliminating the necessity of steaming out after each usage. Attempts to develop a semi-micro-method on the same principles were unsuccessful. J. W. S.

Simplified combustion tube filling for micro-determinations of carbon and hydrogen. J. B. Niederl and V. Niederl (Mikrochem., 1939, **26**, 28).—It is not necessary to use $PbCrO_4$ in micro-combustions when metallic Ag is present, as the latter absorbs the oxides of S quantitatively. J. W. S.

Modifications of Pregl's method for the micro-analytical determinations of carbon and hydrogen in the humid summer atmosphere of a tropical country. M. C. Nath (Mikrochem., 1939, **26**, 165—169).—Pregl's method yields low vals. for C in the hot humid atm. of India. Under such conditions it has been found necessary to extend the period of combustion from 10 to 15 min., and to increase the O_2 current to 4—5 c.c. per min. Escape of gas through rubber connexions is minimised by cleaning these with glycerol on a glass rod, the glycerol being removed again with a dry rod. No cotton is used inside the tubes. Connexions between the combustion and $CaCl_2$ tubes are renewed after each combustion, and other rubber parts after three combustions. Before weighing, the capped absorption tubes are allowed to come into equilibrium with the atm. in a balance room, the moisture content of which is kept const. Blank tests are run before and after each combustion. J. W. S.

Micro-combustion analysis of very volatile liquids. E. Eigenberger (Mikrochem., 1939, **26**, 273—276).—In the method recommended the liquid is contained in a small capillary tube itself inserted into a projection in the combustion tube which can be cooled. The tip of the capillary tube is blown out by heating with an electrically-heated wire. The arrangement is equally suitable for determination of C, H, and N. J. W. S.

Use of lead peroxide in micro-elementary analysis. J. Lindner (Mikrochem., 1938, **25**, 197—207; cf. A., 1933, 80).—Data showing that different preps. of PbO_2 possess different absorptive powers for NO_2, that this absorption increases with a decrease in particle size, and that the hygroscopic effect increases to an even greater extent are discussed. Previous conclusions concerning the efficacy of PbO_2 and the difficulty of ascertaining the correct amount of the prep. to be used are supported. More active PbO_2 preps. make it possible to effect a satisfactory removal of NO_2, but a smaller interference in the H_2O determination does not necessarily follow. The use of a smaller amount of PbO_2, frequently renewed, instead of the universal filling leads to an improvement in the H_2 determination, but one of the advantages of using PbO_2 is thereby lost. Metallic Cu is preferable to PbO_2 since it decomposes the NO_2 completely, and produces no interference in the H_2 determination. L. S. T.

Discussion of important and difficultly-accessible microchemical literature. F. Canal (Mikrochem., 1938, **25**, 182—183).—The catalytic method of Contardi and Ferri (A., 1934, 1375) for the determination of C and H, and the electrical method of Contardi and Erighian (A., 1937, I, 152) for the semi-micro-determination of N are described. L. S. T.

Semi-micro-method for determining carbon and hydrogen in organic compounds. G. Ingram (J.S.C.I., 1939, **58**, 34—37).—The micro-method of Friedrich (cf. A., 1932, 71, 921) is adapted for use as a semi-micro-method (10—21 mg. of substance), involving a modified tube filling on which all types of substances can be analysed. The PbO_2 is contained in a porcelain boat, the oxidation filling being in a CuO tube, which allows the PbO_2 to be changed when used up. The complete analysis, which takes <1 hr., is carried out in a stream of O_2, Pregl's absorption tubes being used. The method is simple and quick, taking <1 hr. for each analysis.

Standard solutions in quantitative organic micro-analysis. J. B. Niederl, V. Niederl, and M. Ettingon (Mikrochem., 1938, **25**, 143—150).—0·01N-$KH(IO_3)_2$ can, with advantage, be substituted for 0·01N-HCl in all the acidimetric and alkalimetric titrations used in org. micro-analysis. It also serves as a standard for the iodometric titrations. No change in titre could be detected after storage for 6 months. For the precision required in org. analysis (5 in 1000), 0·01N-NaOH requires re-standardisation monthly and 0·01N-$Na_2S_2O_3$ weekly. Details of the prep. of the $KH(IO_3)_2$, the standard solutions of $KH(IO_3)_2$, NaOH, and $Na_2S_2O_3$, and the indicator solutions of phenolphthalein, Me-red, and starch are given. The high mol. wt. of the iodate renders the use of a micro-balance unnecessary. Test data for the determination of the equiv. of 3 org. acids, and the determination of NH_3, S, I, Cl, and Br are recorded. A device for steaming-out conical flasks is illustrated. L. S. T.

Ultra-micro-Kjeldahl technique.—See A., 1939, I, 214.

Determination of halogens in organic compounds. H. B. Feldman and L. Powell (Ind. Eng. Chem. [Anal.], 1939, **11**, 89—90).—Reduction by Cook and Cook's modification (A., 1933, 731) of the Stepanow technique followed by titration with 0·1N-$AgNO_3$ using dichlorofluorescein for Cl and eosin for Br and I as absorption indicators affords accurate results for a variety of org. halides. F. N. W.

Determination of chlorine in organic compounds. V. Dostál (Chem. Listy, 1939, **33**, 78—79).—The material is heated with KOH–KNO_3 mixture in a hard glass tube, and Cl′ is determined in the melt by the Volhard method. R. T.

Hygroscopic substances in micro-analysis.—See A., 1939, I, 223.

Determination of water in organic liquid mixtures. R. A. Day, jun., and R. N. Pease (J. Amer. Chem. Soc., 1939, **61**, 524—525).—H_2O in org. liquids is determined by adding powdered, anhyd. $CuSO_4$, filtering, washing with liquid C_4H_{10}, and determining the gain in wt. of the $CuSO_4$. R. S. C.

Micro-technique of organic qualitative analysis. F. Schneider and D. G. Foulke (Ind. Eng. Chem. [Anal.], 1939, **11**, 111—113; cf. A., 1938, II, 423).—Reactions capable of classifying compounds containing C, H, and O, as aldehyde, carbohydrate, phenol, anhydride and lactone, ketone, and alcohol are recorded together with micro-methods for the titration of acids and hydrolysis of esters. F. N. W.

Pyridine–acetic anhydride method for determining hydroxyl: preparation of pyridine of suitable quality. H. N. Wilson and W. C. Hughes (J.S.C.I., 1939, **58**, 74—77).—The method of determining OH by boiling with excess of Ac_2O in C_5H_5N, to acetylate the OH, the excess of AcOH being subsequently determined, will give accurate results only if the C_5H_5N is freed from certain impurities and contains 0·3—0·5% of H_2O, to prevent reaction between the C_5H_5N and Ac_2O. Methods of purifying "technical pure" C_5H_5N were evolved, and a specification for suitable C_5H_5N is appended.

Nitroprusside test for ·SH and ·S·S·.—See A., 1939, III, 344.

Determination of ethylene. B. E. Christensen, E. Hansen, and V. H. Cheldelin (Ind. Eng. Chem. [Anal.], 1939, **11**, 114—116).—A micro-method (for which an extractor, purification train, and reaction flask are described) based on the bromination method of Davis *et al.* (B., 1931, 324), capable of determining 0·001—0·06 c.c. of C_2H_4 in a total vol. of 35—40 c.c., is described. The C_2H_4 contents of a no. of fruit and vegetable tissues are recorded. F. N. W.

[Azides. X.] *p*-Bromobenzazide as a reagent for the identification of alcohols. P. P. T. Sah and K. Y. Tao (Rec. trav. chim., 1939, **58**, 12—16).—*p*-Bromobenzazide (A., 1936, 1006) with the following alcohols in boiling petroleum at 80—120° gives p-*bromophenylurethanes* (m.p. in parentheses): MeOH (125°; cf. lit.); EtOH (84°; cf. lit.); $Pr^{\alpha}OH$ (77—78°); $Pr^{\beta}OH$ (102—104°); $Bu^{\alpha}OH$ (64—65°); $Bu^{\beta}OH$ (96—98°); *n*-C_5H_{11}·OH (76—77°); $CHEt_2$·OH (54—55°); *n*-C_6H_{13}·OH (75°); *n*-C_7H_{15}·OH (83—84°); *iso*-C_7H_{15}·OH (65—66°); *n*-C_8H_{17}·OH (78—79°); *n*-C_9H_{19}·OH (73—74°); *n*-$C_{10}H_{21}$·OH (79°); CH_2:CH·CH_2·OH (65°); CH_2Ph·OH (123—124°); furfuryl alcohol (105—106°); *cyclo*hexanol (113—114°); 4-methyl*cyclo*hexanol (160—161°); benzoin (122°); menthol (114°); cholesterol (175—176°); borneol (116—117°); $(CH_2$·$OH)_2$ (194°); glycerol [229° (decomp.)]; CH_2Cl·CH_2·OH (88—89°); and CH_2Br·$CHBr$·CH_2·OH (93—94°). E. W. W.

Determination of linalool, cineole, and terpineol. T. Ikeda and S. Takeda (J. Chem. Soc. Japan, 1936, **57**, 442—448).—40 g. of the material are heated with 1 g. of $ZnCl_2$ which has been dried for 1 hr. at 156° and 50 c.c. of xylene at 195—200° for 2 hr., and the H_2O liberated by the dehydration of the linalool, cineole (I), or terpineol is collected and measured. For (I) 3 hr. heating is necessary. A blank must be run to determine the H_2O retained by the $ZnCl_2$, and a correction applied. Ch. Abs. (*e*)

Application of drop analysis to the investigation of medicinal materials. VII. Detection of polyhydroxy-compounds. O. Frehden and K. Fürst. **VIII. Detection of aldehydes with stable reagent paper.** O. Frehden and C. H. Huang (Mikrochem., 1939, **26**, 36—38, 39—40).—VII. The test for HCO_2H (following abstract) can be applied to detection of polyhydric alcohols, which are first oxidised to HCO_2H by $NaIO_4$ and H_2SO_4. The HCO_2H is oxidised to CO_2 by Br–H_2O and detected by the turbidity produced by the gas in aq. $Ba(OH)_2$. The reaction permits detection of 3—5 μg. of polyhydroxy-compounds. Aldehydes other than CH_2O do not interfere with the test.

VIII. Malachite-green (0·8 g.) is dissolved as the leuco-base by addition of Na_2SO_3 (3 g.) and after addition of further Na_2SO_3 (2 g.) the solution is filtered and imbibed on thin test paper, which is allowed to dry in the cold. A drop of test solution placed on the colourless dry test paper produces a green spot if an aldehyde is present. The reaction is favoured by the fine state of distribution of the leuco-base on the paper. The solutions must be neutral, as both acid and alkali cause colour changes. The method is capable of detecting 20—300 μg. of aldehyde. J. W. S.

Application of drop analysis to the investigation of medicinal materials. Selective test for formic acid. O. Frehden and K. Fürst (Mikrochem., 1938, **25**, 256—257).—The test, based on the reaction $HCO_2H + Br_2 = 2HBr + CO_2$, permits the detection of 2·5 μg. of HCO_2H. A few drops of solution are treated with aq. Br until yellow in colour, and the solution is heated to boiling. The evolved gases are passed into saturated aq. $Ba(OH)_2$ protected from atm. CO_2 by a layer of paraffin. The small amounts of HBr and Br which also distil do not interfere with the test. L. S. T.

Determination of fumaric and maleic acids. S. C. Ganguly (J. Indian Chem. Soc., 1938, **15**, 611—614).—The KBr–$KBrO_3$–$HgSO_4$ method (A., 1937, I, 314; 1938, II, 210) may be used successfully to determine maleic or fumaric acid, in presence of $(CH_2$·$CO_2H)_2$ and Na_2HPO_4. E. W. W.

Iodometric determination of acetone by a turbidimetric method. E. K. Nikitin and M. E. Egorova (Zavod. Lab., 1938, **7**, 1363—1367).—1 ml. of 15% I in KI and 1 ml. of 10% KOH are added to 1 ml. of 5% aq. $COMe_2$, and the time t_1 elapsing before appearance of turbidity is noted. An equal vol. of

H_2O is added to the aq. $COMe_2$, and the experiment is repeated (time $= t_2$). Finally, the time t required for development of turbidity in the unknown solution is determined. The $[COMe_2]$ is then given by $(x + c)/2$, where $x = c/\{1 + (t - t_1)/(t_2 - t_1)\}$, and c is the $[COMe_2]$ of the standard solution. A second, more dil. standard $COMe_2$ solution (0·01%) is used, with 0·2% instead of 10% KOH, for comparison with very dil. $COMe_2$ solutions. R. T.

Determination of water in acetone. R. Gaspart and L. Gillo (Bull. Soc. chim. Belg., 1938, **47**, 933—939).—The presence of an absorption band at 3500 cm.$^{-1}$, traced to the H_2O–$COMe_2$ complex, permits the spectroscopic determination of 1 part of H_2O in 100,000 parts of $COMe_2$ with a precision of 0·5%. E. S. H.

Use of periodate in the volumetric determination of polyhydric alcohols and reducing aldoses (monosaccharides), and the determination of periodate and iodate in presence of each other. Use of periodate in the volumetric determination of ketoses (monosaccharides). (A) P. Fleury. (B) F. Rappaport (Mikrochem., 1938, **25**, 263—265, 265—266; cf. A., 1937, II, 530; 1938, II, 219).—(A) Attention is directed to the author's previous work on this subject.

(B) The method of Fleury differs in principle and in execution. L. S. T.

Micro-method for the determination of the *iso*propylidene group in sugar derivatives. D. J. Bell and K. Harrison (J.C.S., 1939, 350).—The $:CMe_2$ derivative is steam-distilled in N-H_2SO_4, and the $COMe_2$ is determined. An apparatus is described by which 1 mg. of $COMe_2$ may be determined with an accuracy of ±1%. J. D. R.

Determination of pentose especially in adenylic acid derivatives. W. Mejbaum (Z. physiol. Chem., 1939, **258**, 117—120).—Free and/or combined pentose (1—20 μg.) is determined by adding to 0·5 c.c. of the solution 0·5 c.c. of fresh Bial's reagent (5 mg. of orcinol in conc. HCl containing 0·1% $FeCl_3$), heating for 20 min. at 100°, cooling, and measuring the depth of colour produced in a step photometer. The pentose solution must be diluted if its concn. exceeds 20 μg. per c.c. Glucose, $Pb^{..}$, and NO_3' (but not $Ba^{..}$) interfere. W. McC.

Determination of uronic groups in polysaccharides. A. G. Norman (Nature, 1939, **143**, 284—285).—The rate of evolution of CO_2 with acid under standard conditions of heating etc. affords a method for detecting the presence of uronic groups. The curves indicate that these give an early max., whilst hexose material provides a longer and more regular evolution of CO_2. L. S. T.

Determination of 0·3—50 mg. of glucose by the method of Hagedorn and Jensen.—See A., 1939, III, 221.

Reaction between amines and sodium 1 : 2-naphthaquinone-4-sulphonate. E. G. Schmidt (Ind. Eng. Chem. [Anal.], 1939, **11**, 99—100).—The reaction, which is the basis of Folin's colorimetric method (A., 1922, ii, 536, 540) for the determination of the NH_2-acid content of blood, is influenced by the amount of alkali and acid added to the reaction medium. The quant. nature of the reaction is followed by comparing the colour intensities produced by interaction of aq. NH_3 and 26 different amines with that obtained from an equiv. amount of glycine. F. N. W.

Amino-acids and peptides. V. Function of iodine in amino-nitrogen analyses by the nitrous acid method. M. S. Dunn and I. Porush (J. Biol. Chem., 1938, **127**, 261—268; cf. Kendrick and Hanke, A., 1937, III, 108).—The effect of added I′ on the NH_2-N vals. obtained in the analyses is explained by supposing that slightly sol. or only slightly ionised HgI_2 complexes of the NH_2-acids are produced, low results indicating production of insol. complexes. The rate of oxidation of cystine by I, as measured by production of SO_4'', is much slower than that by HNO_2 in comparable concn. N_2 is produced from HNO_2 when $Na_2S_2O_3$ is present and hence high results are sometimes obtained. No explanation is provided of the fact that addition of KI results in a 15% decrease in the NH_2-N content of blood filtrates. W. McC.

Detection of α-amino-β-hydroxybutyric acid and its distribution in various proteins. T. Higasi, S. Mayeda, and H. Matsuoka (Sci. Papers Inst. Phys. Chem. Res., Tokyo, 1939, **35**, 170—173).—$OH{\cdot}CHMe{\cdot}CH(NH_2){\cdot}CO_2H$ (I) is heated with Br–H_2O (and a little Br + $FeSO_4$) at 100° (bath) for 5—8 min., cooled, decolorised by $Na_2S_2O_4$, and boiled with NH_2OH,HCl for 1 min. Addition of aq. NH_3 to the cold solution affords a characteristic reddish colour (mechanism of reaction discussed). The test is sp. for (I) (apart from aspartic acid) and can be used for its detection and approx. estimation in the hydrolysis products of proteins. A. T. P.

Determination of small amounts of aspartic acid by the malic acid method of Pucher. A. A. Arhimo (Suomen Kem., 1939, **12**, B, 6).—Aspartic acid is determined by direct bromination to dibromomalic acid, oxidation of this ($KMnO_4$) to dibromooxalacetic acid (?), and further treatment according to Pucher (A., 1934, 1048). Tyrosine and dihydroxyphenylalanine, but not glutamic acid, can be determined in this way. M. H. M. A.

Determination of thiourea and thiocyanates. H. E. Williams (J.S.C.I., 1939, **58**, 77—79).—CNS′ is determined by titration with $Hg(NO_3)_2$ in presence of dil. HNO_3 and Fe^{III} alum solution until the red colour disappears. $CS(NH_2)_2$ is titrated in a similar manner after adding a known vol. of standard NH_4CNS. The method can be used with N- or 0·1N-$Hg(NO_3)_2$, and gives results accurate to 0·02—0·035%. With mixtures containing $CS(NH_2)_2$ and CNS′, the former is eliminated by adding $CdSO_4$ and NaOH and boiling, and the latter determined as above. HgO or $HgSO_4$, but not Pb salts, can replace the $CdSO_4$. Determinations with the $Hg(NO_3)_2$ are unaffected by the presence of $CO(NH_2)_2$, $CN{\cdot}NH_2$, or guanidine, but excessive amounts of dicyanodiamide interfere. Heavy metals should, in general, be absent. Chlorides lead to high

results, and when present the CNS′ is first pptd. as CuCNS, or as the Cl′ is removed as basic Bi chloride. In mixtures with CNS′, $CS(NH_2)$ can be determined directly by adding aq. $NaAg(CN)_2$ and NaOH, diluting, and boiling. The filtrate is titrated with $AgNO_3$ to a permanent opalescence (KI as indicator). The reactions occurring are $2NaAg(CN)_2+CS(NH_2)_2+2NaOH=CN\cdot NH_2+Ag_2S+4NaCN+2H_2O$, and $4NaCN+2AgNO_3=2NaAg(CN)_2+2NaNO_3$. L. S. T.

[**Azides. IX.**] ***m*-Bromobenzazide as a reagent for the identification of amines.** P. P. T. Sah and L. H. Chang (Rec. trav. chim., 1939, **58**, 8—11; cf. A., 1937, II, 129).—*m*-Bromobenzazide, an oil (from the hydrazide, A., 1936, 873), with the following amines etc. in PhMe at 120° yields m-*bromophenylcarbamides* (m.p. in parentheses): NH_2Ph (196—197°); *o*- (212—213°), *m*- (248—249°), and *p*-$C_6H_4Me\cdot NH_2$ (222—223°); *p*-xylidine (227—228°); α- (259—260°) and β-$C_{10}H_7\cdot NH_2$ (240—241°); *p*-$C_6H_4Ph\cdot NH_2$ (235—236°); *o*- (175—176°), *m*- (218—219°), and *p*-$NO_2\cdot C_6H_4\cdot NH_2$ (245—247°); *p*-$C_6H_4Cl\cdot NH_2$ (236—237°); *p*-$C_6H_4Br\cdot NH_2$ (252—253°); 2 : 1 : 4- (196—190°) and 3 : 1 : 4-$NO_2\cdot C_6H_3Me\cdot NH_2$ (213—214°); 1 : 3 : 4-$C_6H_3MeBr\cdot NH_2$ (237—238°); $NHPh_2$ (141—142°); *o*-$NH_2\cdot C_6H_4\cdot OH$ (236—237°); NH_2Bz (211—212°); NH_2Ac (201—202°); NHPhAc (118—119°); *o*- (208—209°) and *m*-$NH_2\cdot C_6H_4\cdot CO_2H$ (282—283°). E. W. W.

Determination of phenolic and naphtholic hydroxyl groups by means of benzoic anhydride. A. Leman (Compt. rend., 1939, **208**, 357—359; cf. A., 1938, II, 274).—A phenol (0·01 mol.) or a dihydroxybenzene (0·005 mol.) with C_5H_5N–Bz_2O at 100°/1 hr. is benzoylated quantitatively (±1—2%) as shown by the titrimetric determination of BzOH obtained after hydrolysing the excess of Bz_2O. J. L. D.

Determination of carbonyl compounds by means of 2 : 4-dinitrophenylhydrazine. H. A. Iddles, A. W. Low, B. D. Rosen, and R. T. Hart (Ind. Eng. Chem. [Anal.], 1939, **11**, 102—103).—The method originally devised for H_2O-sol. CO-compounds (A., 1935, 101) is extended to EtOH-sol. compounds (I). 10 c.c. of an EtOH solution of (I) are added dropwise to excess of a saturated solution of 2 : 4-$(NO_2)_2C_6H_3\cdot NH\cdot NH_2$ in 2N-HCl (II) and after dilution with 50 c.c. of (II) is kept at room temp. for 2—24 hr. The ppt. is washed with (II) and dried at 105—110°. The average yields obtained with the following are given in parenthesis: COPhMe (99·6), *p*-$OH\cdot C_6H_4\cdot CHO$ (97·6), CHPhBz·OH (99·6), mesityl oxide (93·2), benzylideneacetophenone (97·7), Bz_2 (97·7), $COPh_2$ (95·6), piperonal (96·5), *cyclo*hexanone (97·3), *cyclo*pentanone (98·6), and carvone (99·38). F. N. W.

Condensations of furan derivatives. X. Furan derivatives analogous to chalkones. V. V. Tschelincev (Bull. Soc. chim., 1939, [v], **6**, 70—79; cf. A., 1932, 1140; 1933, 1179).—Ketones, CHR:CH·CO·R′, give with 50—60% H_2SO_4 or conc. HCl a bright yellow colour if R is aromatic, violet or red-violet if R is furyl. Only indefinite colours are obtained with the corresponding acids or aldehydes, or if R is aliphatic. The colours are supposed to be due to oxonium compounds resembling quinones. A. Li.

Determination of aneurin. Enzymic conversion of cocarboxylase (aneurin pyrophosphate) into the free vitamin.—See A., 1939, III, 401.

Colorimetric reaction for determination of nicotinic acid. E. Bandier and J. Hald (Biochem. J., 1939, **33**, 264—271).—An aq. solution of nicotinic acid (containing 0·005—0·25 mg.) is heated at 75—80° for 5 min. and 1 c.c. of 4% aq. CNBr is added. After a further 5 min. heating, the solution is cooled, 10 c.c. of saturated aq. metol are added, and, after dilution to 20 c.c., the mixture is left for 1 hr. in the dark. The colour developed is then read with a Pulfrich photometer, using a S.43 filter. Solutions containing nicotinamide must first be hydrolysed. A modified technique for use with org. materials is described. Yeast contains 16—61 mg. per 100 g. dry wt. P. G. M.

Iodometric titration of SH groups; micro-determination of cysteine and methionine in proteins. R. Kuhn, L. Birkofer, and F. W. Quackenbush (Ber., 1939, **72**, [*B*], 407—416).—The compound is hydrolysed by boiling HI (*d* 1·7) containing a little KH_2PO_2 and the volatile products are conveyed by pure N_2 through an aq. suspension of red P, a solution (I) of 20% $CdCl_2$ + 20% $BaCl_2$ to retain H_2S, saturated $HgCl_2$ solution, and AcOH (II) containing 10% of KOAc and Br. Methionine (III) is determined in (II) by addition of HCO_2H to decolorise Br, treatment with solid KI, acidification, and titration with 0·004N-$Na_2S_2O_3$. (I) is treated with excess of 0·004N-I and 2N-HCl and, after disappearance of CdS, the excess of I is determined with 0·004N-$Na_2S_2O_3$. For the determination of cysteine (IV) the residue in the hydrolysing flask is treated with AcOH and repeatedly evaporated to dryness at 100°/vac. with intermediate addition of 30% AcOH until the odour of PH_3 is no longer perceptible. The residue is treated in 90% AcOH with an excess of 0·004N-I and after 1 min. unchanged I is determined by 0·004N-$Na_2S_2O_3$. The total S determined thus for casein, ovalbumin, globin, insulin, vitellin, and phalloidin is identical with that determined directly as $BaSO_4$. Under the experimental conditions aneurin (V) and lactoflavin (VI) do not evolve sufficient EtI to influence the determination of (III) in proteins in the structure of which these vitamins form part. On the side of (IV), an error is not introduced by (V) but a slight correction is required for (VI). Proteins with adermin, nicotinamide, or astaxanthin as prosthetic group can be directly analysed. Immediate analysis of hæmoglobins is scarcely possible, the main disturbing factor being porphyrin. The results depend so greatly on experimental conditions that a correction cannot be given. The substances to be examined for (III) must be free from OAlk and NAlk. S, present in SO_4 esters, is smoothly removed as H_2S. With sulphanilamide the total S is volatilised as H_2S whilst the basic fragments in the flask give a false val. for (IV) owing to their reducing power. The adenylthiomethylpentose from yeast gives only about 66% of MeI and 33% of MeSH. Thiomethylpentose triacetate behaves similarly. H. W.