BRITISH CHEMICAL ABSTRACTS

A., II.—Organic Chemistry

NOVEMBER, 1937.

Recent investigations on thermal changes in simple organic compounds. M. W. Travers (Trans. Faraday Soc., 1937, **33**, 1342—1353).—The results of recent studies of the thermal decomp. of MeCHO, simple hydrocarbons, $(CH_2)_2O$ + MeCHO, NH_2Me, ethers, and alkyl nitrites, and the conclusions reached from them, are discussed. For such reactions the determination of order of reaction from the half-life period is impossible. The importance of the initial stages of the reaction is emphasised.

J. W. S.

Structure of aliphatic compounds: Walden inversion. W. Taylor (Rec. trav. chim., 1937, **56**, 898—899; cf. A., 1, 417).—In simple reactions (*e.g.*, hydrolysis and esterification) of Me, Et, Pr^{β}, and Bu^{γ} compounds, the high relative speed of reaction of Bu^{γ} is interpreted by assuming that in primary and *sec.* aliphatic compounds, RX, X is partly bound by the α-H. This view conforms with the theories of Polanyi and others to account for the Walden inversion.

F. L. U.

Mechanism of the reaction of substitution and Walden inversion. P. A. Levene, A. Rothen, and M. Kuna (J. Biol. Chem., 1937, **120**, 777—797).—It is shown that in normal saturated aliphatic derivatives, substitution on the asymmetric C by a negative group or atom is connected with an inversion of configuration. In substances CHRR′X when R = ·CH:CH_2, substitution of a N_3 group for halogen proceeds without inversion of configuration, whilst when R′ = Ph substitution of Br for OH by HBr or PBr_3 in absence of C_5H_5N takes place without inversion of configuration, but in presence of C_5H_5N with inversion. For normal, saturated alkyl derivatives substitution is connected with inversion provided the mechanism of substitution of N_3 for halogen proceeds by the same mechanism as the substitution of one halogen for another. A general theory of the Walden inversion is not yet possible. d-δ-*Chloro-octane*, b.p. 92°/50 mm., d_D^{25} +0·28° (l = 1), and d-γ-*chloro-octane*, b.p. 98°/33 mm., α_D^{25} +5·10° (l = 1), are obtained from the requisite I-compound and LiCl in MeOH at 37°. Δ$^{\alpha}$-*Hepten-γ-ol*, b.p. 103—106°/147 mm., $[\alpha]_D^{25}$ −23·2°, and PCl_5 in dry Et_2O give d-γ-*chloro*-Δ$^{\alpha}$-*heptene* (I), b.p. 92—94°/125 mm., $[\alpha]_D^{25}$ +9·76°, converted by NaN_3 in H_2O–MeOH at 25° into γ-*azido*-Δ$^{\alpha}$-*heptene*, b.p. 78—81°/32 mm., $[\alpha]_D^{27}$ −0·04°, reduced (Adams) to l-γ-*aminoheptane*, b.p. 100—106°/148 mm., $[\alpha]_D^{27}$ −0·02°; another sample of the latter substance, b.p. 99—101°/150 mm., $[\alpha]_D^{27}$ −0·45°, was obtained by hydrogenating (Adams) l-γ-*amino*-Δ$^{\alpha}$-*heptene*, b.p. 95—105°/155 mm., α_D^{25} −4·80° (l = 1), derived, with a sec. *amine*, b.p. 92—95°/1 mm., $[\alpha]_D^{25}$ +0·52° (l = 1), from (I) in NH_3–MeOH at 25° and then at 50°. l-γ-*Bromo*-Δ$^{\alpha}$-*heptene*, b.p. 92—94°/50 mm., $[\alpha]_D^{25}$ −4·64°, is converted by LiCl in MeOH at 25° into d-γ-*chloro*-Δ$^{\alpha}$-*heptene*, b.p. 87—88°/90 mm., $[\alpha]_D^{25}$ +0·90°. *r*-α-Phenylethan-α-ol is converted into the *H phthalate*, m.p. 108°, from which, after resolution with brucine, l-α-*phenylethan-α-ol*, b.p. 75°/1 mm., $[\alpha]_D^{25}$ −42·0°, is obtained. This is converted by $SOCl_2$ into l-α-*chloro*-α-*phenylethane*, b.p. 101°/50 mm., $[\alpha]_D^{25}$ −24·0°, whence successively d-α-*azido*-α-*phenylethane*, b.p. 114°/50 mm., $[\alpha]_D^{25}$ +18·6°, and d-α-*amino*-α-*phenylethane*, b.p. 75°/15 mm., $[\alpha]_D^{25}$ +3·14°. l-α-*Phenylpropan-α-ol* (II), b.p. 94—95°/10 mm., $[\alpha]_D^{25}$ −22·2° (obtained by resolving the *r*-alcohol through the strychnine phthalate), and $SOCl_2$ afford l-α-*chloro*-α-*phenylpropane*, b.p. 77—80°/10 mm., $[\alpha]_D^{25}$ −28·9°, whence d-α-*azido*-α-*phenylpropane*, b.p. 100—101°/22 mm. α_D^{25} +32·95° (l = 1), and d-α-*amino*-α-*phenylpropane*, b.p. 81°/10 mm., $[\alpha]_D^{25}$ +4·57°. PBr_5 and (II) in C_5H_5N give *l*-α-*bromo*-α-*phenylpropane*, b.p. 57—61°/0·6 mm., α_D^{25} −47·7°, converted by 40% NH_3–MeOH into the *amine*, b.p. 88—90°/16 mm., $[\alpha]_D^{25}$ +3·65°. l-α-*Phenylbutan-α-ol*, b.p. 121—123°/18 mm., $[\alpha]_D^{25}$ −7·62° [hydrogenated (Adams) to l-α-cyclo*hexylbutyl*-α-ol, b.p. 76—77°/1·5 mm., $[\alpha]_D^{25}$ −4·61°], is converted by PBr_5 in $CHCl_3$–C_5H_5N into d-α-*bromo*-α-*phenylbutane*, b.p. 67—75°/0·5—1 mm., $[\alpha]_D^{25}$ −17·6°, and by PBr_5 in $CHCl_3$ into l-α-*bromo*-α-*phenylbutane*, b.p. 67—72°/0·5—1 mm., $[\alpha]_D^{25}$ −1·98°, whereas the alcohol and PBr_3 gave a sample of b.p. 65—72°/0·5—1 mm., $[\alpha]_D^{25}$ −0·20°. PCl_5 and the alcohol gave a *hydrocarbon*, $C_{10}H_{12}$, b.p. 147—152°/1·5 mm. Inversion occurs during the transformation of the bromide into the chloride by LiCl. l-α-*Amino*-α-*phenylbutane* has b.p. 105°/10 mm., $[\alpha]_D^{25}$ −2·28° (*hydrochloride*, $[\alpha]_D^{25}$ +0·66° in H_2O), if derived from l-α-*azido*-α-*phenylbutane*, b.p. 85—90°/4 mm., $[\alpha]_D^{25}$ −16·4°, but b.p. 103—104°/15 mm., $[\alpha]_D^{25}$ −0·83°, when obtained from the bromide and NH_3.

H. W.

Catalytic isomerisation of *n*- and *iso*-butane. C. W. Montgomery, J. H. McAteer, and N. W. Franke (J. Amer. Chem. Soc., 1937, **59**, 1768—1769).—5% of $AlBr_3$ equilibrates *n*- and *iso*-C_4H_{10}, giving about 20% of the former; as by-products only 2—3% of CH_4 and C_2H_6 are formed.

R. S. C.

Synthesis of branched hydrocarbons with long chains. K. H. Meyer and P. Streuli (Helv. Chim. Acta, 1937, **20**, 1179—1183).—Octadecyl alcohol is converted by PCl_5 into *octadecyl chloride*, m.p. 18°, and by HBr at 150° into the corresponding

bromide, m.p. 41°, neither of which reacts with Mg. *Octadecyl benzoate*, m.p. 42°, decomposes at 300° into BzOH and *octadecene*, b.p. 179—180°/18 mm., m.p. 18°, the dibromide, m.p. 22°, of which is transformed by KOH at 270°/0·1 mm. into Δ^{α}-*octadecinene* (I), m.p. 28° (*Ag* derivative and salt $C_{16}H_{33}\cdot C{:}CAg,AgNO_3$, which when heated in xylene gives $\Delta^{\alpha\gamma}$-*hexatriacontadiinene*, m.p. 59°). Reaction does not occur between MgMeI in boiling Et_2O, whereas CH_4 is evolved from solution in boiling Bu^{α}_2O, but the Grignard compound (II) does not react with PhCHO, BzCl, MeOBz, $AsCl_3$, $SiCl_4$, or thapsonitrile (III) and is not hydrogenated (Pt). With CO_2 it affords Δ^{α}-*nonadecinenoic acid*, m.p. 59·5°, in 25% yield and with $COPh_2$ it gives α-*hydroxy*-αα-*diphenyl*-Δ^{β}-*nonadecinene*, m.p. 54°. Treatment of (III) with MgEtI in Et_2O–Bu^{α}_2O at 60° affords *eicosane*-γσ-*dione*, m.p. 93°, converted by (II) into 19 : 34-*dihydroxy*-19 : 34-*diethyl*-$\Delta^{17\ 35}$-*dopentacontadi-inene*, $C_{14}H_{28}[CEt(OH)\cdot C{:}C\cdot C_{16}H_{33}]_2$, m.p. 42° (yield 88%), reduced to 19 : 34-*diethyldopentacontane*, m.p. 26°. H. W.

Ratio of substitution to addition in the reaction of chlorine with olefines in dilute carbon tetrachloride solution. T. D. Stewart, K. Dod, and G. Stenmark (J. Amer. Chem. Soc., 1937, **59**, 1765—1766).—Rates of reaction with Cl_2 in CCl_4 are Δ^{β}-C_5H_{10} > Δ^{γ}-C_7H_{14} > Δ^{β}-C_6H_{12} > Δ^{β}-C_7H_{14} ≫ Δ^{α}-C_5H_{10} > Δ^{α}-C_7H_{14}. The ratio of addition to substitution is determined for these olefines. Excess of olefine or Cl_2 increases and decreases, respectively, substitution. With Δ^{α}-C_5H_{10} increase in concn. increases substitution, but with C_7H_{14} decreases it. R. S. C.

Catalytic polymerisation of ethylene at atmospheric pressure. III—V. Y. Konaka (J. Soc. Chem. Ind. Japan, 1937, **40**, 236—237B; cf. this vol., 43).—III. The Co catalyst is improved by the addition of 20% of Cu to Ag. The influence of a no. of metallic oxides and salts has been examined.

IV. The Co–Ag catalyst is best prepared by pptg. the nitrates with K_2CO_3 followed by reduction at 350°. A good catalyst is given by Co–Ag–U_3O_8–kieselguhr (10 : 2 : 2 : 12).

V. The optimum temp. (290—300°) varies slightly with the catalyst used and the rate of flow of the C_2H_4 has a considerable influence on the yield of liquid polymeride. F. R. G.

Gaseous polymerisations.—See A., I, 569.

Isomeric Δ^{β}-pentenes. H. J. Lucas and A. N. Prater (J. Amer. Chem. Soc., 1937, **59**, 1682—1686).—The hydriodides, m.p. 42—42·5° and an oil, respectively of *trans*-, b.p. 106·5°/10 mm., m.p. 24·1°, n_D^{25} 1·4578 (p-*phenylphenacyl* ester, m.p. 90—91°; dibromide, m.p. 97—98°), and *cis*-α-methyl-Δ^{α}-pentenoic acid, b.p. 94—94·4°/10 mm., m.p. —42°, n_D^{25} 1·4488 (dibromide, an oil; p-*phenylphenacyl* ester, m.p. 44·5—45·8°) (prep. from $OH\cdot CMePr^{\alpha}\cdot CO_2H$), with aq. $NaHCO_3$ give pure *trans*- (I), b.p. 36·2°, f.p. —180° to —178°, n_D^{20} 1·3817, and nearly pure *cis*-Δ^{β}-pentene (II), b.p. 36·2°, f.p. —135° to —136°, n_D^{20} 1·3799, which afford the dibromides, b.p. 91°/50·1 and 92·4°/50·1 mm., f.p. —55° to —53° and —44° to —41°, n_D^{20} 1·5096 (both), d_4^{20} 1·6809 and 1·6817, respectively, and with HBr bromopentenes, b.p. 117·5° and 116·5—118·5°, n_D^{20} 1·4435 and (?) 1·4425, respectively. The properties of pentenes prepared by other investigators are considered in the light of these data; many samples were mixtures. The experimental basis of the hypothesis of electronic isomerism of olefines is removed. R. S. C.

Constitution of lycopene. R. Kuhn and C. Grundmann (Ber., 1937, **70**, [*B*], 1905—1906).—In reply to Karrer and Solmssen (this vol., 378) it is pointed out that the authors' conclusions with regard to the formula of lycopenal are independent of the yields of methylheptenone and the dialdehyde $C_{24}H_{28}O_2$ obtained by its oxidation (A., 1932, 749). H. W.

Hydrogenation of acetylene and ethylene with palladium as catalyst.—See A., I, 524.

Hydrogenation of acetylene to ethylene. P. Ackermann (Brennstoff-Chem., 1937, **18**, 357—361).—By passing mixtures of C_2H_2 with excess of H_2 over Ni–kieselguhr at 80—150°, using narrow tubes and a short layer of catalyst, up to 70% of the C_2H_2 is converted into C_2H_4. C_2H_6 and liquid polymerides are also formed. The formation of C_2H_6 is diminished by using narrow tubes having their inner surface coated with a thin layer of catalyst, or Ni tubes the surface of which has been activated. By hydrogenation in the liquid phase even at relatively low temp. some polymerides are formed. A. B. M.

The "peroxide" or "oxygen" effect. J. C. Smith (Chem. and Ind., 1937, 833—839).—A review of the available data on the effect of O_2 and peroxides on the addition of H halides to unsaturated compounds. J. D. R.

Kinetics and mechanism of polymerisation processes. S. Medvedev (Prom. Org. Chim., 1937, **3**, 472—481).—Polymerisation of $CH_2{:}CCl\cdot CH{:}CH_2$ consists in aggregation of the active units $\cdot CH_2\cdot CCl{:}CH\cdot CH_2\cdot$ (I), to yield chains, followed by development of units of the type $\cdot CH_2\cdot \dot{C}Cl\cdot \dot{C}H\cdot CH_2\cdot$ (II) in the straight-chain polymeride, to yield branched chains and rings. Approx. expressions are derived for velocity of polymerisation; the exact equations cannot be derived, owing to differences in the probability of attachment of (I) to (II) units, according to whether the latter are situated at the surface or near the centre of an aggregate. It is shown that the velocity rises with increasing concn. of monomeride, to a limiting val. determined by the free surface of the polymeride. R. T.

Synthesis of polychloro-compounds by aluminium chloride. IV. Condensation of hexachloropropylene with *s*-dichloroethylene. H. J. Prins (Rec. trav. chim., 1937, **56**, 779—784; cf. this vol., 174).—$CCl_3\cdot CCl{:}CCl_2$ and $AlCl_3$ at 80° form a cryst. additive compound, which reacts vigorously with $(CHCl)_2$, but the only product isolated was a *compound*, $C_9H_5Cl_{11}$, m.p. 113—114°, b.p. 190°/2 mm., formed by reaction of 3 mols. of $(CHCl)_2$. Cautious reaction in CH_2Cl_2 at 5—6° affords a good yield of ααβγγδεε-*octachloro*-Δ^{α}-*pentene*, b.p. 113—113·5°/2 mm., which with ≮96% H_2SO_4 gives SO_3, HCl, αβγδδ-*pentachloro*[(?)-Δ^{α}-]*pentenoic acid*, m.p. 120—124·5° (loses

1 HCl to KOH–EtOH), and an isomeric *acid*, m.p. 133—136·5°. Both acids lose 4—5 Cl to Na_2CO_3. R. S. C.

Kinetics of the synthesis of methyl alcohol.—See A., I, 525.

Heterogeneous catalytic racemisation of *l-iso*butyl alcohol.—See A., I, 573.

Synthesis of a glycerol-d_1 from optically active *iso*propylidene-*d*-glyceraldehyde. H. Erlenmeyer, H. O. L. Fischer, and E. Baer (Helv. Chim. Acta, 1937, **20**, 1012—1014).—Treatment of *iso*propylidene-*d*-glyceraldehyde in EtOAc containing D_2O and Ni (Rupe) with D_2 gives d-iso*propylidene-glycerol*-d, $C_5H_9O_2{\cdot}CH_{1\cdot62}D_{1\cdot38}O$, b.p. 78·5—79·5°/11 mm, $[\alpha]_D$ +11·8°, whence *glycerol*-d, $C_2H_5O_2{\cdot}CH_{2\cdot1}D_{0\cdot9}O$, b.p. 165—166°/12 mm., $[\alpha]$ 0·00±0·01°. H. W.

Naturally occurring monoanhydrohexitols. W. Freudenberg and E. F. Rogers (J. Amer. Chem. Soc., 1937, **59**, 1602—1605).—Styracitol, m.p. 155°, $[\alpha]_D^{24}$ −48·5° in H_2O, $[\alpha]_D^{23}$ −50·5° in aq. H_3BO_3, is oxidised by $Pb(OAc)_4$ more rapidly than is polygalitol (I), m.p. 142—143°, $[\alpha]_D^{19}$ +42·86° in H_2O, $[\alpha]_D^{23}$ +45° in aq. H_3BO_3 (prep. from *Polygala senega* in 0·22% yield). The former is thus αε-anhydromannitol and the latter αε-anhydrosorbitol, configurations which are confirmed by consideration of optical superposition. Aceritol and (I) are identical. Hydrogenation (Pd-black) of oxygalactal tetra-acetate, freed from (?) β-*d*-galactose 2 : 3 : 4 : 6-tetra-acetate by crystallisation, gives *αε-anhydro-dulcitol* [(?) *-talitol*] *tetra-acetate*, m.p. 108°, $[\alpha]_D^{22}$ −15·31° in $CHCl_3$, hydrolysed by $Ba(OH)_2$ to *αε-anhydro-dulcitol* [(?) *-talitol*], a syrup, $[\alpha]_D^{23}$ −7·34° in H_2O. R. S. C.

Synthesis of glycerides. II. P. E. Verkade, J. van der Lee, J. C. de Quant, and E. de Roy van Zuydewijn (Proc. K. Akad. Wetensch. Amsterdam., 1937, **40**, 580—583; cf. A., 1935, 326).—In glycerides of the type $OR{\cdot}CH(CH_2{\cdot}O{\cdot}CPh_3)_2$ (I) and $CPh_3{\cdot}O{\cdot}CH_2{\cdot}CH(OR){\cdot}CH_2{\cdot}OR'$ (II) (R, R' is acyl), the CPh_3 may be removed by H_2–Pd in EtOH without wandering of the acyl groups. On the basis of this and lit. data on the wandering of acyl groups in the hydrolysis of CPh_3 from glycerides of the type (I) and (II) with acid, the following general method for the synthesis of glyceryl esters is outlined. Reduction of (I) or (II) with H_2–Pd in EtOH affords β-glycerides and βγ-diglycerides, respectively; fission of (II) with HCl yields αγ-diglycerides of known structure. The βγ- and αγ-diglycerides with R''Cl and C_5H_5N afford triglycerides containing three different acyl groups and of definite structure. J. D. R.

Reduction of glycerides by Bouveault and Blanc's method. V. M. Mitchovitch and G. Stefanovitch (Compt. rend., 1937, **205**, 386—388).—Interaction of olein and palmitin with Na in boiling EtOH, $Bu^{\alpha}OH$, or amyl alcohol affords oleyl and cetyl alcohol. Similarly, olive oil, lard, cod-liver oil, and chaulmoogra oil afford mixtures of alcohols. J. L. D.

Glycerides of elaidic acid. A. Bömer and W. Kappeller (Fette u. Seifen, 1937, **44**, 340—343).—The elaidoglycerides *α-palmito-βα'-dielaidin*, m.p. 46·3°, *α-stearyl-βα'-dielaidin*, m.p. 49·9°, *α-elaido-βα'-dipalmitin*, m.p. 51·7°, *α-elaido-βα'-distearin*, m.p. 60·7°, and trielaidin, m.p. 40·7°, have been synthesised from glycerol and the respective acids. E. L.

Fission of Robison's ester by triphosphopyridine nucleotide. O. Warburg and W. Christian (Biochem. Z., 1937, **292**, 287—295).—Phosphohexonic acid (Robison and King, A., 1931, 523) is oxidised by systems containing the nucleotide and protein intermediary enzymes I and II (Negelein and Gerischer, A., 1936, 638), the oxidation being more complete in the presence of glucose or, to a greater extent, fructose. The end products include two esters with C : P = 3 : 1 and 6 : 1, respectively. F. O. H.

Preparation of esters from alcohols and acid chlorides in the presence of magnesium. Esterification of tertiary alcohols. A. Spassov (Ber., 1937, **70**, [*B*], 1926—1930).—A solution of the acid chloride in Et_2O is gradually added to the carbinol in Et_2O containing Mg powder. Reaction is usually vigorous and after about 1 hr. at room temp. is completed during 2 hr. on the water-bath, after which the product is cooled, treated with dil. $NaHCO_3$, and the ester is extracted with Et_2O. The change is $CR_3{\cdot}OH + R'{\cdot}COCl = OH{\cdot}CR'Cl{\cdot}O{\cdot}CR_3$ (I); (I) = $R'CO_2CR_3 + HCl$; $Mg + 2HCl = MgCl_2 + H_2$. In addition to reacting with HCl, the Mg has a secondary action, since it cannot be replaced by Fe, Al, or Zn. This sp. action is obvious in the acceleration of esterification and the suppression of the dehydrating action of the acid chloride on the *tert.* alcohol. $Bu^{\gamma}OH$, $CMe_2Et{\cdot}OH$, $CMeEt_2{\cdot}OH$, and $CEt_3{\cdot}OH$ are smoothly and rapidly acylated, the yield being >60%. $CPh_3{\cdot}OH$ could not be thus esterified, but $C(CH_2Ph)_3{\cdot}OH$ gives a 50% yield of ester. AcCl, EtCOCl, PrCOCl, and $Pr^{\beta}COCl$ react readily with primary, *sec.*, and *tert.* alcohols (yields 50—90%). $CH_2Ph{\cdot}COCl$ reacts readily with $Bu^{\gamma}OH$, but with BzCl the reaction proceeds less favourably. The following appear new: *trimethylcarbinyl propionate*, b.p. 115—116·5°, and *phenylacetate*, b.p. 114—117°/14 mm.; *dimethylethylcarbinyl propionate*, b.p. 153—156°/710 mm.; *tribenzylcarbinyl acetate*, m.p. 80—81°; *triethylcarbinyl butyrate*, b.p. 83—86°/13 mm., and *phenylacetate*, b.p. 142—146°/13 mm. H. W.

Replacement series of alkyl groups as determined by alcoholysis of esters. II. G. B. Hatch and H. Adkins (J. Amer. Chem. Soc., 1937, **59**, 1694—1696; cf. A., 1935, 472).—The equilibrium ratios, ROAc/ROMe, obtained in the reaction ROAc + MeOH ⇌ ROH + MeOAc, at 200° (actually measured for reaction of EtOAc and calc. for MeOAc), are R = Et 0·81, Pr^{α} 0·79, Bu^{α} 0·80, *n*-amyl 0·98, -hexyl, -heptyl, -nonyl, and -decyl 0·88, -octyl 0·85, and -dodecyl 0·84, Pr^{β} 0·55, *sec.*-Bu 0·53, $CHMePr^{\alpha}$ 0·80, CHMeBu 0·7, $CHMe{\cdot}C_5H_{11}$ 0·71, $CHMe{\cdot}C_6H_{13}$ 0·68, $CHMe{\cdot}C_7H_{15}$ 0·63, Bu^{β} 0·66, $CH_2{\cdot}CHEt_2$ 0·92, $CH_2{\cdot}CHEtBu^{\alpha}$ 1·01, $CHMeBu^{\beta}$ 0·72, *cyclo*hexyl 0·57, allyl 0·62, benzyl 0·59, $CH_2Ph{\cdot}CH_2$ 0·63, $Ph{\cdot}[CH_2]_3$ 0·83. Substitution by Me or unsaturated residues reduces the ratio, unless Me is sterically near O. R. S. C.

Thermal transformations of potassium and sodium formate in presence of alkali hydroxides. —See A., I, 523.

Hydrolysis of acid chlorides. IV.—See A., I, 571.

Basic lead acetates. R. DUBRISAY and A. SAINT-MAXEN (Compt. rend., 1937, **205**, 325—326; cf. A., 1936, 1464).—Addition of aq. NH_3 in increasing amounts to solutions of neutral $Pb(OAc)_2$ does not alter the ultra-violet absorption spectrum, in which there is no definite band until the mixture, which contains two basic Pb acetates, contains 0·5 g.-mol. of NH_3 and 1 g.-mol. of Pb. With higher concns. of NH_3, the spectrum is altered. The *X*-ray diffraction spectrum of the more sol. compound is identical with that of Plöchl's compound, $Pb_2(OAc)_3{\cdot}OH$. The less sol. exhibits a characteristic *X*-ray spectrum which indicates that it is not a mixture and is not hydrocerusite. J. L. D.

Hydration of acetylenes. I. Δ^9-Undecynoic acid (undecolic acid). (MISS) M. L. SHERRILL and J. C. SMITH (J.C.S., 1937, 1501—1503).—Hydration of Δ^9-undecynoic acid with H_2SO_4 yields 59% of θ- and 41% of ι-ketoundecoic acid, whilst with $Hg(OAc)_2$ the respective proportions formed are 46% and 54%. J. D. R.

Exchange reaction of organic compounds with D_2SO_4. R. SCHOENHEIMER, D. RITTENBERG, and A. S. KESTON (J. Amer. Chem. Soc., 1937, **59**, 1765).—D has been introduced into palmitic acid, *dl*-alanine, *d*-leucine (I), and cholesteryl chloride dibromide by exchange with D_2SO_4 in H_2SO_4. (I) was racemised. E. S. H.

Kolbe electrosynthesis of several organic acids. S. KITAURA (Bull. Inst. Phys. Res. Japan, 1937, **16**, 765—772).—Kolbe electrolysis of oleic, ricinoleic, palmitic + phenylacetic, and palmitic + β-phenylpropionic acids gives tetratriacontadiene, the glycol $(CH_2)_{14}[CH{:}CH{\cdot}CH_2{\cdot}CH(OH){\cdot}(CH_2)_5Me]_2$, cetylbenzene, and heptadecylbenzene, respectively. E. W. W.

Isomerides formed in the course of the hydrogenation of erucic acid. Y. TOYAMA (J. Soc. Chem. Ind. Japan, 1937, **40**, 283—285B).—Et erucate is hydrogenated (Ni–kieselguhr at 180—185°) to a product hydrolysed to a mixture containing behenic (I) and brassidic (II) acid, and other isomerides of erucic acid. Products of oxidation ($KMnO_4$) of the mixed Et esters from (I), (II), and (III) suggest that the Δ^{μ}-ethylenic linking has migrated partly to the Δ^{λ}- and partly to the Δ^{ξ}- and perhaps the Δ^{o}-positions. E. W. W.

Optical activity of lactic acid produced by *Lactobacillus acidophilus* and *L. bulgaricus*.—See A., III, 316.

Specificity of the salicylaldehyde reaction [for pyruvic acid] of Csonka-Straub. A. E. BRAUNSTEIN (Nature, 1937, **140**, 427).—The reaction is positive with all compounds containing Ac linked directly to H or C. It is negative with *O*- and *N*-Ac compounds, the CO of which is not a genuine carbonyl group. The mechanism of the reaction is discussed, and the need for care in its application to quant. investigations on the metabolism of $AcCO_2H$ emphasised. L. S. T.

Ethyl acetoacetate and metallic copper. B. CIOCCA (Gazzetta, 1937, **67**, 346—351).—In presence of air, Cu reacts slowly with $CH_2Ac{\cdot}CO_2Et$ (I) at 50—60° to give the Cu derivative of (I), also obtained from Cu_2O, or from CuO that has not been strongly heated. Cu reacts similarly with CH_2BzAc or with CH_2Ac_2, but not with $COMe_2$, COMeEt, or $COPh_2$. E. W. W.

Peroxide effect in the rearrangement of α-bromoacetoacetic ester. M. S. KHARASCH, E. STERNFELD, and F. R. MAYO (J. Amer. Chem. Soc., 1937, **59**, 1655—1657).—$CHAcBr{\cdot}CO_2Et$ and $CMeAcBr{\cdot}CO_2Et$ rearrange to γ-Br-esters in the absence of light and air only if HBr and a peroxide (ascaridole) are present; HBr or a peroxide alone is ineffective. As normally prepared $CHAcBr{\cdot}CO_2Et$ is slowly rearranged by HBr in vac., but this is due to traces of peroxide present, since prep. in H_2 usually gives a stable α-Br-ester. Light accelerates the change by HBr. HCl does not effect rearrangement. The peroxide effect is due to a chain mechanism involving liberation of Br atoms from HBr by a peroxide and/or O_2. R. S. C.

Paramagnetic isomerisation of maleic acid into fumaric acid.—See A., I, 573.

Ozonisation of maleic anhydride. Production of a very explosive ozonide. E. BRINER and D. FRANK (Helv. Chim. Acta, 1937, **20**, 1211—1213).—Ozonisation of maleic anhydride in $CHCl_3$ or EtCl at −60° to −80° gives a particularly unstable and explosive *ozonide*. According to the quantity of O_3 absorbed it has the composition $(CH{\cdot}CO)_2O{,}xO_3$. H. W.

Enzymic hydrogenation of fumaric acid.—See A., III, 392.

Synthesis of *trans-trans*-muconic acid from fumaric acid. H. ERLENMEYER and W. SCHOENAUER (Helv. Chim. Acta, 1937, **20**, 1008—1012).—Me H fumarate is converted by $SOCl_2$ into the corresponding chloride, b.p. 70—71°/14 mm., m.p. 16°, converted by 5% H_2O_2 in presence of C_5H_5N into the *peroxide*, decomp. 129°. This passes when heated mainly into Me_2 *trans-trans*-muconate, m.p. 158°, but a more fundamental reaction resulting in the evolution of C_2H_2 also occurs. H. W.

Synthesis of Hildebrandt's acid; synthesis of methylated polyenedicarboxylic acids. R. KUHN and C. GRUNDMANN (Ber., 1937, **70**, [*B*], 1894—1904).—$Bu^{\alpha}CHO$, obtained by oxidising *n*-amyl alcohol with $Na_2Cr_2O_7$ and H_2SO_4 at 100°, is brominated at −20° to −15° in $CHCl_3$ in strong light and then converted by EtOH into *α-bromo-n-valeraldehyde Et$_2$ acetal*, b.p. 92—96°/12 mm. This is transformed by solid KOH at 150° into *Δ^{α}-pentenal Et$_2$ acetal*, b.p. 163—165°, hydrolysed by 2N-H_2SO_4 to *Δ^{α}-pentenal*, b.p. 122—125°, which is condensed with $CHMeBr{\cdot}CO_2Et$ and Zn turnings in boiling C_6H_6 and then dehydrated by $KHSO_4$ to *Et α-methyl-$\Delta^{\alpha\gamma}$-heptadienoate* (I), m.p. 94—95°/11 mm. Condensation of (I) with $Et_2C_2O_4$ and KOEt in EtOH–Et_2O affords *Et_2 α-keto-βζ-dimethyl-$\Delta^{\gamma\epsilon}$-hexadiene-αζ-dicarboxylate*, m.p. 70°. This is con-

verted by Ac_2O at 200° into the corresponding *Ac* derivative, reduced (Al–Hg in moist Et_2O) to the *compound*, $CO_2Et{\cdot}CH(OAc){\cdot}CMe{:}CH{\cdot}CH{:}CH{\cdot}CHMe{\cdot}CO_2Et$, which is hydrolysed to *αε-dimethyl-*$\Delta^{\alpha\gamma\epsilon}$*-hexatriene-αζ-dicarboxylic acid* (I), m.p. 271° (*Me_2* ester, m.p. 109°), which is reduced (Na–Hg) to *αε-dimethyl-*$\Delta^{\beta\delta}$*-hexadiene-αζ-dicarboxylic acid* (II), m.p. 109°, isomeric with Hildebrandt's acid (III) (A., 1901, ii, 180; 1936, 1231). Addition of HBr in AcOH to (II) gives a non-cryst. acid transformed by $AgNO_3$ in C_5H_5N into *αε-dimethyl-*$\Delta^{\gamma\epsilon}$- or -$\Delta^{\alpha\gamma}$*-hexadine-αζ-dicarboxylic acid*, m.p. 147° (Hildebrandt's *ψ*-acid). [The conversion of $\Delta^{\beta\delta}$-hexadiene-αζ-dicarboxylic acid into $\Delta^{\alpha\gamma}$-hexadiene-αζ-dicarboxylic acid under similar conditions shows that the reactions are accompanied by migration of the double linkings.] Hydrogenation ($Pt–SiO_2$ in AcOH) of (I) affords *αε-dimethylhexane-αζ-dicarboxylic acid*, b.p. 168—174°/0·07 mm. (*di-p-bromophenacyl* ester, m.p. 103—104° or m.p. 90° when rapidly cryst. from 70—90% EtOH), the *dichloride* of which is converted by Br in strong light followed by EtOH into *Et_2 αζ-dibromo-αε-dimethylhexane-αζ-dicarboxylate*, b.p. 153—158°/0·08 mm. This is converted by NaI in $COMe_2$ into the corresponding I_2-compound, which is transformed by 35% KOH–MeOH into *αε-dimethyl-*$\Delta^{\alpha\epsilon}$*-hexadiene-αζ-dicarboxylic acid*, m.p. 193°, identical with (III).

The following examples are cited of the influence of choice of materials on the synthesis of methylated polyenedicarboxylic acids by the $Et_2C_2O_4$ process. Et Δ^{α}-pentenoate, b.p. 156—158°, $Et_2C_2O_4$, and KOEt afford *Et_2 δ-keto-γ-methyl-*Δ^{α}*-butene-αδ-dicarboxylate*, m.p. 60°, converted by the successive action of Ac_2O and Al–Hg followed by hydrolysis into β-methylmuconic acid, m.p. 232°, in 36·5% yield, whereas a yield of 34·5% is secured when $CMe_2{:}CH{\cdot}CO_2Et$ is the initial material. *Et* $\Delta^{\alpha\gamma}$*-heptadienoate*, b.p. 90—92°/12 mm., is transformed into *Et_2 ζ-keto-ε-methyl-*$\Delta^{\alpha\gamma}$*-hexadiene-αζ-dicarboxylate*, whence *ε-methyl-*$\Delta^{\alpha\gamma\epsilon}$*-hexatriene-αζ-dicarboxylic acid*, m.p. 245—246°, in 13% yield. The yield is only about 5% when the acid is obtained similarly from Et β-methylsorbate through the non-cryst. *Et_2 ζ-keto-β-methyl-*$\Delta^{\alpha\gamma}$*-hexadiene-αζ-dicarboxylate*. H. W.

Glyoxal. IV. *dl*-Tartronaldehydic acid. H. O. L. Fischer, E. Baer, and H. Nidecker (Helv. Chim. Acta, 1937, **20**, 1226—1236).—The prep. of cryst. dl-*tartronaldehydic acid* (I) or of salts thereof of const. composition has not been accomplished, but it is shown that in aq. solutions it has the reactions expected of a OH-aldehyde, whilst in acid solution the reducing power is so marked as to resemble that of reductone or ascorbic acid. Glyceraldehyde CH_2Ph *cyclo*acetal in AcOH is converted by conc. H_2SO_4 followed by CrO_3 into *tartronaldehydic acid* *CH_2Ph* cyclo*acetal*, $\begin{matrix}CO_2H{\cdot}CH{\cdot}O{\cdot}CH{\cdot}O{\cdot}CH_2Ph\\ CH_2Ph{\cdot}O{\cdot}CH{\cdot}O{\cdot}CH{\cdot}CO_2H\end{matrix}$, m.p. 180—181°, [*$Na_2$* salt (+$1H_2O$); *$Me_2$* ester, m.p. 137—138°], converted by reductive fission or by hydrolysis into (I). Alternatively, glyoxal semi-acetal is transformed by $ClCO_2Me$ and KCN into the *Et_2 acetal* of *carbomethoxytartronaldehydonitrile*, $(OEt)_2CH{\cdot}CH(O{\cdot}CO_2Me){\cdot}CN$, b.p. 131—133°/12 mm. (corresponding *CO_2Et*-compound, b.p. 85—88°/0·01—0·03 mm., 103—105°/1 mm.), whence the *amide*, m.p. 122—123° (corresponding *carbethoxy-amide*, m.p. 75°), transformed into the *Et_2 acetal* of *Ba tartronaldehydate*, which is converted by CO_2 into (I). Treatment of warm solutions of (I) with $NHPh{\cdot}NH_2$ gives CO_2 and glyoxaldiphenylhydrazone. The *phenylosazone* of (I), m.p. 209° when rapidly heated, has been obtained in small amount. The *Et_2 acetal* of *Et carbomethoxytartronaldehydate* and the corresponding *carboethoxy*-compound have b.p. 85—90°/0·02 mm. and 90—95°/0·02 mm., respectively. H. W.

Sensitised photolysis of malic acid. E. Baur (Helv. Chim. Acta, 1937, **20**, 974—977).—Irradiation of malic acid and $HgCl_2$ in presence of UO_2SO_4 gives HgCl and CO_2 (1 : 1), whilst $AcCO_2H$ is produced. In presence of $Fe_2(SO_4)_3$ the ratio is 1 : 2 and MeCHO arises secondarily from $AcCO_2H$, whilst in presence of quinine the ratio becomes approx. 1 : 3 and MeCHO is not formed solely from $AcCO_2H$. H. W.

Derivatives of hydroxymethoxysuccinic acids, and some related amides. R. T. Williams (J.C.S., 1937, 1517—1518).—*meso*-Tartaric acid, methylated (Me_2SO_4–KOH) and esterified (MeOH–HCl) affords *Me_2* dl-*erythro-α-hydroxy-β-methoxysuccinate*, b.p. 107—109° (bath)/0·5 mm., $[\alpha]_D$ 0° in MeOH (*diamide*, m.p. 195—196°; *bismethylamide*, m.p. 125°). Similarly, *r*-tartaric acid yields *Me_2* dl-*threo-α-hydroxy-β-methoxysuccinate*, b.p. 140° (bath)/2 mm. (*diamide*, m.p. 192—193°; *bismethylamide*, m.p. 152—153°). The following are also described: dl-*tartramide*, m.p. 226°, meso-*tartramide*, m.p. 189—190°, dl-*dimethoxysuccindiamide*, m.p. 268—272° (decomp.), dl-*tartarobismethylamide*, m.p. 204—205°, meso-*tartarobismethylamide*, m.p. 182—183°, dl-*dimethoxysuccinobismethylamide*, m.p. 194—195°. J. D. R.

Crystallised *l*-threonolactone and synthesis of *l*-threonic acid α-methyl ether. K. Gätzi and T. Reichstein (Helv. Chim. Acta, 1937, **20**, 1298—1303).—Oxidation of *l*-ascorbic acid with $KMnO_4$ leads to cryst. *l*-threonolactone (I), m.p. 65—68° (corr.), b.p. 145—147°/0·3 mm., $[\alpha]_D^{21}$ +30·7° to +27·3° in H_2O, $[\alpha]_D^{20}$ +47·0° in MeOH, +45·1° in $COMe_2$, readily transformed into *l*-threonphenylhydrazide, m.p. 161—161·5° (corr.), $[\alpha]_D^{20}$ +30·9° in H_2O, $[\alpha]_D^{21}$ +48·6° in MeOH. NH_3–MeOH and (I) at room temp. afford *l*-threonamide, m.p. 105·5—107° (corr.), $[\alpha]_D^{21}$ +56·0° in H_2O, $[\alpha]_D^{20}$ +82·1° in MeOH. Brucine and (I) in H_2O–MeOH afford brucine *l*-threonate, m.p. 209—210° (corr.), $[\alpha]_D^{22}$ −19·3° in H_2O; the corresponding *quinine* and *strychnine* salts have m.p. 169·5—170·5° (corr.), $[\alpha]_D^{22}$ −116·7° in H_2O, and m.p. 182—184° (corr.), $[\alpha]_D^{21}$ −18·5° in H_2O, respectively. Treatment of (I) in dioxan with a large excess of CH_2N_2 in Et_2O gives *l-threonolactone Me ether*, m.p. 111—114°/0·12 mm., $[\alpha]_D^{13}$ +78·8° in MeOH, characterised as *l*-threonamide α-Me ether, m.p. 105·5—107°, identical with that derived from *iso*propylideneascorbic acid, the structure of which is thereby elucidated. H. W.

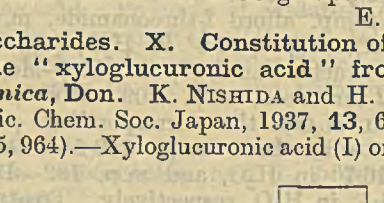
Reductones. F. Micheel, G. Bode, and R. Siebert (Ber., 1937, **70**, [*B*], 1862—1866).—Tetronic

acid is converted by PhN_2Cl into the sparingly sol. monophenylhydrazone of hydroxydehydrotetronic acid, which with $NHPh{\cdot}NH_2$ gives the corresponding diphenylhydrazone. This is suspended in abs. EtOH and hydrogenated (Pd sponge) to 3 : 4-*diaminotetrone* (I), $\begin{matrix}C(NH_2)—CO\\ C(NH_2){\cdot}CH_2\end{matrix}>O$, m.p. 198—201° (decomp). Dehydro-*l*-ascorbic acid diphenylhydrazone is similarly transformed into *hydroxy*-3 : 4-*diamino*-5-l-*tetronylacetic acid* (II), $\begin{matrix}C(NH_2)——CH{\cdot}CH(OH){\cdot}CO_2H\\ C(NH_2){\cdot}CO{\cdot}O\end{matrix}$. In H_2O (I) and (II) are nearly neutral to indicators. In acid solution $AgNO_3$ is reduced to Ag and 2 I are absorbed, but the changes do not occur so readily as with ascorbic or scorbamic acid. The absorption spectra of (I) and (II) suggest the presence of the forms $\begin{matrix}C(:NH)——CO\\ CH(NH_2){\cdot}CH_2\end{matrix}>O$ and $\begin{matrix}C(:NH){\cdot}CO{\cdot}O\\ CH(NH_2)—CH{\cdot}CH(OH){\cdot}CO_2H\end{matrix}$ in neutral solution. H. W.

Duality of the reversibly oxidised forms of vitamin-*C* and the polarisation of its dienol group. N. Bezssonoff and M. Woloszyn (Nature, 1937, **139**, 469).—The reversible behaviour of the blue and green solutions obtained by treating acid solutions of vitamin-*C* (I) with phosphomolybdic acid (II) affords further evidence of the existence of two reversibly oxidised forms of (I). Quinol (III), but not pyrocatechol, gives the same colour reactions with (II) as does (I), which indicates that in both (I) and (III) the dienol group is polarised. L. S. T.

βε-Anhydromannono-γ-lactone. F. Valentin (Coll. Czech. Chem. Comm., 1937, **9**, 315—326).—3 : 6-Anhydromannose treated with Br in H_2O for several days gives non-cryst. *βε-anhydromannonic acid* (I) (amorphous *Ba* salt), which yields a *phenylhydrazide*, m.p. 190·5° (decomp.), $[\alpha]_D$ +19·7° in MeOH. This with EtOH–H_2O–PhCHO at the b.p. gives the *γ-lactone*, m.p. 113°, $[\alpha]_D$ +126·5° in H_2O, falling slowly to +115·3° after 282 hr. K_2 saccharate reacts violently with AcCl–H_2SO_4, giving *αδ-diacetylsaccharo-γγ′-dilactone*, m.p. 190—192°, $[\alpha]_D$ +155° in Ac_2O. It is concluded that the two rings of these and of other sugar compounds containing the dicyclic system $C<\begin{matrix}O{\cdot}C{\cdot}C\\ C{\cdot}C{\cdot}O\end{matrix}>C$ have the same optical character, [α] thus being augmented, and that the effect increases with the no. of CO groups. E. W. W.

Polysaccharides. X. Constitution of new disaccharide "xyloglucuronic acid" from *Kadsura japonica*, Don. K. Nishida and H. Hashima (Bull. Agric. Chem. Soc. Japan, 1937, **13**, 660—672; cf. A., 1935, 964).—Xyloglucuronic acid (I) on methyl-

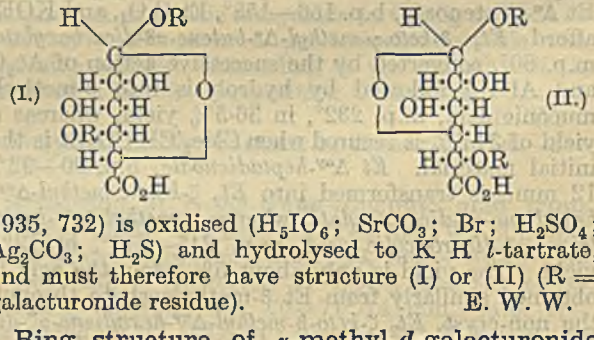


(I.)

ation with Me_2SO_4 + NaOH and MeI + Ag_2O yielded *Me hexamethylaldobionate*, $[\alpha]_D^{20}$ +90·7°, which on hydrolysis with 2% HCl gave 2 : 3-dimethylxylose and *αβγ*-trimethylglucuronic acid. J. N. A.

Derivatives of *d*-galacturonic acid. III. Synthesis of a mercaptal of *d*-galacturonic acid and methyl tetra-acetylaldehydo-*d*-galacturonate. H. A. Campbell and K. P. Link (J. Biol. Chem., 1937, **120**, 471—479).—The reaction product of *d*-galacturonic acid and EtSH in conc. HCl gives, with NaOH–MeOH, the *Na* salt (I), $[\alpha]_{5893}^{25}$ −13·6° in H_2O, of *digalacturonic acid Et₂ mercaptal* (II), m.p. 132·5°, $[\alpha]_{5893}^{25}$ +17° in MeOH. An aq. solution of (II) evaporated at 100° gives d-*galacturonolactone Et₂ mercaptal*, m.p. 79°, $[\alpha]_{5893}^{25}$ +36° in H_2O. CH_2N_2 and (II), or MeOH–HCl and (I) or (II), or Me *d*-galacturonate and EtSH in HCl, give the *Me* ester (III), m.p. 133—134°, $[\alpha]_{5893}^{25}$ +17·8° in 95% EtOH, of (II). Acetylation of (III) (Ac_2O–C_5H_5N) yields *Me tetra-acetyl*-d-*galacturonate Et₂ mercaptal*, m.p. 112·5—113·5°, $[\alpha]_{5893}^{25}$ +20·5° in $CHCl_3$. This is converted ($CdCO_3$–$HgCl_2$–$COMe_2$–H_2O) into the *Et hemiacetal* (IV), sintering at 113°, m.p. 139°, $[\alpha]_{5893}^{25}$ +16·5° after 10 min., −3·0° after 36 hr., in $C_2H_2Cl_4$, of *Me tetra-acetylaldehydo*-d-*galacturonate*, m.p. 136·5—137·5°, $[\alpha]_{5893}^{25}$ −16·2° in $C_2H_2Cl_4$, of which the *semicarbazone*, m.p. 219—220° (decomp.), $[\alpha]_{5893}^{25}$ +83·4° in $CHCl_3$, is obtained from (IV). E. W. W.

Oxidation and hydrolysis of polygalacturonide methyl ester to *l*-tartaric acid. P. A. Levene and L. C. Kreider (J. Biol. Chem., 1937, **120**, 591—595).—Polygalacturonide Me ester (A., 1934, 633;



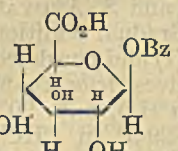
(I.) (II.)

1935, 732) is oxidised (H_5IO_6; $SrCO_3$; Br; H_2SO_4; Ag_2CO_3; H_2S) and hydrolysed to K H *l*-tartrate, and must therefore have structure (I) or (II) (R = galacturonide residue). E. W. W.

Ring structure of α-methyl-*d*-galacturonide and its derivatives. P. A. Levene and L. C. Kreider (J. Biol. Chem., 1937, **120**, 597—606).—The pyran structure of methylgalacturonide (A., 1934, 281) is confirmed. α-Methyl-*d*-galacturonide Me ester monohydrate (I) (A., 1934, 280) is dehydrated in vac. at 78° over P_2O_5 to the *anhyd.* form, m.p. 148°, which with MeI–Ag_2O–MeOH (repeated methylation) yields *α-methyl*-2 : 3 : 4-*trimethyl*-d-*galacturonide Me ester*, m.p. 70·2—70·3°, $[\alpha]_D^{26}$ +142·1° in $CHCl_3$. This is oxidised (HNO_3, *d* 1·42, at 65—95°) to *βγδ-trimethoxymucic acid*, m.p. 100—101°, $[\alpha]_D^{23}$ +42·0° in $COMe_2$ [*Me₂* ester, m.p. 100·5° (mixed m.p. with acid, 79—82°), $[\alpha]_D^{24}$ +28·9° in H_2O; *di*(*methylamide*), m.p. 207°, $[\alpha]_D^{23}$ +12·6° in MeOH], with a syrup from which MeOH–HCl gives trimethoxy-*l*-araboglutardi(methylamide) (A., 1927, 1059). With NH_3–MeOH, (I) gives *α-methyl*-d-*galacturonamide* (II), m.p. 225—226°, $[\alpha]_D^{23}$ +127·2° in H_2O. After attempted "Weerman degradation" (A., 1917, i, 546) of (II), only (II) is isolated. Attempted Hofmann degradation

gives only α-methyl-*d*-galacturonide dihydrate (A., 1934, 280). E. W. W.

Chemical constitution of benzoylglycuronic acid. W. F. Goebel (Science, 1937, **86**, 105—106).—Benzoylglycuronic acid (I) in MeOH with CH_2N_2 at −10° yields the *Me* ester, m.p. 190—191°, $[\alpha]_D^{25}$ −16·3° in MeOH, acetylated (C_5H_5N–Ac_2O at 0°) to *Me triacetylmonobenzoylglycuronate*, m.p. 145°, $[\alpha]_D^{25}$ −16·6° in $CHCl_3$. Synthetic Me α-benzoyl-βγδ-triacetylglycuronate, from Me α-bromo-βγδ-triacetylglycuronate (II) and AgOBz in $CHCl_3$, is identical with the corresponding derivative prepared from natural (I). It is regarded as having the same structure and configuration as (II), which is a pyranose derivative with the β configuration (A., 1936, 1231). (I) is as (*A*) in which Bz is attached to the first C. L. S. T.



(*A*.)

Reactions of the thiol group. IV. N. Hellström (Svensk Kem. Tidskr., 1937, **49**, 201—207).—$SH{\cdot}CH_2{\cdot}CO_2Na$ (I) and $CH_2Cl{\cdot}CH_2{\cdot}OH$ after 17 days at room temp. are treated with $CuSO_4$ to give *Cu α-(β-hydroxyethyl)thiolacetate*, decomp. 171°. By similar methods (I) yields with $OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2Cl$ (II), *Cu α-(βγ-dihydroxypropyl)thiolacetate*, (III), decomp. 182°. (III) is also made from (I) and glycide. (II) and carbyl sulphate give a *compound*, $C_4H_7O_2Cl$, b.p. 146°, probably α-chloro-βγ-methylenedioxypropane, which with (I) yields (III). (I) and epichlorohydrin give *Cu α-(γ-chloro-β-hydroxypropyl)thiolacetate*, decomp. 157—158°, and *Cu αγ-(β-hydroxypropyl)dithioldiacetate*, decomp. 149°. M. H. M. A.

Mechanism of homogeneous thermal decomposition of gaseous acetaldehyde.—See A., I, 523.

Influence of traces of oxygen on thermal decomposition of gaseous acetaldehyde.—See A., I, 571.

Electrolytic reduction of *n*-valeraldehyde to *n*-pentane. S. Swann, jun., and E. W. Field (Trans. Electrochem. Soc., 1937, **72**, Preprint 16, 229—233).—Highest yields are obtained under conditions similar to those used for reduction of $COMePr^a$ (A., 1935, 310) using a Cd cathode, although the yield of C_5H_{12} is much less from Bu^aCHO. The next best yield is given by >99·99% Pb, but this is very sensitive to impurities. A Zn cathode also gives a good yield. A 99·9% Pb cathode "prepared" according to Tafel (A., 1900, ii, 588) is not as efficient as pure Pb. F. R. G.

Polyene pigment of the orange. II. Citraurin. L. Zechmeister and P. Tuzson (Ber., 1937, **70**, [*B*], 1966—1969; cf. A., 1936, 1435).—The finely-powdered, dried skins are extracted with Et_2O free from peroxides. The extract is evaporated, the residue is dissolved in light petroleum and chromatographed ($CaCO_3$). The ester fraction is hydrolysed and the hydrolysate is again chromatographed, thereby yielding *citraurin* (I), $C_{20}H_{40}O_2$, m.p. 146—147° (*oxime*). A method of determining (I) is given. H. W.

Ketones from higher fatty acids. II. Comparison of the degrees of decomposition of the carboxyl group during the action of iron or magnesium powder on higher fatty acids at high temperatures. K. Kino (J. Soc. Chem. Ind. Japan, 1937, **40**, 235—236B).—Decomp. is more rapid when higher temp. and large amounts of metal are used, and is greater with Fe, which also gives a more highly coloured product than Mg. Prolonged heating lowers the m.p. of the product, especially with Fe. F. R. G.

Determination of acetoin. Y. Tomiyasu (J. Agric. Chem. Soc. Japan, 1937, **13**, 787—790).—Acetoin (I) in neutral or slightly acid solution is mixed with $FeCl_3$ and distilled into a solution containing NH_2OH, NaOAc, and $NiCl_2$; wt. of ppt. × 0·72 = (I). With a mixture of Ac_2 and (I), two determinations are necessary, the first without $FeCl_3$. Wt. of ppt. × 0·596 = Ac_2. J. N. A.

Syntheses of simpler methylated sugars. H. O. L. Fischer, E. Baer, H. Pollock, and H. Nidecker (Helv. Chim. Acta, 1937, **20**, 1213—1226).—The action of 0·1N-H_2SO_4 on $\begin{matrix}CH_2{\cdot}O\\O{\cdot}CH_2\end{matrix}>C{:}CH_2$ gives equiv. amounts of CH_2O and acetol which condense after addition of a small excess of $Ba(OH)_2$ to *butane-αβ-diol-γ-one* (I), b.p. 65—70°/0·02 mm., m.p. 37·5°, also obtained by hydrolysis of *iso*propylidenebutane-αβ-diol-γ-one or by oxidation of $COMe{\cdot}CH{:}CH_2$ with $NaClO_3$ in presence of OsO_4 or, less advantageously, of $KMnO_4$. (I) affords a *hydrazone*, m.p. 110—111°, 2 : 4-*dinitrophenylhydrazone*, m.p. 118°, 2 : 4-*dinitrophenylosazone*, a *diacetate*, b.p. 51—64°/0·01—0·02 mm., and its p-*nitrophenylhydrazone*, m.p. 105°, a *dibenzoate*, m.p. 87°, and a *methylcycloacetal* (bimol.), m.p. 177—178°. Distillation with P_2O_5 transforms (I) into Ac_2. Condensation of (I) with CH_2O or of $COMe{\cdot}CH_2{\cdot}OH$ with CH_2O (1 : 2) affords *γ-hydroxymethylbutane-γδ-diol-β-one* (*dihydroxymethylacetol*), b.p. 105—107°/0·02—0·05 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 156—157°; *tri*-p-*nitrobenzoate*, m.p. 192—194°; *anhydride* $C_{10}H_{16}O_6$, m.p. 196—197°, and its *diacetate*, m.p. 196°).

Oxidation of mesityl oxide in $COMe_2$ by $NaClO_3$ and a little OsO_4 in H_2O and treatment of the mixture with Zn powder yields *β-methylpentane-βγ-diol-δ-one* (*trimethylglycerose*), b.p. 94—99°/9 mm., m.p. 20—21° (2 : 4-*dinitrophenylhydrazone*, m.p. 157—158°; *di*-p-*nitrobenzoate*, m.p. 154—155°). H. W.

Dioximes. CXXII. G. Tappi (Gazzetta, 1937, **67**, 388—392).—Dimethyltriketone trioxime (I) with N_2O_4 gives *methylacetylglyoxime peroxide oxime*, $\begin{matrix}CMe—C{\cdot}CMe{:}N{\cdot}OH\\N{\cdot}O{\cdot}O{\cdot}N\end{matrix}$ (II), m.p. 130—131° (*Ac*, m.p. 73°, and *Bz*, m.p. 172°, derivatives), which in HNO_3 (*d* 1·40) gives *dinitromethylacetylglyoxime peroxide*, m.p. 72—73°, converted by $SnCl_2$–HCl into methylacetylglyoxime peroxide. Hydrolysis of (II) by 20% HCl gives *methylacetylglyoxime peroxide*, m.p. 32—33° (*phenylhydrazone*, m.p. 169°; *semicarbazone*, m.p. 230°). Using excess of N_2O_4, (I) also yields traces of *dimethyltriketone*-1 : 3-*dioxime peroxide* 2-*oxime*, m.p. 182° (decomp.), converted by NH_2OH,HCl in C_5H_5N into (I). E. W. W.

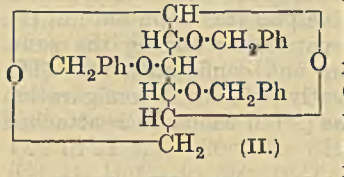
Oxidation as a route to carbohydrates. N. A. Orlov and L. S. Mustafin (Compt. rend. Acad. Sci. U.R.S.S., 1937, **16**, 107—108).—Dipentene, allyl alcohol, and styrene in H_2O with $Ca(OH)_2$, active C, and O_2 at 100—110° in 34 days afford pentosans (0·03—0·1% yield). J. D. R.

Sugars in solution and in the cell. E. F. Armstrong (Chem. & Ind., 1937, 816—818).—The tautomerism of sugars in solution and the probable modes of biogenesis of sugars are discussed. R. S. C.

2 : 5-Dimethylxylofuranose and 2 : 3-dimethylxylose. G. J. Robertson and D. Gall (J.C.S., 1937, 1600—1604).—1 : 2-*iso*Propylidenexylose 5-benzoate 3-*p*-toluenesulphonate is hydrolysed (NaOMe in C_6H_6) to 1 : 2-iso*propylidenexylose* 3-p-*toluenesulphonate*, m.p. 89—90°, $[\alpha]_D^{17}$ −28·6° in $CHCl_3$, which with MeI–Ag_2O yields 5-*methyl*-1 : 2-iso*propylidenexylose* 3-p-*toluenesulphonate*, m.p. 81—82°, $[\alpha]_D^{18}$ −31·8 in $CHCl_3$, converted by MeOH–HCl into 5-*methyl*-β- (I), m.p. 89°, $[\alpha]_D^{18}$ −51·7° in $CHCl_3$, and -α-*methylxylofuranoside* 3-p-*toluenesulphonate* (II) (a syrup), $[\alpha]_D^{18}$ +44·5° in $CHCl_3$; the α- and β-forms are converted by HCl–MeOH into an equilibrium mixture, $[\alpha]_D$ +11·7° in $CHCl_3$. Methylation of (I) and (II) (MeI–Ag_2O) affords respectively 2 : 5-*dimethyl*-β- (a syrup), $[\alpha]_D^{18}$ −49·9°, and -α-*methylxylofuranoside* 3-p-*toluenesulphonate* (a syrup), $[\alpha]_D^{17}$ +34·7° in $CHCl_3$, which are hydrolysed (KOH–aq. EtOH) to 2 : 5-*dimethyl*-β-, b.p. 85°/0·02 mm., $[\alpha]_D^{17}$ −56° in $CHCl_3$, and -α-*methylxylofuranoside*, b.p. 110°/0·03 mm., $[\alpha]_D^{17}$ +54·3° in $CHCl_3$, both of which are converted (HCl–aq. $COMe_2$) into 2 : 5-*dimethylxylofuranose* (a syrup), $[\alpha]_D^{17}$ +46° in H_2O, +16·4° in EtOH. This, with *p*-$C_6H_4Br{\cdot}NH{\cdot}NH_2$ yields the *p*-bromophenylosazone of 5-methylxylose. 1 : 2-*iso*Propylidenexylose 5-benzoate, hydrolysed (MeOH–HCl) and methylated (Ag_2O–MeI), gives 2 : 3-*dimethyl*-γ-*methylxyloside* 5-*benzoate* (a syrup), hydrolysed (NaOH–aq. EtOH) to 2 : 3-*dimethyl*-γ-*methylxyloside*, b.p. 95°/0·15 mm., $[\alpha]_D^{15}$ +12·5° in $CHCl_3$, and further hydrolysed (aq. HCl) to 2 : 3-dimethylxylose, identical with that obtained from xylan by Robertson and Speedie (A., 1934, 871). 1 : 2-*iso*Propylidenexylose 5-*p*-toluenesulphonate when methylated (MeI–Ag_2O) yields 3-*methyl*-1 : 2-iso*propylidenexylose* 5-p-*toluenesulphonate*, m.p. 114°, $[\alpha]_D$ −27·2° in $CHCl_3$, hydrolysed (HCl–MeOH) to monomethylmethylxyloside. J. D. R.

β-*d*-Talose and *d*-talose acetates and ortho-esters. W. W. Pigman and H. S. Isbell (J. Res. Nat. Bur. Stand., 1937, **19**, 189—213).—Oxidation (BzO_2H) of galactal by Levene and Tipson's method (A., 1931, 938) affords galactose, α- (I) and β-*d*-talose (II), m.p. 120—121°, and d-*talose benzoate* (III), m.p. 150—170° (decomp.). Acetylation (C_5H_5N–Ac_2O; 0°; 3 days) of (I) yields α-d-*talose penta-acetate*, m.p. 106·5—107°, $[\alpha]_D^{20}$ +70·2° in $CHCl_3$, which with AcOH containing 38% of HBr (0°, 1 hr. followed by room temp., 2½ hr.) affords 1-*bromo*-d-*talose tetra-acetate* (IV), m.p. 84—84·5° (sinters 83°), $[\alpha]_D^{20}$ +165·6° in $CHCl_3$. (IV) with AcOH–Ag_2CO_3 (0°, 1¼ hr.) gives d-*talose triacetate* 1 : 2-o-*methylacetate*, m.p. 91·5—92·5°, $[\alpha]_D^{20}$ +3·7° → +2·2° (19 hr.), and with AgOBz in moist $COMe_2$ (−4°; 1½ hr.) yields α-d-*talose tetra-acetate*, m.p. 112—113°, $[\alpha]_D^{20}$ +42·8° in $CHCl_3$. Mutarotation and oxidation (Br–H_2O) rates are given for (I) and (II), and evidence is given suggesting that (III) has an orthobenzoic acid structure. The conditions for ortho-ester formation are discussed. F. N. W.

Benzylated derivatives of β-glucosan and of glucose. G. Zemplén, Z. Csürös, and S. Angyal (Ber., 1937, **70**, [*B*], 1848—1856).—Gradual addition of a mixture of β-glucosan triacetate (I) and powdered KOH to CH_2PhCl at 95—100° gives *tribenzyl*-β-*glucosan* (II), m.p. 90°, $[\alpha]_D^{20}$ −29·5° in $CHCl_3$ (a modified procedure for the determination of CH_2Ph is recorded). (II) with Ac_2O containing a trace of conc. H_2SO_4 at room temp. gives α-2 : 3 : 4-*tribenzylglucose* 1 : 6-*diacetate*, m.p. 66°, $[\alpha]_D^{21}$ +62·5° in $CHCl_3$, $[\alpha]_D^{22}$ +81·5° in EtOH, and the corresponding β-derivative. The mixture is hydrolysed by NaOMe–MeOH at room temp. to a mixture of α- and β-tribenzylglucose, giving after treatment with Ac_2O and anhyd. NaOAc at 100° a product from which β-2 : 3 : 4-*tribenzylglucose* 1 : 6-*diacetate*, m.p. 63—63·5°, $[\alpha]_D^{21}$ +17·4° in $CHCl_3$, is isolated. This, or its mixture with the α-isomeride, in $CHCl_3$ is transformed by HBr–AcOH followed by $CH_2Ph{\cdot}OH$ and Ag_2CO_3 in C_6H_6 into 2 : 3 : 4-*tribenzyl*-β-*benzylglucoside* 6-*acetate*, m.p. 115·5—116°, $[\alpha]_D^{21}$ +2·9° in $CHCl_3$, which with CH_2PhCl and KOH at 95—100° affords 1 : 2 : 3 : 4 : 6-pentabenzylglucose, m.p. 82—82·5°. 2 : 4-*Dibenzyl*-β-*glucosan* (III), m.p. 103°, $[\alpha]_D^{20}$ −28·5° in $CHCl_3$, is invariably produced during the prep. of (II) and is conveniently obtained when solid KOH is added to a mixture of (I) and CH_2PhCl in xylene at 90°; it passes into 2 : 4-*dibenzylglucose*, m.p. 75—79°, $[\alpha]_D^{15}$ +25·1° in EtOH. The constitution of (III) is established by converting it into 2 : 4-*dibenzyl*-β-*glucosan*-3-p-*toluenesulphonate*, m.p. 105·5—106°, $[\alpha]_D^{17}$ −5·7° in $CHCl_3$; this is debenzylated by hydrogenation (Pd–C in EtOH–AcOH) and the product is transformed by Ac_2O in C_5H_5N at room temp. into β-*glucosan* 2 : 4-*diacetate* 3-p-*toluenesulphonate* (IV), m.p. 87—87·5°. Treatment of (IV) with Ac_2O–H_2SO_4 followed by HBr–AcOH affords α-bromoglucose 2 : 4 : 6-triacetate 3-*p*-toluenesulphonate, m.p. 150°, which with Ac_2O and TlOAc yields β-glucose 1 : 2 : 4 : 6-tetra-acetate 3-*p*-toluenesulphonate, m.p. 171—172°. H. W.



Aldehydo-derivatives of dibenzylideneglucose. M. L. Wolfrom and L. J. Tanghe (J. Amer. Chem. Soc., 1937, **59**, 1597—1602).—When glucose Et_2 mercaptal 6-benzoate (I), PhCHO, and $ZnCl_2$ react, [α] rapidly passes through a min. and then rises. This min. α corresponds with a max. yield of *dibenzylidene*-d-*glucose* Et_2 *mercaptal* 6-*benzoate* (II), m.p. 130·5—131·5°, $[\alpha]_D^{23}$ −15·5° in $CHCl_3$, −11° in PhCHO [hydrolysed to (I) by hot aq. AcOH], which passes by further reaction into dibenzylidene-*d*-glucose 6-benzoate (III), m.p. 160—160·5°, $[\alpha]_D^{25}$ +15° in $CHCl_3$, $[\alpha]_D^{23}$ +18° in $C_2H_2Cl_4$, +20° in

PhCHO (does not reduce Fehling's solution or $AgNO_3$). $CdCO_3$–$HgCl_2$ in aq. $COMe_2$ converts (II) into *di-benzylidene*-aldehydo-d-*glucose* 6-*benzoate*, m.p. 185—187°, non-reducing, $[\alpha]_D^{26}$ +43° (stable) in $C_2H_2Cl_4$, $[\alpha]_D^{23}$ +51° → +14° (24 hr.) in $CHCl_3$ containing EtOH [*thiosemicarbazone*, m.p. 191—192° (decomp.), $[\alpha]_D^{24}$ +47° → +40° in $CHCl_3$], which gives Schiff's test and is converted by PhCHO–$ZnCl_2$ into (II). Hot 0·5N-NaOH hydrolyses (II) to 2 : 3 : 4 : 5-*dibenzylidene*-d-*glucose* *Et*$_2$ *mercaptal*, m.p. 159·5—160·5°, $[\alpha]_D^{24}$ −17° in $CHCl_3$, reconverted into (II) by benzoylation and giving with $HgCl_2$–$CdCO_3$ 2 : 3 : 4 : 5-*dibenzylidene*-d-*glucose*, amorphous [*thiosemicarbazone*, m.p. 223—224° (decomp.), $[\alpha]_D^{24}$ +91° in C_5H_5N]. Hydrolysis of (III) gives dibenzylidene-*d*-glucose, m.p. 163—165°, $[\alpha]_D^{24}$ +35° in C_5H_5N, reconverted into (III) by benzoylation. R. S. C.

Acetylation and methylation of agar-agar and the isolation of 2 : 4 : 6-trimethyl-α-*d*-galactose by hydrolysis. E. G. V. Percival and J. C. Somerville (J.C.S., 1937, 1615—1619).—Agar acetate with Me_2SO_4–NaOH yields a *product*, $[\alpha]_D^{17}$ −92° in $CHCl_3$, which is hydrolysed (H_2SO_4 followed by MeOH–HCl) to Me lævulate (p-*nitrophenylhydrazone*, m.p. 136°), an unidentified dimethylmethylketoside, and 2 : 4 : 6-*trimethylmethylgalactoside monohydrate* (I), m.p. 37°, $[\alpha]_D^{15}$ +101° in H_2O, further hydrolysed (HCl) to 2 : 4 : 6-trimethyl-α-galactose (II), m.p. 104—105°, $[\alpha]_D^{15}$ +124° in H_2O, which with $NHPh{\cdot}NH_2$ yields 4 : 6-*dimethylgalactosazone*, m.p. 158°, $[\alpha]_D^{26}$ −25° in EtOH. When treated with Br and dehydrated, (I) gives 2 : 4 : 6-*trimethyl*-δ-*galactonolactone*, $[\alpha]_D^{15}$ +50° in H_2O (*amide*, m.p. 167°, $[\alpha]_D^{12}$ +74° in H_2O). With HCl–MeOH, (II) regenerates (I). J. D. R.

Reduction of potassium dichromate by sucrose. —See A., I, 577.

Influence of the walls of the vessel on the course of alcoholytic reactions. E. Berner and A. Hjulstad (Ber., 1937, **70**, [*B*], 2028—2031).—Alcoholysis of heptamethyl-β-methyl-lactoside occurs almost twice as quickly in a steel tube (construction described) as in a glass tube. Similar observations are recorded for β-phenolglucoside and MeOH at 205—210° and for the action of MeOH on $CH_2Ph{\cdot}OAc$ at about 210°. H. W.

Emulsin. XXXI. Mono- and di-β-*d*-glucosides of dihydric alcohols and their hydrolysis by sweet almond emulsin. B. Helferich and R. Hiltmann (Annalen, 1937, **531**, 160—175).—The ease of hydrolysis of monoglucosides $OH{\cdot}[CH_2]_n{\cdot}OR$ increases somewhat with increase in the length of the C chain. Diglucosides $OR{\cdot}[CH_2]_n{\cdot}OR$ are hydrolysed at about the same rate as the corresponding monoglucosides if $n = 2$ or 3, but much more slowly when $n = 4$. $OH{\cdot}[CH_2]_2{\cdot}OMe$, acetobromoglucose (I), and Ag_2CO_3 give β-β′-*methoxyethyl*-d-*glucoside* *tetra-acetate*, m.p. 81—82°, $[\alpha]_D^{20}$ −20·6° in $CHCl_3$, hydrolysed (Zemplén) to β-β′-*methoxyethyl*-d-*glucoside*, m.p. 117·5—119° (corr.), $[\alpha]_D^{22}$ −28·7° in H_2O. β′-Hydroxyethyl-β-*d*-glucoside tetra-acetate, (I), Ag_2CO_3, $CaCl_2$, and I in anhyd. $CHCl_3$ yield *glycoldi*-β-d-*glucoside* *octa-acetate*, m.p. 170·5—171°, $[\alpha]_D^{20}$ −31·8° in $CHCl_3$, whence *glycoldi*-β-d-*glucoside*, m.p. 113—115°, $[\alpha]_D^{20}$ −35·2° in H_2O. (I) and $CH_2(CH_2{\cdot}OH)_2$ with Ag_2CO_3 give γ′-*hydroxypropyl*-β-d-*glucoside* *tetra-acetate* (II), m.p. 97·5—98·5° (corr.), $[\alpha]_D^{20}$ −17·0° in $CHCl_3$, de-acetylated to γ′-*hydroxypropyl*-β-d-*glucoside*, m.p. 100—101·5° (corr.), $[\alpha]_D^{20}$ −36·2° in H_2O. (II) and (I) in anhyd. $CHCl_3$ containing Ag_2CO_3, $CaCl_2$, and I give *propane*-α′γ′-*dioldi*-β-d-*glucoside* *octa-acetate*, m.p. 175—176·5° (corr.), $[\alpha]_D^{20}$ −16·9° in $CHCl_3$, whence *propane*-α′γ′-*dioldi*-β-d-*glucoside*, m.p. 152—154° (corr.) after softening, $[\alpha]_D^{20}$ −40·5° in H_2O. Analogous methods are used in the prep. of the following: δ′-*hydroxybutyl*-β-d-*glucoside*, m.p. 98—100° (corr.), $[\alpha]_D^{20}$ −35° [*tetra-acetate*, m.p. 78—80° (corr.), $[\alpha]_D^{20}$ −19·2° in $CHCl_3$], and *butane*-αδ-*dioldi*-β-d-*glucoside*, m.p. 184—185° after softening, $[\alpha]_D^{21}$ −41·9° in H_2O, n-*pentane*-α′ε′-*dioldi*-β-d-*glucoside*, m.p. 90—92° (corr.) after softening at about 80°, decomp. 100°, $[\alpha]_D^{23}$ −40·0° in H_2O (*octa-acetate*, m.p. 122·5—124°, or, occasionally, m.p. 134·5—137°, $[\alpha]_D^{20}$ −24·5° in $CHCl_3$); n-*hexane*-α′ζ′-*dioldi*-β-d-*glucoside* (+1H_2O), m.p. (anhyd.) 152·5—153·5° (corr.), $[\alpha]_D^{22}$ −40·1° in H_2O [*octa-acetate*, m.p. 142—143·5° (corr.), $[\alpha]_D^{20}$ −24·6° in $CHCl_3$]; l-trans-cyclo*pentane*-1 : 2-*diol*-β-d-*glucoside*, $[\alpha]_D^{25}$ −28·5° in H_2O; cis-cyclo*pentane*-1 : 2-*diol*-β-d-*glucoside*, two diastereoisomeric *forms*-I, m.p. 165—167·5° (corr.), $[\alpha]_D^{18}$ −24·0° in H_2O and, -II, m.p. 135·5—137·5°, $[\alpha]_D^{18}$ −36·3° in H_2O; n-*butane*-α′δ′-*diol*-α′-β-d-*glucoside*-δ′-β-d-6-*methanesulphonylglucoside*, m.p. 122·5—124°, $[\alpha]_D^{23}$ −38·0° in H_2O [*hepta-acetate*, m.p. 142—143° (corr.), $[\alpha]_D^{22}$ −20·4° in $CHCl_3$]. H. W.

Constitution of the glucoside butrin isolated from *Butea frondosa* flowers. I. J. B. Lal (J.C.S., 1937, 1562—1564).—Butrin (I), $[\alpha]_D^{30}$ −81·7° in C_5H_5N (dihydrate, $[\alpha]_D^{31\cdot5}$ −73·27° in H_2O), with $Pb(OAc)_2$ yields a *Pb* salt, $C_{27}H_{39}O_3(O{\cdot}Pb{\cdot}OAc)_2,2H_2O$, m.p. 128°. The following derivatives of (I) are described: *nonabenzoyl* (monohydrate), m.p. 141°, $[\alpha]_D^{30}$ +77·28° in C_5H_5N, *deca-acetyl* (monohydrate) (by NaOAc–Ac_2O), m.p. 119—120°, $[\alpha]_D^{30}$ −79·86° in C_5H_5N, *oxime* (dihydrate), m.p. 180°, *tetra*-p-*nitrobenzoyl* (monohydrate), m.p. 154° $[\alpha]_D^{30}$ (anhyd. material) −44·30° in C_5H_5N. (I) with Me_2SO_4–KOH yields O-*methylbutrin*, m.p. 82—84°, whilst with MeI–K_2CO_3 in MeOH, O-*dimethylbutrin* (heptahydrate), m.p. 234°, is formed. (I) with Na_2CO_3–EtI in EtOH affords O-*diethylbutrin* (+7·5H_2O), m.p. 238°, and an isomeric *chalkone derivative*, m.p. 183°, whilst on oxidation (H_2O_2–KOH), fisetin is formed. J. D. R.

Placing the oleander glycoside in the digitalis group. W. Neumann and W. Lindner (Arch. exp. Path. Pharm., 1937, **185**, 630—643).—The aglucone of oleandrin is identical with acetylgitoxigenin, and that of deacetyloleandrin with gitoxigenin. Both glycosides belong therefore to the digitalis group; this is borne out by the pharmacological activity. P. W. C.

Gossypitrin. Attempt to define the position of the glucose residue. K. Neelakantam and T. R. Seshadri (Proc. Indian Acad. Sci., 1937, **6**, A, 12—15).—Methylation (CH_2N_2) of gossypitrin and subsequent hydrolysis gives *gossypetin* (?) 3 : 8 : 3′ : 4′-

Me_4 ether, m.p. 227—230° after softening at 225° *Ac_2* derivative, m.p. 142—143° after softening at 135°), methylated (Me_2SO_4) to the Me_6 ether. The glucose residue is probably in position 7. F. R. G.

Mechanism of the reduction of aromatic *N*-glucosides to arylglucamines. P. KARRER and E. HERKENRATH (Helv. Chim. Acta, 1937, **20**, 1016—1019).—*N*-*p*-Toluidineglucoside tetra-acetate, from acetobromoglucose and *p*-$C_6H_4Me{\cdot}NH_2$ or by acetylation of *p*-toluidineglucoside, is reduced (Ni–H_2) as readily as the Ac-free compound. Under similar conditions *N*-methylanilineglucoside tetra-acetate and *theophylline*-d-*glucoside tetra-acetate* are unaffected. It appears therefore that in all cases reduction affects the Schiff's base which in solution is in equilibrium with the *N*-glucoside form. H. W.

Rapid volumetric determination of pentosans. I. K. CHRISTITSCH (Zavod. Lab., 1937, **6**, 558—561).—Furfuraldehyde (I) obtained from pentosans and boiling acid is determined by Bertrand's instead of by the usual phloroglucinol method. The Cu equiv. of (I) is almost identical with that of glucose. R. T.

Asparagose. S. MURAKAMI (Acta Phytochim., 1937, **10**, 43—62).—The tubers of *Asparagus officinalis* contain a non-reducing fructosan, *asparagose* (I), m.p. 215°, $[\alpha]_D^{20}$ −35·7°, mol. wt. 1160 (=7 fructose units) (*triacetate*, m.p. 125°, $[\alpha]_D^{20}$ −35·6° in $CHCl_3$, −42·6° in AcOH, mol. wt. 2211; *Me* derivative, m.p. 138—142°, $[\alpha]_D^{20}$ −50·4° in $CHCl_3$). (I) with NaOMe in MeOH gave a *product*, $[\alpha]_D^{20}$ −35·5°, mol. wt. 1280 (=8 fructose units). Under the same conditions, sucrose, (I), and inulin are hydrolysed by acid in 391, 558, and 840 min., the degree of hydrolysis with (I) being 87% and 94% as determined by reduction and polarimetric methods, respectively. The max. aldose val. was 1·6%. (I) in glycerol at 140° gave a product still having the same rotation, but the mol. wt. corresponded with that of a dihexosan. This re-associated on keeping. Similar depolymerisation occurs on heating in $HCO{\cdot}NH_2$ and in NH_2Ac. Hydrolysis of the Me derivative in $H_2C_2O_4$–HCl gave an oil, b.p. 110—120°, $[\alpha]_D^{20}$ +26·9°, containing 41% OMe (phenylosazone, m.p. 127—128°), which resembled in properties 3 : 4 : 6-trimethylfructose. P. W. C.

"Cremastramannan," the mannan of Japanese saleps. T. OHTSUKI (Acta Phytochim., 1937, **10**, 1—28).—The tubers of *Cremastra variabilis* contain but little starch and considerable amounts of *cremastramannan* (I) $[\alpha]_D^{22}$ −46·6°±6·6° in dil. NaOH, which on acid hydrolysis gives *d*-mannose and *d*-glucose (3 : 1). Treatment with pancreatin and diastase gives *cremastramannin*-A (II), $[\alpha]_D^{23}$ −46·6° in 0·02N-NaOH, and with takadiastase *cremastramannin*-B, $[\alpha]_D^{25}$ −40° in 0·02N-NaOH (III), both of which on acid hydrolysis give mannose and glucose (3 : 1). (I), (II), and (III) all give *acetates* in which each hexose mol. has 3 OAc groups, the m.p. being 269°, 245°, and 220°, respectively; all are optically inactive in $COMe_2$. The dissociation by heat is followed in terms of change of viscosity. (I) gives Cu and Pb complexes, the metal contents of which correspond with the requirements of the formulæ $(C_6H_{10}O_5)_8Cu$, $(C_6H_{10}O_5)_{12}Cu$, and $(C_6H_{10}O_5)_4Pb$. (I) after 15 and (II) and (III) after ten treatments with Me_2SO_4–NaOH give sol. *derivatives* of m.p. 240°, 242°, and 247° containing >40% OMe and having $[\alpha]_D^{18}$ −36·1°~−39·7°, −37·5°, and −42·2°, respectively. P. W. C.

Bletillamannan, a mannan from the tubers of *Bletilla striata*. T. OHTSUKI (Acta Phytochim., 1937, **10**, 1—28).—The tubers contain but little starch and considerable amounts of *bletillamannan* (I), $[\alpha]_D^{20}$ −40°±5·3° in 0·5% NaOH, which on acid hydrolysis gives *d*-mannose and *d*-glucose in the ratio 4 : 1. Treatment with pancreatin gives *bletillamannin*-A (II), $[\alpha]_D^{20}$ −44·4° in 0·5% NaOH, and with takadiastase *bletillamannin*-B (III), $[\alpha]_D^{20}$ −44·4° in 0·5% NaOH, both of which on acid hydrolysis give mannose and glucose (4 : 1). (I), (II), and (III) give *acetates*, m.p. 270°, 268°, and 258°, respectively, in which each hexose mol. has 3 OAc groups, and all have $[\alpha]_D^{20}$ −32° in $CHCl_3$. (I), (II), and (III) on treatment 10—13 times with Me_2SO_4–NaOH give sol. derivatives of m.p. 250° containing >40% of OMe and having $[\alpha]_D^{20}$ −58°, −50°, and −40° in $CHCl_3$, respectively. P. W. C.

Dextrins and the constitution of starch; phosphorus content of starch and dextrins. K. MYRBÄCK and K. AHLBORG (Svensk Kem. Tidskr., 1937, **49**, 216—230).—The constitution of starch is critically reviewed with especial reference to the production of dextrins by enzymic fission. Hydrolysis of starch with β-amylase, followed by fractional pptn. of the products with EtOH, yields dextrins with *M* 8000—80,000, whilst with maltase or ptyalin, dextrins with *M* 2500—1100 are obtained. The dextrins are considered to originate from portions of the starch mol. lying between "anomaly" points, which may be chain-branching points, or points where a phosphate group occurs. Determination of the P content of native starches and of sol. starches obtained therefrom by acid hydrolysis indicates that the P-containing portion of the mol. is most resistant to hydrolysis, and similarly, determination of P in the dextrins prepared by hydrolysis with takadiastase or β-amylase shows that the P-containing portion is almost completely resistant to hydrolysis to maltose by β-amylase. J. D. R.

Starch. IV. Hydrolysis of starch by 7·5 and 15% hydrochloric acid at low temperatures [20°]. V. Phosphoric acid content of potato-starch. A. TYCHOWSKI and S. MASIOR (Biochem. Z., 1937, **292**, 141—147, 218—220; cf. A., III, 312).—IV. Results for the formation of maltose, H_2O-sol. and -insol. fractions, changes in hydrolytic products of α- and α + β-amylase action, and ash and P_2O_5 contents are tabulated and discussed.

V. Starch paste heated under pressure in presence of $CaCO_3$ yields the Ca salt of amylophosphoric acid (I) which is more thermostable than the original (I), decomp. only at temp. >150°. The stability is not due to p_H but is sp. for the Ca salt. F. O. H.

Cellulose, starch, and glycogen. H. STAUDINGER (Naturwiss., 1937, **25**, 673—681).—A lecture.

Oxidation of cellulose in a heterogeneous medium. L. Brissaud (Mém. Poudres, 1937, **27**, 195—213).—Samples of cellulose (I) were oxidised with 0·1N-NaOCl to products containing 0·069, 0·077, 0·154, 0·235, and 0·312 atoms of O per mol. of $C_6H_{10}O_5$, respectively. Reducing power and methylene-blue absorption increase rapidly with degree of oxidation. This differentiates (I) degraded by hydrolysis, which have a lower methylene-blue val. than the original (I) and relatively low reduction nos. Nitration also differentiates oxidised and hydrolysed (I); the former seem to undergo nitration like (I), but partly decompose during stabilisation. The CO_2H content increases with degree of oxidation. By treating oxidised (I) with boiling H_2O and cold 2% aq. NaOH, respectively, products having similar properties to the original (I), or rather to (I) degraded by acids, were obtained. The extracts do not appear to be impurities, that have been fixed by adsorption, but seem to form parts of chains to which they are attached by main valencies. W. J. W.

Action of sodium hypoiodite on cellulose. L. Brissaud (Mém. Poudres, 1937, **27**, 214—229).—Prolongation of the hypoiodite treatment beyond ½ hr. does not affect the amount of I consumed, but if after ½ hr. treatment and separation of the wash waters the sample is again treated there is a further considerable consumption. This varies with the concn. of the reagents. Reducing groups are formed or appear during the treatment in addition to the development of acidity, which seems to imply the superimposing of two actions. One of these is caused by the oxidising agent and induces degradation and is analogous to the action of NaOCl. The other action causes changes on the surface of the micelles, which facilitate the passage of sol. products in the micelles. The intervention of surface effects and secondary oxidising reactions invalidates the I val. as an accurate measure of the mol. wt. of cellulose. W. J. W.

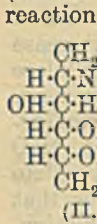
Highly polymerised compounds. CLXVIII. Determinations of the viscosity of cellulose nitrates. H. Staudinger and M. Sorkin (Ber., 1937, **70**, [*B*], 1993—2017).—Cellulose nitrates (I) are obtained by the action of HNO_3–H_2SO_4 on cellulose of varying degree of polymerisation. They can be preserved almost unchanged over P_2O_5 if the acid has been removed completely. For sol solutions the relationship $\eta_{sp.}/c_{gm.} = K_m M$ is shown to hold good by comparison of the mol. wt. determined osmometrically with that based on viscosimetric measurements in $COMe_2$ or BuOAc. For gel solutions, the expression $\log \eta_{sp.}/c_{gm.} = [\log \eta_{sp.}/c_{gm.}]_{c\to 0} + c.K_{st.}$ holds for (I) and the relationship between mol. wt. and increment const. is $M = (K_{st.} + 7)/K_{mst.}$ The dependence of viscosity on temp. has been investigated. The viscosity of (I) in BuOAc with increasing amounts of C_6H_6, in BuOAc + light petroleum, *cyclo*hexane, EtOH, $CHCl_3$, CCl_4, or PhCl, and in $COMe_2$–H_2O gives results dissimilar to those observed with the polystyrenes. The low viscosity of (I) in C_5H_5N is due to degradation. The departures of solutions of (I) from the Hagen–Poiseuille law are discussed. H. W.

***X*-Ray diffraction study of the action of liquid ammonia on cellulose and its derivatives.** G. L. Clark and E. A. Parker (J. Physical Chem., 1937, **41**, 777—786).—Fibres of native and mercerised cellulose, treated with liquid NH_3 at −75°, increase in diameter about threefold. Swollen NH_3-cellulose is reverted to cellulose by treatment with conc. aq. NH_3. Slow evaporation of NH_3 yields a new *modification*, cellulose III, which on boiling with H_2O reverts to cellulose, reversion being more complete for cellulose III derived from native than for that derived from mercerised cellulose. On acetylation, cellulose III gives the same acetate as native and mercerised cellulose. The actions of heat, dil. and conc. NH_3, and AcOH on cellulose III have also been examined. Commercial cellulose acetates are saponified by liquid NH_3 after several days. C. R. H.

Rotatory dispersion of configuratively related amines. P. A. Levene, A. Ruthen, and M. Kuna (J. Biol. Chem., 1937, **120**, 759—775).—The correlation of the configuration of primary and *sec.* amines is similar to that of primary and *sec.* alcohols and the direction of rotation of the former is identical with that of the corresponding alcohols. In all alkylamines the absorption regions nearest to the visible region are not anisotropic. The following new compounds have been prepared: d-β-*benzamidobutane*, m.p. 86—88°, $[\alpha]_D^{25}$ +6·7° in abs. EtOH; d-β-*benzamidooctane*, m.p. 73—74°, $[\alpha]_D^{25}$ +28·5° in abs. EtOH; d-*hexan*-β-*ol*, b.p. 99—100°/168 mm., $[\alpha]_D^{25}$ +10·7°, converted by anhyd. HI into l-β-*iodohexane*, b.p. 90—91°/70 mm., $[\alpha]_D^{25}$ −30·7°; this with NaN_3 in H_2O–MeOH at 80° gives d-β-*azidohexane*, b.p. 96—98°/160 mm., $[\alpha]_D^{25}$ +27·8°, hydrogenated (Adams) to l-β-*aminohexane*, b.p. 70°/155 mm., $[\alpha]_D^{27}$ +4·30° (*hydrochloride*, $[\alpha]_D^{25}$ −5·68° in abs. EtOH, transformed into d-β-*benzamidohexane*, m.p. 86—88°, $[\alpha]_D^{25}$ +14·3° in abs. EtOH); d-γ-*heptanol*, b.p. 104—106°/117 mm., $[\alpha]_D^{25}$ +5·12°, converted successively into l-γ-*iodoheptane*, b.p. 76°/12 mm., $[\alpha]_D^{25}$ −8·25°, d-γ-*azidoheptane*, b.p. 79—81°/43 mm., $[\alpha]_D^{28}$ +1·78°, and d-γ-*aminoheptane*, b.p. 75°/70 mm., $[\alpha]_D^{25}$ +4·15° (homogeneous), $[\alpha]_D^{25}$ +2·6° in abs. EtOH (*hydrochloride*, $[\alpha]_D^{25}$ +1·00° in 10% HCl; d-γ-*benzamidoheptane*, m.p. 66—68°, $[\alpha]_D^{25}$ +2·0° in abs. EtOH); d-γ-*nonanol*, b.p. 96—98°/19 mm., $[\alpha]_D^{25}$ +7·08°, converted successively into l-γ-*iodononane*, b.p. 99—100°/10 mm., $[\alpha]_D^{25}$ −14·2°, d-γ-*azidononane*, b.p. 105—107°/30 mm., $[\alpha]_{5780}^{25}$ +3·04°, d-γ-*aminononane*, b.p. 102°/50 mm., $[\alpha]_D^{27}$ +4·61° (homogeneous), $[\alpha]_D^{25}$ +3·7° in abs. EtOH (*hydrochloride*, $[\alpha]_D^{25}$ +1·5° in H_2O; d-γ-*benzamidononane*, m.p. 86°, $[\alpha]_D^{25}$ +12·5° in abs. EtOH); l-δ-*octanol*, b.p. 79—80°/17 mm., $[\alpha]_D^{28}$ +0·64°, giving successively l-δ-*iodo-octane*, b.p. 97°/22 mm., $[\alpha]_D^{25}$ −1·76°, l-δ-*azido-octane*, b.p. 92—93°/35 mm., $[\alpha]_D^{25}$ −0·82°, l-δ-*amino-octane*, b.p. 92—93°/80 mm., $[\alpha]_D^{27}$ +0·45° (*hydrochloride*, $[\alpha]_D^{25}$ −0·50° in 10% HCl; d-δ-*benzamido-octane*, m.p. 99—100° $[\alpha]_D^{25}$ +1·30° in abs. EtOH). The rotatory dispersions of configuratively related primary and *sec.* amines in the homogeneous state and their corresponding hydrochlorides in H_2O are recorded. H. W.

A catalytically induced reaction [of glucosamine] resembling the Cannizzaro reaction.

P. A. Levene and C. C. Christman (J. Biol. Chem., 1937, **120**, 575—590).—Glucosamine (I) with H_2 (Adams' Pt) is converted, by a pseudo-Cannizzaro reaction, half into *aminosorbitol* (II) [*Ac*$_6$ derivative, m.p. 99—100°, b.p. 160—180°/0·3 mm., $[\alpha]_D^{25}$ +21·0° in $CHCl_3$, converted by $Ba(OMe)_2$–MeOH into N-*acetyl*-β-*aminosorbitol* (IV), m.p. 152—153°, $[\alpha]_D^{25}$ −10·4° in H_2O], and half into *glucosaminic acid* (III) [as (II) but with CO_2H for upper $CH_2{\cdot}OH$], $[\alpha]_D^{26}$ −13·4° in 20% HCl, which is determined by titration. Slightly increased yields of (II) are obtained under high pressure of H_2, and of (III) under atm. pressure. The reaction is unimol. until 70—80% completed. In absence of H_2 or of Pt there is no reaction. The hydrochloride of (I) with H_2–Pt gives only *aminosorbitol*, m.p. 157—158°, $[\alpha]_D^{26}$ −2·4° in 20% HCl, whilst *N*-acetylglucosamine gives (IV). In H_2, reduced Adams' Pt converts (I) into (II) and (III), but under reduced pressure of H_2, especially in presence of NaOH, there is almost quant. formation of (III). The mechanism of the reaction is discussed.



(II.)

E. W. W.

Formation and breakdown of amino-acids by intermolecular transfer of the amino-group. A. E. Braunstein and M. G. Kritzmann (Nature, 1937, **140**, 503—504).—The reaction between glutamic acid (I) and $AcCO_2H$ (II) is reversible, since these acids are rapidly formed by muscle tissue from alanine and α-ketoglutaric acid (III), and equilibrium mixtures of similar composition are obtained in both the direct and the reversed reaction. The enzyme system responsible is present in muscle, heart, brain, liver, and kidney. α-Keto-acids other than (II) can serve as acceptors for the NH_2 of (I), but, on the other hand, all α-NH_2-acids give up their NH_2 to (III) in presence of muscle tissue; the formation of (I) with 16 different natural and racemic NH_2-acids, including such as glycine or histidine, has been established. No transfer of NH_2 occurs unless either the NH_2- or the keto-acid is dicarboxylic. L. S. T.

Oxidative deamination of amino-acids. B. C. Kar (J. Indian Chem. Soc., 1937, **14**, 381—387).—NH_2-acids (glycine, leucine, alanine) are oxidised to aldehyde, CO_2, and NH_3 by phenols in the presence of H_2O_2 and Na_2WO_4 or H_2WO_4 sol, or by quinones alone (*o*- or *p*-). Since phenols are oxidised by H_2O_2 + catalyst, the deamination must be due to quinones. Resorcinol deaminates better with H_2O_2 alone. The rate of deamination is measured by the decrease in NH_2-N (Van Slyke). A. Li.

Non-labile deuterium of amino-acids treated in dilute deuterium oxide media. J. A. Stekol and W. H. Hamill (J. Biol. Chem., 1937, **120**, 531—536).—Treatment of *l*-cystine, arginine, histidine, and lysine with hot aq. D_2O–HCl yields products containing D in positions other than the NH_2, NH, or CO_2H groups. Tryptic digestion of caseinogen in aq. H_2O yields tyrosine containing D in positions other than the OH, NH_2, or CO_2H groups. The use of D in the study of NH_2-acid metabolism is discussed. F. O. H.

Amino-acids of the yellow enzyme. R. Kuhn and P. Desnuelle (Ber., 1937, **70**, [*B*], 1907—1926).—Colorimetric determinations establish the presence of the following NH_2-acids in the yellow enzyme (% in parentheses): arginine (I) (8·2), histidine (II) (2·75), lysine (III) (13·7), hydroxyproline (~0·0), tyrosine (7·75), phenylalanine (5·75), tryptophan (4·86), cystine (IV) (0·34), and glutamic acid (V) (7·1). As far as the method is valid, therefore, there is no fundamental difference in nature or amount between the identified NH_2-acids and other known proteins. Only (V) has been obtained in substance (as hydrochloride). The % S in the enzyme is about thrice that required by the amount of (IV) which is present, so that other NH_2-acids containing S must be expected. In all, account is rendered of 65% of the total N. The bases are of peculiar interest since lactoflavin-5-phosphoric acid is united to basic groups of the protein component in at least two positions, the PO_4 residue and NH at position 3. The sum of (I), (II), and (III) is very similar to that of the best known chromoprotein, hæmoglobin, but the distribution is widely different. The protein of the yellow enzyme is poor in (II) but rich in (III) whereas the globin contains much (II) and little (III). H. W.

Dipeptides of β-amino-acids. E. Dyer and E. Ballard (J. Amer. Chem. Soc., 1937, **59**, 1697—1699).—$CH_2Cl{\cdot}CH_2{\cdot}COCl$ and the appropriate NH_2-acid give N-β-*chloropropionyl-glycine*, m.p. 133—135° (*Et* ester, m.p. 71—72·5°; *amide*, m.p. 174—175°), -β-*phenyl*-α-*alanine*, m.p. 123—125°, and -β-*phenyl*-β-*alanine*, m.p. 71—72·5°. $CHPhBr{\cdot}CH_2{\cdot}CO_2H$ and glycine give mainly cinnamoylglycine. None of these products give dipeptides with NH_3. *Carbobenzyloxy*-β-*alanyl-glycine*, m.p. 145—146°, -β-*phenyl*-α-*alanine*, m.p. 144·5—145°, and -β-*phenyl*-β-*alanine*, m.p. 151·5—153°, with H_2 and colloidal Pd give β-*alanyl-glycine*, m.p. 230° (decomp.) (*hydrochloride*), -β-*phenyl*-α-*alanine*, m.p. 264—265° (decomp.) (*hydrochloride*, m.p. 205·5—207°), and -β-*phenyl*-β-*alanine*, m.p. 235—236° (decomp.) (*hydrochloride*, m.p. 180—182°), which are unchanged by HCO_2H. M.p. are corr. R. S. C.

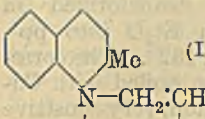
Biuret reaction of sarcosyldiglycine and glycylsarcosyldiglycine. J. Feldman (J. Amer. Chem. Soc., 1937, **59**, 1657—1659).—Rising's theory of the biuret reaction is confirmed. Sarcosine anhydride gives no Cu complex. *Sarcosyldiglycine* (from chloroacetyldiglycine and NH_2Me), $+H_2O$, m.p. 237—239°, with $Cu(OH)_2$ and NaOH in absence of CO_2 gives the *complex*, $Na_4CuC_{14}H_{20}O_8N_6$. Hydrogenation of carbobenzoxyglycylsarcosyldiglycine gives *glycylsarcosyldiglycine*, a syrup, which affords the *complex*, $NaCuC_9H_{13}O_5N_4$. R. S. C.

Protective colloids "protalbinic" and "lysalbinic" acids. S. Inoue (J. Soc. Chem. Ind. Japan, 1937, **40**, 268B).—Increase in [NaOH] gives acids having a decreasing N content and the Na salts have an increasing Au no. and decreasing γ which lowers the protective action (cf. Bechhold, A., 1904, ii, 650). F. R. G.

Derivatives of aminohydroxypropanesulphonic acid. Biuret reaction. S. Tsunoo (J. Biochem. Japan, 1937, **25**, 375—391; cf. A., 1935, 1111).—

The following were prepared: γ-o-, m.p. 235°, -m-, m.p. 195°, and -p-*toluidino*-, m.p. 247°, -m-*xylidino*-, m.p. 213° (decomp.), -(2-*methylquinolyl*)- (I), -(α-*naphthylamino*)-, m.p., 165—170°, -*ethylamino*-, -*diethylamino*-, -*propylamino*-, -*allylamino*-, -*butylamino*-, -*guanido*-, m.p. 225°, -(2-*naphthalenesulphonylmethylamino*)-, m.p. >280°, -(*p*-toluenesulphonamido)- (as *Na* salt, decomp. 260°), and -(*p*-toluenesulphonylmethylamino)-β-hydroxypropanesulphonic acid (as *Na* salt, m.p. >280°). γ-Chloro-β-hydroxypropanesulphonic acid, resolved by means of the *brucine*, m.p. 232°, and *strychnine* salts, yielded the l- (*strychnine* salt, m.p. 104—105°) and d-*isomeride* (*strychnine* salt, m.p. 85°), the following respective *d*- and *l*-derivatives being subsequently prepared: γ-*amino*-, m.p. 265°, 265°, $[\alpha]_D^{13}$ +9·13°, $[\alpha]_D^{19}$ −9·67°; -*methylamino*-, m.p. 223°, 225° (decomp.), $[\alpha]_D^{19}$ +19·86°, $[\alpha]_D^{12}$ −17·25°; -*dimethylamino*-, m.p. 251°, 243° (decomp.), $[\alpha]_D^{16}$ +31·96°, $[\alpha]_D^{30}$ −29·49°; -(n-*butylamino*)-, $[\alpha]_D^{19}$ +22·34°, $[\alpha]_D^{30}$ −23·08°; -*trimethylamino*-, m.p. >295°, 285° (decomp.), $[\alpha]_D^{13}$ +28·54°, $[\alpha]_D^{23}$ −26·63°; also the *strychnine* salt, m.p. 125°, of γ-benzamido-β-hydroxypropanesulphonic acid. All rotations are in H_2O; all m.p. uncorr. γ-Amino-β-hydroxypropanesulphonic acid, fed to rabbits, is excreted unchanged. The response of the above compounds to the ninhydrin (II) and biuret (III) reactions indicates that the group ·CH(OH)·CH_2·NRR′ gives both reactions when R = H and R′ = alkyl, (III) but not (II) when both R and R′ = alkyl, and neither reaction on betaine formation. With R or R′ = aryl or with SO_2·NH_2 neither reaction is given but substitution of ·NH·C(:NH)·NH_2 for NH_2 does not inhibit (III).

F. O. H.



(I.)

Ferroaminopentacyanides.—See A., I, 528.

Preparation of azomethane. F. P. Jahn (J. Amer. Chem. Soc., 1937, **59**, 1761—1762).—Me_2N_2 is best obtained from NMe_2·NH_2,2HCl by conversion by $CuCl_2$ into Me_2N_2,Cu_2Cl_2, which is dried in vac. and heated. Me_2N_2 and Hg vapour do not explode. Explosions are caused by distilling a high-boiling oil, which is formed by oxidising old samples of the hydrazine. R. S. C.

Improved preparations of aliphatic diazo-compounds and certain of their properties. D. W. Adamson and J. Kenner (J.C.S., 1937, 1551—1556).—An improved prep. of Me nitroso-β-methylamino*iso*butyl ketone (cf. A., 1933, 398; 1935, 479) is described. Interaction of pulegone and the appropriate primary amine in H_2O, followed by nitrosation, yield the following: 5-*methyl*-2-*nitroso*-α-*methyl*-, m.p. 116·5°, -*ethyl*-, m.p. 108·5°, -n-*propyl*-, m.p. 125·5°, -n-*butyl*-, m.p. 89°, -n-*amyl*-, m.p. 88·5°, -n-*heptyl*-, m.p. 70°, and -*allyl*-iso*propyl*cyclo*hexanone*, m.p. 108°. From CH_2N_2 to $CHPrN_2$, aliphatic diazo-compounds are prepared from the appropriate Me nitroso-β-alkylamino*iso*butyl ketone in PhOMe by treatment with NaO·CH_2Ph or Na *cyclo*hexoxide under reduced pressure. Homologues higher than $CHPrN_2$ are similarly prepared using the NO-ketones prepared from pulegone. The following b.p. are recorded: $CHMeN_2$, −19° to −17°/89·5 mm., $CHEtN_2$ −8° to −7·5°/41·5 mm., $CHPr^{\alpha}N_2$, −3·5° to −5·5°/26 mm., $CHPr^{\beta}N_2$, 1° to −1°/32 mm., and the absorption spectra of these and CH_2N_2 from 2500 to 5500 A. are measured in *cyclo*hexanol. The reactivities of $CHMeN_2$, $CHEtN_2$, and CH_2N_2 are compared by measurement of N_2 evolution when treated with PhOH, and found to be (II) > (I) > (III). CMe_2:CHAc with (III) in Et_2O yields 5-*acetyl*-4 : 4-*dimethylpyrazoline*, b.p. 110°/18 mm., m.p. 51·5—52·5°, and with (I), 5-*acetyl*-3 : 4 : 4-*trimethylpyrazoline*, m.p. 76·3°, which when heated with Cu gives 2 : 2 : 3-trimethyl*cyclo*propyl Me ketone (*semicarbazone*, m.p. 139—140°). J. D. R.

Phosphine and arsine derivatives of the group I(*b*) metals: volatile derivatives of gold. F. G. Mann and A. F. Wells (Nature, 1937, **140**, 502).—The trialkyl-phosphine and -arsine derivatives of AgI, like those of CuI, have the fourfold mol. $[R_3P(As)\rightarrow AgI]_4$. The Ag compounds have the same constitution as the Cu^+ compounds, since $[AsPr^{\alpha}_3\rightarrow AgI]_4$ is strictly isomorphous with $[AsEt_3\rightarrow CuI]_4$, the effect of replacing Cu by Ag being compensated by that of Et by Pr^{α}; both the 4-covalent Cu^+ and Ag^+ atoms have a tetrahedral configuration. The aurous compounds, $[R_3P(As)\rightarrow AuX]$, where X is Cl, I, or CNS, are unimol., and the Au shows a true co-ordination no. of 2. The compounds $[PR_3\rightarrow AuX]$, where X is Cl or I, are very stable and can be freely distilled under reduced pressure. $[PBu^{\alpha}_3\rightarrow AuCl]$ can be volatilised even at 1 atm., and deposits a film of Au when the vapour is passed through a heated tube. L. S. T.

Mechanism of the reaction between sulphuric acid and mono- and di-methylarsinic acids. G. Petit (Compt. rend., 1937, **205**, 322—325).—$AsMeO(OH)_2$ (I) with H_2SO_4 at 315° in a sealed tube rapidly affords As_2O_3 and SO_2. At 250°, the reaction is much slower. In each case, the amount of SO_2 liberated is < that expected from the stoicheiometric equation and is explained on the basis of two consecutive reactions: (*a*) scission of (I) to give MeOH and $As(OH)_3$ (which is also accomplished by H_3PO_4) and (*b*) oxidation of MeOH by H_2SO_4. $AsMe_2$·O_2H with H_2SO_4 in a sealed tube at 315° rapidly affords As_2O_3 and SO_2 in the proportions demanded by the stoicheiometric equation. At lower temp., the reaction mechanism resembles that for (I). J. L. D.

Organo-magnesium compounds as reducing agents. M. Mousseron and R. Granger (Compt. rend., 1937, **204**, 986—989).—The organo-magnesium derivative (I) of *cyclo*hexylcarboxylic acid (1 part) with C_6H_{11}·MgBr (2 parts) in Et_2O in an atm. of N_2 at 0° affords *cyclo*hexene (II), *cyclo*hexanol (III), *cyclo*hexylcarbinol, di*cyclo*hexyl-methane (IV) and -carbinol, and di*cyclo*hexyl. Two types of reaction are utilised to explain the formation of these products. The reaction is of fairly general application and is applied to straight-chain analogues of (I). *cyclo*-Hexylcarboxyl chloride or Et *cyclo*hexylcarboxylate with C_6H_{11}·MgBr similarly affords di*cyclo*hexyl ketone, (II), (III), and (IV). Aromatic aldehydes and alicyclic ketones react similarly. J. L. D.

Preparation of stannic alkyl iodides and their action on aromatic amines. T. KARANTASSIS and C. VASSILIADÈS (Compt. rend., 1937, **205**, 460—462; cf. A., 1897, 918).—Prolonged interaction of Sn (2 parts) with alkyl iodides (4 parts) in a sealed tube at 130—180° affords Sn^{IV} dialkyl iodides. The following are prepared: *Sn* Me_2, m.p. 30°, *Et*$_2$, m.p. 42—42·5°, *Pr*^{2}, b.p. 166—167°/10 mm. (slight decomp.), *Bu*$^\beta_2$, b.p. 290—295°, and *di*-iso*amyl iodide*, b.p. 202—205°/8 mm. The Me_2 and Et_2 derivatives are stable at 180°, but the others decompose extensively to give, for example, SnI_2, C_3H_8, and propylene from $SnPr_2I_2$. The above iodides (1 mol.) form additive compounds with aromatic bases (2 mols.) in EtOH. The following are prepared: *Sn*Me_2I_2 + 2C_5H_5N, m.p. 151—152°; + 2NH_2Ph, m.p. 109—110°; + 2o-$C_6H_4Me{\cdot}NH_2$, m.p. 69—70°; + *picoline*, liquefies in air; + 2*NPhEt*$_2$, m.p. 88—89°; + 2*quinaldine*, m.p. 110—111°; *SnEt*$_2I_2$ + 2C_5H_5N, m.p. 115—116°; *SnPr*$_2I_2$ + 2C_5H_5N, m.p. 64—65°; + 2$NHPh_2$; + 2*NPhEt*$_2$, m.p. 63—64°; + 2*quinaldine*, m.p. 71—72°; and *SnBu*$^\beta_2I_2$ + 2*NPhEt*$_2$.

J. L. D.

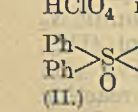
Theory of unsaturated and aromatic compounds. E. HÜCKEL (Z. Elektrochem., 1937, **43**, 752—788).—A summary. J. W. S.

Combustion of aromatic and alicyclic hydrocarbons.—See A., I, 522.

Bromination of bromo-, chloro-, and fluorobenzene in the gas phase. Effect of temperature and catalyst on the substitution type. M. VAN LOON and J. P. WIBAUT (Rec. trav. chim., 1937, **56**, 815—838).—The bromination of gaseous PhBr, PhCl, and PhF is investigated in an automatically functioning apparatus. In the presence of C the reaction changes at 400—450° from *o*–*p* to mainly *m* in all cases, a change which is inexplicable on any known theory of substitution. In the presence of $FeBr_3$ on C the reaction is of the *o*–*p* type from 200° to 500°, although the proportions of isomerides formed change considerably; these changes agree excellently for PhBr with Scheffer's equations and are determined by differences in the energies of activation which appear to be const. from 200° to 500°; differences in the entropies of activation are negligible. Mixed m.p. curves are given for *o*–*m*-C_6H_4ClBr, *p*–*o*- and *p*–*m*-C_6H_4BrF. R. S. C.

Thermal polymerisation of styrene.—See A., I, 523.

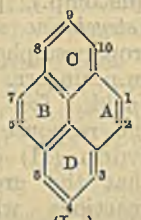
β-Phenyl sulphide. IV. O. HINSBERG (Ber., 1937, **70**, [*B*], 2027—2028; cf. this vol., 288).—β-Diphenyl sulphone (I) is converted by boiling 70% $HClO_4$ into β-*diphenyl sulphone oxide* (II), m.p. 120—122° or (+1H_2O) m.p. 82° (with a *compound*, m.p. 150°). (II) cannot be acetylated and is unchanged by Zn filings and boiling 20% HCl. (I) retains 0·5H_2O very obstinately. H. W.

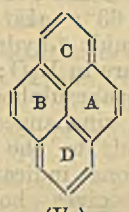

(II.)

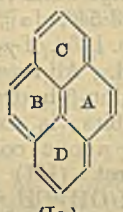
Synthesis of diradicals. *pp'*-Triphenylenediphenylmethyl. E. MÜLLER and G. SOK (Ber., 1937, **70**, [*B*], 1990—1992; cf. A., 1936, 1370).—*cyclo*Hexane-1 : 4-dione and LiPh in Et_2O give 1 : 4-*diphenylcyclohexane*-1 : 4-*diol*, m.p. 225°, dehydrated and aromatised by Se at 200° to *p*-$C_6H_4Ph_2$ (I), m.p. 210°, in 70—80% yield. BzCl, $AlCl_3$, and (I) afford *pp'-dibenzoylterphenyl*, m.p. 294° transformed in decahydronaphthalene by LiPh in Et_2O into *pp'-tetraphenylterphenylene*-*pp'-diol*, m.p. 162°. The corresponding *dichloride*, m.p. 236°, when boiled with Cu-bronze in C_6H_6 gives a dark red solution, very sensitive to air. It doubtless contains the diradical. H. W.

Molecular constitution of naphthalene. G. B. BONINO (Gazzetta, 1937, **67**, 343—346).—A reply to Oddo on a question of priority (cf. this vol., 373). E. W. W.

Pyrene and its derivatives. H. VOLLMANN, H. BECKER, M. CORELL, and H. STREECK [with, in part, G. LANGBEIN] (Annalen, 1937, **531**, 1—159).—Monosubstitution of pyrene (I) occurs very readily and without exception in position 3. Similarly mixtures of 3 : 8- and 3 : 10-di-derivatives are invariably produced by the ready, direct disubstitution. 3 : 5 : 8-Derivatives and 3 : 5 : 8 : 10-compounds are formed by direct tri- and tetra-substitution. Higher substitution causes entry into the 1 : 2 : 6 : 7 and finally in the 4 : 9 positions. The behaviour of (I) towards


(Ia.)


(Ib.)

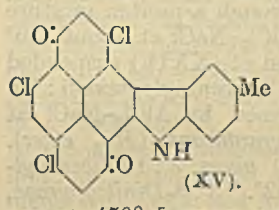

(Ic.)

substituents causes it to be regarded mainly as a Ph_2 derivative the *o*-positions of which are bridged by two ·CH:CH· residues; the mobility of H at 3, 5, 8, and 10 is attributed to the action of these residues on the typically benzenoid rings C and D. The behaviour of (I) is expressed by the formula (I*a*) or (I*b*) but the older formulation (I*c*) is less satisfactory since it contains a *p*-quinoid nucleus A whereas (I) is colourless when pure. The assumption of an alternation of the linkings according to all these schemes accounts for the predominance of 3 : 10- over 3 : 8-di-derivatives in all cases of di-substitution.

Crude pyrene-3 : 8-quinone, obtained by oxidation of (I) with H_2SO_4 and $K_2Cr_2O_7$, is purified with difficulty by successive crystallisations from AcOH, PhCl, and $PhNO_2$ respectively. The pure substance is best obtained through 3 : 8-dihydroxypyrene or by catalytic dehalogenation of 2 : 5 : 7 : 10-tetrachloropyrene-3 : 8-quinone; the former method gives opportunity of isolating pyrene-3 : 10-quinone through 3 : 10-*diacetoxypyrene*, m.p. 190°. SO_2Cl_2 and (I) in CCl_4 yield 3-*chloropyrene*, m.p. 119°, whilst 3 : 5 : 8 : 10-*tetrachloropyrene* (II), m.p. 368°, is obtained from (I) and Cl_2 in CCl_4 at 60° or by treatment of 3 : 5 : 8 : 10-tetranitropyrene with PCl_5. Br and (I) in $PhNO_2$ at room temp. and then at 120—130° give 3 : 5 : 8 : 10-*tetrabromopyrene* (III), m.p. 402°. With oleum at 85° (II) gives 5 : 10-*dichloropyrene*-3 : 8-*quinone*, m.p. 278° (decomp.), obtained also by dehalogenation of 2 : 5 : 7 : 10-tetrachloropyrene-3 : 8-quinone.

3 : 5 : 8 : 10-*Tetraketo*-3 : 4 : 5 : 8 : 9 : 10-*hexahydropyrene* (naphthalene-1 : 8 : 4 : 5-di-indandione) (IV) is

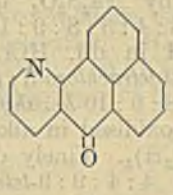
obtained by treating (II) with oleum at 80°, diluting the solution with H_2SO_4, and raising the temp. to 200° or by the action of Zn dust and NaOH on 4 : 9-*dibromo*-3 : 5 : 8 : 10-*tetraketo*-3 : 4 : 5 : 8 : 9 : 10-*hexahydropyrene* (V) [derived from (III) and conc. H_2SO_4 at 140—150°, reduced and then oxidised to 4 : 9-*dibromo*-3 : 5 : 8 : 10-*tetraketopyrene*, and converted by Ac_2O containing a trace of H_2SO_4 into 4 : 9-*dibromo*-3 : 8-*diacetoxypyrene*-5 : 10-*quinone*, m.p. 270° (decomp.)]. With boiling BzCl–$NPhMe_2$ (IV) gives 3 : 5 : 8 : 10-*tetrabenzoyloxypyrene*, m.p. 340° (decomp.), hydrolysed to 3 : 5 : 8 : 10-*tetrahydroxypyrene*. Analogously (V) gives 4 : 9-*dibromo*-3 : 5 : 8 : 10-*tetrabenzoyloxypyrene*, m.p. >370° (decomp.). (IV) in 2% NaOH is converted by $NaNO_2$ and 6% H_2SO_4 into 4 : 9-*dinitroso*-3 : 5 : 8 : 10-*tetraketohexahydropyrene* (VI), violent decomp. >200°. 4 : 9-*Dinitro*-3 : 5 : 8 : 10-*tetraketo*-3 : 4 : 5 : 8 : 9 : 10-*hexahydropyrene* is obtained from (IV) and HNO_3 (*d* 1·4) or from (VI); its *Na* salt is reduced by $Na_2S_2O_4$ to 4 : 9-*diamino*-3 : 5 : 8 : 10-*tetraketo*-3 : 4 : 5 : 8 : 9 : 10-*hexahydropyrene*. (IV) suspended in dil. HCl is converted by Cl_2 into 4 : 4 : 9 : 9-*tetrachloro*-3 : 5 : 8 : 10-*tetraketo*-3 : 4 : 5 : 8 : 9 : 10-*hexahydropyrene*, decomp. >340°, which is oxidised in alkaline solution to 1 : 4 : 5 : 8-$C_{10}H_4(CO_2H)_4$. Finely divided (V) and Br at 50—70° give 4 : 4 : 9 : 9-*tetrabromo*-3 : 5 : 8 : 10-*tetraketo*-3 : 4 : 5 : 8 : 9 : 10-*hexahydropyrene*, decomp. >250°, which gives $CHBr_3$ when treated with alkali. Prolonged chlorination of (I) in $C_6H_3Cl_3$ yields 1 : 2 : 3 : 5 : 6 : 7 : 8 : 10-*octachloro*-1 : 2 : 6 : 7-*tetrahydropyrene* (VII), m.p. about 292° with evolution of HCl when rapidly heated and m.p. about 375° after re-solidification; it passes when heated at 400° into *hexachloropyrene* (VIII), m.p. 383° after softening at 360—370°, also obtained by use of KOH–EtOH. Treatment of (VIII) with oleum yields 2 : 6-, m.p. 390°, and 2 : 7-, m.p. 296°, *-dichloronaphthalene-tetracarboxylic dianhydride*; the last-named is also obtained from 3 : 8-dichloroacenaphthene-5 : 6-dicarboxylic acid, the *anhydride*, m.p. 289° after darkening at 275°, of which is described. The mother-liquors from the prep. of (VII) contain 1 : 2 : 3 : 5 : 6 : 7 : 8 : 10-*octachloropyrene* (IX), m.p. 238°. Treatment of (VIII) with Cl_2 and I in $ClSO_3H$ gives *perchlorohydropyrene*, decomp. about 260°, and *decachloropyrene* (X), m.p. 264°, converted by 20% oleum at 110° followed by H_2SO_4 and HNO_3 at 180° into 2 : 3 : 6 : 7-*tetrachloronaphthalenetetracarboxylic dianhydride*, m.p. >400° after darkening at 350°. Oxidation of (VIII) with HNO_3 (*d* 1·5) at ≯5° yields 2 : 5 : 7 : 10-*tetrachloropyrene*-3 : 8-*quinone*, m.p. 320—325° after darkening at 310°. Similar treatment of (IX) affords 1 : 2 : 5 : 6 : 7 : 10-*hexachloropyrene*-3 : 8-*quinone*, m.p. 274°, whilst (X) yields 1 : 2 : 4 : 5 : 6 : 7 : 9 : 10-*octachloropyrene*-3 : 8-*quinone*, m.p. 304°. 4 : 5 : 9 : 10-*Tetrachloro*-4 : 5 : 9 : 10-*tetrahydropyrene*-3 : 8-*quinone*, from the 3 : 8-quinone and Cl_2 in $C_6H_3Cl_3$ at 100°, passes when distilled with steam into 4 : 9-*dichloropyrene*-3 : 8-*quinone* (XI), m.p. >500° after darkening at 330°. 5-*Chloropyrene*-3 : 8-*quinone*, m.p. 248°, obtained by use of SO_2Cl_2 in $PhNO_2$ at 100°, and 4 : 5 : 9 : 10-*tetrachloropyrene*-3 : 8-*quinone*, m.p. 377°, prep. by chlorination in $C_6H_3Cl_3$ at 150—170°, are described. Chlorination of 3 : 8-dimethoxypyrene (XII) with SO_2Cl_2 in $C_6H_3Cl_3$ containing $CaCO_3$ at 150° yields 5 : 10-*dichloro*-3 : 8-*dimethoxypyrene*, m.p. 279°, also obtained by the action of Me_2SO_4 and NaOH on 5 : 10-*dichloro*-3 : 8-*dihydroxypyrene*, decomp. >350°, prep. by reducing the corresponding quinone with $NHPh{\cdot}NH_2$ in $C_6H_3Cl_3$. Treatment of (XII) in PhCl with SO_2Cl_2 and dioxan gives 5-*chloro*-3 : 8-*dimethoxypyrene*, m.p. 315°. Reduction of (XI) in $C_6H_3Cl_3$ by $NHPh{\cdot}NH_2$ at 130—140° gives 4 : 9-*dichloro*-3 : 8-*dihydroxypyrene*, m.p. 274°, whence 4 : 9-*dichloro*-3 : 8-*dimethoxypyrene*, m.p. 256°. 5-*Nitropyrene*-3 : 8-*quinone* has m.p. 335° (decomp.). (XII) and HNO_3 (*d* 1·4) in boiling AcOH afford 5 : 10-*dinitro*-3 : 8-*dimethoxypyrene* (XIII), m.p. 357° (decomp.), whilst addition of $NaNO_2$ to (XII) in boiling PhCl containing AcOH yields 5-*nitro*-3 : 8-*dimethoxypyrene*, m.p. 237°, catalytically reduced to 5-*amino*-3 : 8-*dimethoxypyrene*, m.p. 255°, and oxidised by HNO_3 to (XIII). The tetrachloroquinone is converted by NH_2Ph at 50°, by cryst. NaOAc and NH_2Ph at 130—140°, and by boiling NH_2Ph containing Cu powder into 3 : 6 : 8-*trichloro*-1-*anilinopyrene*-5 : 10-*quinone*, m.p. 269—270°, 3 : 8-*dichloro*-1 : 6-*dianilinopyrene*-5 : 10-*quinone* (XIV), m.p. 335°, and 1 : 3 : 6 : 8-*tetra-anilinopyrene*-5 : 10-*quinone*, m.p. 390—395°, respectively, and by anhyd. KOAc in boiling $PhNO_2$ followed by boiling dil. AcOH into 3 : 6 : 8-*trichloro*-1-*hydroxypyrene*-5 : 10-*quinone*, m.p. 322° (decomp.) (*Na* salt), by NH_3 at 120° into 3 : 6 : 8-*trichloro*-1-*aminopyrene*-5 : 10-*quinone*, m.p. >350° (decomp.) (*Bz* derivative, m.p. 323°), and by *p*-$C_6H_4Me{\cdot}NH_2$ and NaOAc in boiling PhCl into 3 : 6 : 8-*trichloro*-1-*p*-*toluidinopyrene*-5 : 10-*quinone*, m.p. 297° [whence the *carbazole derivative* (XV)]; (XIV) yields the analogous *dicarbazole* compound, m.p. 338°. 2 : 6-$C_{10}H_6(OBz)_2$ with NaCl–$AlCl_3$ at 155—200° gives 1 : 6-*dihydroxy*-3 : 4 : 8 : 9-*dibenzpyrene*-5 : 10-*quinone* (XVI), m.p. >450° [corresponding *Me*$_2$ derivative (XVII), m.p. 360° (decomp.)]. (XVI) with PCl_5 in boiling PhCl yields a *keto-chloride*, hydrolysed by conc. H_2SO_4 at 100° to 1 : 6-*dichloro*-3 : 4 : 8 : 9-*dibenzpyrene*-5 : 10-*quinone*, m.p. >400°, or, under other conditions, into 1 : 5 : 6 : 10-*tetrachloro*-3 : 4 : 8 : 9-*dibenzpyrene*, m.p. about 336° after softening at 300°. (XVI) or (XVII) with boiling *p*-$C_6H_4Me{\cdot}NH_2$ affords 1 : 6-*di*-*p*-*toluidino*-3 : 4 : 8 : 9-*dibenzpyrene*-5 : 10-*quinone*, m.p. 379—380°. 2 : 6-*Dichloro*-, m.p. 400°, and 2 : 6-*dianilino*-, m.p. 400°, *-naphthalene*-1 : 4 : 5 : 8-*tetracarboxydiphenylimide* are described.



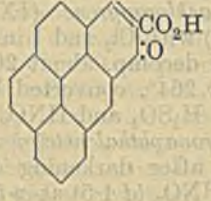
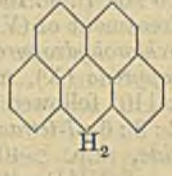
(XV).

$ClSO_3H$ and (I) in CCl_4 at 0—5° yield *pyrene*-3-*sulphonic acid* [*Na* salt (XVIII), converted by PCl_5 in $POCl_3$ into the corresponding *chloride*, m.p. 120° (decomp.)]. 3-*Hydroxypyrene*, m.p. 179° (*Ac* derivative, m.p. 102°; *Me ether*, m.p. 93°), from (XVIII) and NaOH at 270—290°, does not couple with diazotised aromatic amines. 3-*Nitropyrene* (XIX), m.p. 153—154°, is obtained from (I) and HNO_3 (*d* 1·4) in AcOH at 50°. Successive addition of $POCl_3$ and (I) to formylmethylaniline in *o*-$C_6H_4Cl_2$ leads to *pyrene*-3-*aldehyde*, m.p. 126° (*phenylhydrazone*, m.p. 201—202°). 3-*Acetylpyrene* (XX), m.p. 90°, is

obtained from (I) and $ZnCl_2$ in AcOH–Ac_2O at 80°. 3-Benzoylpyrene (XXI) gives an *oxime*, m.p. 220°, isomerised by PCl_5 in C_6H_6 to *pyrene-3-carboxyanilide*, m.p. 255°. Reduction of (XIX) by NaSH in EtOH–H_2O yields 3-*aminopyrene*, m.p. 117—118° (*Ac* derivative, m.p. 260°). 3-Chloropyrene is transformed by CuCN at 300—340° into 3-*cyanopyrene*, m.p. 153°, hydrolysed by aq. NaOH at 180° to *pyrene-3-carboxylic acid*, m.p. 274° (corresponding *chloride*, m.p. 152°, and *anilide*, m.p. 255°), also obtained by oxidising (XX) in boiling C_5H_5N by aq. NaOCl. (XXI) with $AlCl_3$–NaCl at 160—165° gives 2 : 3(CO)-*benzoylenepyrene*, m.p. 242°; this with molten KOH at 170—245° gives 1-*phenylpyrene-o-carboxylic acid*, m.p. 218°, converted by dry distillation of the *Ba* salt into 1-*phenylpyrene*, m.p. 169°. $CH_2Cl{\cdot}CO_2H$ and (I) in *o*-$C_6H_4Cl_2$ at 180—190° yield *pyrenyl-3-acetic acid*, m.p. 220° (decomp.), which when distilled with NaOH–CaO affords 3-*methylpyrene*, m.p. 71—72° (*picrate*, m.p. 211—212°), obtained also from pyrene-3-aldehyde and N_2H_4,H_2O at 200°. Distillation of (XX) with Zn dust gives 3-*ethylpyrene*, m.p. 94—95°. Gradual addition of $CH_2Cl{\cdot}COCl$ to (I) and $AlCl_3$ in CS_2 gives 3 : 8-, m.p. 288°, and 3 : 10-, m.p. 202°, *-dichloroacetylpyrene*, oxidised by NaOCl in $Bu^{\alpha}OH$–EtOH–H_2O at 90° to *pyrene-3 : 8-dicarboxylic acid*, m.p. >365° (decomp.) [corresponding *chloride* (XXII), m.p. 262°], and *pyrene-3 : 10-dicarboxylic acid*, m.p. >365° (decomp.) [*chloride* (XXIII), m.p. 235°]. With C_6H_6 and $AlCl_3$ (XXII) gives 3 : 8- (XXIV), m.p. 239°, and (XXIII) gives 3 : 10- (XXV), m.p. 165°, *-dibenzoylpyrene*, the mixture of which is obtained from (I), $AlCl_3$, and BzCl in CS_2 at room temp. Passage of dry O_2 through a molten mixture of (XXIV) or (XXV) with $AlCl_3$–NaCl at about 120° gives pyranthrone. Oxidation of (XXIV) suspended in AcOH by CrO_3 yields 3 : 8-*dibenzoylpyrene*-5 : 10-*quinone*, m.p. 292°, transformed by $AlCl_3$–NaCl at 140—150° into *dihydroxypyranthrone* (*Me*$_2$ *ether*). Similar oxidation of (XXV) gives 3 : 10-*dibenzoylpyrene*-5 : 8-*quinone*, m.p. 242°. 3 : 8-*Dinitropyrene*, m.p. 309°, is obtained mixed with the 3 : 10-isomeride by the addition of HNO_3 (*d* 1·4) to (I) in AcOH at 90°; reduction of the mixture by NaSH in EtOH–H_2O leads to 3 : 8-*diaminopyrene*, m.p. 232—233° (*sulphate*; *Ac*$_2$ derivative, m.p. about 410° after blackening at about 375°), and 3 : 10-*diaminopyrene*, m.p. 160—162° (*Ac*$_2$ derivative, decomp. about 350°). Nitration of 3-acetamidopyrene gives a mixture, reduced (Na in EtOH) and separated into 3-*amino*-8-, m.p. 280°, and 3-*amino*-10-, m.p. 250—251°, *-acetamidopyrene*. 3 : 5 : 8 : 10-*Tetranitropyrene*, m.p. 332°, is described. KCN and (III) in boiling $CH_2Ph{\cdot}CN$ yield 3 : 5 : 8 : 10-*tetracyanopyrene*, m.p. about 450°, hydrolysed by 10% NaOH at 180° to *pyrene-3 : 5 : 8 : 10-tetracarboxylic acid* (*Et*$_2$ ester, m.p. 194°), the *tetrachloride*, m.p. 226°, of which is transformed by C_6H_6 and $AlCl_3$ in CCl_4 into 3 : 5 : 8 : 10-*tetrabenzoylpyrene*, m.p. 282°. 3 : 5 : 8 : 10-*Tetrachloropyrene*, m.p. 299—300°, from (II), $AlCl_3$, and C_6H_6, is oxidised by CrO_3 in AcOH to 1 : 4 : 5 : 8-*tetrabenzoylnaphthalene*, m.p. 373°, which is very stable towards further oxidation. 2 : 3 : 3′ : 2′-*Dipyrenylene* has m.p. 212—214°. (I), *o*-$C_6H_4(CO)_2O$, and $AlCl_3$ in C_6H_6 yield o-3-*pyrenoylbenzoic acid*, m.p. 225—226°, which with BzCl in boiling 1-$C_{10}H_7Cl$ gives 3 : 4-*phthaloylpyrene*, m.p. 254°. *Diphthaloylpyrene*, m.p. >420°, is described. β-3-Pyrenoylpropionic acid, m.p. 184°, is reduced by Zn dust and NaOH to *γ-3-pyrenylbutyric acid*, m.p. 184°, transformed by the successive action of PCl_5 and $AlCl_3$ in C_6H_6 into 3 : 4-4′-*keto*-1′ : 2′ : 3′ : 4′-*tetrahydrobenzpyrene*, m.p. 171°, and thence by distillation with Zn dust into 3 : 4-*benzpyrene* (XXVI), m.p. 175°. 3 : 4 : 8 : 9-*Dibenzpyrene* has m.p. 315°. Oxidation of (XXVI) by CrO_3 yields 3 : 4-*benzpyrene*-5 : 8-*quinone*, m.p. 245° (corresponding *quinol diacetate*, m.p. 204°), and 3 : 4-*benzpyrene*-5 : 10-*quinone*, m.p. 295° (corresponding *quinol diacetate*, m.p. 242°). Under other conditions (XXVI) affords benzanthrone*peri*dicarboxylic anhydride, m.p. 364—365°. Treatment of (XIX) with 3-aminopyrene, glycerol, and conc. H_2SO_4 leads to 3 : 4-*pyridinopyrene* (XXVII), m.p.

(XXVII.)   (XXVIII.)

157°, oxidised to 3 : 4-*pyridinopyrene*-5 : 10-*quinone*, m.p. 330°, converted by NaOCl in boiling C_5H_5N into 11-*azabenzanthrone*per*idicarboxylic acid* [the corresponding *anhydride*, m.p. 349°, is converted by *o*-$C_6H_4(NH_2)_2$ into a *benziminazole* derivative], the *Ba* salt of which passes into 11-*azabenzanthr*-7-*one* (XXVIII), m.p. 159—160°. *Et*$_2$ 3-*pyrenylidenemalonate*, m.p. 114°, from the aldehyde and $CH_2(CO_2Et)_2$ in boiling Ac_2O, is hydrolysed to 3-*pyrenylidenemalonic acid*, decomp. about 230° (3-*pyrenylacrylic acid*, m.p. 270°), transformed by $ZnCl_2$ in Ac_2O into *pyreneindenonecarboxylic acid* (XXIX), decomp. 302—303°; this yields 1 : 8 : 9-*naphthanthrene* (XXX), m.p. 135°, also obtained by the

(XXIX.)   (XXX.)

distillation of 1 : 8 : 9-naphthanthrone (XXXI) with Zn dust. (XXX) or (XXXI) is oxidised by CrO_3 in AcOH to 1 : 8 : 9-*naphthanthrone*-10-*naphtha*-1 : 2-*quinone*, m.p. 378° (decomp.) [corresponding *phenazine* derivative, m.p. (indef.) 352°]. *Pyrene*-4-*carboxylic acid*, m.p. 326° (*Me*, m.p. 136°, and *Et*, m.p. 117°, ester; corresponding *chloride*, m.p. 166°), is converted into the corresponding *hydrazide*, m.p. 230° and m.p. (indef.) >300° after re-solidification (*Ac* derivative, m.p. 290° (decomp.); *di*-4-*pyrenoylhydrazine*, m.p. 368—369°), which is transformed through the *azide* and 4-*acetamidopyrene*, m.p. 229°, into 4-*aminopyrene* (XXXI), m.p. 207°. 3-Aminopyrene sulphate passes in boiling *o*-$C_6H_4Cl_2$ into

3-*aminopyrene*-4-*sulphonic acid*, the *Na* salt (XXXII) of which is converted by NaOH at 160° into 4-*hydroxypyrene*, m.p. 206—207° (*acetate*, m.p. 114°; *Me ether*, m.p. 105—106°), also obtained from (XXXI) (Sandmeyer); it couples with diazotised aromatic amines. (XXXII) is converted into the corresponding hydrochloride, which gives 3-*cyanopyrene*-4-*sulphonic acid* (*Na* salt; corresponding *chloride*, m.p. 265°) when diazotised and treated with $K_3Cu(CN)_4$. *Pyrene*-4-*carboxylamide* and PCl_5 in $C_6H_3Cl_3$ give 4-*cyanopyrene*, m.p. 203—204°, also obtained by distilling Na pyrene-4-sulphonate with KCN; it is converted by N_2H_4, H_2O at 200° into 4-methylpyrene, m.p. 143—143·5° (*picrate*, m.p. 192°). Under differing conditions hexahydropyrene (XXXIII) is transformed by Br into 1-*bromo*-, m.p. 130—131°, and 1 : 6-*dibromo*-, m.p. 194°, -3 : 4 : 5 : 8 : 9 : 10-*hexahydropyrene* (XXXIV). (XXXIII) and SO_2Cl_2 containing a little $AlCl_3$ yield 1 : 6-*dichloro*-3 : 4 : 5 : 8 : 9 : 10-*hexahydropyrene*, m.p. 182—183°. $ClSO_3H$ and (XXXIII) in $PhNO_2$ at 16—25° give *hexahydropyrene*-1-*sulphonic acid* whereas the 1 : 6-*disulphonic acid* is obtained from (XXXIII) and conc. H_2SO_4 at room temp.; the corresponding *Na* salts did not give satisfactory results when fused with NaOH. 1-*Acetyl*-, m.p. 85—86°, and 1 : 6-*diacetyl*-, m.p. 182°, -*hexahydropyrene* are oxidised by NaOCl in presence of C_5H_5N to *hexahydropyrene*-1-, m.p. 241° (*Na* salt), and -1 : 6-*di*-, m.p. 322° (decomp.), -*carboxylic acid*. 1-*Benzoyl*-, m.p. 109°, and 1 : 6-*dibenzoyl*-, m.p. 275°, -*hexahydropyrene* are described; the latter did not undergo ring-closure satisfactorily when fused with $AlCl_3$–NaCl in presence of O_2. CuCN and boiling (XXXIV) yield 1 : 6-*dicyanohexahydropyrene* (XXXV), m.p. 303°, whereas at 320—350° they give *pyrene*-1 : 6-*dinitrile*, m.p. 406°, also obtained by dehydrogenating (XXXV) with Se in boiling ethylcarbazole. *Pyrene*-1 : 6-*dicarboxylic acid*, decomp. about 420°, is converted by PCl_5 in $C_6H_3Cl_3$ at 170—180° into the corresponding *dichloride*, which with C_6H_6 and $AlCl_3$ affords 1 : 6-*dibenzoylpyrene* (XXXVI), m.p. 237°, and (?) 1-*benzoylpyrene*-6-*carboxylic acid*, m.p. 252°. Oxidative treatment of (XXXVI) with $AlCl_3$–NaCl at 140—150° leads to 1 : 10-6 : 5-*dibenzoylenepyrene*. Ozonisation of (I) in AcOH gives 4-*aldehydophenanthrene*-5-*carboxylic acid* (XXXVII), m.p. 276°, oxidised by CrO_3 in AcOH at 80° to *phenanthrene*-4 : 5-*dicarboxylic acid*, m.p. 298° (decomp.) (corresponding *azine*, m.p. 330°, and its *anhydride*, m.p. 340°). Oxidation of (XXXVII) by $KMnO_4$ in alkaline solution gives *diphenyl*-2 : 2′ : 6 : 6′-*tetracarboxylic acid*, m.p. about 390° (decomp.), converted by heating with $Cu(OAc)_2$ into Ph_2 and fluorenone.

2-*Amino*-1-*hydroxypyrene*, decomp. 250°, obtained by reduction of 2-*benzeneazo*-1-*hydroxypyrene*, m.p. 197°, is oxidised by CrO_3 to *pyrene*-1 : 2-*quinone* (XXXVIII), m.p. 310° (corresponding *azine*, m.p. 262°), also obtained by fusion of (XXXVII) with KOH. Oxidation of (XXXVIII) with CrO_3 in AcOH at 90° gives *pyrene*-1 : 2 : 6 : 7-*diquinone*, m.p. about 365° (decomp.), which affords a *diphenazine* derivative, m.p. >420°. 1-*Hydroxypyrene* (XXXIX), m.p. 206—207° (*Ac* derivative, m.p. 113—114°), is prepared from (XXXVII) and N_2H_4,H_2O in boiling AcOH or by the energetic reduction of (XXXVIII). It is converted by aq. $(NH_4)_2SO_3$ at 150° into 1-*aminopyrene*, m.p. 182° (*hydrochloride*; *sulphate*; *Ac* derivative, m.p. 276°). Glycerol, 80% H_2SO_4, amd (XXXIX) at 120—125° give 1 : 8 : 9-*naphthanthr*-10-*one*, m.p. 243°, also obtained similarly from (I). H. W.

Polyterpenes and polyterpenoids. CXV. Synthesis of 1 : 8-dimethyl- and 2-methoxy-1 : 8-dimethyl-picene and their identification with the products of the dehydrogenation of pentacyclic triterpenes. L. Ruzicka and K. Hofmann [with H. Bauer, P. Müller, G. Ruffoni, and P. Rusconi] (Helv. Chim. Acta, 1937, 20, 1155—1164).—1-Keto-7-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene is converted by Zn and $CH_2Br{\cdot}CO_2Et$ in C_6H_6 into *Et* 7-*methyl*-3 : 4-*dihydro*-1-*naphthylacetate*, b.p. 112—122°/0·4 mm., reduced by Na and EtOH to β-7-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthylethyl alcohol*, b.p. 115—118°/0·1 mm., whence the corresponding *bromide* (I), b.p. 104—105°/0·1 mm. The Mg derivative of this reacts with 1-*keto*-5-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. 143—145°/10 mm., m.p. 49—50°, to form α-7-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthyl*-β-5′-*methyl*-3′ : 4′-*dihydro*-1′-*naphthylethane*, b.p. 185—186°/0·1 mm., dehydrogenated (Pd–C at 320°) to α-7-*methyl*-1-*naphthyl*-β-5′-*methyl*-1′-*naphthylethane*, which after purification through Al_2O_3 (Brockmann) has m.p. 74—75°. It is transformed by $AlCl_3$ in CS_2 at room temp. into 1 : 8-*dimethylpicene*, m.p. 305—306°, identical with that derived from gypsogenin, hederagenin, quinovaic acid, ursolic acid, fricdelinol, and β-amyrene. Condensation of $CHNa(CO_2Et)_2$ with ω-chloro-3-methoxy-2-methylacetophenone gives the corresponding *malonate*, b.p. 140—150°/0·5 mm., hydrolysed and decarboxylated to γ-*keto*-γ-3-*methoxy*-o-*tolylbutyric acid*, m.p. 130—130·5°. This is reduced (Clemmensen) to γ-3-*methoxy*-o-*tolylbutyric acid*, b.p. 144—145°/0·1 mm., m.p. 109—110°, cyclised by successive treatments with $SOCl_2$ and $AlCl_3$ in CS_2 to 1-*keto*-6-*methoxy*-5-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. 123—124°/0·1 mm., m.p. 114—115°. This is transformed by the Grignard compound from (I) into α-6-*methoxy*-5-*methyl*-3 : 4-*dihydro*-1-*naphthyl*-β-7′-*methyl*-1′ : 2′ : 3′ : 4′-*tetrahydro*-1′-*naphthylethane*, b.p. 197—198°/0·02 mm., dehydrogenated to α-6-*methoxy*-5-*methyl*-1-*naphthyl*-β-7′-*methyl*-1′-*naphthylethane*, m.p. 121—122°, which is cyclised by $AlCl_3$ in CS_2 to 2-*methoxy*-1 : 8-*dimethylpicene*, m.p. 358—359°, identical with that derived from amyrin. H. W.

Aromatic nitro-derivatives. X. Naphthalene derivatives. A. Mangini and B. Frenguelli. **XI. Action of some diamines on 1-chloro-2 : 4-dinitronaphthalene.** A. Mangini (Gazzetta, 1937, 67, 358—370, 373—380).—X. The structure of substituted C_6H_6 derivatives is discussed on Bonino's theory (A., 1935, 1057), and extended to substituted naphthalenes. The rate of reaction of 1 : 2 : 4-$C_{10}H_5Cl(NO_2)_2$ (I) with NH_2Ph and other amines is studied: it is always > that of 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$. The following are described: N-4-*diphenylyl*-, m.p. 174—174·5°, -p-*bromophenyl*-, m.p. 223·5—224·5°, -p-*carboxyphenyl*-, m.p. 269—270° (decomp.), -p-

carbethoxyphenyl-, m.p. 146·5—148°, and -p-*hydroxyphenyl*-2′ : 4′-*dinitro*-1′-*naphthylamine*, m.p. 219·5—220·5°; and 4-(2′ : 4′-*dinitroanilino*)*diphenyl*, m.p. 144—145°.

XI. With diamines (I) gives compounds of type $NH_2{\cdot}R{\cdot}NH{\cdot}C_{10}H_5(NO_2)_2$ or type $R[NH{\cdot}C_{10}H_5(NO_2)_2]_2$, according to reactivity and proportion of amine used. The following are described: N-o-, m.p. 177·5—178° [*hydrochloride*; *Ac* derivative, m.p. 218—219° (decomp.)], N-m-, m.p. 195—196° (decomp.) (*Ac* derivative, m.p. 205—206°), and N-p-*aminophenyl*-2′ : 4′-*dinitro*-1′-*naphthylamine*, m.p. 232—233° (decomp.) (*Ac* derivative, m.p. 245—246°); and NN′-*bis*-(2′ : 4′-*dinitro*-1′-*naphthyl*)-m-, m.p. 252—253° (decomp.), and -p-*phenylenediamine*, m.p. >290°. 2 : 4′-$NH_2{\cdot}[C_6H_4]_2{\cdot}NH_2$ gives a mixture from which only NN′-*bis*-(2″ : 4″-*dinitro*-1″-*naphthyl*)-2 : 4′-*diaminodiphenyl*, m.p. ⩽290°, is isolated. Benzidine yields N-2″ : 4″-*dinitro*-1″-*naphthylbenzidine*, m.p. 228·5—229·5° (*Ac* derivative, m.p. 205—206·5°), and NN′-*bis*-(2″ : 4″-*dinitro*-1″-*naphthyl*)*benzidine*, m.p. ⩽290°. $(CH_2{\cdot}NH_2)_2$ yields NN′-*bis*-(2 : 4-*dinitro*-1-*naphthyl*)-*ethylenediamine*, m.p. 170°, resolidifying to melt again at 250—260° (variable), converted by Ac_2O into N-β-*acetamidoethyl*-2 : 4-*dinitro*-1-*naphthylamine*, m.p. 162—163°. E. W. W.

Condensation products of the diphenylamine series [methylsulphonyldiphenylamines].—See B., 1937, 885.

***cis*-Form of azobenzene.** G. S. Hartley (Nature, 1937, **140**, 281).—The *cis*-form of azobenzene has been separated by extraction of a $COMe_2$ solution, which has been exposed to light, with H_2O, and extraction of the aq. extract with $CHCl_3$ after treatment with light petroleum. The m.p. is at least 2° > that of the normal form; the absorption coeff. for blue light is greater, and the dipole moment in C_6H_6 is 3·0 D units. Equilibrium is attained under the usual conditions with approx. 27% of the *cis*-form. L. S. T.

Decomposition of benzenediazonium chloride. W. A. Waters (Nature, 1937, **140**, 466—467).—When suspended in an org. liquid, PhN_2Cl (I) appears to melt at approx. 50° with violent decomp. HCl is often formed and is always accompanied by PhCl. In $COMe_2$ with excess of $CaCO_3$, the chief reaction is (I) + $COMe_2$ = N_2 + C_6H_6 + $CH_2Cl{\cdot}CO{\cdot}Me$. Free neutral radicals are supposed to be formed as (I) decomposes. When this decomp. in $COMe_2$ + $CaCO_3$ is carried out in presence of Sb, Bi, Pb, or Hg, the metal is rapidly attacked at room temp.; with Hg, HgPhCl is formed. L. S. T.

"Catalytically polar" materials.—See A., I, 523.

[Metallic salts of] diazoamino-compounds. IV. A. Mangini (Gazzetta, 1937, **67**, 384—388; cf. A., 1935, 969).—2 : 2′- (I), 3 : 3′- (II), and 4 : 4′-dinitro- (III), and 4 : 4′-dimethyl- (IV), and 4 : 4′-dibromo-diazoaminobenzene (V) give salts as follows: (I) and (II), intensely coloured *K* salts; (II) and (III), *Ag* salts in yellow, orange, and red forms; (IV) and (V), yellow *Ag* salts; and (II), yellow, and (III), orange-yellow and red, *Hg* salts. The *Hg* salts of (IV) and (V) are obtained in yellow forms only, but these give red solutions in $PhNO_2$. E. W. W.

Refractive indices of aniline–*o*-chlorophenol mixtures and the nature of the molecular compound. C. D. Ellyett (Trans. Faraday Soc., 1937, **33**, 1212—1217).—The vals. of n_D^{20} have been determined for NH_2Ph–*o*-$C_6H_4Cl{\cdot}OH$ mixtures. The departures of the mol. refractivity from the mixture law are within experimental error. Trew's results (A., 1932, 801) for $CHBr_3$–$COMe_2$ mixtures are recalc. The conclusion of Smyth *et al.* (A., 1929, 994) that in such cases only dipole association occurs is criticised and a resonance link is proposed. It is considered to be most probable that in the intermediate compound the N of the NH_2Ph is linked to the phenolic H of the *o*-$C_6H_4Cl{\cdot}OH$ mol. This is supported by the fact that the large heat of mixing, and therefore the compound formation, disappears when the OH is replaced by H or OMe. The existence of a chelate ring in *o*-$C_6H_4Cl{\cdot}OH$ is discussed. J. W. S.

Heats of reaction and specific heats of aniline–*o*-chlorophenol mixtures.—See A., I, 507.

Thermal decomposition of cresol on a glowing wire. K. Peters and K. Winzer (Brennstoff-Chem., 1937, **18**, 357).—The reactions occurring when cresol (b.p. 190—210°) was decomposed by immersing in it an electrically-heated wire (cf. B., 1936, 133) can be represented approx. by; $30C_6H_4Me{\cdot}OH = 15C_6H_6 + 5PhMe + Ph_2 + 30CO + 15CH_4 + 20H_2 + 28C$. The rate of decomp. of cresol is ⩽ that of paraffin hydrocarbons under similar conditions. A. B. M.

Pyrolysis of 2 : 4 : 6-trialkylphenyl allyl ethers. C. D. Hurd and W. A. Yarnall (J. Amer. Chem. Soc., 1937, **59**, 1686—1690).—Diallyl and $CH_2{:}CHMe$, but not allene, are evolved during pyrolysis of Ph allyl ethers; the rearrangement is in part intermol. *p*-Tolyl allyl ether (modified prep.), b.p. 97—98°/16 mm., gives 69% of 3-*allyl*-p-*cresol* (I), b.p. 115—118°/14 mm. (gives 3-*allyl*-p-*tolyloxyacetic acid*, m.p. 124—125°), and a little *p*-cresol and 3 : 5-*diallyl*-p-*cresol* (II), b.p. 134—141°/15 mm., hydrogenated to 3 : 5-*diisopropyl*-p-*cresol* (III), b.p. 138—142°/17 mm., m.p. 21° (3 : 5-*dinitrobenzoate*, m.p. 96°). 1 : 3 : 4-$C_6H_3MePr^{\alpha}{\cdot}OH$, prepared by hydrogenation of (I) (gives 3-*propyl*-p-*tolyloxyacetic acid*, m.p. 114—115°), gives an *allyl ether*, b.p. 123—124°/16 mm., which at 230—275° affords 67% of 3-*propyl*-5-*allyl*-p-*cresol*, b.p. 135°/13 mm. [hydrogenated to (III)], with 24% of (I). The *allyl ether*, b.p. 148°/15 mm., of (II) at 250—270° gives diallene, (III), and $CH_2{:}CHMe$. R. S. C.

Nitrated *o*-alkyl-phenolic compounds.—See B., 1937, 878—879.

Introduction of the triphenylmethyl group. II. III. Mobility of the bromine atom in triphenylmethyl*iso*chavibetol and its derivatives. I. E. Funakubo (Ber., 1937, **70**, [*B*], 1981—1982, 1983—1986; cf. A., 1936, 1388).—II. *iso*-Chavibetol is converted by short heating with CPh_3Cl in C_5H_5N at 155° into the oxonium salt, which passes into *iso*chavibetol CPh_3 ether (the yield of which attains its max. in 10 hr. and then slowly

declines) and triphenylmethyl*iso*chavibetol [2-methoxy-6-triphenylmethyl-5-Δ^{α}-propenylphenol] (I) max. production of which is observed after 40 hr. The product of the action of HI on (I) is 1 : 2-*dihydroxy*-3-*triphenylmethyl*-4-*propylbenzene*, m.p. 93—96°.

III. The presence of ·CPh_3 confers mobility on α-Br. Addition of Br to (I) in Et_2O gives the corresponding *dibromide* (II), m.p. 128° (decomp.) when freshly prepared or decomp. 155° after preservation or crystallisation from light petroleum. (II) is transformed by short boiling with MeOH into 2-*methoxy*-6-*triphenylmethyl*-5-β-*bromo*-α-*methoxy*-n-*propyl*-*phenol* (III), m.p. 184·5° (decomp.), and by boiling EtOH into the corresponding -α-*ethoxy*-compound, m.p. 174° (decomp.). Br and triphenylmethyl*iso*chavibetol Me ether in Et_2O at 15° afford 2-*methoxy*-6-*triphenylmethyl*-5-αβ-*dibromopropylanisole*, m.p. 150·5—151° (decomp.), converted by MeOH into 2-*methoxy*-6-*triphenylmethyl*-5-β-*bromo*-2-*methoxy*-n-*propyl*-*anisole*, m.p. 172—172·5° (decomp.) [also obtained by methylation (Me_2SO_4) of (III)], and by EtOH into the corresponding -α-*OEt*-compound, m.p. 159—160° (decomp.). Indications of the replacement of β-Br are not observed and *iso*chavibetol dibromide and its Me ether are stable under these treatments. H. W.

System: pyrogallol–*p*-phenylenediamine.—See A., I, 517.

Pentahydroxybenzene series. I. G. Aulin and H. Erdtman (Svensk Kem. Tidskr., 1937, **49**, 208—215).—2 : 6-Dimethoxybenzoquinone with Br in $CHCl_3$ in the cold affords 4 : 6-*dibromo*-2 : 5-*dihydroxy*-1 : 3-*dimethoxybenzene*, m.p. 140·5—142·5° (*diacetate*, by Ac_2O–C_5H_5N, m.p. 103—104°), whilst at 100°, 3 : 5-*dibromo*-2 : 6-*dimethoxy*-1 : 4-*benzoquinone* (I), m.p. 174·5—176·5°, is formed. (I) with MeOH–NaOH affords 6-*bromo*-2 : 5-*dihydroxy*-3-*methoxy*-1 : 4-*benzoquinone* (II), decomp. 203—205°, converted by Zn–Ac_2O–C_5H_5N into 6-*bromo*-3-*methoxy*-1 : 2 : 4 : 5-*tetra-acetoxybenzene* (III), m.p. 165—166·5°, and reduced (Pd–H_2) to 2 : 5-*dihydroxy*-3-*methoxy*-1 : 4-*benzoquinone*, m.p. 158—160°. 3-*Methoxy*-1 : 2 : 4 : 5-*tetra-acetoxybenzene*, m.p. 182—182·5°, obtained in the same manner as (III), is hydrolysed (MeOH–H_2SO_4) and methylated (Me_2SO_4–NaOH) to *pentamethoxybenzene*, m.p. 59—60°. 1 : 2 : 3 : 4-$C_6H_2(OMe)_4$ with Br in $CHCl_3$ affords 5 : 6-*dibromo*-1 : 2 : 3 : 4-*tetramethoxybenzene*, b.p. 153—155°/0·6 mm., oxidised (HNO_3) to 5 : 6-*dibromo*-2 : 3-*dimethoxybenzoquinone*, m.p. 126—127°, which is hydrolysed (NaOH) to (II). J. D. R.

Alkanolamines. II. Reaction of the chloronitrobenzenes with monoethanolamine. C. B. Kremer (J. Amer. Chem. Soc., 1937, **59**, 1681—1682; cf. A., 1936, 485).—*o*-$C_6H_4Cl{\cdot}NO_2$, $NH_2{\cdot}[CH_2]_2{\cdot}OH$, and Na_2CO_3 give 60—70% of N-β-*hydroxyethyl*-*o*-*nitroaniline*, m.p. 76°, and 5—8% of *o*-$C_6H_4Cl{\cdot}NH_2$; Sn–HCl affords N-β-*hydroxyethyl*-*o*-*phenylenediamine*, m.p. 107°. *p*-$C_6H_4Cl{\cdot}NO_2$ gives 15—20% of N-β-*hydroxyethyl*-*p*-*nitroaniline*, m.p. 111—111·5°, with 5—8% of *p*-$C_6H_4Cl{\cdot}NH_2$ and 15—20% of (*p*-$C_6H_4Cl{\cdot}N{:})_2$. *m*-$C_6H_4Cl{\cdot}NO_2$ gives only 50—60% of *m*-$C_6H_4Cl{\cdot}NH_2$ and 30—40% of (*m*-$C_6H_4Cl{\cdot}N{:})_2$. R. S. C.

Some bases of physiological interest. H. C. Bhatnagar, N. N. Chopra, K. S. Narang, and J. N. Ray (J. Indian Chem. Soc., 1937, **14**, 344—348).—$NMe_2{\cdot}CN$ with NH_2Ph,HCl at 120° gives *phenyldimethylguanidine*, m.p. 90° [*methiodide*, m.p. 188° (decomp.)], but does not react at atm. pressure with $OH{\cdot}CHPh{\cdot}CH_2{\cdot}NH_2$ (I) [*picrolonate*, m.p. 198° (decomp.); *oxalate*, m.p. 171—172°; *methiodide*, m.p. 222°, NO-Bz_2 derivative, m.p. 131—132°; *piperonylidene* derivative, m.p. 105—106°, converted by MeI followed by dil. HCl into $OH{\cdot}CHPh{\cdot}CH_2{\cdot}NHMe$ (*picrolonate*, m.p. 196—198°)]. Piperonaldehyde cyanohydrin is reduced (Na–Hg) to β-*hydroxy*-β-3 : 4-*methylenedioxyphenylethylamine* [*carbonate*, m.p. 116—119° (decomp.); *hydrochloride*, m.p. 182—183°; *picrolonate*, m.p. 200° (decomp.); *oxalate*, m.p. 197°; N-Bz_1 derivative, m.p. 152—153°; NO-Bz_2 derivative, m.p. 141—142°; *methiodide*, m.p. 229—230°], the *piperonylidene* derivative, m.p. 155—156°, of which, when methylated and hydrolysed, yields 3 : 4-*methylenedioxyadrenaline* (*picrolonate*, m.p. 203°). (I) condenses with $SMe{\cdot}C(:NH){\cdot}NH_2$,HI in boiling EtOH, giving β-*hydroxy*-β-*phenylethylguanidine hydriodide*, m.p. 133°. A. Li.

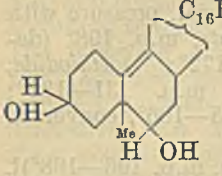
Preparation of a homologue of *epi*coprosterol in the ergosterol series. F. Wetter and K. Dimroth (Ber., 1937, **70**, [*B*], 2033).—Further details of the measurements of absorption spectra are given (cf. this vol., 416). H. W.

Bile acids, sterols, neutral saponins, cardiac poisons, hormones, and vitamins and their mutual chemical relationships. D. van Os (Pharm. Weekblad, 1937, **74**, 1161—1178, 1194—1218).—A review of the chemical relationships of representative members of each of the above types of compounds. S. C.

Stereochemistry of the sterols and the bile acids. D. A. Peak (Nature, 1937, **140**, 280—281).—A discussion. The fusion of the C and D rings appears to be in the *cis* and not in the *trans* position as hitherto believed. L. S. T.

Transformations of cholestanetriol. H. Lettré and M. Müller (Ber., 1937, **70**, [*B*], 1947—1952).—Removal of H_2O from cholestanetriol (I), unlike that from the ergostadienetriols, does not lead to 7-dehydrosterols but is accompanied by stabilisation to the oxide or by intramol. transformations. Distillation at 220—240°/1 mm. of (I) causes decomp. without formation of well-defined substances. The corresponding dibenzoate at 210°/1 mm. gives BzOH and α-*cholesteryl oxide benzoate*, m.p. 181°. The diacetate is unchanged when distilled but passes when heated with $BaCO_3$ at 220° into α-cholesteryl oxide acetate, m.p. 97—98°. To exclude the possible formation of an oxide, derivatives of (I) in which OH at $C_{(5)}$ is removed or replaced are examined. Cholestanetriol diacetate is converted by Ac_2O–conc. H_2SO_4 into a cholestenediol diacetate, hydrolysed to a cholestenediol, m.p. 99—108° (*di*-3 : 5-*dinitrobenzoate*, m.p. 231°); the corresponding *dibenzoate*, m.p. 160—161° and, after solidification, m.p. 177—178°, loses a little BzOH at 210°/1 mm. but is mainly unchanged. Oxidation of the enediol by CrO_3 in AcOH at 4°

gives a substance (II), $C_{27}H_{42}O_3$ (?), m.p. 142—143°. (I) is transformed by HCl–MeOH into the chlorohydrin, $C_{27}H_{47}O_2Cl$, converted into a *diacetate*, m.p. 107—108°, and a *dibenzoate* (III), m.p. 181°, proving that the *tert.* OH at $C_{(5)}$ in (I)

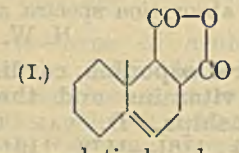


is replaced by Cl. (III) when heated at 210°/1 mm., or with quinoline at 180° loses partly HCl and partly BzOH giving a *cholestenediol dibenzoate*, m.p. 179°, hydrolysed to a *cholestenediol*, m.p. 137—138°, oxidised to cholestane-3 : 6-dione. Assuming that a retropinacolin transformation has occurred, the annexed formula is suggested for (II). H. W.

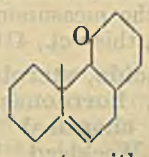
Derivatives of 3 : 17-diols of the *cyclo*pentanopolyhydrophenanthrene series.—See B., 1937, 980.

Unsaturated neutral oxidation products of stigmasterol compounds.—See B., 1937, 980.

Diene synthesis applicable to the sterol group. A. B. Meggy and R. Robinson (Nature, 1937, **140**, 282).—1-*Methyl*-2-*vinyl*cyclo*hexene*, obtained from 2-methyl*cyclo*hexenylethyl alcohol by an application of the xanthate reaction, condenses with maleic anhydride in C_6H_6 to form the *anhydride* (I), m.p. 111·5°. This and the related dibasic acid, m.p. 171°,



(I.)



(II.)

gave analytical vals. in agreement with theory. With crotonaldehyde, the diene yields an *adduct*, $C_{19}H_{24}O_4N_4$ (*dinitrophenylhydrazone*, m.p. 192°). The 2 : 4-*dinitrophenylhydrazone* of the adduct (II) from the diene and *cyclo*hexenone has m.p. 164°. Advantages of the method in relation to the synthesis of cholesterol and analogous substances are discussed. L. S. T.

Preparation of plant growth-promoting substances. I. Ethyl α-naphthylglyoxylate; α-naphthylglycollic acid; α-naphthylacetic acid. F. Wilcoxon (Contr. Boyce Thompson Inst., 1937, **8**, 467—472).—α-$C_{10}H_7$·CH_2·CO_2H is prepared by condensation of $C_{10}H_8$ with Et chloroglyoxylate (47% yield) followed by reduction with HI and red P (90% yield of crude product). Reduction with Na–Hg or with H_2–Ni gave α-naphthylglycollic acid. A. G. P.

Halogen migrations under the influence of aluminium chloride. IV. C. D. Nenitzescu and J. Gavăt (Ber., 1937, **70**, [*B*], 1883—1886; cf. this vol., 140).—Further examples of migration are recorded. Gradual addition of Δ^1-*cyclo*hexenyl- or -*cyclo*hexylidene-acetic acid in C_6H_6 to $AlCl_3$ in C_6H_6 gave p-*phenyl*cyclo*hexylacetic acid*, b.p. 180°/2 mm., m.p. 112° [*Et* ester (I), b.p. 168°/5 mm.; corresponding *chloride*, b.p. 182—183°/14 mm., and *amide*, m.p. 195·5°], the constitution of which is established by its transformation by MgPhBr into the corresponding carbinol, which is oxidised by CrO_3 in AcOH to *p*-phenyl*cyclo*hexanecarboxylic acid. β-*cyclo*-Hexylacrylic acid and $AlCl_3$ in C_6H_6 afford β-p-*phenylcyclohexylpropionic acid* (II), b.p. 186—189°/1·5 mm., m.p. 145·5° (*Et* ester, b.p. 159°/2 mm.). Reduction of (I) by Na and EtOH gives β-p-*phenyl*cyclo*hexylethyl alcohol*, b.p. 157°/3·5 mm., m.p. 78°, transformed by red P and I in $CHCl_3$ at room temp. into β-p-*phenyl*cyclo*hexylethyl iodide*, b.p. 188°/2 mm. (corresponding *bromide*, b.p. 171°/6 mm.), whence the *nitrile*, b.p. 194°/1 mm., and (II). Gradual addition of $AlCl_3$ to *cyclo*hexene, BzCl, and *cyclo*hexane gives Ph *cyclo*hexyl ketone, b.p. 131—134°/5 mm., m.p. 54°, which condenses with Mg and CH_2Br·CO_2Et in C_6H_6 to *Et* β-*hydroxy*-β-*phenyl*-β-cyclo*hexylpropionate*, b.p. 155—158°/5 mm. This is hydrolysed to β-*hydroxy*-β-*phenyl*-β-cyclo*hexylpropionic acid*, m.p. 175°, dehydrated by boiling Ac_2O to β-*phenyl*-β-cyclo*hexylacrylic acid*, b.p. 183°/4 mm., m.p. 144·5°, reduced by Na–Hg to β-*phenyl*-β-cyclo*hexylpropionic acid*, m.p. 101°. H. W.

Addition of Schiff's bases to methylenecarbonyl compounds. C. Lazzareschi (Gazzetta, 1937, **67**, 371—373).—CN·CH_2·CO_2Et, $CH_2(CO·NH_2)_2$, and CN·CH_2·CO·NH_2 resemble $CH_2(CO·)_2$ compounds in combining with NPh:CHPh. The respective products are *Et* β-*anilino*-α-*cyano*-β-*phenylpropionate*, m.p. 140°, β-*anilino*-β-*phenylmethylmalonamide*, m.p. 196—197°, and β-*anilino*-α-*cyano*-β-*phenylpropionamide*, m.p. 118—119°. E. W. W.

Homologues of thioprocaine. C. F. Lischer and C. N. Jordan (J. Amer. Chem. Soc., 1937, **59**, 1623—1624).—NaSH and CH_2Br·CH_2·NEt_2,HBr in abs. EtOH give only *bis*-β-*diethylaminoethyl disulphide*, b.p. 160°/16 mm. (*dihydrobromide*, m.p. 223°). *p*-NO_2·C_6H_4·CO·SK and Cl·$[CH_2]_3$·Br in EtOH give γ-*chloropropyl* p-*nitrothiobenzoate*, m.p. 59—60°, reduced (Fe–HCl) to the p-*aminothiobenzoate*, m.p. 50—51°, which with the appropriate diamine at 100° gives the following γ-*dialkylaminopropyl* p-*aminothiobenzoate dihydrochlorides*: Et_2, m.p. 190—191°, Pr^{α}_2, m.p. 167°, Pr^{β}_2, m.p. 196°, diallyl, m.p. 143°, Bu^{α}_2 (1 : 1 compound of the mono- and di-hydrochloride), m.p. 162°, and di-*n*-amyl, m.p. 183°. The ester hydrochlorides are local anæsthetics. M.p. are corr. R. S. C.

Dissociation constants of *o*-substituted acids. Alkaline hydrolysis of benzoic esters.—See A., I, 516.

Formation of anilides of acids.—See A., I, 522.

Catalytic hydrogenation of amides of α-hydroxy-acids (cont.). H. Ôeda (Bull. Chem. Soc. Japan, 1937, **12**, 377—381; cf. this vol., 235).—Hydrogenation of CH_2Ph·CH(OH)·CO·NH_2 yields CH_2Ph·CH(OH)·CH_2·OH (cf. A., 1936, 189) together with two forms (presumed to be *meso* and *r*) of αδ-*diamino*-βγ-*dibenzylbutane*, m.p. 153—155° (*Bz* derivative, m.p. 199—201°) and m.p. 166—167° (*Bz*, m.p. 280—282°, and *Ph*·SO_2· derivatives, m.p. 226—227°). F. R. G.

Sulphur studies. XII. Thioaldehydes in the naphthalene and anthracene series. J. H. Wood and R. W. Bost (J. Amer. Chem. Soc., 1937, **59**, 1721—1723; cf. this vol., 342).—Naphthalene-(*A*) and anthracene-thioaldehydes (*B*) are more

stable than thiobenzaldehydes. The influence of the size of the radical is shown by the fact that PhCHS gives mainly the *trans*-cyclic trimeride, (*A*) give only the *trans*-cyclic compound, and (*B*) give only linear polymerides. 1-$C_{10}H_7$·CHO is best obtained from 1-naphthylcarbithoic acid by way of the semicarbazone. 2 : 1-OEt·$C_{10}H_6$·CHO (2 : 4-*dinitrophenylhydrazone*, m.p. 258°), best obtained from 2-$C_{10}H_7$·OMe (I), NPhMe·CHO, and $POCl_3$, with H_2S and a trace of H_2SO_4 in EtOH gives 2-*ethoxynaphthalene*-1-*thioaldehyde* (II), an oil, and some of the cyclic *trimeride* (III), m.p. 283°, the latter being the sole product if H_2S is passed into a solution of (II) and HCl in EtOH. (II) and 2-$C_{10}H_7$·CHS are stable in dil. solution for 24—36 hr., give colours with Grote's reagent, eliminate H_2S with 2 : 4-$(NO_2)_2C_6H_3$·NH·NH_2 to give the hydrazones, and give ppts. with $HgCl_2$. At 300°/5 mm. (III) gives 70% of s-*di*-2-*ethoxy*-1-*naphthylethylene*, m.p. 213°, but, when distilled with a little H_2SO_4, is partly depolymerised to (II). H_2S and anthracene-9-aldehyde (best obtained from anthracene, NPhMe·CHO, and $POCl_3$) give a *polymeride*, m.p. 178°, of *anthracene*-9-*thioaldehyde*, obtained faster in presence of HCl; with H_2S and HCl in EtOAc–C_6H_6 at 0° a *polymeride*, m.p. 266°, is obtained, and at 23° a *polymeride*, m.p. about 263°; in KOH a *polymeride*, m.p. 223°, is formed; distillation of these polymerides gives H_2S and tars. R. S. C.

Preparation of vanillin. I—III. S. Kimura (J. Soc. Chem. Ind. Japan, 1937, **40**, 277—278B).—The influence of [KOH], of quantity of KOH and of $PhNO_2$, and of time, temp., solvents, and catalysts on the oxidation of safrole (I) in the prep. of vanillin (II) is studied. The process (I) → 4 : 3 : 1- + 3 : 4 : 1-OH·C_6H_3(O·CH_2·OMe)·CH:CHMe → 3 : 4 : 1-$C_6H_3(OH)_2$·CH:CHMe → $C_6H_3(OH)_2$·CHO → (II) gives improved yields. E. W. W.

3 : 4-Diphenylchloro*cyclo*pentenones and related compounds. C. F. H. Allen and H. Rudoff (Canad. J. Res., 1937, **15**, B, 321—330).—2-Hydroxy-3 : 4-diphenyl-Δ²-*cyclo*pentenone with $POCl_3$ affords 2-*chloro*-3 : 4-*diphenyl*-Δ²-cyclo*pentenone*, (I), m.p. 142° (2 : 4-*dinitrophenylhydrazone*, m.p. 216—217°), reduced (P–HI–AcOH) to 3 : 4-*diphenyl*cyclo*pentanone*, m.p. 92° (2 : 4-*dinitrophenylhydrazone*, m.p. 228°), which is dehydrogenated (SeO_2 in dioxan) to 3 : 4-diphenyl-Δ³-*cyclo*pentenone (2 : 4-*dinitrophenylhydrazone*, m.p. 233°). Ozonolysis of (I) in EtOAc affords β-benzoyl-β-phenylpropionic acid, and with Na_2CO_3 in MeOH it gives a bimol. *compound*, $C_{35}H_{28}O_3$, m.p. 208°. 4-Chloro-3 : 4-diphenyl-Δ³-*cyclo*pentenone (II) (2 : 4-*dinitrophenylhydrazone*, m.p. 216°) with HBr in AcOH yields 2-chloro-3 : 4-diphenyl-Δ³-*cyclo*pentenone (III) (2 : 4-*dinitrophenylhydrazone*, m.p. 216°) and 4 : 7-*endo*keto-3 : 5 : 6 : 8-tetraphenyl-4 : 7 : 8 : 9-tetrahydroindenone (cf. A., 1933, 1164), which is also formed from (II) by oxidation ($KMnO_4$ in $COMe_2$). 2-Chloro-3 : 4-diphenyl-Δ³-*cyclo*pentenone (V) with 2 : 4-$(NO_2)_2C_6H_3$·NH·NH_2 affords a 2 : 4-*dinitrophenylhydrazone*, $C_{23}H_{16}O_4N_4$, m.p. 265° (decomp.), from which (V) cannot be regenerated. With NaOH–MeOH, (V) yields 4 : 7-*endo*keto-2-chloro-3 : 5 : 6 : 8-tetraphenyl-2 : 3 : 4 : 7 : 8 : 9-hexahydroindenone, the Cl_1-dimeride, $C_{34}H_{23}O_2Cl$, of Burton and Shoppee (A., 1934, 409), from which (IV) is regenerated by NaOMe–MeOH. (IV) with CrO_3 in AcOH affords an *isomeride* (trans ?), m.p. 264°, which at 265—270° yields 3 : 3 : 5 : 6-*tetraphenylhydrindone* (VI), m.p. 182°, oxidised (SeO_2) to 3 : 3 : 5 : 6-*tetraphenylindan*-1 : 2-*dione*, m.p. 199—200° (*monoxime*, m.p. about 200°), which with *o*-$C_6H_4(NH_2)_2$ gives an *anil*, m.p. 272°. With HBr–AcOH (VI) affords a *dibromide*, $C_{33}H_{22}OBr_2$, m.p. 265°, and with SO_2Cl_2 a *dichloride*, $C_{33}H_{22}OCl_2$, m.p. 252°, from which (VI) is regenerated by Zn–AcOH. 1-Phenyl*cyclo*hexene and AcCl in CS_2 with $SnCl_4$ yield 2-*acetyl*-1-*phenyl*-Δ¹-cyclo*hexene*, b.p. 145—147°/7 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 165°). The reaction product of CH_2:CMe·CMe:CH_2 and 2 : 5-diphenylbenzoquinone in MeOH yields on reduction a *compound*, $C_{22}H_{24}O_2$, m.p. 169—170°. J. D. R.

Synthesis of benzanthrones. F. G. Baddar and F. L. Warren (Nature, 1937, **140**, 321; cf. A., 1936, 1388).—The αγ-Et_2 ethers of β-substituted glycerols can be used for the synthesis of 2-alkyl- and 2-aryl-benzanthrones under the conditions of Bally and Scholl's synthesis (A., 1911, i, 676). L. S. T.

Infra-red absorption as a measure of enolisation. A. M. Buswell, W. H. Rodebush, and M. F. Roy (J. Amer. Chem. Soc., 1937, **59**, 1767).—The absence of an absorption band characteristic of OH in the region 2·75—3·0 μ. for dibenzoylmethane is believed to indicate that it is not largely in the enolic form (cf. A., 1936, 703). E. S. H.

Carvacrol. VI. Removal of the *iso*propyl group. VII. Halogenoacylmethyl*iso*propylphenols. I. H. John and P. Beetz (J. pr. Chem., 1937, [ii], **149**, 164—170, 171—174; cf. A., 1936, 76).—VI. $AlCl_3$ in PhCl (not $PhNO_2$) at 50° removes the Pr^{β} from carvacrol, 5-acetyl-, -propionyl-, -*n*-butyryl-, -*iso*valeryl-, and -benzoyl-carvacrol, thymol, 6-acetyl-, -propionyl-, -*n*-butyryl-, -*iso*valeryl-, and -benzoyl-thymol to give 53—80% yields of the phenol or OH-ketone. The acyl group is also removed to a small extent. 4-*Hydroxy*-3-*methylpropio*-, m.p. 86°, -*butyro*-, m.p. 133°, and -iso*valerophenone*, m.p. 83°, and 4-*hydroxy*-2-*methyl*-*butyro*-, m.p. 104°, and -iso*valero*-*phenone*, m.p. 51°, b.p. 115—120°/0·008 mm., are described.

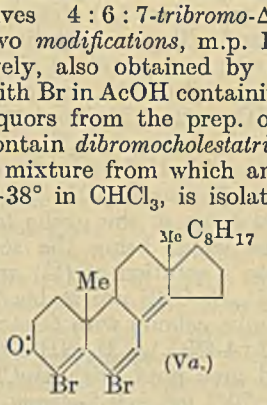
VII. Thymol with Br (4 mols.) in $CHCl_3$ in light gives a *Br*-derivative, m.p. 113°, and with CH_2Cl·COCl and $AlCl_3$ in $PhNO_2$ at 50° gives a 20—23% yield of 6-*chloroacetylthymol*, m.p. 133°, b.p. 175—178°/0·0018 mm. (*acetate*, m.p. 83°), sensitive to alkali, with much oily by-product. R. S. C.

Syntheses in the indene series. H. Simonis and G. Wojack (Ber., 1937, **70**, [*B*], 1837—1848).—Treatment of CHMeBz·CO_2Et with 96% H_2SO_4 at 100° affords 2-methylindandione (I), m.p. 85°, whereas with P_2O_5 2 : 2′-*dimethyliso*bindone (II), $C_6H_4<^{CO}_{CO}>$CMe·C$<^{C_6H_4}_{CMe}>$CO m.p. 198°, is produced, also formed when (I) is warmed with P_2O_5 or boiled with $POCl_3$. Its constitution is established by its formation from 3-*chloro*-2-*methylindone*, m.p. 61° (from CPhCl:CMe·CO_2H and 96% H_2SO_4 at 45—50°), and sodio-2-methylindandione. (II) gives a

p-*nitrophenylhydrazone*, m.p. 269°, and a p-*bromophenylhydrazone*, m.p. 222° (decomp.), and is converted by *p*-$C_6H_4Me{\cdot}NH_2$ and anhyd. $ZnCl_2$ in boiling EtOH into the *tri*-p-*tolil*, $C_{20}H_{14}(N{\cdot}C_6H_4Me)_3$, decomp. 240—250° after softening at 175°. (II) is transformed by PCl_5 in boiling CCl_4 and subsequently at 160° into the corresponding *dichloride*, m.p. 182°, converted by Cu powder in boiling EtOH into (II) and by HI (*d* 1·7) into *dihydro*-2 : 2′-*dimethylisobindone* (3-2′-methylindandionyl-2-methylindanone), m.p. 154°, also derived from (II), HI (*d* 1·7), and red P in boiling AcOH. 2 : 2′-*Dimethylisobindone dibromide* is obtained from (II) and Br in boiling CS_2 in sunlight. Fuming HNO_3 and (II) in boiling AcOH yield a *dinitrodimethylisobindone*, m.p. 167° (decomp.). Et *o*-toluoylmethylacetate and conc. H_2SO_4 give 2 : 4-*dimethylindan*-1 : 3-*dione* (III), m.p. 110°. The corresponding *p*-tolyl derivative affords 2 : 6-*dimethylindan*-1 : 3-*dione*, m.p. 112°, whereas the *m*-tolyl compound yields a *substance*, m.p. 87°. Et α-*m*-xyloylpropionate is converted into 2 : 4 : 6-*trimethylindan*-1 : 3-*dione*, m.p. 104°, whereas Et benzoylbenzylacetate with H_2SO_4 or P_2O_5 gives 2-benzoylindanone, m.p. 98°. The formation of benzylindandione could not be detected. *o*-$C_6H_4Me{\cdot}CO{\cdot}CHMe{\cdot}CO_2Et$ is converted into 2 : 2′ : 4 : 4′-*tetramethylisobindone*, m.p. 129° (p-*nitrophenylhydrazone*, m.p. 218°), also derived from (III), NaOEt–EtOH, and 3-*chloro*-2 : 4-*dimethylindone*, m.p. 107° (obtained from β-*chloro*-α-*o*-*dimethylcinnamic acid*, m.p. 103°). *p*-$C_6H_4Me{\cdot}CO{\cdot}CHMe{\cdot}CO_2Et$ and P_2O_5 at 140° afford 2 : 2′ : 6 : 6′-*tetramethylisobindone*, m.p. 193° (p-*nitrophenylhydrazone*, m.p. 251°), obtained also from 3-*chloro*-2 : 6-*dimethylindone*, m.p. 80° [from β-*chloro*-α-*methyl*-p-*methylcinnamic acid*, m.p. 108° (*Et* ester)], and 2 : 6-dimethylindandione. Et α-2 : 4-dimethylbenzoylpropionate and P_2O_5 give a cryst. mass which yields 2 : 4 : 6 : 2′ : 4′ : 6′-*hexamethylisobindone*-p-*nitrophenylhydrazone*, m.p. 232°. Similarly the resinous product from Et α-anisoylpropionate and P_2O_5 affords 6 : 6′-*dimethoxy*-2 : 2′-*dimethylisobindone*-p-*nitrophenylhydrazone*, m.p. 230—235° after softening. 2 : 2′-*Dichloroisobindone* has m.p. 224°.

H. W.

Bromination of Δ⁴-cholesten-3-one, cholestane-3 : 6-dione, and Δ⁴-cholestene-3 : 6-dione. A. Butenandt, G. Schramm, and H. Kudbus (Annalen, 1937, **531**, 176—208; cf. A., 1936, 1512).—The bromination of cholestenone is a complex process the final result of which depends greatly on the experimental conditions. A scheme for the probable course of the changes is given. Gradual addition of Br in AcOH to cholestenone (I) in Et_2O containing HBr gives 4 : 6 : 6-tribromo-Δ⁴-cholesten-3-one (II), m.p. 182—183° (decomp.) or m.p. 194° when very rapidly heated, also obtained from the stereoisomeric 4 : 6-dibromo-Δ⁴-cholesten-3-ones. (II) is unchanged by short warming with KOAc or Zn dust in EtOH. 4 : 6-Dibromo-Δ⁴·⁶-cholestadien-3-one (III), m.p. 183° (cf. Ruzicka *et al.*, A., 1936, 1382), is obtained by treatment of (I) in $CHCl_3$ with Br–AcOH at room temp., of (II) in EtOAc by conc. HBr, and from 4 : 4 : 5 : 6-tetrabromocholestanone by KOAc in EtOH–C_6H_6 or by HBr in Et_2O–AcOH at room temp.; it is unchanged when heated with Ac_2O. Gradual addition of Br in AcOH to (I) in $CHCl_3$ gives 4 : 6 : 7-*tribromo*-Δ⁴·⁶-*cholestadien*-3-*one* (IV), two *modifications*, m.p. 165—166° and 130° respectively, also obtained by treatment of (III) in Et_2O with Br in AcOH containing conc. HBr. The mother-liquors from the prep. of (IV) by the first method contain *dibromocholestatrienone* (V*a* or V*b*), probably a mixture from which an *individual*, m.p. 203°, $[\alpha]_D^{20}$ —38° in $CHCl_3$, is isolated; it is best obtained by



the action of Br in AcOH on (I) in Et_2O and is also derived from (IV), m.p. 165—166°, in $CHCl_3$ and conc. HBr–AcOH. It is stable towards quinoline at 185° and $NPhEt_2$ at 215°. It is unaffected by CH_2N_2, maleic anhydride in boiling xylene, Ac_2O, AcCl, AcOH + conc. HCl, $Hg(OAc)_2$ in EtOH, or by SeO_2 in AcOH or amyl alcohol. The *oxime* has m.p. 118°. (II) with NaI in boiling C_6H_6–EtOH gives 4-bromo-6-ethoxycholestenone (VI), m.p. 111°; if MeOH is used 4-bromo-6-methoxycholestenone, decomp. 101°, is produced. Debromination of (VI) by Zn dust in boiling C_6H_6–MeOH yields (?) 6-*ethoxycholestenone*, m.p. 109°. Cholestenedione Et ether, m.p. 163°, is produced by the action of HBr–AcOH in boiling EtOH on (IV). Cholestenedione (VII), m.p. 122—123°, is converted by Br in Et_2O–AcOH into 4 : 7-*dibromo*-Δ⁴-*cholestene*-3 : 6-*dione* (VIII), m.p. 174°, which yields a *diquinoxaline* derivative, m.p. 209°; it gives oils containing Br under the influence of $AgNO_3$ in C_5H_5N. Cholestanedione in $CHCl_3$ is converted by Br in $CHCl_3$ containing a little HBr–AcOH into (VIII). (VII) in AcOH with Br at 30—35° affords 4 : 7 : 7-*tribromo*-Δ⁴-*cholestene*-3 : 6-*dione* (IX), m.p. 195°, also obtained from (VIII). Gradual addition of (IX) in C_6H_6 to a boiling mixture of $NaHCO_3$, Zn dust, and EtOH gives cholestanedione (X) and coprostanedione (XI), similarly derived from (VIII); the respective *dioximes* have m.p. 216° and 143—144°. (XI) is isomerised to (X) in AcOH containing HCl at 100°. Bromination of (XI) in $CHCl_3$ containing HBr–AcOH gives (VIII). (IX) and $AgNO_3$ in C_5H_5N at room temp. afford 4 : 7-*dibromo*-Δ⁴·⁷-*cholestadiene*-3 : 6-*dione* (XII), m.p. 183°, reduced by Zn dust and AcOH to (X). Cautious treatment of (XII) with Zn dust and boiling EtOH gives 7-*bromo*-Δ⁴-*cholestene*-3 : 6-*dione*, m.p. 216°, transformed by Br in $CHCl_3$ into (XII). Fe powder and boiling EtOH convert (XII) into 7-*bromo*-Δ⁴·⁷-*cholestadiene*-3 : 6-*dione*, m.p. 182°, obtained also from (IX) in boiling C_5H_5N and brominated to (XII).

H. W.

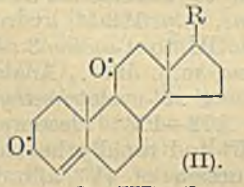
Oxidation of cholesterol and dehydroandrosterone by means of osmic acid. M. Ushakov and A. Lutenberg (Nature, 1937, **140**, 466).—Oxidation of cholesterol and dehydroandrosterone with OsO_4 yields *cis*-cholestanetriol, and *cis*-androstanonetriol, m.p. 243·5—244° (corr.; sinters at 242·5°), respectively.

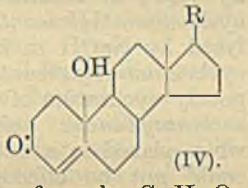
L. S. T.

Application of Darzens' reactions to dehydroandrosterone. A. Ercoli and L. Mamoli (Chim. e l'Ind., 1937, **19**, 435; cf. this vol., 294).—Dehydroandrosterone (I) and $CHCl_2{\cdot}CO_2Et$ (Mg–Hg) give the *dichloroacetate*, m.p. 198—199°, of (I). E. W. W.

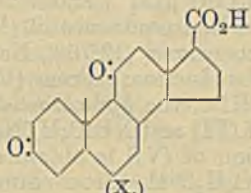
Sterols. XVIII. Preparation of *epiallo*pregnanolone from *allo*pregnanediol. R. E. Marker, O. Kamm, and D. M. Jones (J. Amer. Chem. Soc., 1937, **59**, 1595—1596).—A good yield of *epiallo*pregnan-3-ol-20-one is obtained from *allo*pregnanediol by esterifying the 3-OH thereof with Ac_2O–AcOH, oxidising the monoacetate with CrO_3, and separating and purifying the product by means of Girard's reagent and the H succinate. 4-Bromo-20-acetoxypregnan-3-one and KOAc–AcOH give 4 : 20-*diacetoxypregnan*-3-*one*, m.p. 247°. Hydrogenation (PtO_2; 3 atm.) of pregnanedione, m.p. 120°, in AcOH gives iso*pregnanediol*, m.p. 174° (*diacetate*, m.p. 111°). *allo*Pregnanonedicarboxylic acid (from *allo*pregnanedione and CrO_3–AcOH), m.p. 218°, when heated first with Ac_2O and then at 200—280°, and finally distilled at 2 mm., gives *pyro*all*opregnanedione*, $C_{20}H_{30}O_2$, m.p. 180°. R. S. C.

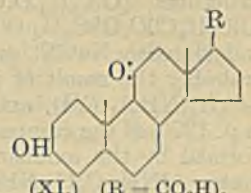
Adrenal cortex. III. Structures of compounds *A*, *B*, and *H*. H. L. Mason, W. N. Hoehn, B. F. McKenzie, and E. C. Kendall (J. Biol. Chem., 1937, **120**, 719—741; cf. this vol., 25).—Compound *A* (I) (A., 1936, 1117), new formula $C_{21}H_{28}O_4$, is probably (II) ($R = CO{\cdot}CH_2{\cdot}OH$). Com-

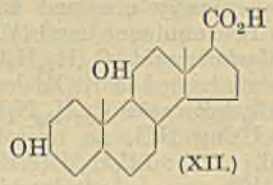

(II).

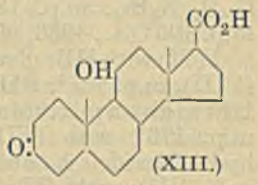

(IV).

pound *B* (III) (*loc. cit.*), new formula $C_{21}H_{30}O_4$, m.p. 177—180° (not 135—139°, cf. *loc. cit.*), $[\alpha]_D^{25}$ +222° (all rotations in EtOH) (contains 2 OH and 2 CO), is identified with corticosterone (this vol., 105), and is probably (IV) ($R = CO{\cdot}CH_2{\cdot}OH$). With HIO_4, (III) gives CH_2O and acid-2 (V) [formula (IV), $R = CO_2H$], new m.p. 253—258° (decomp.), new $[\alpha]_{5461}^{25}$ +218° (contains 2 active H and 1 CO). Acid-1 (VI) [formula (II), $R = CO_2H$], new m.p. 267—269° (*Me* ester, m.p. 178—179°; *mono-oxime*, m.p. 258—260°), from (I) and HIO_4, is also obtained from (V) and $K_2Cr_2O_7$–H_2SO_4 in $COMe_2$. Hydrogenation (Pd) of (I) gives *dihydro*-compound-*A*, $C_{21}H_{30}O_4$ (VII), m.p. 174—176°, $[\alpha]_{5461}^{25}$ +163°, and hydrogenation (Pd) of (III) a *dihydro*-compound-*B*, $C_{21}H_{32}O_4$ (VIII), m.p. 181—187°, $[\alpha]_{5461}^{25}$ +157°, further hydrogenated (PtO_2) to *hexahydro*-compound-*B*, $C_{21}H_{36}O_4$, m.p. 220—222·5°, $[\alpha]_{5461}^{25}$ +39°. Oxidation (HIO_4) of (VIII) gives *dihydro-acid*-2 (IX), m.p. 265—270°, $[\alpha]_{5461}^{25}$ +100° (*Me* ester, m.p. 170—171°). Reduction of (VI) is carried out in steps, and gives first (Pd in EtOH) *acid*-1*A*, $C_{20}H_{28}O_4$ (X), m.p. 272—273°, $[\alpha]_{5461}^{25}$ +114° (*mono-oxime*), then (PtO_2 in EtOH–NaOH), *acid*-1*B*, $C_{20}H_{30}O_4$ (XI), m.p. 272—274°, $[\alpha]_{5461}^{25}$ +78° (*Me* ester, m.p. 188—189°; no oxime obtained), and, finally (PtO_2–AcOH) *acid*-1*C* (XII), $C_{20}H_{32}O_4$, m.p. 284—286°, $[\alpha]_{5461}^{25}$ +71°. Alternatively (X) is obtained by action of $K_2Cr_2O_7$–H_2SO_4 on (IX) or on (XI) in $COMe_2$. Similar oxidation of (XII) gives *acid*-1*D* (XIII), $C_{20}H_{30}O_4$, m.p. 265—266°, $[\alpha]_{5461}^{25}$ +93° (*Me* ester, m.p. 170—171°), but the *acetate* of (XII) with CrO_3–AcOH gives the *acetate*, m.p. 210—213°, of (XI). With PCl_5 in $CHCl_3$, (XII) gives a *chloro-acid*, $C_{20}H_{31}O_3Cl$, m.p. 214—217° [*Me* ester, m.p. 128—130°, also obtained by chlorination of the *Me* ester of (XII)]. Filtrates from which (III) has been separated give a gum from which a *compound-H*, $C_{21}H_{32}O_4$ (XIV), m.p. 172—176°, $[\alpha]_{5461}^{25}$ +118°, oxidised (HIO_4) to CH_2O and (XI), and ($K_2Cr_2O_7$–H_2SO_4–$COMe_2$) to (X) (2 : 4-*dinitrophenylhydrazone*), is obtained. The annexed structures are proposed.


(X.)


(XI.) (R = CO_2H).
(XIV.) (R = $CO{\cdot}CH_2{\cdot}OH$).


(XII.)


(XIII.)

As hydrogenation of (I) and (III) largely destroys cortin activity, it is assumed that this is associated with the Δ^a-unsaturated ketone group. E. W. W.

Artostenone, a ketonic sterol from *Artocarpus integrifolia*. IV. Oxidation of artostenone. V. Platinichloride of artostenamine. Determination of carbon and hydrogen in stenones. VI. Constitution of artostenone. M. C. Nath (Z. physiol. Chem., 1937, **249**, 71—75, 76—78, 78—81; cf. this vol., 294).—IV. Artostenone (I) in $COMe_2$ with $KMnO_4$ in neutral or acid (H_2SO_4) aq. $COMe_2$ gives *diketoartostanic acid*, $C_{30}H_{50}O_4$, m.p. 136° (*dioxime*, m.p. 173°; *anilide* m.p. 140—141°), and with HNO_3, a nitrocarboxylic *acid*, $C_{11}H_{17}O_4N$, m.p. 157—159° (decomp.), containing two condensed rings. Artostanone in AcOH with CrO_3 gives a keto-*acid*, $C_{20}H_{30}O_3$ or $C_{21}H_{32}O_3$, m.p. 88—90°.

V. The oxime of (I) in EtOH with Zn and NaOH in EtOH gives *artostenamine*, m.p. 169—170° (*platinichloride*), which with AcOH and $NaNO_2$ gives artosterol. The magnitude of the differences between the C and H contents of such platinichlorides (II) of homologues renders (II) suitable for use in elementary analysis.

VI. (I) in EtOH with H_2SO_4 at 79° for 4 hr. gives *α-artostenone*, m.p. 99—100° (*oxime*, m.p. 193—194°; *CHPh*: compound, m.p. 89—90°). Dihydroartostenone (III) yields a *CHPh*: compound, m.p. 91—92°, but (I) does not. 1 mol. of (I) takes up 2 Br and 1 mol. of (III) 3 Br. (I) is an αβ-unsaturated ketone with the keto-group at $C_{(12)}$ and the double linking most probably at $C_{(9)}{=}C_{(11)}$. W. McC.

Unsaturated diketones related to the corpus luteum hormone.—See B., 1937, 980.

Dihydrofollicle hormone.—See B., 1937, 981.

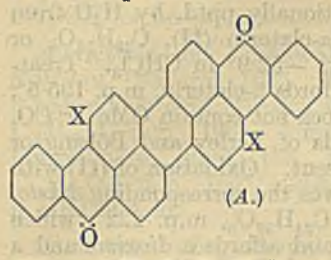
Quinhydrones. R. Ciusa and L. Brull (Gazzetta, 1937, **67**, 392—398).—Quinol (I) treated in EtOH with NaOEt and with benzoquinone (II) gives *disodium quinhydrone* $[O{:}C_6H_4{:}O,O'{\cdot}C_6H_4{\cdot}O']Na_2^{\cdot}$, violet, also obtained from quinhydrone and NaOEt, or from (II) and NaOEt. Chloroquinol (III) and chlorobenzoquinone (IV) similarly give *disodium dichloroquinhydrone*. From either (III) and (II), or (I) and (IV), a *disodium chloroquinhydrone* is obtained; it is not clear whether these are identical, or whether they have the different structures $[O{:}C_6H_4{:}O,O'{\cdot}C_6H_3Cl{\cdot}O']Na_2^{\cdot}$ and $[O{:}C_6H_3Cl{:}O,O'{\cdot}C_6H_4{\cdot}O']Na_2^{\cdot}$. Benzoquinoneanil (V) and (I) with NaOEt give a *compound* (12·76% Na), probably the result of partial reduction. From (V), p-$C_6H_4(NH_2)_2$ (VI), and aq. HBr, the *hydrobromide*, m.p. 127°, of the compound of (VI) and $NH{:}C_6H_4{:}NH$ [formed by the oxidising action of (V)] is obtained, thus: $[NH_2{\cdot}C_6H_4{\cdot}NH_2,NH{:}C_6H_4{:}NH_2{\cdot}]Br$. Similarly (V) and p-$C_6H_4(NHPh)_2$ give the dihydrobromide, $C_{36}H_{32}N_4Br_2$, m.p. 180°, previously obtained with m.p. 195° (A., 1936, 991). Benzoquinonedianil (VII) and (VI) with HBr give a *dihydrobromide*, $C_{24}H_{24}N_4Br_2$ (VIII), m.p. 188°, which when heated in EtOH loses HBr to give a mixture of the *hydrobromide*, $C_{24}H_{23}N_4Br$, m.p. 173°, with (VIII). Using HCl, an unstable hydrochloride is obtained. 1 : 2 : 5-$C_6H_3Me(NH_2)_2$ and (VII) with HBr or HCl give a *hydrobromide*, $C_{25}H_{26}N_4Br$, and a *hydrochloride*, m.p. 135°. Similarly p-$C_6H_4(NMe_2)_2$,2HCl and (VII) give a green *hydrochloride*, m.p. 125° (11·65% Cl). E. W. W.

Colouring matters of *Drosera Whittakeri*. V. Constitution of droserone. J. W. H. Lugg, A. K. Macbeth, and F. L. Winzor (J.C.S., 1937, 1597—1600).—The isolation of pure droserone (I) is described, and the measurement of its normal reduction potential supports the proposed structure, 2 : 5(or 2 : 8)-dihydroxy-1 : 4-naphthaquinone, and shows the close relationship to hydroxyjuglone (*diacetate*, m.p. 137°) and phthiocol. The 1 : 4-naphthaquinone structure of (I) is shown by the absorption spectra of its *acetate*, m.p. 119°. The absorption spectra of phthiocol and naphthapurpurin (*triacetate*, m.p. 164°) are discussed, showing their relationship to lawsone and hydroxydroserone respectively. F. R. S.

Friedel–Crafts reaction. II. Action of phthalic anhydride on acylarylamides. P. Kränzlein (Ber., 1937, **70**, [*B*], 1952—1963).—o-$C_6H_4(CO)_2O$ and 3 : 4-$C_6H_3Me_2{\cdot}NHAc$ react very slowly in CS_2, Et_2O, or C_6H_6 and slowly in $PhNO_2$ at 120—140°. In $C_2H_2Cl_4$ at 100—110° o-2′-*acetamido*-4′ : 5′-*dimethylbenzoylbenzoic acid* (I), m.p. 192°, is obtained in 68% yield. Conc. H_2SO_4 at 100° converts (I) into 1-*amino*-3 : 4-*dimethylanthraquinone* (II), m.p. 218·5°, with small amounts of o-2′-*acetamido*-4′ : 5′-*dimethylbenzoylbenzlactam* (III), $C_6H_4\langle{}^{CO{\cdot}NH}_{CO}\rangle C_6H_2Me_2$, m.p. 255—256°. Br in boiling AcOH transforms (II) into 2-*bromo*-1-*amino*-3 : 4-*dimethylanthraquinone*, m.p. 206·5°, which is transformed by CuCl and NaOAc in $PhNO_2$ at 180—190° into 3 : 4 : 3′ : 4′-*tetramethylindanthrene*; this does not give a vat. Similarly 2-acetamido-5 : 6 : 7 : 8-tetrahydronaphthalene and o-$C_6H_4(CO)_2O$ in $C_2H_2Cl_4$ at 70° afford o-2′-*acetamido*-4′ : 5′-cyclo*tetramethylenebenzoylbenzoic acid* (IV), m.p. 193°, and 5-acetamidohydrindene yields o-2′-*acetamido*-4′ : 5′-cyclo*trimethylenebenzoylbenzoic acid*, (V), m.p. 210°. Attempts to effect ring-closure with (IV) or (V) by H_2SO_4 alone or in presence of H_3BO_3 fail by reason of the more ready sulphonation. Acid chlorides, P_2O_5, or $AlCl_3$–NaCl are ineffective. Attempts to hydrolyse the NHAc groups by prolonged boiling with dil. HCl lead quantitatively to the *lactams* of (IV) and (V), m.p. 209° and 269°, respectively. The lactams are readily hydrolysed by NaOH–MeOH. Thereby (III) yields o-2′-*amino*-4′ : 5′-*dimethylbenzoylbenzoic acid*, m.p. 152° (decomp.) and after re-solidification, m.p. 285°; it is transformed into (II). o-2′-*Amino*-4′ : 5′-cyclo*tetramethylenebenzoylbenzoic acid*, m.p. 146·5°, is obtained similarly but its cyclisation is inhibited by sulphonation. Reduction of (IV) by Zn and NH_3 or preferably by H_2 at 170°/40 atm. in neutral or somewhat alkaline solution in a Ni bomb yields o-2′-*acetamido*-4′ : 5′-cyclo*tetramethylenebenzylbenzoic acid*, m.p. 220°, which with conc. H_2SO_4 at 40—45° gives 1-*acetamido*-3 : 4-cyclo*tetramethyleneanthrone*, m.p. 283° after softening and darkening at 280°; this is oxidised by H_2O_2 in alkaline solution to 1-*acetamido*-3 : 4-cyclo*tetramethyleneanthraquinone*, m.p. 192·5°, hydrolysed by NaOH in boiling MeOH to 1-*amino*-3 : 4-cyclo*tetramethyleneanthraquinone*, m.p. 189°. Analogously cyclisation of o-2′-*amino*-4′ : 5′-cyclo*trimethylenebenzoylbenzoic acid*, m.p. 172—173° (decomp.) when placed in a bath at 165° and rapidly heated, could not be effected. Reduction of (V) affords o-2′-*acetamido*-4′ : 5′-cyclo*trimethylenebenzylbenzoic acid*, m.p. 238°, whence successively 1-*acetamido*-3 : 4-cyclo*trimethyleneanthrone*, m.p. 277—278° after darkening at 272° and softening at 274°, 1-*acetamido*-3 : 4-cyclo*trimethyleneanthraquinone*, m.p. 212°, and 1-*amino*-3 : 4-cyclo*trimethyleneanthraquinone*, m.p. 212·5°. NHPhAc, *o*-, *m*-, and p-$C_6H_4Cl{\cdot}NHAc$, 3 : 4-, 2 : 4-, and 2 : 5-$C_6H_3Cl_2{\cdot}NHAc$, and p-$NH_2{\cdot}C_6H_4{\cdot}NHAc$ do not react with $C_6H_4(CO)_2O$ and $AlCl_3$ in $C_2H_2Cl_4$. m-$C_6H_4Me{\cdot}NHAc$ is transformed mainly into o-2′-*acetamido*-4′-*methylbenzoylbenzoic acid* (VI), m.p. 184°, transformed by prolonged boiling with dil. HCl into the corresponding *lactam*, m.p. 268°, with a smaller amount of o-4′-*acetamido*-2′-*methylbenzoylbenzoic acid*, m.p. 241°, which with conc. H_2SO_4 at 130° affords 2-*amino*-4-*methylanthraquinone*, m.p. 265°. Similarly (VI) yields 1-*amino*-3-*methylanthraquinone*, m.p. 193°. H. W.

Regularities of substitution in polynuclear vat dyes. I. Constitution of a dichloro*iso*violanthrone and preparation of some *Bz*-2 : *Bz*-3′-*iso*violanthrone derivatives. II. Dinitro- and diamino-*iso*violanthrones of the *Bz*-2 : *Bz*-2′-series. T. Maki and Y. Nagai (Ber., 1937, **70**, [*B*], 1867—1872; 1872—1874).—I. Treatment of *iso*violanthrone suspended in $PhNO_2$ with SO_2Cl_2 at

room temp. and then at 60° gives violet trichloro*iso*violanthrone, chlorodihydroxy*iso*violanthrone, and Bz-3 : Bz-3′-*dichloro*iso*violanthrone* (I) (*A*; X = Cl). (I) with KOH–MeOH at 165°/18 atm. or with 25% NH_3 and Cu powder at 200°/48 atm. gives respectively Bz-3 : Bz-3′-*dimethoxy*- (II) and Bz-3 : Bz-3′-*diamino*- (III) -iso*violanthrone*. The constitution of (I), (II), and (III) follows from the observation that each yields a blue vat which is regarded as characteristic of dibenzanthrone or *iso*dibenzanthrone derivatives disubstituted in the *Bz* nuclei. Further, oxidation of (I) with CrO_3–H_2SO_4 causes almost complete removal of Cl and production of Bz-2 : 3-Bz-2′ : 3′-iso*violanthrone-diquinone*. Again (I), (II), and (III) dissolves so readily in alkaline $Na_2S_2O_4$ that vat formation takes place at 40—50° whereas *iso*violanthrone disubstituted in the *o*- or *m*-position to CO yields vats with greater or less difficulty on account of steric hindrance. The two Cl of (I) are readily replaced by OMe or NH_2, whereas Cl in β-position of the anthraquinone nucleus reacts with difficulty. 8 : 8′-Dimethoxy*iso*violanthrone is a red-violet vat dye whereas (II) gives considerably darker, violet-blue shades on cotton. Bz-2 : Bz-2′-*Dimethoxy*iso*violanthrone* is described.



(*A*.)

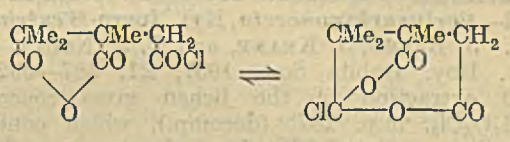
II (cf. A., 1936, 338). *iso*Violanthrone suspended in AcOH is converted by HNO_3 (*d* 1·48) at 60° into Bz : 2-Bz : 2′-*dinitro*iso*violanthrone*, reduced by $Na_2S_2O_4$ and NaOH to Bz : 2-Bz : 2′-*diamino*iso*violanthrone*. The greenish-blue shades of the latter on cotton become grey or fast black when the material is treated with NaOCl; warming with NaOH–$Na_2S_2O_4$ on exposure to air reproduces the blue-green colour. The black dye is regarded as *Bz* : 2-*Bz* : 2′-*iso*violanthrone in which a N_2 group is present either as an intramol. bridge or 2 N_2 groups are distributed between two *iso*violanthrone mols.

H. W.

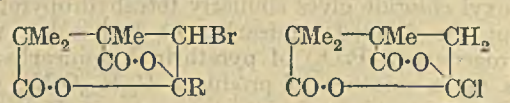
Synthetic cyperones and their comparison with α- and β-cyperones. P. S. Adamson, F. C. McQuillin, R. Robinson, and J. L. Simonsen (J.C.S., 1937, 1576—1581).—Application of different processes has given cyperones structurally identical with α- and β-cyperones. The respective oximes, semicarbazones, and 2 : 4-dinitrophenylhydrazones of the natural and synthetic ketones exhibit undepressed m.p. on admixture and closely resemble each other in most respects. They show, however, certain optical and crystallographic divergencies, so that complete identity is not claimed. $CH_2Cl{\cdot}CH_2{\cdot}CO_2Et$ and $NHEt_2$ give 1-*diethylaminopentan*-3-*one*, b.p. 84°/13 mm., the methiodide of which with *l*-dihydrocarvone and $NaNH_2$ affords 1-*methyl*-1-*γ-ketoamyl*-4-iso*propenyl*cyclo*hexan*-2-*one*, m.p. 103°. Cyclisation of this compound with NaOEt yields 1 : 10-*dimethyl*-7-iso*propenyl*-$\Delta^{1(9)}$-*octal*-2-*one* (I), b.p. 160—163°/11 mm. $[\alpha]_{5461}$ +88° [*oxime* (O_α), m.p. 144°; *semicarbazone* (O_α), m.p. 202°, $[\alpha]_{5461}$ +91·5° in $CHCl_3$], and with H_2SO_4 leads to the *isomeride*, b.p. 130°/1 mm., $[\alpha]_{5461}$ +342° [*oxime* (O_β), m.p. 152—153°, $[\alpha]_{5461}$ +147° in EtOH; *semicarbazone* (O_β), m.p. 204° (decomp.), $[\alpha]_{5461}$ +201° in EtOH; 2 : 4-*dinitrophenylhydrazone*, m.p. 226°]. *l*-Dihydrocarvone, $NaNH_2$, and $CH_2Cl{\cdot}CH_2{\cdot}CO_2Et$ give *Et* 1-*methyl*-4-iso*propenyl*cyclo*hexan*-2-*one*-1-β-*propionate* (II), b.p. 181—182°/13 mm., $[\alpha]_{5461}$ −10·65° in $CHCl_3$, which with $Et_2C_2O_4$ followed by loss of CO affords *Et* 3-*carbethoxy*-1-*methyl*-4-iso*propenyl*cyclo*hexan*-2-*one*-1-β-*propionate*, b.p. 170—175°/3 mm., $[\alpha]_{5461}$ −29·4° in $CHCl_3$ (*semicarbazone*, m.p. 147—148°). This ester is hydrolysed to the acid (*semicarbazone*, decomp. 192—193°), re-esterified to (II). $CHMeBr{\cdot}CO_2Et$ and (II) yield the β-form of (I), b.p. 173—175°/14 mm., $[\alpha]_{5461}$ +111·7°, purified through the *semicarbazone* (B_β), decomp. 209—210° [*oxime* (B_β), m.p. 141—144°, $[\alpha]_{5461}$ +112° in EtOH; 2 : 4-*dinitrophenylhydrazone*, m.p. 225—227°]. Reduction (Na) of this compound gives *ακ-dimethyl*-η-iso*propenyldecal*-β-*ol*, b.p. 160°/12 mm. (3 : 5-*dinitrobenzoate*, m.p. 150—152°), dehydrated to an impure *hydrocarbon*, b.p. 148°/22 mm., $[\alpha]_{5461}$ +47·0°.

F. R. S.

Desmotropic rearrangements of camphoronic acid derivatives. Constitution of camphoranic and *iso*camphoranic acids. J. Bredt [with F. Demeure (J. pr. Chem., 1937, [ii], **149**, 153—163).—α- (I) and β-Camphoronyl chloride (II) with HCO_2H give anhydrocamphoronic acid (III) and with piperidine give a *piperidide*, m.p. 131·5—132·5°, probably that of (III). Reactions of (I) and (II) and of their Br-derivatives and of camphoranic and *iso*camphoranic acid, regarded as *cis*- and *cis-trans*-isomerides, $CMe_2{<}\begin{matrix}CMe(CO_2H)\\CO\end{matrix}{-\!-\!-}\begin{matrix}\\O\end{matrix}{>}CH{\cdot}CO_2H$, are discussed on the basis of desmotropic rearrangement of the chlorides, as annexed.



The following formulæ are assigned: liquid Me_2 camphoronate $CO_2Me{\cdot}CMe_2{\cdot}CMe(CO_2H){\cdot}CH_2{\cdot}CO_2Me$; Me α- and β-anhydrocamphoronate $O{<}\begin{matrix}CO{\cdot}CMe_2\\CO{\cdot}CMe{\cdot}CH_2{\cdot}CO_2Me\end{matrix}$ and $\begin{matrix}CO_2Me{\cdot}CMe_2{-\!-\!-}CO\\CMe{\cdot}CH_2{\cdot}CO\end{matrix}{>}O$, respectively; Me camphoronate, m.p. 141—142°, $CO_2Me{\cdot}CMe_2{\cdot}CMe(CO_2H){\cdot}CH_2{\cdot}CO_2H$; (III) $O{<}\begin{matrix}CO{\cdot}CMe_2\\CO{\cdot}CMe{\cdot}CH_2{\cdot}CO_2H\end{matrix}$; bromoanhydrocamphoronic acid, m.p. 154°, $O{<}\begin{matrix}CO{\cdot}CMe_2\\CO{\cdot}CMe{\cdot}CHBr{\cdot}CO_2H\end{matrix}$, and its chloride, m.p. 168° (IV; R = Cl), and α-Me ester, m.p. 100° (IV; R = OMe), and β-Me ester, m.p. 142°, $\begin{matrix}CO_2Me{\cdot}CMe_2{\cdot}CMe{-\!-\!-}CO\\CHBr{\cdot}CO\end{matrix}{>}O$; α-anhydrocamphoronyl chloride (V).



R. S. C.

Bornyl and menthyl *tert.*-butylacetates.—See B., 1937, 1134.

Water-soluble ligninsulphonic acid from an extracted oak lignin. H. Hibbert and W. H. Steeves (J. Amer. Chem. Soc., 1937, 59, 1768).—Acetylation and hydrolysis of solvent-extracted oak wood meal gives a $CHCl_3$-sol. (10%) (OMe 23·6%) and -insol. (90%) lignin (OMe 20·6%), sol. in aq. $NaHSO_3$ at 100—125°; the sulphonic acid with NaOH gives 4·6% of vanillin and syringaldehyde. R. S. C.

Lignin. IX. Sulphonation of lignin. H. Friese and E. Clotofski (Ber., 1937, 70, [*B*], 1986—1989).—The product of the action of H_2SO_4–Ac_2O–AcOH on Ca ligninsulphonate [obtained by the action of $Ca(HSO_3)_2$ on lignin (I)] is the *salt*, $C_{36}H_{41}O_{20}S_2Ca$, closely analogous to the compound, $C_{36}H_{39}O_{21}S_2Ba$ (II), derived directly from (I) and H_2SO_4–Ac_2O–AcOH. A portion of the unsaturated linkings of (I) is unaffected by $Ca(HSO_3)_2$ but is sensitive to H_2SO_4. The presence of an aromatic ring in lignin would be expected to cause a much more energetic action with H_2SO_4 leading to a more highly sulphonated product. $Ca(HSO_3)_2$ has no action on (II) at 135°. Nitrolignin is not sulphonated by H_2SO_4–AcOH–Ac_2O but the presence of a sugar residue becomes evident during the change. H. W.

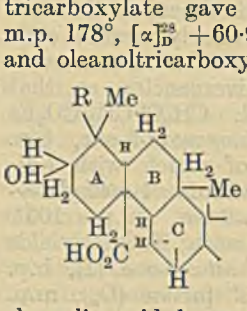
Catalytic isomerisation of the acids of pine oleo-resin and rosin. E. E. Fleck and S. Palkin (J. Amer. Chem. Soc., 1937, 59, 1593—1595).—Isomerisation of *l*-abietic acid (I) by various common catalysts, mostly at 250°, is recorded. Pd–C is the most effective, giving α-pyroabietic acid, $[\alpha]_D^{23}$ about +53°, from (I), α- and β-pimaric and the sapinic acids, and various resins. The reaction is much faster than when heat alone is applied. R. S. C.

Chemical constituents of lichens found in Ireland—*Pertusaria concreta*, Nyl., form *Westringii*, Nyl. J. Breen, J. Keane, and T. J. Nolan (Sci. Proc. Roy. Dublin Soc., 1937, 21, 587—592).—Et_2O extraction of the lichen gives *concretin*, $C_{14}H_7O_5Cl_3$, m.p. 287° (decomp.), which contains 3 readily acetylated OH (*Ac*$_3$ derivative, m.p. 220—222°) and is methylated with difficulty by CH_2N_2 to a *Me*$_3$ derivative, m.p. 200—202°. Extraction of the residue with boiling $COMe_2$ yields mannitol and norstictic acid, m.p. 267° (decomp.). P. G. M.

Constituents of pyrethrum flowers. IX. Optical rotation of pyrethrolone and the partial synthesis of pyrethrins. H. L. Haller and F. B. LaForge (J. Amer. Chem. Soc., 1937, 59, 1678—1681).—Pyrethrolones, obtained from pyrethrins I and II, are identical, being dextrorotatory in both cases. Pyrethrolone and Me chrysanthemumcarboxylate-carboxyl chloride, b.p. 88—92°/0·2 mm., yield an oil, which gives no cryst. semicarbazone, but tetrahydropyrethrolone gives tetrahydropyrethrin II, identified as semicarbazone. Chrysanthemumcarboxyl chloride gives similarly tetrahydropyrethrin I, but the derived semicarbazone had a low m.p. Hydrogenation (PtO_2) of pyrethrin I semicarbazone gives (?) a mixture of products, $C_{22}H_{35}O_3N_3$, m.p. 82—84°. R. S. C.

α-Elaterin. L. Reichel and K. H. Eisenlohr (Annalen, 1937, 531, 287—296).—Elaterin (I) (Merck), from *Ecballium Elaterium*, is extracted with light petroleum and then fractionally pptd. by H_2O from dioxan, thereby giving α-elaterin (II), $C_{23}H_{32}O_6$ or $C_{24}H_{34}O_6$, m.p. 234°, $[\alpha]_D^{23}$ −52·9° in $CHCl_3$. Treatment of (I) with PhMe affords β-elaterin, m.p. 195·5°, in small amount. (II) does not contain OMe or CO. According to the methods of Verley and Bölsing or Zerevitinov 2 OH are present. Oxidation of (II) with Ag_2O in boiling $CHCl_3$ gives the corresponding *diketo*-compound, $C_{23}H_{30}O_6$ or $C_{24}H_{32}O_6$, m.p. 222°, which reddens fuchsin–H_2SO_3, and affords a *dioxime* and a *mono-p-nitrophenylhydrazone*. The OH groups are therefore *sec.* Amorphous, ill-defined compounds are obtained from (II) and BzCl, *p*-$C_6H_4Me{\cdot}SO_2Cl$, diphenylcarbamyl chloride, PCl_5, or $SOCl_2$. Titration of (II) with 0·1N-KOH shows the presence of 1 lactone ring and treatment with 2N-KOH establishes that of 1 Ac, thus accounting for the 6 O. Distillation of (II) with Zn dust gives 1 : 4-$C_{10}H_8Me_2$, also obtained by use of Se; hence (II) is derived from a hydronaphthalene. Quaternary Me is absent since dehydrogenation of (II) by S does not give MeSH. With $C(NO_2)_4$ (II) gives a distinct yellow colour. Bromination is accompanied by loss of HBr; it yields amorphous products from which fractions, decomp. 172° and 142°, respectively, have been separated. Hydrogenation (PtO_2 in AcOH) of (II) gives an amorphous H_6-derivative, transformed by Se at 320° into 1 : 4-$C_{10}H_6Me_2$ and other substances. Ozonisation of (II) affords AcOH, $COMe_2$, and HCO_2H establishing the presence of :CHMe, :CMe_2, and :CH_2 in the side-chains. H. W.

Constitution of acid sapogenins. XIII. Hederagenin and oleanolic acid. Z. Kitasato [with H. Shishido] (Acta Phytochim., 1936, 10, 199—210; cf. A., 1936, 1261).—Oleanonic acid monobromolactone with CrO_3 in AcOH–H_2SO_4 gave (*a*) the *monobromolactone* of *oleanintricarboxylic acid*, m.p. 270° (decomp.). This is converted by CH_2N_2 into the *Me*$_2$ ester, m.p. 190°, which with Zn–AcOH gave *Me*$_2$ *oleanintricarboxylate*, m.p. 203—205°, $[\alpha]_D^{28}$ +57·3° in $CHCl_3$. The free *acid* has m.p. 289—290° (decomp.), and the *Me*$_3$ ester, m.p. 167—169°, the latter with KOH–MeOH giving a neutral *product*, $C_{28}H_{44}O_3$, m.p. 181—183°, $[\alpha]_D^{28}$ +159·4° in $CHCl_3$ (*oxime*, m.p. 215—216°); (*b*) the monobromolactone of oleanoltricarboxylic acid which on reduction and methylation as above gave *Me*$_3$ *oleanoltricarboxylate*, m.p. 183°, $[\alpha]_D^{28}$ +73·3° in $CHCl_3$. Me_3 keto-oleanintricarboxylate gave a neutral *product*, $C_{28}H_{42}O_4$, m.p. 178°, $[\alpha]_D^{28}$ +60·9° in $CHCl_3$, with KOH–MeOH, and oleanoltricarboxylic acid gave an *acid*, $C_{32}H_{50}O_6$, m.p. 222—224°. The lactone of Me_2 acetyloleanoldicarboxylate (A., 1936, 1262) is converted by treatment with HBr–AcOH into an isomeric form, m.p. 267—270° (decomp.), which with CH_2N_2 gave a Me_2 ester, m.p. 269—270°, identical with that from the lactone of ketoacetyloleanolic acid by oxidation and methylation. The results fix the structure of the A, B, and C rings as shown, and the structure of the D and E rings is



discussed. Here R = Me for oleanolic acid and CH_2·OH for hederagenin. P. W. C.

Structure of β-boswellinic acid. J. C. E. Simpson (Nature, 1937, **140**, 467).—Oxidation of β-boswellinic acid (I) with CrO_3 yields a *monoketone*, $C_{29}H_{46}O$, m.p. 196°. Similar oxidation of Me β-boswellinate gives the corresponding *keto-ester*, $C_{31}H_{48}O_3$, m.p. 160° (*oxime*, m.p. 200°). Thus (I) is a β-OH-acid. L. S. T.

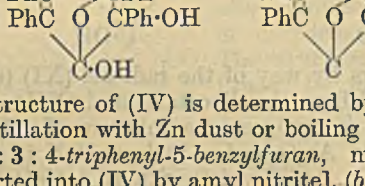
Structure of gossypol. I. K. N. Campbell, R. C. Morris, and R. Adams. **II. Acylation.** R. F. Miller, D. J. Butterbaugh, and R. Adams. **III. Gossypol ethers.** R. C. Morris and R. Adams. **IV. Anhydrogossypol and its derivatives.** R. F. Miller and R. Adams (J. Amer. Chem. Soc., 1937, **59**, 1723—1728, 1729—1731, 1731—1735, 1736—1738).—I. Gossypol (I), $C_{30}H_{30}O_8$, exists in *forms*, m.p. 184° (from Et_2O), 199° (from $CHCl_3$), and 214° (from ligroin), respectively, and in a red *form*, m.p. 184—185° (photomicrographs), shown by *X*-ray examination to be cryst., forms 1 : 1 *compounds* with AcOH, m.p. 187°, HCO_2H, m.p. 197—198°, $EtCO_2H$, m.p. 177—178°, and $Pr^{\alpha}CO_2H$, m.p. 159—160°, and with $SnCl_4$ gives a *complex* containing 1 Sn and 2 Cl. Its isolation is improved. Colour reactions are described.

II. The prep. of the white, m.p. 276—279° (decomp.; sinters at 265°), and yellow hexa-acetates, m.p. 184—186° (decomp.; sinters at 138°), is improved. The former with Ac_2O–NaOAc gives the latter. With conc. H_2SO_4 both or with $Ba(OMe)_2$ the latter yield (I). Tetra-acetylgossypolone is obtained in 57% yield from the white, but only in 7% yield from the yellow, form. Ozonisation of the white form gives a substance, $C_{19}H_{20}O_8$, m.p. 140°. A *hexabenzoate*, m.p. 202—204° (decomp.), is obtained.

III. Me_2SO_4 containing 25% of H_2SO_4 converts (I) into a red *Me_6 ether* (II), m.p. 158—160° after sintering at 140°, giving in H_2SO_4 an orange colour, hydrogenated to an autoxidisable, colourless H_2-derivative, which could not be isolated, and unaffected by hot 40% aq. KOH, 30% KOH–EtOH, *o*-$C_6H_4(NH_2)_2$, or NHPh·NH_2. With Me_2SO_4 in MeOH a colourless *Me_4 ether* (III), *forms*, m.p. 259° (decomp.) and 190°, respectively, is obtained, which gives a scarlet colour with H_2SO_4, is indifferent to CH_2N_2, alkali, and $FeCl_3$, but is readily oxidised, and gives a *Ac_2* derivative, m.p. 264—265° [by further acetylation affords a (?) dehydration product, m.p. about 188° after sintering at 140°; hydrolysed to (III) by KOH–EtOH]. Addition of KOH–MeOH to (I) in Me_2SO_4 gives a mixture of (II) and (III). Addition of Me_2SO_4 to (I) in KOH gives a white *Me_6 ether* (IV), *forms*, m.p. 235—237° and 221°, respectively, which gives an orange colour in H_2SO_4 and resembles (II) in properties, but with Ac_2O–NaOAc gives a product, m.p. 179—181° after sintering at 160°. Gradual addition of $Na_2S_2O_4$ to (II) in MeOH gives a (?) *H_2*-derivative, m.p. 110—126°, converted by KOH–MeOH in N_2 into (IV), which regenerates (II) when an excess of 25% NaOH is added to its solution in conc. H_2SO_4. Addition of 25% NaOH to (I) in Et_2SO_4–H_2SO_4 gives a *Et_6 ether* (V), m.p. 128—130° after sintering at 118°; addition of KOH–EtOH to (I) in Et_2SO_4–EtOH gives a *Et_6 ether*, *forms*, m.p. 211—212° and 231—232°, respectively.

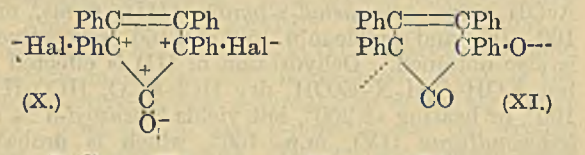
IV. Anhydrogossypol, $C_{30}H_{26}O_6$, m.p. 230°, best obtained from (I) by C_5H_5N,HCl in boiling PhMe, probably contains 2 OH (Zerevitinov), with Ac_2O gives a mixture of the two hexa-acetates of (I), regenerates (I) very readily in cold, dil. acids, and affords (II) or (IV) (according to the conditions of methylation) and (V) even in anhyd. media; in liquid NH_3 it gives *diaminogossypol* (VI), $C_{30}H_{32}O_6N_2$, m.p. 228—230° after decomp. at 187—195° (unstable *hydrochloride*), also obtained similarly from (I) and giving with Ac_2O–NaOAc a NN′-*Ac_2 tetra*-O-*acetate*, m.p. 282° (decomp.), and hydrolysed even by warm dil. AcOH to (I). Probably (I) is a symmetrical mol., containing 2 enolic OH; in anhydrogossypol these and two other OH lose 2 H_2O to give C·C·O·C rings, and (VI) probably contains two C·C·NH_2. R. S. C.

Heteropolarity. XXX. Oxidation and reduction products of tetracyclone. R. Pütter and W. Dilthey (J. pr. Chem., 1937, [ii], **149**, 183—216; cf. this vol., 425).—Tetracyclone (tetraphenyl-*cyclo*pentadienone) (I) is converted by various reactions into furan and α-pyrone derivatives. 65% HNO_3 in AcOH or, better, dioxan converts (I) into 2 : 5-*dihydroxy*-2 : 3 : 4 : 5-*tetraphenyl*cyclo*pentenone* (II), m.p. 191—192° [2 active H (Zerevitinov)]; in AcOH some *tetraphenyl-α-pyrone* (III), *forms*, m.p. 166—167° and double m.p. 158° and 166°, respectively, is also obtained. Dehydration of (II) is effected by hot KOH–C_5H_5N–EtOH, dry HCl–Et_2O, HCO_2H at 100°, or heating at 200°, but yields 2-*benzoyl*-3 : 4 : 5-*triphenylfuran* (IV), m.p. 166°, which is probably formed by way of the half-acetal (V) and radical (VI).

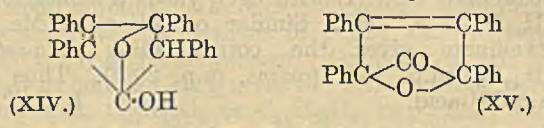


The structure of (IV) is determined by (*a*) reduction by distillation with Zn dust or boiling with HI–red P to 2 : 3 : 4-*triphenyl*-5-*benzylfuran*, m.p. 163° [reconverted into (IV) by amyl nitrite], (*b*) conversion by MgPhBr into *diphenyl*-1-2 : 3 : 4-*triphenylfurylcarbinol*, unstable, m.p. 179° (*perchlorate*, m.p. 267°, a coloured carbenium salt, which with H_2O_2–AcOH–Ac_2O gives a colourless *hydroperoxide*, m.p. 235—238°), (*c*) Beckmann rearrangement of the *oxime*, m.p. 230° (formed only slowly), by PCl_5 in Et_2O into 2-*chloro*-3 : 4 : 5-*triphenylfuran*, m.p. 168° (stable to AgOAc), (*d*) reduction by Zn dust in AcOH to αβ-*diphenyl*-αβ-*di*-2-3 : 4 : 5-*triphenylfurylethylene* (VII), m.p. 233° (green halochromy in H_2SO_4), and by Al–Hg in KOH–EtOH to 2-3 : 4 : 5-*triphenylfurylbenzyl alcohol* (VIII), m.p. 176—177° (red halochromy in H_2SO_4; *acetate*, m.p. 180—181°). Br adds as ions to (VII) in $CHCl_3$, giving a bluish-green solution, which soon becomes colourless when EtOH is added, owing to formation of the pinacone; disproportionation then gives (IV), but the (VIII) formed could not be isolated. The compound, m.p. 193°, considered by Kohler and Jones (A., 1919, i, 533) to be 2 : 4-diphenyl-5-benzylfuran, is probably by analogy αβ-*diphenyl*-αβ-*di*-2-3 : 5-*diphenylfurylethylene*. The colourless product (Dilthey *et al.*, A., 1934, 297), intermediate in the form-

ation of (I), is $C_{58}H_{42}O_2$, gives with Br HBr and a coloured solution, which is decolorised by EtOH and then gives (IV); by analogy with (VII) it is thus *αβ-diphenyl-αβ-di-2-3 : 4 : 5-triphenylfurylethane*; this is confirmed by its conversion by SeO_2 into (VII); it is unaffected by HI–P or Na–Hg in PrOH, but, when distilled with Zn dust, gives triphenylbenzylfuran. (III), best obtained from (I) by H_2O_2–Ac_2O–AcOH, with MgPhBr, followed by $HClO_4$, gives pentaphenylpyrenium perchlorate, m.p. 195°, identified by conversion by NH_3 into pentaphenylpyridine, and obtained also from (II) by MgPhBr. C_6H_4Me·MgBr converts (III), but not (II), into 3 : 4 : 5 : 6-*tetraphenyl-2-tolylpyrenium perchlorate*, m.p. 297°. In cold KOH–EtOH (III) instantly gives a coloured solution, probably containing CPh<CPh·CPh(OH) / CPh=C(OK)>O, from which it is recovered by CO_2, but heating with alkali causes decomp. With soda-lime at 200° (III) gives tetraphenylfuran (IX). With Cl_2 in cold C_6H_6 (I) gives a (? 2 : 5-)*dichloride*, m.p. 206°, which with alkali or Ag_2O or when dissolved in conc. H_2SO_4 or heated alone regenerates (I) and with AgOAc in AcOH gives (III); these reactions are undergone also by the known dichloride, m.p. 188°, and the dibromide, and are due the accumulation of positive charges, as in (X); the second reaction



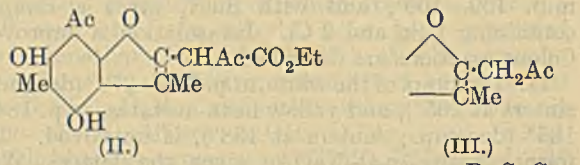
probably occurs by way of the radicals (XI) (formed by loss of Ac_2O from the diacetate) and (XII). With hot Ac_2O (II) rearranges to a mixture of (III) and (IV); with cold Ac_2O and a little C_5H_5N it gives a *monoacetate*, m.p. 145°, which with HCl–MeOH gives (III) only, but with HCl–Et_2O, hot HCO_2H, or hot KOH–EtOH, or, when heated above the m.p., gives (IV) by way of coloured products; the former change probably occurs by way of (XIII), the O in position 2 penetrating into the ring between $C_{(1)}$ and $C_{(2)}$; the latter change is best explained by (VI) and it remains undecided whether (II) is not rather the 2 : 3-$(OH)_2$-compound or the half-acetal (XIII). $Pb(OAc)_4$ with (II) gives an 80% yield of 2-*benzoyloxy-3 : 4 : 5-triphenylfuran*, m.p. 114°, which with NHPh·NH_2 gives NHPh·NHBz and with 3% HCl–MeOH gives 2-*hydroxy-3 : 4 : 5-triphenylfuran*, m.p. 125°; this or its benzoate with MgPhBr gives (IX). The colourless "hydrate" of (I), obtained from Bz_2 and $CO(CH_2Ph)_2$ in the cold or from MgPhBr and CPh<CPh— / CO·O>C:CHPh, is formulated as (XIV), since the known and the following reactions demand sometimes the structure, 3-hydroxy-2 : 3 : 4 : 5-tetraphenyl-Δ^4-*cyclo*pentenone, and sometimes 2-hydroxy-5-benzylidene-2 : 3 : 4-triphenyl-2 : 5-dihydrofuran. With SeO_2 in aq. AcOH (XIV) gives a little (IV), with Cl_2 in C_6H_6 at 50° HCl and 2-*chloro-5-hydroxy-2 : 3 : 4 : 5-tetraphenyl-*Δ^3-*cyclopentenone*, m.p. 206°, which with AgOAc gives (III), with KOH–EtOH yields 20% of (I), with Zn dust and AcOH gives tetraphenyl*cyclo*pentenone, and loses HCl to $NaHCO_3$ in hot MeOH



to yield 2 : 5-*oxido-2 : 3 : 4 : 5-tetraphenyl-*Δ^3-*cyclopentenone* (XV), m.p. 149°; this is unstable in light, yielding (in $COMe_2$) (III), which is also obtained by heating at 160° or treating with HCl in Et_2O.

R. S. C.

Constitution of usnic acid. Y. Asahina, S. Mayeda, and M. Yanagita (Proc. Imp. Acad. Tokyo, 1937, **33**, 270—271).—Usnic acid (I) in abs. EtOH at 150° gives *Et acetousnetate* (II), m.p. 150°, the structure of which is proved by alkaline fission to usnetic acid and AcOH or acetousnetol (deacetyldecarboxyusnic acid) (III), m.p. 197—198°, and CO_2. This proves the position of the CO_2H in the side-chain and the pyronone formula for (I).



R. S. C.

Anthocyanins. II. Pigment of red autumn leaves of species of *Acer*. S. Hattori and K. Hayashi. **III. Pigment of the scarlet blossoms of *Lycoris radiata*.** K. Hayashi (Acta Phytochim., 1937, **10**, 129—138, 139—146; cf. A., 1936, 1307).—II. Extraction of the autumn leaves of *A. circumlobatum*, Maxim (1759 g.), and of *A. ornatum*, Carr., var. *Matsumuræ* (247 g.), with 1% HCl–MeOH, treatment of the extract with basic Pb acetate and of the Pb salt with 5% HCl–MeOH followed by pptn. of the filtrate with Et_2O leads to the separation of 50 and 10 mg. respectively of a *pigment* [*picrate*, m.p. 173° (decomp.)], which on hydrolysis gave an aglucone closely resembling cyanidin chloride. The pigment is probably identical with chrysanthemin (I), a specimen of which was prepared for comparison from the red blossoms of *Chrysanthemum sinense*, Sabine.

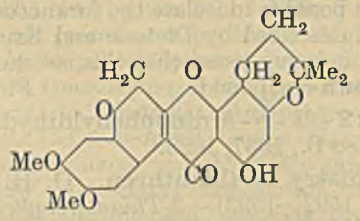
III. The blossoms of *L. radiata* were similarly extracted and gave a pigment [*picrate*, m.p. 173° (decomp.)], hydrolysed to glucose and an aglucone closely resembling cyanidin chloride. The pigment is probably (I). P. W. C.

Heterocyclic compounds. III. Synthesis of *cyclo*penteno-1′ : 2′ : 2 : 3-chromones and a discussion on the mechanism of the Pechmann and Simonis reactions. S. Z. Amed and R. D. Desai (Proc. Indian Acad. Sci., 1937, **6**, A, 6—11).—Et *cyclo*pentanone-2-carboxylate with PhOH, *m*- and *p*-cresol, and β-$C_{10}H_7$·OH yields respectively cyclo*penteno*-, m.p. 120° (*styryl* derivative, m.p. 161°), 6-*methyl*cyclo*penteno*-, m.p. 144°, and 7-*methyl*cyclo*penteno*-1′ : 2′ : 2 : 3-*chromone*, m.p. 83—84°, and cyclo*penteno*-(1′ : 2′ : 2 : 3)-1 : 4-β*α*-*naphthapyrone*, m.p. 165—

166° (*styryl* derivative, m.p. 220°). Alkaline hydrolysis to the corresponding *o*-hydroxybenzoic or naphthoic acid was complete in each case. The mechanism of the reaction is discussed. F. R. G.

Synthesis of rotenone and its derivatives. XIII. W. Bridge, A. J. Crocker, T. Cubin, and A. Robertson. **XV. Structure of toxicarol.** S. W. George and A. Robertson (J.C.S., 1937, 1530—1535, 1535—1542).—XIII. 7-Hydroxy-2 : 2-dimethylchromanone gives no red ferric reaction and forms an *acetate*, m.p. 91°, p-*nitrobenzoate*, m.p. 137°, and Me ether [2 : 4-*dinitrophenylhydrazone*, m.p. 221°; *product* with semicarbazide acetate, m.p. 226° (decomp.)]. The chromanone is reduced (Clemmensen) to 7-*hydroxy*-2 : 2-*dimethylchroman* (I), m.p. 72° (p-*nitrobenzoate*, m.p. 126°). 7-Hydroxycoumarin (*benzyl ether*, m.p. 154°) is hydrogenated to β-2 : 4-dihydroxyphenylpropionic acid, converted into 7-hydroxy-3 : 4-dihydrocoumarin. 7-Benzyloxy-3 : 4-dihydrocoumarin and MgMeI yield 7-*benzyloxy*-2 : 2-*dimethylchroman*, b.p. 160—165°/0·4 mm., debenzylated to (I). 6-Hydroxy-2-*iso*propylcoumaranone is acetylated to 3 : 6-*diacetoxy*-2-iso*propylbenzofuran*, m.p. 56°, and methylated (MeI) to 6-*methoxy*-2-iso*propyl*-β-*coumaranone* (II), m.p. 78°. Resorcinol Me ether and Et α-bromo*iso*valerate form α-3-*methoxyphenoxy*i*sovaleric acid*, b.p. 148—153°/·01 mm., which is cyclised through the acid chloride to (II). The semicarbazone of 7-methoxychromanone has m.p. 231° (lit. 222°). 7-*Benzyloxy*-4-*methylcoumarin*, m.p. 117·5°, from the OH-compound, with MgMeI gives 7-benzyloxy-2 : 2 : 4-trimethyl-Δ^3-chromen (III), m.p. 58°, hydrolysed to the 7-*OH*-compound, m.p. 130°, also obtained through 7-*benzyloxy*-2 : 2-*dimethylchromanone*, m.p. 73°, and MgMeI. Catalytic reduction of (III) affords 7-hydroxy-2 : 2 : 4-trimethylchroman (p-*nitrobenzoate*, m.p. 137°). In forming 2-hydroxy-4-benzyloxyacetophenone on ozonolysis the behaviour of 7-hydroxy-2 : 2 : 4-trimethylchromen is strictly analogous to that of xanthyletin and xanthoxyletin. The foregoing experiments support the structure assigned to 5 : 7-dihydroxychroman.

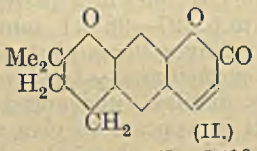
XIV. 5 : 7-Dihydroxy-2 : 2-dimethylchromanone and MeI–K_2CO_3 give the 5-*hydroxy*-7-*methoxy*-compound (IV), m.p. 65—66° (2 : 4-*dinitrophenylhydrazone*, m.p. 254°), reduced (Clemmensen) to 5-*hydroxy*-7-*methoxy*-2 : 2-*dimethylchroman* (V), b.p. 125—128°/0·4 mm. (p-*nitrobenzoate*, m.p. 122°). Benzylation of (IV) gives 5-*hydroxy*-7-*benzyloxy*-2 : 2-*dimethylchromanone*, m.p. 134° (2 : 4-*dinitrophenylhydrazone*, m.p. 242°), methylated (MeI–K_2CO_3) to the 7-*benzyloxy*-5-*methoxy*-compound, m.p. 111° (+H_2O, m.p. 81—82°; 2 : 4-*dinitrophenylhydrazone*, m.p. 215°), which is debenzylated to the 7-*OH*-derivative, m.p. 208—209° [2 : 4-*dinitrophenylhydrazone*, m.p. 275° (decomp.)]. This substance is also obtained by condensation of phloroglucinol Me ether and ββ-dimethylacryl chloride, and is reduced (Clemmensen) to 7-*hydroxy*-5-*methoxy*-2 : 2-*dimethylchroman* (VI), m.p. 103—104° (p-*nitrobenzoate*, m.p. 143°). Toxicarol forms an *oxime*, m.p. 236—237°. Dehydrodihydrotoxicarol (VII) with Me_2SO_4–K_2CO_3 gives the *Me ether*, m.p. 216°, hydrolysed (KOH–Zn) to *dihydrotoxicarolic acid Me ether*, m.p. 203°, which with hot KOH is converted into derric acid and (V) and not (VI). This confirms the structure (VII). 5 : 7-Dihydroxy-2 : 2-dimethylchroman



(VII.)

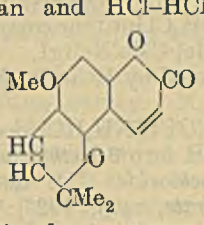
and Me 2-cyanomethyl-4 : 5-dimethoxyphenoxyacetate after reduction give allo*dihydrotoxicarolic* acid (+H_2O), m.p. 148°, converted (NaOAc–Ac_2O) into the *monohydrate* of the *O*-Ac_2 derivative, m.p. 211—212°. Me 2-cyanomethylphenoxyacetate and phloroglucinol afford *phenoxyacetic acid*-2-*phloracetophenone*, m.p. 184—185°, which with Ac_2O–NaOAc yields the *diacetate*, m.p. 240—241°, hydrolysed to 5 : 7-*dihydroxychromeno*-(3′ : 4′ : 2 : 3)-*chromone*, m.p. 256—257°. F. R. S.

Constituents of the bark of *Zanthoxylum americanum* (Mill). IV. Constitution of xanthyletin. (Miss) J. C. Bell, W. Bridge, and A. Robertson. **V. Structure of *allo*xanthoxyletin.** A. Robertson and T. S. Subramaniam (J.C.S., 1937, 1542—1545, 1545—1549).—IV. Cresorcylaldehyde, 2 : 4 : 5-$(OH)_2C_6H_2Me$·CHO, m.p. 105—106° (cf. Clemmensen, A., 1914, i, 271), is obtained by reduction of resorcylaldehyde and is itself reduced to *m*-xylorcin. This verifies its orientation and that of 7-hydroxy-6-methylcoumarin (cf. this vol., 72). 7-Hydroxy-2 : 2-dimethylchroman and HCN–HCl give 7-*hydroxy*-6-*formyl*-2 : 2-*dimethylchroman* (I), m.p. 104° [2 : 4-*dinitrophenylhydrazone*, m.p. 302° (decomp.)], also obtained by ozonolysis of dihydroxanthyletin (II). The structure of (II) is confirmed by its synthesis by decarboxylation of *dihydroxanthyletin* - 3 - *carboxylic acid*, m.p. 158—159°, prepared from (I) and CN·CH_2·CO_2H, followed by hydrolysis. Xanthyletin is reduced (Pd–H_2) to the H_4-compound, m.p. 156°.

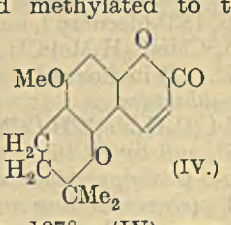


(II.)

V. allo*Xanthoxyletin* (III), $C_{15}H_{14}O_4$, m.p. 115·5°, has been isolated in small amount from the bark. It is hydrolysed (KOH) to $COMe_2$ and phloroglucinol Me ether and is reduced (Pd–H_2) to the H_2-compound (IV), m.p. 155°. (IV) is hydrolysed and methylated to O-*methyldihydro*allo*xanthoxyletinic acid*, m.p. 178° (decomp.), hydrogenated to the H_4-compound, m.p. 108·5°. Ozonolysis of (IV) affords 7-*hydroxy*-5-*methoxy*-8-*formyl*-2 : 2-*dimethylchroman* (V), m.p. 90°, also obtained from 7-hydroxy-5-methoxy-2 : 2-dimethylchroman and HCl–HCN, and methylated to the



(III.)



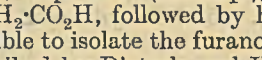
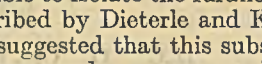
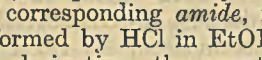
(IV.)

5 : 7-*dimethoxy*-compound, m.p. 107°. (IV) may be prepared by decarboxylation of *dihydro*allo*xanthoxyl*-

etin-3-carboxylic acid, m.p. 240° (decomp.), obtained from (V) and CN·CH_2·CO_2H, followed by hydrolysis. It has not been possible to isolate the furanocoumarin, m.p. 99—100°, described by Dieterle and Kruta (this vol., 112), and it is suggested that this substance is a mixture of known compounds. F. R. S.

1-Keto-2:2-di-*p*-aminophenyldihydrothionaphthen.—See B., 1937, 1025.

Stereochemistry of thianthren. G. H. Keats (J.C.S., 1937, 1592—1593).—*2-Thianthrenyltrimethylammonium iodide*, m.p. 190°, could not be resolved through the *d*-camphor-10- or α-bromo-*d*-camphor-π-sulphonate or H *d*-diacetyltartrate. A val. calc. for the energy for transforming thianthren from the folded to the planar state indicates little configurational stability. F. R. S.

2:3-Diketopyrroline, a uninuclear substance related to isatin. O. Mumm and H. Hornhardt (Ber., 1937, **70**, [*B*], 1930—1947; cf. A., 1911, i, 79).—*Hydroxymethylenepinacolindioxime*, m.p. 84°, is transformed by AcCl into *tert.-butylisooxazole*, b.p. 156°/760 mm., the *methosulphate* of which is converted by KCN at 0° into *α-methylimino-γ-keto-δδ-dimethylhexonitrile*, m.p. 42°. This is gradually converted by conc. HCl into *αγ-diketo-δδ-dimethylhexoic acid* (+1H_2O), m.p. 64°, or by less drastic treatment into the corresponding *amide*, m.p. 115°. The nitrile is transformed by HCl in EtOH into the non-cryst. *pyrroline* derivative, the constitution of which is established by its scission to *γ-imino-α-keto-δδ-dimethylhexoic acid*, m.p. 185°, or by aq. EtOH in absence of HCl into *αγ-diketo-δδ-dimethylhexomethylimide*, m.p. 183°. Analogously Me hexyl ketone and HCO_2Et with NaOEt give the *hydroxymethylene* compound, the *monoxime*, m.p. 118°, of which passes readily into *hexylisooxazole*, m.p. 97—98°/11 mm. (*platinichloride*); the corresponding *methosulphate* is converted by KCN into *α-methylimino-γ-ketodeconitrile*, which could not be distilled unchanged; when treated with HCl–EtOH it appears to give a pyrroline derivative which could not be isolated, whilst in absence of EtOH it is transformed by aq. dil. or conc. HCl into *αγ-diketodecoamide*, m.p. 99°. *p*-C_6H_4MeAc gives the corresponding CH·OH derivative the *oxime*, m.p. 133°, of which is converted by AcCl into p-*tolylisooxazole*, m.p. 60°, the methosulphate of which is transformed by KCN into *α-methylimino-β-p-toluoylpropionitrile* (I), m.p. 126°. The constitution of (I) is established by the observation that it yields with MgMeI a product which is decomposed by HCl to the *substance* OH·CMe(C_6H_4Me)·CH_2·C(:NMe)·CMe:N·MgI, m.p. 175° (decomp.), by AcOH into the *compound* OH·CMe(C_6H_4Me)·CH_2·C(:NMe)·CMe(OH)·NH·MgI, m.p. 183° (decomp.), and by NH_4Cl into the *compound*, NH_2·CMe(C_6H_4Me)·CH_2·C(:NMe)·CMe:N·MgI, m.p. 197°. (I) in dioxan is transformed by HCl–EtOH into the *substance* OH·C(C_6H_4Me):CH·C(:NMe)·C(OEt):NH,HCl, decomp. 145°, and by HCl in abs. EtOH into *3-methylimino-2-keto-5-p-tolylpyrroline dihydrochloride* (II), decomp. 183° (corresponding *monopicrate*, m.p. 192°); if a trace of H_2O is present, *Me α-keto-β-p-toluoylpropionate*, m.p. 84° [hydrolysed to *α-keto-β-p-toluoylpropionic acid* (+1H_2O)], m.p. 143°, is also produced. $NaHCO_3$ solution and (II) at 0° give the yellow-green *ψ-base*,  , which gives *K* (+2H_2O), *Ag* (+1MeOH), decomp. 172°, and *Cu* (+4H_2O), decomp. 191°, salts. NH_3 transforms (II) in EtOH into the *compound*,  , m.p. 153°. Cold H_2O slowly transforms (II) into 2:3-*diketo-5-p-tolylpyrroline*, m.p. 229—230° [*K* (+2H_2O) salt], converted by aq. NaOH into *γ-imino-α-keto-γ-p-tolylbutyric acid*, m.p. 155°. *γ-Imino-α-keto-γ-p-tolylbutyr-piperidide*, m.p. 184°, *-amide* (+0·5H_2O), m.p. 179°, and *-methylamide* (+0·5H_2O), m.p. 169°, are formed analogously. The great similarity of (II) to isatin is shown during hydrogenation (PtO_2 in EtOH). Initially a compound resembling isatide is produced which regenerates the parent on contact with air but alternately the air-stable *γ-amino-α-hydroxy-γ-p-tolyl-Δ$^{\beta}$-butenoic acid*, decomp. 245—250°, results. NH_2Ph and (II) in EtOH afford *3-phenylimino-2-keto-5-p-tolylpyrroline* (III), m.p. 237°, which under non-standardised conditions yields a *mono-* and a *di-hydrochloride*. KOEt and (III) give the *K* salt. Hydrogenation (PtO_2 in EtOH) of (III) affords *Et γ-amino-α-anilino-γ-p-tolylbutyrate*, m.p. 123°. $CH_2(CN)_2$ and (III) in EtOH yield *2-keto-5-p-tolyl-3-dicyanomethylenepyrroline*,  , which has a very high m.p. It is slowly converted by alkali or piperidine into *γ-amino-γ-p-tolyl-α-dicyanomethylene-Δ$^{\beta}$-butenoic acid*, m.p. 276°, transformed by boiling HCl–EtOH into the *dihydrochloride*, m.p. 148—149°, of the substance, NH_2·C(C_6H_4Me):CH·C(CO_2H):CH·C(:NH)·OEt. H. W.

***dicyclo*[1:2:2]Aza-1-heptane.** G. R. Clemo and T. P. Metcalfe (J.C.S., 1937, 1523—1526).—*Et* 2:2:5:5-*tetramethylpyrrolidine-3-carboxylate-1-acetate*, b.p. 169°/16 mm., prepared from $CH_2Cl·CO_2Et$ and Et 2:2:5:5-tetramethylpyrrolidine-3-carboxylate, could not be ring-closed by the Dieckmann reaction. *3-Carboxy-2:2:5:5-tetramethylpyrrolidine-1-acetic acid* (+0·5H_2O), m.p. 261°, is obtained by hydrolysis of the ester. 2-Pyrrolidone and $Et_2C_2O_4$ give *Et 2-pyrrolidone-3-oxalate*, m.p. 132°, which could not be ring-closed. Pyridine-4-carboxylic acid, obtained from 2:4-lutidinic acid, is reduced (Na–C_5H_{11}·OH) and esterified to *Et piperidine-4-carboxylate*, b.p. 74°/1 mm. (*picrate*, m.p. 172°), which is reduced (Bouveault) to *4-piperidylcarbinol*, b.p. 122°/12 mm. (*picrate*, m.p. 120°). The carbinol with PBr_5 gives the bromide, which in alkaline solution is converted into *dicyclo*[1:2:2]aza-1-heptane, b.p. 130°/755 mm. [*methiodide*, m.p. 320° (decomp.); *aurichloride*, m.p. 280° (decomp.); *picrolonate*, m.p. 255° (decomp.); *picrate*, m.p. 274° (decomp.)] (cf. Prelog *et al.*, A., 1936, 1388). F. R. S.

Purification of piperidine and its physiological significance. E. S. Cook and T. H. Rider (J. Amer. Chem. Soc., 1937, **59**, 1739—1741).—The following are recorded for the carefully fractionated materials: piperidine, b.p. 106·3°/751 mm. (hydrochloride, m.p. 248·4—249·9°); 2-methylpiperidine,

b.p. 117—119° (uncorr.)/750 mm. (hydrochloride, m.p. 216—217°); piperidino-, m.p. 172·6—173·6°, and 2-methylpiperidino-formanilide, m.p. 127·9°. M.p. are corr. R. S. C.

Effect of the purification of piperidine on the activity of derived local anæsthetics. T. H. Rider and E. S. Cook (J. Amer. Chem. Soc., 1937, **59**, 1741—1742).—Drugs prepared from pure piperidine often differ in activity from those prepared from material containing 2-methylpiperidine. The following are prepared from the pure bases: piperidinopropanediol diphenylurethane hydrochloride, m.p. 203·5—205°, more active than the crude drug; 2-methylpiperidinopropanediol, m.p. 69—71°, and its *diphenylurethane hydrochloride*, m.p. 192·2—194°; γ-piperidinopropyl benzoate hydrochloride, m.p. 190·6—192·6°; *γ-2-methylpiperidinopropyl alcohol*, b.p. 110—112°/10 mm., and *phenylurethane*, m.p. 218·5—219°. M.p. are corr. Anæsthetic activities of the urethanes and benzoates are recorded, the Me derivatives being more and less active in the latter and former series, respectively. R. S. C.

Piperidinoacetanilide.—See B., 1937, 1131.

Modification of the Guareschi pyridine synthesis. II. N. Palit (J. Indian Chem. Soc., 1937, **14**, 354—357).—In presence of NaOMe, CN·CH:CAr·NH_2 condenses with Et benzylideneacetoacetate to give the 5-cyano-3-carbethoxy-4-phenyl-6-aryl-2-methylpyridine: *Ph*, m.p. 189° (together with 3 : 5-*dicyano*-2 : 4 : 6-*triphenyldihydropyridine*, m.p. 268°), p-*tolyl*, m.p. 189°, p-*anisyl*, m.p. 187°; and with Et benzylidenecyanoacetate to give the 3 : 5-dicyano-4-phenyl-6-aryl-$\Delta^{3:6}$-dihydro-2-pyridone: *Ph*, m.p. 250—251° ($NHEt_2$ as catalyst gives the *diethylammonium* salt, m.p. 208—210°), *p-tolyl*, m.p. 293°, p-*anisyl*, m.p. 296°. A. Li.

Manufacture of [pyridinium] methine and polymethine dyes.—See B., 1937, 1032.

Syntheses in the octahydropyrrocoline and octahydropyridocoline series. G. R. Clemo and T. P. Metcalfe (J.C.S., 1937, 1518—1523).—*Et piperidyl*-1 : 2-*diacetate*, b.p. 155°/12 mm., from the monoacetate and $CH_2Cl·CO_2Et$, and K give 2-*keto-octahydropyrrocoline* (I), b.p. 76—77°/11 mm. [*picrate*, m.p. 187° (decomp.)], which with MgEtI yields 2-*hydroxy*-2-*ethyloctahydropyrrocoline*, b.p. 82°/1 mm. (*picrolonate*, m.p. 198°). Dehydration (PCl_5) of the alcohol yields 2-*ethylhexahydropyrrocoline* (II), b.p. 50°/1 mm. (*picrolonate*, m.p. 191°), catalytically reduced to the H_8-compound, b.p. 41°/1 mm. [*picrate*, m.p. 149°, *picrolonate*, m.p. 161° (slight decomp.); methiodide, m.p. 232° (decomp.)]. 1-Keto-octahydropyrrocoline (III) and MgEtI give 1-*hydroxy*-1-*ethylhexahydropyrrocoline*, b.p. 85—87°/1 mm., dehydrated (PCl_5) to 1-*ethylhexahydropyrrocoline*, b.p. 74—75°/1 mm. (*picrolonate*, m.p. 185°), which is catalytically reduced to the H_8-compound (IV), b.p. 64°/11 mm. (*picrate*, m.p. 134°; *picrolonate*, m.p. 176°). Et piperidyl-2-acetate and $CH_2Cl·CH_2·CO_2Et$ give *Et piperidyl*-2-*acetate*-1-β-*propionate*, b.p. 165—169°/11 mm. Et 1-keto-octahydropyridocoline-2-carboxylate, MeI, and KOEt yield 1-*keto*-2-*methyloctahydropyridocoline*, b.p. 80°/1 mm. (*picrate*, m.p. 176°), which is reduced (Clemmensen) to 2-*methyloctahydropyridocoline* (V), b.p. 56—57°/1 mm. (*picrate*, m.p. 182°), and by the Wolff method to the isomeric compound (*picrate*, m.p. 158°). MgMeI and (III) yield 1-*hydroxy*-1-*methyloctahydropyrrocoline*, b.p. 72—73°/1 mm. (*picrate*, m.p. 142°; *picrolonate*, m.p. 207°), dehydrated to 1-*methylhexahydropyrrocoline* (*picrolonate*, m.p. 183°), reduced to the H_8-compound, b.p. 62°/11 mm. [*picrate*, m.p. 191° (decomp.); *picrolonate*, m.p. 198° (decomp.)]. Reduction of (I) by the Wolff and Clemmensen methods gives octahydropyrrocoline, and by the latter method 2-*hydroxyoctahydropyrrocoline*, b.p. 90°/11 mm. [*picrate*, m.p. 133°; *picrolonate*, m.p. 174° (decomp.)], is also obtained. The isomeric *form* of the 2-OH-compound, b.p. 95°/14 mm. (*picrate*, m.p. 175°), is obtained by reducing (I) with Na–Hg. Et 2-carbethoxypiperidyl-1-β-propionate and K give *Et* 1-*keto-octahydropyrrocoline*-2-*carboxylate*, b.p. 103°/1 mm. It has now been shown that of the degradation products of strychnine (cf. this vol., 38) the base *A* is 4-methyl-3-ethylpyridine but *B* is not (II), (IV), or (V), although it may be another form of (V). F. R. S.

3 : 3-Di-*p*-aminophenyloxindole.—See B., 1937, 1025.

Condensation of 4-hydroxy-2 : 6- and -2 : 8-dimethylquinolines and of their derivatives with aromatic aldehydes. A. Meyer and H. Drutel (Compt. rend., 1937, **205**, 462—464; cf. A., 1935, 758, 1506; this vol., 389, 431).—The ethiodides of 4-hydroxy-2 : 6- (I) and -2 : 8-dimethylquinoline (II) with an excess of aromatic aldehyde and a little piperidine at 130—140° interact at position 2. Thus (I) with the appropriate aldehyde affords: 4-*hydroxy*-2-(δ-*phenyl*-Δ^{γ}-*butenyl*)-, m.p. 198—199°, -2-(3′ : 4′-*methylenedioxy*)*styryl*-, m.p. 271—272°, -2-(4′-*methoxy*)-*styryl*-, m.p. 260—261°, and -2-(4′-*dimethylamino*)-*styryl*-6-*methylquinoline ethiodide*, m.p. 253°. Similarly, (II) affords 4-*hydroxy*-2-(2′-*hydroxy*)*styryl*-, m.p. 248—249°, -2-(4′-*hydroxy*-3′-*methoxy*)*styryl*-, m.p. 210—212°, -2-(3′ : 4′-*methylenedioxy*)*styryl*-, m.p. 208—209°, and -2-(4′-*dimethylamino*)*styryl*-8-*methylquinoline ethiodide*, m.p. 218—219°. The OEt-derivative of (II) with *p*-$NMe_2·C_6H_4·CHO$ (III) at 140° in presence of $ZnCl_2$ affords 4-*ethoxy*-2-(4′-*dimethylamino*)*styryl*-8-*methylquinoline*, m.p. 174—175°. The reaction is general for the OEt-analogues of (I) and (II). 4-Chloro-2 : 8-dimethylquinoline with an equimol. amount of (III) in boiling Ac_2O containing some EtOH gives 4-*chloro*-2-(4′-*dimethylamino*)*styryl*-8-*methylquinoline*, m.p. 127—128°. Similarly treated, (II) or its Bz derivative affords 4-*hydroxy*-2-(4′-*dimethylamino*)*styryl*-8-*methylquinoline*, m.p. 315—316°, which indicates that acetylation of (II) probably precedes interaction with (III). J. L. D.

Spectrochemical investigations in the *iso*-quinoline series. M. Gerendás and E. Varga (J. pr. Chem., 1937, [ii], **149**, 175—182).—Absorption spectra are recorded for piperonyl- (I) and acet-β-hydroxy-β-3 : 4-methylenedioxyphenyl*iso*propylamide, acet-, piperonyl-, and veratryl-β-hydroxy-β-3 : 4-dimethoxyphenyl*iso*propylamide, 1-methyl-, 1-piperonyl- (II), and 1-veratryl-3 : 4-methylenedioxy-

*iso*quinoline, 1-methyl- and 1-veratryl-3 : 4-dimethoxy*iso*quinoline. The amides have a two-banded and the *iso*quinolines a three-banded spectrum. The intermediate product (A., 1936, 1124) in the synthesis of (II) from (I) is shown by its two-banded absorption spectrum to be *piperonyl-α-piperonylidene-ethylamide*. R. S. C.

Acridine salts of "yeast" and "muscle" adenylic acids. R. S. Tipson (J. Biol. Chem., 1937, **120**, 621—623).—The acridine salt of "muscle" adenylic acid (I) prepared as described by Wagner-Jauregg has the composition $C_{13}H_9N,2C_{10}H_{14}O_7N_5P$, and not that assigned by him (cf. A., 1936, 743), and m.p. 217—218° (darkening), $[\alpha]_D^{25}$ —23·2° in 10% HCl after 5 min. ($[\alpha]_D^{25}$ calc. for (I), —29·2°). The acridine *salt* (same formula) of "yeast" adenylic acid (II) has m.p. 183—184° (no previous darkening), $[\alpha]_D^{25}$ —28·6° in 10% HCl after 10 min. ($[\alpha]_D^{25}$ calc. for (II), —35·9°). E. W. W.

2 : 8-Dialkoxy-10-alkylacridinium derivatives with various kinds of amino-groups on the carbon in position 5. XVI. Synthesis of 5-*m*-aminoanilino-2 : 8-dialkoxy-10-alkylacridinium derivatives and 5 : 5′-*m*-phenylenebis(amino-2 : 8-dialkoxy-*N*-alkylacridinium) derivatives. K. Ishihara (J. Chem. Soc. Japan, 1935, **56**, 1368—1387; cf. this vol., 211).—*m*-$C_6H_4(NH_2,HCl)_2$ and 5-chloro-2 : 8-dimethoxy-10-methylacridinium chloride (I) in H_2O afford 5-m-*aminoanilino*-2 : 8-*dimethoxy*-10-*methylacridinium chloride hydrochloride* (II), +0·9MeOH, m.p. 228°, and 5 : 5′-m-*phenylenebis*-(*amino*-2 : 8-*dimethoxy*-10-*methylacridinium chloride*)*, +4H_2O (III), m.p. 250° (decomp.) (for compounds marked * analysis indicates formation of basic salts), also obtained from (I) and (II). When heated, (II) loses HCl, giving the *acridinium chloride*, which with KOH gives 5-m-*aminoanilino*-2 : 8-*dimethoxy*-10-*methylacridinium hydroxide* (IV), m.p. 110° (decomp.) (with KI in AcOH gives the corresponding *iodide*, +0·4AcOH, m.p. about 225°), also obtained from (III) by KOH. When heated, both the above-mentioned hydroxides dissociate into *m*-$C_6H_4(NH_2)_2$ and 2 : 8-dimethoxy-*N*-methylacridone. KI in HCl converts (II) into the corresponding *acridinium iodide hydriodide*, +H_2O, m.p. 209°, and (III) into the corresponding *bis*(*acridinium iodide*), +0·4AcOH, m.p. 271° (decomp.). KOH converts (III) into the *bis*(*acridinium hydroxide*), m.p. 232°, also obtained from (IV). Similarly are obtained 5-m-*aminoanilino*-2 : 8-*dimethoxy*-10-*ethyl*-, m.p. 173° [corresponding *iodide**, m.p. about 220° (*semihydriodide semihydrochloride*, +1·25H_2O, m.p. 219°)], -2 : 8-*diethoxy*-10-*methyl*-, m.p. 163° [corresponding *iodide**, m.p. 240° (*semihydriodide*, m.p. 237°)], and -2 : 8-*diethoxy*-10-*ethyl-acridinium hydroxide*, m.p. 156° [corresponding *iodide*, +0·166AcOH, m.p. 235° (*hydriodide**, +MeOH, m.p. 224°)], 5 : 5′-m-*phenylenebis*(*amino*-2 : 8-*dimethoxy*-10-*ethyl*-, m.p. 249°, -2 : 8-*diethoxy*-10-*methyl*-, m.p. 193°, and -2 : 8-*diethoxy*-10-*ethyl-acridinium hydroxide*), m.p. 193° [corresponding *dichlorides*, m.p. (*+3H_2O) 240° (decomp.), (*+3H_2O) 251° (decomp.), and (+2H_2O,0·5MeOH) 259° (decomp.), and *di-iodides*, m.p. (+0·4AcOH) 271° (decomp.), 253° (decomp.), and 285° (decomp.), respectively]. The original should be consulted. R. S. C.

1-*cyclo*Hexyl-3-methyl-5-pyrazolone.—See B., 1937, 1025.

Synthesis of anserine from *l*-1-methylhistidine. O. K. Behrens and V. du Vigneaud (J. Biol. Chem., 1937, **120**, 517—522).—*l*-1-Methylhistidine [*l*-α-amino-β-(*N*-methyl-5-glyoxalinyl)propionic acid] (I), from anserine (II), and MeOH–HCl give the *dihydrochloride*, m.p. 205°, of the *Me* ester (III) of (I). Carbobenzyloxy-β-alanyl azide (A., 1935, 629) with (III) in $CHCl_3$ gives a syrup converted by NaOH into *carbobenzyloxyanserine*, isolated as the *reineckate*. This is decomposed by C_5H_5N and the product reduced (Pd–H_2) to (II), isolated through the Cu salt. E. W. W.

Creatinine derivatives. III. Alkylation with methyl and ethyl sulphates. Structure of methylcreatinine. W. R. Cornthwaite (J. Amer. Chem. Soc., 1937, **59**, 1616—1617; cf. A., 1936, 864).—Addition of Me_2SO_4 to creatinine in hot H_2O gives methylcreatinine sulphate, converted by $NaHCO_3$ into methylcreatinine, which yields 5-benzylidene- and furfurylidene-2-methylcreatinine. Et_2SO_4 gives mainly *creatinine Et sulphate*, m.p. 146°, with some ethylcreatinine sulphate. The structure of methylcreatinine is thus confirmed. R. S. C.

Barbituric acids containing the 2-methylallyl group. W. J. Doran and H. A. Shonle (J. Amer. Chem. Soc., 1937, **59**, 1625—1626).—The following are prepared: *Et*$_2$ n-, b.p. 99°/2 mm., and iso-*propyl*-, b.p. 126—127°/9—10 mm., n-, b.p. 131—132°/3 mm., sec.-, b.p. 102—104°/1·5 mm., and iso-*butyl*-, b.p. 110—113°/1 mm., n-, b.p. 112—114°/1 mm., sec.-, b.p. 142—144°/8—9 mm., and iso-*amyl*-, b.p. 115—116°/2·5 mm., β-*methyl*-n-*butyl*-, b.p. 135—137°/7 mm., n-*hexyl*-, b.p. 127—131°/1 mm., β-*ethyl*-n-*butyl*-, b.p. 129—133°/1 mm., and *allyl*-β-*methylallylmalonate*, b.p. 124—127°/6 mm.; *Et*$_2$ β-*methylallyl*-, b.p. 113—116°/14—17 mm., *di*-β-*methylallyl*-, b.p. 114—116·5°/1 mm., and *ethyl*-α-*ethylpropyl-malonate*, b.p. 111—112°/5·5 mm.; 5-*ethyl*-, m.p. 165—167°, -n-, m.p. 173·5—174·5°, and -iso-*propyl*-, m.p. 163—164°, -n-, m.p. 125—126°, -sec.-, m.p. 140—142°, and -iso-*butyl*-, m.p. 179·8—180·5°, -n-, m.p. 111—112°, -sec.-, m.p. 141·5—143°, and -iso-*amyl*-, m.p. 143·6—144·4°, -β-*methyl*-n-*butyl*-, m.p. 142—143·5°, -α-*ethylpropyl*-, m.p. 181·5—183°, -n-*hexyl*-, m.p. 127—129°, -β-*ethyl*-n-*butyl*-, m.p. 148—150°, -*allyl*-, m.p. 165—167°, -cyclo*pentyl*-, m.p. 159—161°, -*phenyl*-, m.p. 203—205°, -5-β-*methylallylbarbituric acid*; 5-β-*methylallyl*-, +0·5H_2O, m.p. 187—189°, 5 : 5-*di*-β-*methylallyl*-, m.p. 207—209°, N : 5-*diallyl*-5-β-*methylallyl*-, m.p. 149—150°, and α-*ethylpropyl-barbituric acid*, m.p. 197·5—198°, 5-n-*propyl*-, m.p. 157—158°, -n-, m.p. 137—137·5°, and -sec.-*butyl*-, m.p. 138—139°, and -sec.-*amyl*-5-β-*methylallylthiobarbituric acid*, m.p. 146·5—148°. The pharmacological properties of the barbituric acids are summarised. R. S. C.

Some new derivatives of barbituric acid. M. Busch and F. Keyser (Biochem. Z., 1937, **293**, 16—21).—Anilinobarbituric acid, heated with Ac_2O, gave an *acetate*, m.p. 255—260° (decomp.). *Et diethylaminomalonate*, b.p. 98—100°/19 mm., was prepared by heating $NHEt_2$ with bromomalonate and when treated with $CO(NH_2)_2$ and NaOEt gave 5-*diethyl*-

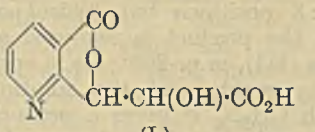
aminobarbituric acid, m.p. 350° (decomp.). *Et diisobutylaminomalonate*, b.p. 148—152°/19 mm., was similarly prepared and converted into 5-*diisobutylaminobarbituric acid*, m.p. 355°. *Et diamylaminomalonate*, b.p. 148—150°/19 mm., with $CO(NH_2)_2$ in NaOEt–EtOH gave 5-*diamylaminobarbituric acid*, m.p. 313°, but when heated in a sealed tube with $CO(NH_2)_2$ gave a *compound*, $C_{15}H_{14}O_3N_4$, m.p. 325°. *Et allylaminomalonate*, b.p. 132—135°/19 mm., gave 5-*allylaminobarbituric acid*, m.p. 232—237°. 5-Bromo-5-ethylbarbituric acid when heated in a sealed tube at 50° with EtOH and $NHEt_2$ gave 5-*diethylamino*-5-*ethylbarbituric acid*, m.p. 218—219°. P. W. C.

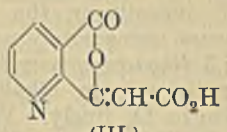
Thiobarbituric acids.—See B., 1937, 1135.

Derivatives of piperazine. X. Reactions with unsaturated esters. II. J. P. Bain and C. B. Pollard (J. Amer. Chem. Soc., 1937, **59**, 1719—1721; cf. A., 1935, 502).—Piperazine (I) with the appropriate Et_2 arylidenemalonate or aryl aldehyde and $CH_2(CO_2Et)_2$ gives 1 : 4-*bis*-ββ-*dicarbethoxy*-α-*phenyl*- (II), m.p. 151—152°, -3 : 4-*methylenedioxyphenyl*-, m.p. 150—151°, -o-*chlorophenyl*-, m.p. 156—157°, -p-*anisyl*- m.p. 146—147°, and -2-*furyl*-*ethylpiperazine*, m.p. 126—127°. By either method 1-phenylpiperazine gives 1-*phenyl*-4-ββ-*dicarbethoxy*-α-*phenyl*-, m.p. 144—145°, -3 : 4-*methylenedioxyphenyl*-, m.p. 144—145°, -p-*anisyl*-, m.p. 146—147°, and 2-*furyl*-*ethylpiperazine*, m.p. 130—104°. With hot KOH–EtOH (II) gives (?) K_2 α-*ethoxybenzylmalonate* and (I). With acid (II) gives (I) and $CHPh{:}C(CO_2Et)_2$, or PhCHO, $CH_2(CO_2Et)_2$, and, in one experiment, $CHPh{:}CH{\cdot}CO_2H$. With H_2 and Raney Ni in dioxan at 100°/68 atm. (II) gives (I), *NN'*-dibenzylpiperazine, $CH_2(CO_2Et)_2$, and $CH_2Ph{\cdot}CH(CO_2Et)_2$. The reaction of PhCHO with $CN{\cdot}CH_2{\cdot}CO_2Et$ is catalysed by (I), but no addition occurs. R. S. C.

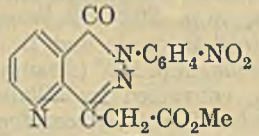
Pyrimidines. I. Preparation of 6-hydroxy-2-methylpyrimidine-5-acetic acid and its derivatives. L. R. Cerecedo and F. D. Pickel (J. Amer. Chem. Soc., 1937, **59**, 1714—1716).—$NH{:}CHMe{\cdot}NH_2$,HCl, $CO_2Et{\cdot}CH(COH){\cdot}CH_2{\cdot}CO_2Et$, and conc. NaOH give *Et* 6-*hydroxy*-2-*methylpyrimidine*-5-*acetate* (I), m.p. 179—180° (*picrate*, m.p. 157—158°), the *acethydrazide*, m.p. 246°, from which with HNO_2 gives 6-*hydroxy*-2-*methyl*-5-*aminomethylpyrimidine hydrochloride*, m.p. 277° (decomp.) (corresponding *picrate*, m.p. 157—158°), converted by HNO_2 into 6-*hydroxy*-2-*methyl*-5-*hydroxymethylpyrimidine*, m.p. 215°. From (I) are obtained the 5-*acetamide*, m.p. 242° (*picrate*, m.p. 207°), and 5-*acetic acid*, m.p. 254—256°, and with $POCl_3$ *Et* 6-*chloro*-2-*methylpyrimidine*-5-*acetate*, m.p. 35—36°, b.p. 108—112°/11 mm., which furnishes the *phenylhydrazide*, m.p. 236°. R. S. C.

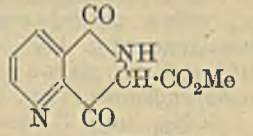
Synthesis of 2 : 5-naphthyridine derivatives. E. Ochiai, K. Miyaki, and S. Soto (Ber., 1937, **70**, [*B*], 2018—2023).—β-2-Carboxyphenylglycerolactone is converted by HCl into *iso*coumarincarboxylic acid and by H_2O at 250° into *iso*coumarin; it is therefore a δ-lactone. β-3-Carboxy-2-pyridylglycerolactone (I) on the other hand loses 1 H_2O and 1 CO_2 giving 2-acetylnicotinic acid (II), the constitution of which is confirmed by its oxidation in alkaline solution to CHI_3 and quinolinic acid. It cannot therefore be a δ-lactone and it appears that it is a γ-lactone (I) which passes into the unsaturated lactone (III) and


(I.)


(III.)

thence by ketonic fission into (II). Therefore (I) is transformed through the *Ca* salt into the *Me* ester, m.p. 154°, converted by $SOCl_2$ in C_5H_5N or by P_2O_5 in boiling xylene into the *enol-lactone* of *Me* 3-*carboxypicolyl*-2-*acetate* (IV) (cf. III), m.p. 160—161°, also formed with a *compound*, $C_{10}H_8O_4NCl$, m.p. 108°, by the action of $SOCl_2$ and C_5H_5N in boiling C_6H_6–PhMe. Warm H_2O transforms (IV) into *Me* 3-*carboxy*-2-*picoloylacetate*, m.p. 94°, converted by *p*-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2$ into the p-*nitrophenylhydrazone anhydride* (V), m.p. 180°, thus proving that β-3-carb-


(V.)

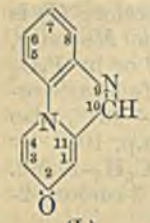

(VI.)

oxy-2-pyridylglyceric acid forms a γ-lactone. CH_2N_2 transforms (IV) into *Me* 3-*carbomethoxy*-2-*picoloylacetate*, b.p. 150—155°/0·04 mm., also prepared from the enol-lactone and anhyd. MeOH at 100—110° with small amounts of a *compound*, m.p. 215°. It gives an *oximino*-derivative, decomp. 186°, transformed by H_2 (Pd–C in HCl) into *Me* 1 : 4-*dihydroxy*-2 : 5-*naphthyridine*-3-*carboxylate* (VI), m.p. 220° (decomp.) after softening at 207°, which with $POCl_3$ at 120—130° affords *Me* 1-*chloro*-4-*hydroxy*-2 : 5-*naphthyridine*-3-*carboxylate*, decomp. 227°. H. W.

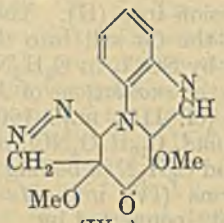
Phthaloylation. Action of quinoxaline-2 : 3-dicarboxylic anhydride on o-phenylenediamine. G. B. Crippa and A. Aguzzi (Gazzetta, 1937, **67**, 352—358; cf. A., 1929, 706).—Quinoxaline-2 : 3-dicarboxylic anhydride (I) and *o*-$C_6H_4(NH_2)_2$ in EtOH give *quinoxaline*-3-*carboxyl*-2′-*aminoanilide*-2-*carboxylic acid* (II), m.p. 168°, with NN′-*o*-*phenylenebis*-(*quinoxaline*-3-*carboxylamide*-2-*carboxylic acid*) (?), m.p. 186—188°. With *o*-$NHAc{\cdot}C_6H_4{\cdot}NH_2$, (I) gives the *Ac* derivative (III), m.p. 217°, of (II), from which it is also obtained. Either (II) or (III) with Ac_2O in excess gives *quinoxaline*-2 : 3-*dicarboxyl*-2′-*acetamidophenylimide*, m.p. 310—315°, which with NaOH followed by HCl yields (III). E. W. W.

Derivatives of glucazidone. K. Maurer and B. Schiedt [with H. Schroeter and, in part, H. Plessing] (Ber., 1937, **70**, [*B*], 1857—1861; cf. A., 1935, 1381).—The typical aromatic reagents attack the pyridone nucleus of glucazidone (I), apparently invariably in position 3. Substitution does not occur with all reagents and if the conditions are made more drastic the ring system is destroyed. Gradual addition of (I) to fuming H_2SO_4 (20% SO_3) gives *glucazidone*-3-*sulphonic acid* (II) (+H_2O), m.p. 275° (decomp.) after darkening (*K*, *Na*, and *Ag* salts). (II) is transformed by fuming HNO_3 into 3-*nitroglucazidone*, m.p. 215°, also obtained from (I). Oxid-

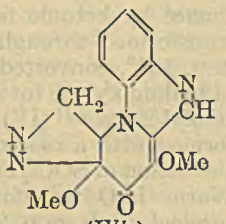
ation of (II) with aq. $KMnO_4$ gives quinoxaline-2-carboxylic acid, m.p. 210°. Br appears to substitute (II) initially in the 1 : 3 positions but hydrolysis occurs immediately and the product is regarded as 1 : 3-*dihydroxyglucazidone* (III), m.p. 206°; it is very readily sol. in alkali hydroxide and the solution absorbs O_2 freely. With CH_2N_2 it gives a *product*, $C_{14}H_{12}O_3N_4$, m.p. 186°, sol. in alkali hydroxide,



(I.)



(IV*a*.)



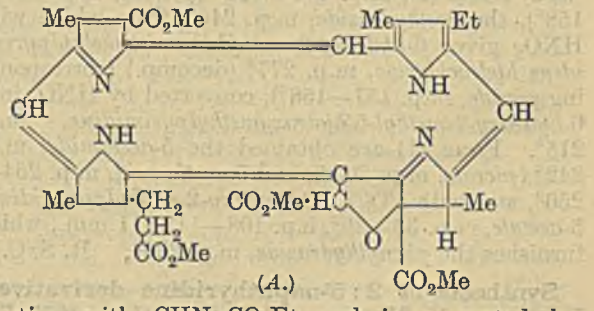
(IV*b*.)

accompanied by a *substance* (IV*a* or IV*b*), m.p. 99—100°. $NHPh{\cdot}NH_2$ and (IV) afford the *phenylhydrazone*, yellow or red crystals, m.p. 202°. 3-*Bromoglucazidone*, m.p. 127°, obtained from (I) and Br in $CHCl_3$ or C_6H_6, gives a *methiodide*, m.p. 194° (decomp.) (*methoperchlorate*, m.p. 230°), converted by alkaline $K_3Fe(CN)_6$ into 3-*bromo*-10-*keto*-9-*methylglucazidone*, m.p. 178°. 3-*Chloroglucazidone* is obtained from (II) and SO_2Cl_2. H. W.

Pyrromethenes and tripyrrylmethanes with bromovinyl groups. H. Fischer and E. Strobel (Annalen, 1937, **531**, 251—267).—2-Formyl-4-methyl-3-bromovinylpyrrole-5-carboxylic acid (I) condenses readily in MeOH at room temp. with 2 : 4-dimethylpyrrole (II) to 2-*carboxy*-3-*methyl*-4-*bromovinyldi*-(2 : 4-*dimethyl*)*tripyrrylmethane*, decomp. 183°. The following 2-*carboxy*-3-*methyl*-4-*bromovinyldi*-( )*tripyrrylmethanes* are obtained similarly: -2 : 4-*dimethyl*-3-*ethyl*-; -2 : 4-*dimethyl*-3-β-*carboxyethyl*-, decomp. 198°; -2 : 3-*dimethyl*-4-*ethyl*-, decomp. 158°; -2 : 3-*dimethyl*-, decomp. 169°; -2-*methyl*-4-*ethyl*-, decomp. 141°; -2 : 3 : 4-*trimethyl*-, decomp. 167°; -2-*methyl*-3 : 4-*diethyl*-, decomp. 156°; 2 : 3-*dimethyl*-4-*propyl*-, decomp. 145°; -3-*carbethoxy*-2 : 4-*dimethyl*-, decomp. 187°; -2-*methyl*-3-*ethyl*-, decomp. 168°. 4-*Bromo*-2-*carboxy*-3-*methyldi*-(2-*methyl*-3-*ethyl*)*tripyrrylmethane* decomposes at 152°. 2-Carboxy-3-methyl-4-bromovinyldi-3-benzoyl-2 : 4-dimethyl- and -3-benzoyl-4-phenyl-2-methyl-tripyrrylmethane and the Et ester of the former could not be thus obtained. Addition of HBr–AcOH to (I) and (II) in Ac_2O affords 4 : 3′ : 5′-*trimethyl*-3-*bromovinylpyrromethene*-5-*carboxylic acid hydrobromide* (*Et* ester *hydrobromide*). The requisite pyrrole and (I) (or its Et ester) analogously give the following -3-*bromovinylpyrromethene*-5-*carboxylic acid hydrobromides*: 4 : 4′ : 5′-*trimethyl*- (*Et* ester *hydrobromide*); 4 : 5′-*dimethyl*-4′-*ethyl*- (*Et* ester *hydrobromide*); 4 : 5′-*dimethyl*-3′-*ethyl*- (*Et* ester *hydrobromide*); 4 : 3′ : 4′ : 5′-*tetramethyl*- (*Et* ester *hydrobromide*); 4 : 5′-*dimethyl*-3′ : 4′-*diethyl*- (*Et* ester *hydrobromide*); 4 : 4′ : 5′-*trimethyl*-3′-*propyl*- (*Et* ester *hydrobromide*). 4′-*Carbethoxy*-4 : 3′ : 5′-*trimethyl*-3-*bromovinylpyrromethene*-5-*carboxylic acid hydrobromide* and its *Et* ester *hydrobromide*, 4′-*benzoyl*-4 : 3′ : 5′-*trimethyl*-3-*bromovinylpyrromethene*-5-*carboxylic acid hydrobromide* and its *Et* ester *hydrobromide*, and *Et* 4′-*benzoyl*-3′-*phenyl*-4 : 5′-*dimethyl*-3-*bromovinylpyrromethene*-5-*carboxylate hydrobromide* are described. 3-Bromo-2-formyl-4-methylpyrrole-5-carboxylic acid and 2-methyl-3-ethylpyrrole yield 3-*bromo*-4 : 5′-*dimethyl*-4′-*ethylpyrromethene*-5-*carboxylic acid hydrobromide*, converted by Br in AcOH into 3 : 5-*dibromo*-4 : 5′-*dimethyl*-4′-*ethylpyrromethene hydrobromide*. 2 : 4-*Dimethyl*-3-*bromovinylpyrrole*-5-*carboxylic acid*, obtained by hydrolysis of the Et ester, is extremely unstable. 5-Carbethoxy-2-methyl-4-ethylpyrrole-3-acrylic acid suspended in CS_2 is transformed by Br into the corresponding dibromide, which loses HBr at 100° with formation of *Et* 2-*methyl*-4-*ethyl*-3-*bromovinylpyrrole*-5-*carboxylate*; this with SO_2Cl_2 in Et_2O yields *Et* 2-*formyl*-4-*ethyl*-3-*bromovinylpyrrole*-5-*carboxylate* (*oxime*), hydrolysed to 2-*formyl*-4-*ethyl*-3-*bromovinylpyrrole*-5-*carboxylic acid*. Substitution of Et for Me does not appear to increase the stability of these compounds. H. W.

Source of the formic acid produced on acid hydrolysis of nucleic acids. C. D. Stevens (J. Biol. Chem., 1937, **120**, 751—757).—Acid hydrolysis of thymonucleic acid (I) yields HCO_2H (II) corresponding with the adenine (III) present, and adenine sulphate gives on hydrolysis large quantities of (II); from (I), (III), and not the carbohydrate, is therefore presumably the main source of (II), of which guanine (IV) is also a minor source. Yeast nucleic acid on hydrolysis gives (II), due mainly to (III), and partly to (IV) and to ribose. Pyrimidines give little or no (II). E. W. W.

Chlorophyll. LXXX. New purpurins and chlorins by the oxidative degradation of chlorophyll. H. Fischer and K. Kahr (Annalen, 1937, **531**, 209—244).—The presence of CO in purpurin-7 (I) could not be established by NH_2OH or $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$, by acetal production or addition of HCl, or by condensation with $CH_2(CO_2Et)_2$, $CH_2(CN)_2$, or $MeNO_2$. Benzoylation is not effected in C_5H_5N. Chlorin-e_6, Me_3 ester is oxidised by $KMnO_4$ in C_5H_5N to dihydroxychlorin-e_6, and application of this method to purpurin-7 Me_3 ester leads to *purpurin*-9 [2-*carboxy*-2-*devinylpurpurin*-7 *Me*$_4$ *ester*] (*A*), m.p. 236° (decomp.), which gives a negative



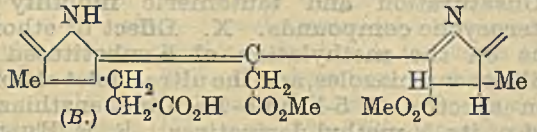
(*A*.)

reaction with $CHN_2{\cdot}CO_2Et$ and is converted by boiling C_5H_5N into 2-*carboxy*-2-*de-ethylrhodoporphyrin Me*$_3$ *ester*, m.p. 270°. Similar energetic oxidation of *iso*chlorin-e_4 Me_2 ester gives a 2-carboxychlorin sol. in alkali and 5 : 6-*dihydroxy*-2-*glycolyl*-2-*devinyl*isochlorin-e_4 *Me*$_2$ *ester*, m.p. 192° (decomp.). Catalytic hydrogenation (Pd in 1% NaOH) of purpurin-7 Me ester (II) gives *meso*-rhodochlorin, m.p. 178°, also obtained with *meso*-purpurin-18 from

purpurin-18 under similar conditions. With PtO_2 in dioxan *meso*-purpurin-7 Me_3 ester is converted into the *perhydro*-compound, m.p. 213°.

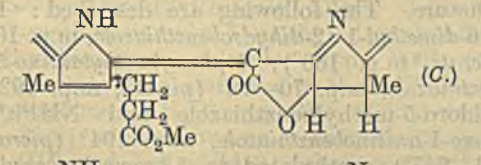
The impossibility of hydrolysing (I) to the tricarboxylic acid depends on the instability in the last stage. Hydrolysis of (II) with $Ba(OH)_2$ gives the sparingly sol. *Ba* salt of the unstable *chlorin*, $C_{34}H_{32}O_7N_4Ba$, $[\alpha]^{20}_{690-730}$ +650° in $COMe_2$.

Treatment of phæophorbide *a* (III) in C_5H_5N with MeOH–anhyd. Na_2CO_3 at 100° gives the *chlorin*-e_6 *Me*$_2$ *ester* (*B*), m.p. 215° (decomp.), $[\alpha]^{20}_{690-730}$ −241°

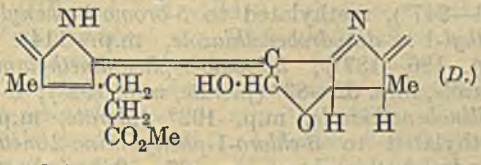


(*B.*)

in $COMe_2$, which when heated above its m.p. yields vinylrhodoporphyrin and a little rhodoporphyrin, both of which are sol. in alkali. (III) is oxidised by $KMnO_4$ in $COMe_2$ to unstable *chlorin Me ester*, decomp. 237°, $[\alpha]^{20}_{690-730}$ −94° in $COMe_2$. Analogously *meso*-phæophorbide-*a* gives unstable meso-*chlorin Me ester*, m.p. 220° (decomp.), $[\alpha]^{20}_{690-730}$ −99° in $COMe_2$. The reactions of these unstable chlorin esters do not differ from those of (I). Gentle oxidation of free chlorin-e_6 with $KMnO_4$ appears to give a mixture of chlorins, $C_{33}H_{34}O_5N_4$ and $C_{32}H_{34}O_4N_4$ or $C_{32}H_{32}O_4N_4$, esterified by CH_2N_2 to *purpurin*-5 *Me*$_2$ *ester* (IV), m.p. 194°, $[\alpha]^{20}_{690-730}$ +242° in $COMe_2$, and the *chlorin ester C* or *D*, m.p. 177°. Free chlorin-e_6

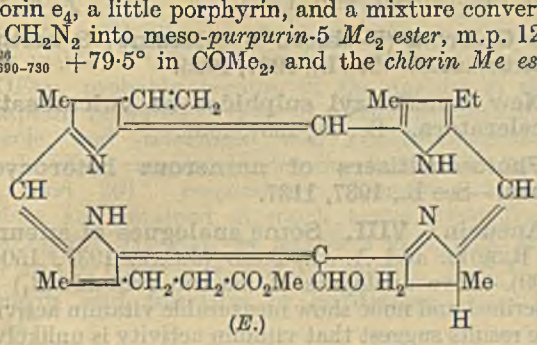


(*C.*)



(*D.*)

is converted by boiling C_5H_5N in N_2 into chlorin-e_4 and another chlorin. Under similar conditions but in presence of O_2 it gives the *ester*, $C_{33}H_{34}O_4N_4$ or $C_{33}H_{36}O_4N_4$, m.p. 176°. Similarly (IV) gives vinylrhodoporphyrin Me_2 ester, m.p. 273°. Analogously *meso*-chlorin-e_6 affords unchanged material, *meso*-chlorin e_4, a little porphyrin, and a mixture converted by CH_2N_2 into meso-*purpurin*-5 *Me*$_2$ *ester*, m.p. 127°, $[\alpha]^{26}_{690-730}$ +79·5° in $COMe_2$, and the *chlorin Me ester*,



(*E.*)

$C_{33}H_{36}O_4N_4$ or $C_{33}H_{38}O_4N_4$, m.p. 149°. *ψ*-Chlorin-p_6 yields *diazomethane*-meso-*chlorinlactone-ester*, $C_{33}H_{34}O_4N_4$, m.p. 176°, $[\alpha]^{20}_{690-730}$ −378° in $COMe_2$, whilst in the absence of O_2 it affords this substance with purpurin-5 Me_2 ester and rhodoporphyrin-*γ*-carboxylic anhydride. The action of O_2 in C_5H_5N followed by CH_2N_2 on *iso*chlorin-e_4 leads to *γ-formylpyrrochlorin Me*$_1$ *ester* (*E*), m.p. 181°, $[\alpha]^{20}_{690-730}$ −401° in $COMe_2$ (*oxime*; *semicarbazone*), also obtained by oxidation with $KMnO_4$ in C_5H_5N. H. W.

Imidoporphyrins. IV. Synthesis of tetraimidoætioporphyrin. H. Fischer and F. Endermann (Annalen, 1937, **531**, 245—250; cf. this vol., 169).—Et_2 3-methyl-4-ethylpyrrole-2 : 5-dicarboxylate is converted by N_2H_4,H_2O at 120—130° into 3-*methyl*-4-*ethylpyrrole*-2 : 5-*dicarboxyhydrazide*, m.p. 241°, whence the corresponding *diazide*, m.p. 66° (decomp.), which could not be transformed satisfactorily into the corresponding diurethane. Treatment of opsopyrrole (I) or opsoic acid (II) with Br (2 mols.) does not lead to recognisable derivatives but the simultaneous action of Br and NH_3 in $CHCl_3$ on (I) gives *tetraimidoætioporphyrin*, m.p. 252—253° (probably a mixture of isomerides) (corresponding *hæmin*, $C_{28}H_{32}N_8FeCl$, m.p. >380°; complex *Cu* salt, $C_{28}H_{32}N_8Cu$, m.p. >350°; *Mg* compound, very sensitive to acid). The method can be applied to (II) or 3-methylpyrrole but not to pyrrole itself on account of its ready decomp. by acids. H. W.

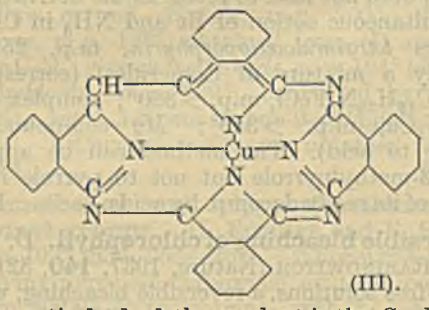
Reversible bleaching of chlorophyll. D. Porret and E. Rabinowitch (Nature, 1937, **140**, 321—322).—In O_2-free solutions, a reversible bleaching, which ∝ the (light intensity)$^{\frac{1}{2}}$, occurs. HCO_2H markedly increases this bleaching, whilst $FeCl_2$ and traces of O_2 suppress it. The quantum yield of the reversible bleaching is ⩾ that of the irreversible oxidation in presence of O_2. Synthetic Et chlorophyllide *a* and the natural chlorophylls *a* and *b* all behave in a similar manner. Possible mechanisms are discussed. L. S. T.

Reactions of nitrite with hæmoglobin derivatives.—See A., III, 411.

***N*-Tripyrazolylmethane.** W. Hückel and H. Bretschneider (Ber., 1937, **70**, [*B*], 2024—2026).—*K pyrazole*, obtained from K and pyrazole (I) in C_6H_6 or from molten (I) and KOH, is converted by $CHCl_3$ in C_6H_6 into N-*tripyrazolylmethane*, m.p. 106°, rapidly transformed by acids into (I) and HCO_2H. BzCl or Bz_2O and (I) afford 1-*benzoylpyrazole*, b.p. 140°/11 mm., m.p. 46°, also obtained in poor yield from Mg pyrazolyl bromide (II) and BzCl. *Me pyrazole*-1-*carboxylate*, b.p. 92°/11 mm., m.p. 35°, from (I) and $ClCO_2Me$ or from (II), gives CO_2 and (I) when hydrolysed. *Di*-1-*phenyl*-3-*methylpyrazolonyl*-4-*ketone* (*semicarbazone*, m.p. 202°) is obtained by the action of H_2O_2 on methenyldi- or methylenedi-phenylmethylpyrazolone. Other attempts to combine three pyrazole residues with one C atom are described. H. W.

Action of cuprous cyanide on *o*-halogenoacetophenones. II. J. H. Helberger and A. von Rebay (Annalen, 1937, **531**, 279—287; cf. this vol., 264).—*o*-*Cyanoacetophenone* (I), b.p. 148°/12 mm., m.p. 48°, is obtained in very modest yield from *o*-$C_6H_4Ac{\cdot}NH_2$ (Sandmeyer); it is prepared from *o*-C_6H_4ClAc and CuCN in quinoline at 150° with a *by-*

product, m.p. 230°, but is best derived from *o*-C_6H_4BrAc in C_5H_5N at 120° (yield 80%). The unexpected stability of (I) suggests a cyclic structure $C_6H_4<^{CO}_{C(:NH)}>CH_2$ or $C_6H_4<^{CO}_{C(NH_2)}>CH$, but the hypothesis is negatived by the conversion of (I) by NH_2OH into the inner anhydride of phenylmethylketoxime-*o*-carboxylic acid, $^{C_6H_4\cdot CMe}_{CO\text{——}O}>N$, m.p. 159°. Similarly, methylphthalazone, m.p. 219°, is obtained from (I) and N_2H_4,H_2O or $NH_2\cdot CO\cdot NH\cdot NH_2$. Mild treatment of (I) with $NHPh\cdot NH_2$ in MeOH gives the additive *product*, $C_{13}H_{15}ON_3$, m.p. 205—207° (decomp.), converted by short boiling with AcOH into phenylmethylphthalazone. CuCl and (I) in quinoline at 200—220° give the Cu derivative of tetrabenzomonoazaporphin (*loc. cit.*), whilst in presence of *o*-$C_6H_4(CN)_2$ (II) [(I) : (II) : CuCl :: 2 : 1 : 2] the Cu salt of tetrabenzodiazaporphin results. If the components



(III).

are in the ratio 1 : 1 : 1 the product is the *Cu derivative* of *tetrabenzotriazaporphin* (III). The intermediate formation of (I) in the production of Cu tetrabenzoazaporphins from *o*-halogenoacetophenones and CuCN is thus established.

Exposure of finely-divided *o*-$CN\cdot C_6H_4\cdot CH{:}CH\cdot CO_2H$ to Br vapour at room temp. gives the corresponding *dibromide*, m.p. 155°, which passes in boiling C_5H_5N into ω-bromo-*o*-cyanostyrene, m.p. 87°, and *bromo-o-cyanocinnamic acid*, m.p. 173°. These compounds with CuCl in quinoline undergo much resinification and do not appear to afford compounds resembling the phthalocyanines (cf. Linstead and Noble, this vol., 352). H. W.

Furfurylbarbituric acids.—See B., 1937, 1135.

Reaction of cysteine with acetone. Titration of cysteine by the acetone–hydrochloric acid method of Linderstrøm-Lang. (Miss) G. E. Woodward and E. F. Schroeder (J. Amer. Chem. Soc., 1937, **59**, 1690—1694).—Cysteine and $COMe_2$ give H_2O and 2 : 2-*dimethylthiazolylidene-4-carboxylic acid* (I), m.p. 134—134·5° (decomp.; corr.), $[\alpha]_D^{22}$ —183° in $COMe_2$, hydrolysed by H_2O. In aq. $COMe_2$ the position of the equilibrium depends on the $[COMe_2]$ and p_H. In the Linderstrøm-Lang method of determining glutathione it is essential to add the HCl before the bulk of the $COMe_2$, as the p_H developed prevents the formation of (I), which cannot be titrated with HCl. R. S. C.

Thiazoles. I. 4-Methylthiazole-5-acetic acid and its derivatives. L. R. Cerecedo and J. G. Tolpin (J. Amer. Chem. Soc., 1937, **59**, 1660—1661).—$HCS\cdot NH_2$ and Et β-bromolævulate in dry EtOH at —5° to 15° give *Et 4-methylthiazole-5-acetate* (I), b.p. 107—112°/3 mm. (*hydrochloride*, m.p. 153°, prepared slowly from the β-Cl-ester; *picrate*, m.p. 130°), hydrolysed to the corresponding *acid*, m.p. 189° {*Me* ester, b.p. 111°/18 mm.; *amide*, 136°; *hydrazide*, m.p. 111° [*picrate*, m.p. 258° (decomp.)]}. The *hydrobromide*, m.p. 164°, of (I) with Na–EtOH gives a trace of β-4-*methylthiazolyl-5-ethyl alcohol*, isolated as *picrate*, m.p. 164°, but other methods of reduction either did not affect the ester or decomposed it. R. S. C.

Unsaturation and tautomeric mobility of heterocyclic compounds. X. Effect of ethoxyl ions on the methylation of 5-substituted 1-anilinobenzthiazoles, and the ultra-violet absorption spectra of 5-bromo-1-anilinobenzthiazole and of its *N*-methyl derivatives. R. F. Hunter and M. A. Wali (J.C.S., 1937, 1513—1517).—On methylation with Me_2SO_4 alone, 1-anilino-5-methyl-, 5-bromo- and 5-chloro-1-anilino-benzthiazole apparently all react exclusively in the amino-aromatic form, yielding 1-phenylimino-2-methyl-1 : 2-dihydrobenzthiazoles. The 5-NO_2-derivative gives a mixture of isomeric Me derivatives. The presence of EtOH–NaOEt causes extensive methylation on the non-nuclear N in the 5-Me, -Br-, and -Cl-bases, and in the 5-NO_2-compound exclusive alkylation at this position. A comparison of the ultra-violet absorption spectrum of 5-bromo-1-anilinobenzthiazole with that of 5-bromo-1-phenylmethylaminobenzthiazole in EtOH indicates that the mol. has the amino-aromatic structure. The following are described: 1-*phenyl*-2 : 5-*dimethyl*-1 : 2-*dihydrobenzthiazole*, m.p. 107—108° (*picrate*, m.p. 180°); 1-*phenylmethylamino*-5-*methylbenzthiazole*, m.p. 70—72° (*picrate*, m.p. 192°), from 1-chloro-5-methylbenzthiazole and NHPhMe; 5-*bromo*-1-*anilinobenzthiazole*, m.p. 194° (*picrate*, m.p. 246—247°), methylated to 5-*bromo*-1-*phenylimino*-2-*methyl*-1 : 2-*dihydrobenzthiazole*, m.p. 114° (*picrate*, m.p. 186—187°); 5-*bromo*-1-*phenylmethylaminobenzthiazole*, m.p. 82—83° (*picrate*, m.p. 198°); 5-*chloro*-1-*anilinobenzthiazole*, m.p. 192° (*picrate*, m.p. 238°), methylated to 5-*chloro*-1-*phenylimino*-2-*methyl*-1 : 2-*dihydrobenzthiazole*, m.p. 125—126° (*picrate*, m.p. 174°); 5-*chloro*-1-*phenylmethylaminobenzthiazole*, m.p. 76—77° (*picrate*, m.p. 196—198°); and 5-*nitro*-1-*anilinobenzthiazole*, m.p. 248°, methylated to 5-*nitro*-1-*phenylimino*-2-*methyl*-1 : 2-*dihydrobenzthiazole*, m.p. 210°, and 5-*nitro*-1-*phenylmethylaminobenzthiazole*, m.p. 152° (*picrate*, m.p. 173°). F. R. S.

5-Chloro-2-(5′-chloro-*o*-toluidino)-3-methylbenzthiazole.—See B., 1937, 1025.

New benzthiazyl sulphides as vulcanisation accelerators.—See B., 1937, 1092.

Photosensitisers of numerous heterocyclic types.—See B., 1937, 1137.

Aneurin. VIII. Some analogues of aneurin. F. Bergel and A. R. Todd (J.C.S., 1937, 1504—1509).—Five analogues of aneurin (vitamin-B_1) are described and none show measurable vitamin activity. The results suggest that vitamin activity is unlikely in a 3-(pyrimidyl-5′-methyl)thiazolium salt unless it contains (*a*) a 4′-NH_2, (*b*) a 5-β-hydroxyethyl group,

(*c*) a free 2-position in the thiazole ring. It is also probable that the nature of the substituents at 2′ and 6′ in the pyrmidine ring influences vitamin activity. 4-Amino-5-thioformamidomethyl-2-methylpyrimidine and CH_2Cl·COMe give 3-(4′-*amino*-2′-*methylpyrimidyl*-5′-*methyl*)-4-*methylthiazolium chloride hydrochloride* (analogue *A*) (+H_2O), sinters 261—262°. 4-Hydroxy-5-thioformamidomethyl-2-methylpyrimidine (I) and Me α-bromo-γ-acetoxypropyl ketone (II) afford 3-(4′-*hydroxy*-2′-*methylpyrimidyl*-5′-*methyl*)-4-*methyl*-5-β-*hydroxyethylthiazolium chloride hydrochloride* (analogue *B*), m.p. 195—197°. CH_2Cl·COMe and (I) yield 3-(4′-*hydroxy*-2′-*methylpyrimidyl*-5′-*methyl*)-4′-*methylthiazolium chloride hydrochloride* (analogue *C*), (+H_2O), softens 220°. Condensation in AcOH at 120° of (II) and 4-*amino*-5-*thioacetamidomethyl*-2-*methylpyrimidine* (III), m.p. 228—229°, obtaind from 4-amino-2-methylpyrimidine and dithioacetic acid, gives the *hydrobromide* of 2 : 7-dimethyldihydro-1 : 3 : 6 : 8-benztetrazine, m.p. 283—284° (*picrate*, m.p. 198—199°; *hydrochloride*, m.p. 269—270°; *base*, m.p. 169—170°), and the *bromide hydrobromide* of O-*acetyl*-2-*methylaneurin*, m.p. 193—194°. This compound is converted through the picrate, m.p. 188—189°, into 3-(4′-*amino*-2′-*methylpyrimidyl*-5′-*methyl*)-2 : 4-*dimethyl*-5-β-*hydroxyethylthiazolium chloride hydrochloride* (*methylaneurin*), m.p. 199°. (II) and (III) in AcOH at 80° lead to the *hydrobromide* of (III), m.p. 198—200°, converted through the picrate into the corresponding *hydrochloride*, m.p. 197—199°. 2 : 4-Dichloro-6-methyl-5-chloromethylpyrimidine (IV) and 4-methyl-5-β-hydroxyethylthiazole afford 3-(2′ : 4′-dichloro-6′-methylpyrimidyl-5′-methyl)-4-methyl-5-β-hydroxyethylthiazolium chloride, m.p. 206° (cf. Bowman, this vol., 213), aminated to the 3-(2′-*chloro*-4′-*amino*-compound (+H_2O), m.p. 200—205° (*picrate*, m.p. 214—215°), which shows no measurable vitamin activity. (IV) and NaI yield 2 : 4-*dichloro*-6-*methyl*-5-*iodomethylpyrimidine*, m.p. 93·5—94·5°, which with 4-methyl-5-β-hydroxyethylthiazole forms 3-(2′ : 4′-*dichloro*-6′-*methylpyrimidyl*-5′-*methyl*)-4-*methyl*-5-β-*hydroxyethylthiazolium iodide*, m.p. 181—182°. Amination of (IV) leads to *bis*-(2 : 4-*dichloro*-6-*methylpyrimidyl*-5-*methyl*)*amine*, m.p. 162—163°, and no 5-aminomethyl compound can be isolated. F. R. S.

Anthraquinonebis-selenazoles.—See B., 1937, 1030.

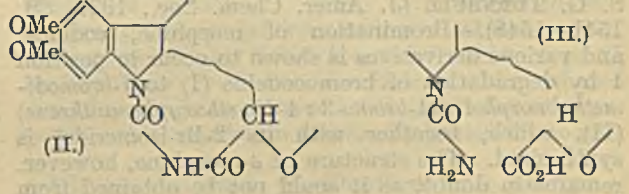
Improved cyanine synthesis (mixed solvent process). Reaction of orthothioformic ester. T. Kimura (Proc. Imp. Acad. Tokyo, 1937, **33**, 261—265).—$CH(SEt)_3$ in Ac_2O at 140° gives much better yields of trinuclear carbocyanines than does $CH(OEt)_3$, probably because of the acidity of the mercaptan liberated; thus, 1-methylbenz-oxazole, -thiazole, and -selenazole, and 1-methyl-naphthothiazole afford *compounds*, decomp. 225°, 260—261°, 239°, and 201°, respectively. Dinuclear carbocyanines are obtained in much better yield from $CH(SEt)_3$ or $CH(OEt)_3$ by mixtures of C_5H_5N and Ac_2O than by either C_5H_5N or Ac_2O alone. R. S. C.

Origin and function of hordenine.—See A., III, 447.

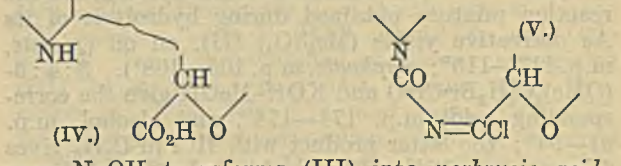
Condensation of 2-aminonicotine with ω-bromoacetophenone. J. L. Goldfarb and M. V. Andrijtschuk (Compt. rend. Acad. Sci. U.R.S.S., 1937, **16**, 473—477).—2-Aminonicotine and COPh·CH_2Br in EtOH yield a mixture of 7-(N-*methylpyrrolidyl*)-2-*phenylpyriminazole* (*picrate*, m.p. 209·5—211°; *dihydrobromide*, m.p. 272—274°; *platinichloride*, m.p. 250—253°) and α-*phenacylaminonicotine* (*picrate*, m.p. 186·5°). J. D. R.

Veratrine alkaloids. II. Basic degradation products of cevine. W. A. Jacobs and L. C. Craig (J. Biol. Chem., 1937, **120**, 447—456; cf. this vol., 355).—The base $C_7H_{15}N$ has been identified as *d*-*N*-methyl-β-pipecoline (*picrate* of *l*-base, m.p. 176—179°, $[\alpha]_{5780}^{23}$ −12·6° in $COMe_2$; *picrate* of *dl*-base, m.p. 165—168°). l-N-*Dimethyl*-β-*pipecolinium iodide*, m.p. 200—201°, $[\alpha]_D^{26}$ +7·0° in H_2O, and *l*-β-*pipecoline* 3 : 5-*dinitrobenzoate*, m.p. 114—116°, $[\alpha]_D^{32}$ −30° in $COMe_2$, are described. Separation of the mixture of bases obtained by heating cevine (I) in H_2 with Zn dust, by means of HNO_2, gave β-pipecoline (II) and similar treatment of the bases obtained by heating with soda-lime gave (II), mainly as the *d*-isomeride, and a very small amount of coniine (3 : 5-dinitrobenzoate, $[\alpha]_D^{25}$ +49° in $COMe_2$). The base $C_8H_{11}N$ obtained by heating (I) in H_2 with Zn, followed by catalytic hydrogenation, is probably 5-methyl-2-ethylpyridine. The dicyclic base $C_{10}H_{19}N$ previously obtained may be a methyloctahydropyridocoline or a dimethyloctahydropyrrocoline. J. N. A.

***Strychnos* alkaloids. XIX. Attempted degradation of oximinobrucine.** H. Wieland and F. Wille (Annalen, 1937, **531**, 268—278; cf. A., 1932, 629).—Oximinobrucine is converted by $SOCl_2$ into a product (I) from which by repeated crystallisation from MeOH the cyclic *carbamide* (II), m.p.

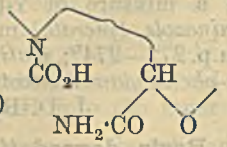


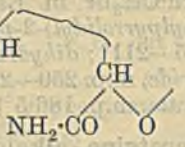
228° (decomp.), is isolated as the *hydrochloride*, $[\alpha]_D^{20}$ +30·1° in H_2O. Boiling 2N-H_2SO_4 converts (II) into the open *carbamide* (III), m.p. 251° (decomp.), $[\alpha]_D^{20}$ +31·2° in 0·1N-NaOH (*sulphate*), reconverted into (II) by HCl in MeOH. Treatment with boiling



conc. NaOH transforms (III) into *norbrucic acid*, $C_{22}H_{26}O_5N_2$, (IV), m.p. 292—293° (decomp.) (also +5H_2O) (*hydrochloride*; *Et* ester, m.p. 231°), hydrogenated (PtO_2 in AcOH) to *dihydronorbrucic acid*, m.p. 286—287° after decomp. from 270° (also +3H_2O). The isolation of an isomeric *acid*, m.p. 259° (decomp.) after softening, is also described; unlike (IV), it is not hydrogenated in presence of Pd. If (I) is treated with N-NaOH (II) present therein is converted into

(III) which dissolves leaving the cyclic *chloroimine* (V), $C_{23}H_{24}O_4N_3Cl$, m.p. 247° (decomp.), converted

(VI.) 

(VII.) 

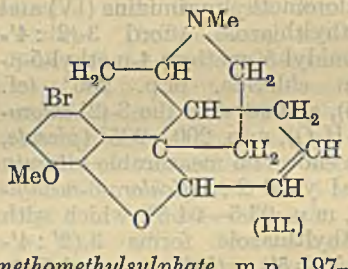
by 2N-H_2SO_4 into (IV), which absorbs 1 H_2 (Pd-black) without loss of Cl. When finely dispersed (V) is transformed by 2N-NaOH into the *carbamic acid* (VI), $C_{23}H_{27}O_6N_3$, m.p. 206—207° (decomp.), which with dil. acid yields CO_2 and *norbrucamide* (VII), $C_{22}H_{27}O_4N_3$, m.p. 156—158°. If a solution of (VII) in dil. HCl is neutralised with $NaHCO_3$ (VI) is obtained. Attempts to remove Cl from (V) by KOH–EtOH yield a *base*, $C_{23}H_{25}O_5N_3$, m.p. 143—145°, isomeric with (II). The *bases*, $C_{22}H_{25}O_4N_3$, m.p. 258° (decomp.), and $C_{21}H_{26}O_6N_2$, m.p. 163° after prolonged softening [orange-yellow *hydrochloride*; H_4-derivative, m.p. 236° (decomp.)], are isolated as by-products of the prep. of (I).

[With H. Beyer.] Re-examination of the acid from 11-hydroxydihydrostrychnine (Wieland and Kaziro, A., 1933, 1175) confirms the conclusions of Leuchs and Beyer (A., 1934, 539). H. W.

[Strychninolone and its derivatives.] H. Leuchs (Ber., 1937, **70**, [*B*], 2031—2033).—In criticism of the publication of Kotake and Mitsuwa (A., 1936, 870) it is suggested that their γ-isomeride is the *c*-form of Leuchs; the ε-isomeride is impure *b*-form and their β-prep. is a mixture. The δ-substance does not appear to be a strychninolone isomeride. H. W.

Structure of bromomorphine. L. Small and S. G. Turnbull (J. Amer. Chem. Soc., 1937, **59**, 1541—1548).—Bromination of morphine, codeine, and various derivatives is shown to occur in position 1 by degradation of bromocodeine (I) to 1-*bromodimethylmorphol* (1-*bromo*-3 : 4-*dimethoxyphenanthrene*) (II), which, together with its 2-Br-isomeride, is synthesised. The structure of ψ-morphine, however, remains in doubt, as it could not be obtained from bromomorphine. Bromoacetylmethylmorphol [from (I) by Hofmann degradation and acetolysis of the methine] is stable to aq. alkali, but with hot 15% KOH–MeOH gives *bromomethylmorphol* (1-*bromo*-4-*hydroxy*-3-*methoxyphenanthrene*), m.p. 141·5—142·5°; this is too sensitive to alkali to be methylated, but the reaction mixture obtained during hydrolysis of its Ac derivative yields (Me_2SO_4) (II), an oil (*picrate*, m.p. 113—115°; *styphnate*, m.p. 105—108°). 3 : 4 : 6-$(OMe)_2C_6H_2Br$·CHO and KOH–MeOH give the corresponding acid, m.p. 174—178°, and alcohol, m.p. 91—94°; the latter product with HCl in C_6H_6 gives 6-*bromoveratryl chloride*, m.p. 66·5—68·5°, and thence the oily *cyanide* and 6-*bromohomoveratric acid*, m.p. 114—116°; condensation with *o*-NO_2·C_6H_4·CHO and reduction gives 2-*amino*-α-6′-*bromo*-3′ : 4′-*dimethoxyphenylcinnamic acid*; diazotisation and treatment with Naturkupfer-*C* eliminates Br, but Gattermann's Cu paste gives 1-*bromo*-3 : 4-*dimethoxyphenanthrene*-10-*carboxylic acid*; dry distillation of this acid gives an oily *substance*, (?) the *Me* ester (*picrate*, m.p. 113—115°), not identical with (II), and decarboxylation with Cu eliminates the Br.

3 : 4 : 6 : 2-$(OMe)_2C_6HBr(NO_2)$·CHO and $CH_2Ph·CO_2Na$ in Ac_2O at 100° give 30% of 6-*bromo*-2-*nitro*-3 : 4-*dimethoxy*-α-*phenyl*-, m.p. 206—208°, and 12% of 6-*bromo*-2-*nitro*-3 : 4-*dimethoxy*-*cinnamic acid*, m.p. 200—201°, and thence ($FeSO_4$–NH_3) the *NH_2-acids*, m.p. 202—203° and 150—151°, respectively, catalytic hydrogenation of which gives Br-free *substances*, m.p. 169—170° and 120—122°, respectively; the first-mentioned NH_2-acid, when treated with $BuNO_2$ and HCl–EtOH and then with Cu paste, gives 1-*bromo*-3 : 4-*dimethoxyphenanthrene*-9-*carboxylic acid*, decomp. 260—270°, converted by distillation at 75 mm. into the *Me* ester, m.p. 123·5—125° (no picrate), and by Cu paste in quinoline at 240° into (II). By a similar series of reactions 5-*bromo*-2-*nitroveratraldehyde* (prep. from the vanillin derivative), m.p. 70—72·5°, affords 5-*bromo*-2-*nitro*-, m.p. 231—231·5°, and -2-*amino*-3 : 4-*dimethoxy*-α-*phenylcinnamic acid*, m.p. 175—176° (decomp.), 2-*bromo*-3 : 4-*dimethoxyphenanthrene*-9-*carboxylic acid*, m.p. 237·5—238·5°, the *Me* ester, m.p. 114—116° (obtained by pyrolysis or CH_2N_2), of which with H_2–Pd–$BaSO_4$ gives *Me* 3 : 4-*dimethoxyphenanthrene*-9-*carboxylate*, m.p. 95—96°; decarboxylation of the acid gives 2-bromo-3 : 4-dimethoxyphenanthrene, m.p. 78·5—79·5°. Bromochlorocodide [from (I) and PCl_5 in $CHCl_3$], m.p. 131—133·5°, $[\alpha]_D^{26}$ —288·5° in EtOH, is reduced by Zn dust–EtOH–CO_2 to *bromodeoxycodeine*-C (III), m.p. 210—212·5°, $[\alpha]_D^{26}$ +65·9° in EtOH (*perchlorate*, m.p. 208—210°), cryptophenolic, which absorbs 2 H_2 (Adams) in EtOH to give bromotetrahydrodeoxycodeine, *form*, $+H_2O$, m.p. 119 — 128°, $[\alpha]_D^{26}$ —28·2° in EtOH; the *methomethylsulphate*, m.p. 197—212°, with 5N-NaOH gives, in one step, bromomethylmorphenol, m.p. 119—120°, debrominated by H_2–Pd–$CaCO_3$ to methylmorphenol. Deoxycodeine-*C* and Br in aq. AcOH give a *perbromide*, $C_{18}H_{20}O_2NBr_3$, m.p. 184·5—185·5°, $[\alpha]_D^{26}$ —156·7° in C_6H_6, hydrogenated (Adams) in EtOH to a new phenolic *bromotetrahydrodeoxycodeine* (*hydrobromide*, m.p. 116—117·5°, $[\alpha]_D^{26}$ —3·3° in EtOH), which with Na–EtOH gives a Br-free phenolic *substance* (C 72·5, H 7·9%), m.p. 88—89°. Deoxycodeine-*A* or its hydrobromide with Br in AcOH gives a *substance*, m.p. 189—189·5°, $[\alpha]_D^{25}$ +10·2° in C_6H_6 (contains 2 Br; *hydrobromide*, m.p. 149—151°, $[\alpha]_D^{25}$ —3·8° in EtOH), which with hot NaOAc–Ac_2O gives 1-bromoacetylmethylmorphol. Dihydrodeoxycodeine-*D* with Br–AcOH or aq. Br–AcOH gives a *Br*-derivative, m.p. 156—157°, $[\alpha]_D^{25}$ —37·6° in EtOH.



(III.)

R. S. C.

Curare alkaloids. III. Pot-curare. H. King (J.C.S., 1937, 1472—1482).—By extraction with 1% tartaric acid, the alkaloids of a specimen of pot-curare have been separated into "non-quaternary" bases (38%) and "quaternary" bases (12%). The paralysing dose on frogs under standard conditions has been determined, and, although the former frac-

tion shows weak curare action, most of the activity lies in the "quaternary" fraction. The "non-quaternary" bases may be separated into *protocuridine* (I), $C_{36}H_{38}O_6N_2$ ($+0{\cdot}5C_5H_5N$), m.p. 295° [*dihydrochloride* ($+6H_2O$), m.p. 295° (efferv.), $[\alpha]_{5461}^{20}$ +7·6° in H_2O; *O-methylprotocuridine methiodide*, m.p. 318° (decomp.)] (cf. Boehm, A., 1898, i, 283), and *neoprotocuridine* (II), $C_{36}H_{38}O_6N_2$ ($+8H_2O$), m.p. 232° (efferv.) [*dihydrochloride* ($+6$ or 7 H_2O), m.p. >310°; *O-methylneoprotocuridine methiodide*, m.p. >300°]. The Millon reaction is shown by (I) but not by (II). From the "quaternary" fraction, (II) has been isolated as hydrochloride and also a mixture of alkaloids from which an amorphous iodide of high paralysing activity and showing a Millon reaction has been separated. By methylation of fractions of the alkaloids, *iodide A*, $C_{20}H_{25}O_8NI_2$, m.p. 260° (decomp.), and *iodide B*, $C_{17\text{ or }18}H_{22}O_2NI$, m.p. 318°, have been obtained. (II) has been identified as an internally compensated form of *iso*chondrodendrine; this establishes a close relationship between the alkaloids of pot-curare and those of tube-curare, as both are based on the fusion of two polyphenolic benzyl*iso*quinoline nuclei by ether linkages. The botanical origin is discussed. F. R. S.

***Sinomenium* and *Cocculus* alkaloids. XLVI. Methyl*iso*chondodendrine.** H. Kondo, M. Tomita, and S. Uyeo (Ber., 1937, **70**, [*B*], 1890—1893).—Chromatographic analysis (Al_2O_3, Brockmann) of the crude bases from *Cissampelos insularis*, Makino, does not lead to the isolation of insularine but yields methyl-*iso*chondodendrine, also obtained from *Stephania cepharantha*, Hayata. Its identity with the product of Faltis (A., 1934, 423) is established by direct comparison of the alkaloids, their methine and hydromethine bases. H. W.

***m*-Arsenated phenoxyethanols.** S. B. Binkley and C. S. Hamilton (J. Amer. Chem. Soc., 1937, **59**, 1716—1719).—*m*-OH·C_6H_4·AsO_3H_2 does not condense with $CH_2Cl{\cdot}CH_2{\cdot}OH$, but *m*-$NO_2{\cdot}C_6H_4{\cdot}OH$ in 2N-NaOH gives β-m-*nitrophenoxyethyl alcohol*, m.p. 88°, reduced (H_2–Raney Ni) to m-β-*hydroxyethylaniline*, m.p. 52°, which affords (Bart) m-β-*hydroxyethylphenylarsinic acid*, m.p. 110° (*Na* salt). With HNO_3 (*d* 1·5) this gives a mixture of nitrates, hydrolysed by hot 3N-HCl to 2-, m.p. 270° (I), and 4-*nitro*-3-β-*hydroxyethylphenylarsinic acid* (II), m.p. 164°, which afford (SO_2–HI) the corresponding *arsinoxides*, m.p. >270°, and thence by $Hg(OAc)_2$ β-2-*nitro*-3-, m.p. 150—152°, and β-2-*nitro*-5-*chloromercuriphenoxyethyl alcohol*, m.p. 147—149°, both of which with 3N-HCl give *o*-$NO_2{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, hydrolysed by 6N-NaOH to *o*-$NO_2{\cdot}C_6H_4{\cdot}OH$. With 6N-NaOH (I) and (II) give 2-, m.p. 208° (decomp.), and 4-*nitro*-3-*hydroxyphenylarsinic acid*, m.p. >270°; the 2-NO_2-acid affords successively 2-*nitro*-3-*hydroxyphenylarsinoxide*, m.p. 220—223° (decomp.), 2-*nitro*-3-*chloromercuriphenol*, m.p. 212—214°, and 2 : 3-$NO_2{\cdot}C_6H_3I{\cdot}OH$. R. S. C.

Arsenic derivatives of 1 : 4-benz*iso*oxazine.—See B., 1937, 1136.

Organo-arsenic compounds. V. Synthesis of arsindole derivatives. H. N. Das-Gupta (J. Indian Chem. Soc., 1937, **14**, 349—353).—C_2H_2 and $AlCl_3$ convert $AsPhCl_2$ into a mixture of diphenyl-β-chlorovinyl-, phenyl-ββ′-dichlorodivinyl- (also synthesised from the chloroarsine and MgPhBr) (*double salts* with $HgCl_2$, m.p. 157—158°, and $AgNO_3$, m.p. 170°; *methiodide*, m.p. 232°), and phenyl-β-chlorovinylchloro-arsine (cf. J.C.S., 1925, **127**, 996). The last has been converted into the corresponding *arsinic acid*, m.p. 135°, *Et ether*, b.p. 165—170°/3 mm., *arsenious cyanide*, and *sulphide*, m.p. 141°, and by Grignard reagents into the phenyl- and methyl-arsines. When treated with $AlCl_3$ in CS_2 or heated to 230°, it affords 1-chloroarsindole. A. Li.

Mercury compounds of benzotrifluoride.—See B., 1937, 1136.

Mercuriation of benzanthrone(-7). A. Bernardi (Gazzetta, 1937, **67**, 380—384)—Benzanthrone(-7) with $Hg(OAc)_2$ at 171° yields its 3-*mercuriacetate* (I), which at its m.p., 141—142°, gives *Hg bisbenzanthronyl*, m.p. 70—75°. 0·1N-KOH–EtOH converts (I) into the 3-*mercurihydroxide*, decomp. 260° (*chloride* prepared). With Br–KBr in AcOH, (I) forms 3-bromobenzanthrone(-7). E. W. W.

The cyclol hypothesis and the "globular" proteins. D. M. Wrinch (Proc. Roy. Soc., 1937, **A**, **161**, 505—524).—A further development of the "cyclol" hypothesis (cf. this vol., 394). The general "cyclol" fabric, consisting of hexagonal rings, is folded according to geometrical rules to produce closed "globular" mols. It is shown that several systems can exist, the series formed by folding the cyclol network on to the faces of a truncated tetrahedron being here described. This series consists of a no. of mols. C_1, C_2 . . . C_n in which the no. of NH_2-acid radicals is 72, 288 . . . $72n^2$. It is suggested that the group of proteins with mol. wts. 33,600—40,500 are represented by closed "cyclols" of the type C_2 containing 288 residues. The ionic behaviour of such mols. in solution is discussed with particular reference to reversible association and the hydration of the mol. G. D. P.

Ultracentrifugal purification and study of macromolecular proteins. R. W. G. Wyckoff (Science, 1937, **86**, 92—95).—A review. L. S. T.

Clupein. VIII. K. Felix and A. Mager (Z. physiol. Chem., 1937, **249**, 111—123; cf. A., 1933, 963; Waldschmidt-Leitz and Kofranyi, A., 1936, 110).—The hydrochloride (I) of the Me ester of clupein (II) contains total N 24·99, Cl 16·08, and OMe 0·65%. The N is distributed as follows: as arginine (III) 89·39, $(NH_2)_1$-acid 11·4, alanine (IV) 1·84, serine (V) 1·73, :NH 3·76, and valine (VI) 3·67. Arginylarginine and oxyproline (VII) are obtained as picrates from (I). The nos. of residues of (III), (IV), (V), (VII), and (VI) + others in (II) are 22, 2, 2, 1, and 3, respectively, and the no. of proline residues is 3. The mol. wts. of (II) and its Me ester are 4470 and 5340, respectively. The (II) formula previously suggested is modified in the light of these results. W. McC.

Rapid method for protein dialysis.—See A., III, 447.

Green derivative of hæmoglobin.—See A., III, 370.

Semi-micro methods for determining the elements in organic analysis. H. BERGER (Chem. Fabr., 1937, **10**, 396—398).—A thermostatically controlled electric furnace is preferred for heating the tubes, and in the determination of halogens and S, as well as C, H, and N, the temp. is maintained at 700°. PbO_2 is superior to Cu for removing N oxides. A special Kipp apparatus for preparing air-free CO_2 is described. A bead tube is used for the determination of halogens and S. I. C. R.

Determination of nitrogen and carbon in the same sample. C. T. GAYLEY (Ind. Eng. Chem. [Anal.], 1937, **9**, 422—423).—The gases formed during a Kjeldahl N determination are passed in a stream of O_2 over Pt gauze in an electric furnace, cooled, and passed successively through $K_2Cr_2O_7$, 10% H_2SO_4, Zn, conc. H_2SO_4, and Dehydrite; finally the CO_2 is absorbed and weighed. R. S. C.

Determination of iodine in organic substances. H. DOERING (Ber., 1937, **70**, [*B*], 1887—1889).—In the customary Carius procedure $AgNO_3$ is replaced by $Hg(NO_3)_2$ and the vol. of HNO_3 is increased to 5 c.c. The contents of the bomb tube are treated with aq. $CaOCl_2$, whereby I is converted into HIO_3. Excess of Cl is removed by cautious addition of HCO_2Na, the mixture is cooled, and solid KI is added. The liberated I is titrated with $Na_2S_2O_3$ in presence of starch. H. W.

Simultaneous determination of chlorine, nitrogen, and arsenic in organo-arsenic compounds. H. N. DAS-GUPTA (J. Indian Chem. Soc., 1937, **14**, 358—361).—The compound is slowly heated with a mixture of K_2SO_4, conc. H_2SO_4, and a little Se. The gaseous chlorides are absorbed in alkaline H_2O_2, and the Cl is determined volumetrically, or gravimetrically after boiling, treating with $NaHSO_3$, and acidifying. The NH_3 in the residue is expelled by NaOH and the remaining solution treated with $NaHSO_3$, acidified, boiled, and the As determined with I. A. LI.

Semi-micro-determination of arsenic in organic compounds. E. I. AIZENSCHTADT (Zavod. Lab., 1937, **6**, 503—504).—10 mg. of substance are heated with 0·5 ml. of H_2O and 1 ml. of H_2SO_4 (4 min. at the b.p.), 1 ml. of H_2O is added, and boiling is continued until SO_3 fumes appear. This operation is repeated, the solution is washed into a flask by means of 5 ml. of 20% H_2SO_4, 5 ml. of 10% KI and 30 ml. of H_2O are added, and the solution is titrated with 0·01N-$Na_2S_2O_3$ after 15 min. The vol. of $Na_2S_2O_3$ required in a blank test is subtracted, and the As content is hence calc. R. T.

Determination of arsenic in mineral oil solutions.—See A., I, 579.

Volumetric determination of mercury [in organic compounds]. M. FITZGIBBON (Analyst, 1937, **62**, 654—656).—Org. Hg compounds are destroyed by heating with H_2SO_4. An excess of KI is added, and the solution is made alkaline with NaOH. 40% aq. CH_2O is added at 60°, together with 2·5% aq. gelatin to stabilise the reduced Hg in colloidal suspension. The solution is cooled to 20°, acidified with AcOH, and treated with 0·1N-I, the excess of I being finally titrated back. J. S. A.

Determination of tellurium in organic compounds. E. T. TSAO (Chem. Ind. [China], 1935, **10**, No. 2, 15—21).—0·2—0·3 g. of the Te compound is fused with 14 g. of Na_2O_2, 0·1 g. of $KClO_3$, and 0·2—0·3 g. of sucrose in a Parr bomb. The product is dissolved in H_2O, boiled to remove peroxide, acidified with HCl, and conc. to 100 c.c., 30 c.c. of 12N-HCl are added, and the solution is heated to boiling. 15 c.c. of saturated aq. SO_2, 10 c.c. of 15% N_2H_4,HCl, and a further 15 c.c. of saturated aq. SO_2 are added and the solution is boiled and filtered on a Gooch crucible. The ppt. of Te is washed with H_2O and EtOH and dried at 105°. CH. ABS. (*e*)

Physical method of drying liquefied hydrocarbons. E. E. ROPER (Ind. Eng. Chem. [Anal.], 1937, **9**, 414—415).—0·7 mg. of H_2O in 100 g. of $CH_2{:}CMe_2$ is detectable as a turbidity when the liquid is cooled to −80°. An apparatus for drying hydrocarbons is described. The liquid is placed over glass wool in a closed system at −80°; the wool rests over a capillary tube passing into a vessel containing the hydrocarbon at −135°. Passage of liquid through the wool filter is caused by the difference in v.p. of the liquid at the two temp. R. S. C.

Determination of methoxyl. F. ARNDT and F. NEUMANN (Ber., 1937, **70** [*B*], 1835).—The method of gradual heating advised for highly methylated carbohydrates by Neumann (this vol., 229) has been applied in other circumstances by Arndt (*ibid.*, 283) and thus appears generally useful. H. W.

Microchemical detection of organic compounds by means of drop reactions. F. FEIGL [with A. LENZER, V. DEMANT, O. FREHDEN, and V. ANGER] (Mikrochim. Acta, 1937, **1**, 127—141).—(*a*) Sulphinic acids, sulphonic acids, or sulphones are detected by fusion with NaOH, forming Na_2SO_3. On acidification, the SO_2 liberated induces the oxidation of $Ni(OH)_2$ spread on a slip of filter-paper, which may be impregnated with benzidine (purple colour produced) to increase the sensitivity. (*b*) NH_2OH and oximes in 1 drop of solution are treated successively with NaOAc, 1% sulphanilic acid (I) in dil. AcOH, and 0·1N-I in glacial AcOH. NH_2OH is oxidised to HNO_2, which diazotises (I). On addition of $Na_2S_2O_3$ and then 0·3% $C_{10}H_7{\cdot}NH_2$ (II) in dil. AcOH, a red coloration is produced with 10^{-8} g. of NH_2OH. Oximes are first hydrolysed by warming with HCl before treatment as above. (*c*) Arylhydrazines, -hydrazones, and -osazones are oxidised to diazo-salts by treatment with a drop of HCl + solid SeO_2. On addition of (II), red to violet colorations are produced. (*d*) Glycerol and glycerides are heated with $KHSO_4$, forming acraldehyde, which gives a blue coloration on paper impregnated with *o*-dianisidine or, better, with $Na_2[Fe(CN)_5NO]$ + piperidine. Limit, 0·005 mg. (*e*) *sec.* Aliphatic amines in neutral aq. solution are treated with a drop of aq. $Na_2[Fe(CN)_5NO]$ containing 10% of MeCHO. Addition of Na_2CO_3 gives a blue to violet colour. J. S. A.

Determination of acetone, *n*-butyl and ethyl alcohol, present together. I. Oxidation method. M. N. Bechtereva and N. D. Jerusalimski (J. Appl. Chem. Russ., 1937, **10**, 1314—1320).—$COMe_2$ is determined in a $COMe_2$–BuOH–EtOH–H_2O mixture by the CHI_3 method; a second portion of the mixture is oxidised by Osburn and Werkman's method (B., 1931, 1117), and the acids produced are determined by the method of Virtanen and Pulkki (B., 1928, 688), applying a correction for AcOH produced by oxidation of $COMe_2$ (8% of the no. of ml. of 0·1N-$COMe_2$ present). R. T.

Microchemical determination of butyric acid. L. Kling (Mikrochem., 1937, **23**, 60—61; cf. A., 1936, 1397).—In the method previously described distillation is preferably carried out in apparatus with ground joints. The H_2O_2 should be prepared from Na_2O_2 and 2N-H_2SO_4. The flame must be low during distillation to prevent H_2O_2 passing into the distillate. Preferably the test sample should contain 0·05—2·0 mg. of $PrCO_2H$. J. W. S.

Quantitative micro-analysis of mixtures of fumaric and maleic acid. G. Semerano and I. S. Rao (Mikrochem., 1937, **23**, 9—16).—The determination of maleic (I) and fumaric (II) acid in presence of one another through the difference in their reduction potentials (A., 1932, 1234) has been adapted to the microchemical scale. For determination of (I), the K salts are dissolved in aq. NH_4Cl, and for determination of (II) the Li salts are dissolved in LiCl. The reduction potentials under these conditions are, according to concn., between −1·90 and −1·26 v. for (I) and between −1·90 and −1·84 v. for (II). The heights of the waves in the polarographic diagrams ∝ the concns. With quantities $>10^{-6}$ g. the accuracy is ±1%. J. W. S.

Volumetric analytical notes. [Determination of chloral hydrate, hypophosphite, phosphite, halogen oxyacids, and phenol.] A. Schwicker (Z. anal. Chem., 1937, **110**, 161—184).—(i) Chloral hydrate may be determined (*a*) iodometrically, in the presence of NH_4 borate. (*b*) Bromometrically, by adding an excess of 0·1N-$KBrO_3$ + KBr + conc. HCl, and then borax. The excess of free Br is finally titrated back with AsO_3'''. (*c*) By oxidation with an excess of 0·1N-$KMnO_4$ in Na_2CO_3-alkaline solution; excess of $KMnO_4$ is determined iodometrically. (*d*) By hydrolysis to $CHCl_3 + HCO_2Na$ by means of NaOH at 100°. An equal vol. of saturated aq. NaOAc is added, and the HCO_2Na is titrated at 80° with $KMnO_4$. (*e*) By reduction to Cl′ with Zn dust + 10% $(NH_4)_2SO_4$. The Cl′ is then titrated with $AgNO_3$.

(ii) (*a*) H_2PO_2' reduces $HgCl_2$ to Hg_2Cl_2; the first stage proceeds in HCl solution, but is completed rapidly only in neutral solution. The final solution is acidified with HCl, and Hg_2Cl_2 is dissolved in an excess of 0·1N-$KBrO_3$, which is finally titrated back with AsO_3'''. H_2PO_3' reduces $HgCl_2$ in neutral solution and may be determined similarly. (*b*) H_2PO_2' may be determined also with $KMnO_4$, the excess of which is titrated back iodometrically, or with $H_2C_2O_4$; (*c*) by oxidation with $KBrO_3$ in H_2SO_4 solution at 100°; or (*d*) with $KBrO_3$ + KBr or $KBrO_3$ + HCl. H_2PO_3' is oxidised with $KBrO_3$ + KBr in hot solution, or with NaOCl in a solution neutralised with $NaHCO_3$.

(iii) BrO_3' and IO_3' together are determined (*a*) by iodometric titration of total $BrO_3' + IO_3'$; (*b*) BrO_3' in a separate sample is destroyed by means of HCl, the Br and Cl liberated being bound by addition of PhOH; IO_3' is then determined independently. I′ can be selectively oxidised to IO_3' in the presence of Br′ by means of OCl′ in Na_2CO_3 solution, the IO_3' being finally determined iodometrically. IO_3' in presence of BrO_3' is determined by complete reduction to I′ and Br′ by means of $KHSO_3$. I′ is then oxidised to IO_3' with OCl′ and determined as above. For the determination of I′, IO_3', and BrO_3' together, I′ is determined with standard NaOCl. $IO_3' + BrO_3$ in a separate sample are determined iodometrically, and $I' + IO_3'$ are finally determined with OCl′ after reduction with $KHSO_3$. Alternatively, I′ is oxidised to IO_3', and total IO_3' is determined after destruction of BrO_3' with HCl. I′ in presence of Br′ is oxidised to IO_3' by a slight excess of 0·1N-$KMnO_4$ at 80°. The excess of $KMnO_4$ is destroyed with EtOH, the solution filtered from MnO_2, and the IO_3' in an aliquot part is determined iodometrically. IO_4' in the presence of IO_3' is determined by reducing IO_4' to IO_3' by means of H_2O_2 in alkaline solution. The excess of H_2O_2 is destroyed by boiling, and the total IO_3' is determined iodometrically. $IO_4' + IO_3'$ in a separate portion is determined by titration of the total I liberated with KI + HCl.

(iv) PhOH is determined by the direct titration of an HCl solution, containing KBr, with 0·1N-$KBrO_3$. The excess of $KBrO_3$ is titrated back with AsO_3'''. J. S. A.

Volumetric determination of semicarbazide and aminoguanidine. G. S. Smith (J.C.S., 1937, 1325).—N_2H_4 derivatives are determined by treatment of the hydrochloride or sulphate with KIO_3, KI, and H_2SO_4, followed by determination of the residual I. The guanidine or semicarbazide content is calc. from the reactions $5NHR{\cdot}NH_2 + 4KIO_3 \rightarrow 2I_2$ and $KIO_3 + 5KI \rightarrow 3I_2$. J. D. R.

Extractor for monoamino-acids. D. W. Woolley (Ind. Eng. Chem. [Anal.], 1937, **9**, 433).—An apparatus is described for extraction of NH_2-acids (or other heat-labile substances) without their anhydrides from neutral aq. solution by boiling BuOH (50°/vac.). Only the upper part of the BuOH is heated; the acids crystallise from the cold part and are not subjected to heat. R. S. C.

Effect of aldehydes on the determination of cysteine and cystine. M. X. Sullivan and W. C. Hess (J. Biol. Chem., 1937, **120**, 537—542).—The effect of adding varying amounts of CH_2O (I), MeCHO (II), $(CHO)_2$, AcCHO, and $C_6H_{13}{\cdot}CHO$ (III) on the accuracy of various methods of determining cysteine (IV) and cystine (V) is examined. Freshly added aldehydes have little effect in the Sullivan (A., 1930, 199) and Okuda (A., 1926, 190) methods for (V). The Folin–Marenzi method (A., 1929, 1093) for (V) is inhibited markedly by (I), somewhat by (III), but only slightly by (II). For (IV), aldehydes

have little effect on the Okuda method, some effect in the Sullivan and Folin–Marenzi methods, and marked inhibiting effect in the Mason method (cf. A., 1930, 803). E. W. W.

Determination of thiol and disulphide compounds, with special reference to cysteine and cystine. VIII. Molecular ratio between *A*-phospho-18-tungstic acid and cysteine in their colour reaction. K. Shinohara (J. Biol. Chem., 1937, **120**, 743—749).—*A*-Phospho-18-tungstic acid, new formula for crystals $P_2O_5(WO_3)_{18},26H_2O$ (I) (cf. A., 1920, ii, 625), does not react regularly with 2RSH (cf. A., 1935, 877, 1111; 1936, 60, 353). With cysteine (II) and (I) or its $(NH_4)_6$ salt, at p_H 5, in a first reaction (I) loses 1 equiv. of O per mol. of (II), but with excess of (II), (I) slowly loses a second equiv. of O. Colour intensity is plotted against time under varying conditions; it is const. only at p_H 4·7—7·5, and in presence of excess of (I). E. W. W.

Applicability of Benedict–Denis procedure to determination of methionine-sulphur. C. B. Rutenber and J. C. Andrews (J. Biol. Chem., 1937, **120**, 203—207).—Addition of 10 m.-equiv. of Na_2CO_3 to 10 ml. of Benedict–Denis reagent gave maximal (95·6%) recovery of S in determination of methionine. Larger or smaller amounts of Na_2CO_3 lower the S recovery. Prolonged ignition after evaporation is without advantage. J. L. C.

Determination of nitrogen by hydrogenation in betaine, pyramidone, and sulphanilic acid. H. ter Meulen and H. J. Ravenswaay (Rec. trav. chim., 1937, **56**, 1022—1023).—N can be determined accurately in these compounds by hydrogenation. H. W.

Titration of aromatic amines with nitrous acid. J. Phillips and A. Lowy (Ind. Eng. Chem. [Anal.], 1937, **9**, 381—382).—2:4:6-$(NH_2)_3C_6H_2{\cdot}CO_2H$, 1:2:4:6-$C_6H_2Me(NH_2)_3$, 1:3:5-$C_6H_3(NH_2)_3$, 1:2:4:6-$C_6H_2Cl(NH_2)_3$, metanilic acid, *m*-$C_6H_4(NH_2)_2$, and 1:2:4-$C_6H_3Me(NH_2)_2$ can be determined by addition of excess of $NaNO_2$ to the HCl solution followed by back-titration with either NH_2Ph,HCl or sulphanilic acid. Titration of 2:4:6-$(NH_2)_3C_6H_2{\cdot}OH$, 1:2:4-$C_6H_3(NH_2)_3$, and *o*- and *p*-$C_6H_4(NH_2)_2$ does not give quant. results. E. H. S.

New photo-reaction of pyridine. A. Castiglioni (Annali Chim. Appl., 1937, **27**, 256—257).—Filter-paper soaked in a 1% EtOH solution of quinoline (I), treated with a 0·05% aq. solution of C_5H_5N, and exposed to ultraviolet light, slowly develops a yellow coloration. Using lepidine instead of (I), a similar colour results, and a less intense colour using quinaldine, hydroxyquinoline, *iso*quinoline, or acridine. The reaction can be used to detect C_5H_5N in presence of nicotine, since with (I) the latter slowly gives only a greyish coloration. E. W. W.

Determination of pyridine in presence of pyridine homologues. L. Barta and Z. Marschek (Biochem. Z., 1937, **293**, 118—120).—C_5H_5N homologues (α- and β-picoline, αα′-lutidine, *s*-collidine) and piperidine give with BrCN and β-$C_{10}H_7{\cdot}NH_2$ a red colour similar to that given by C_5H_5N but the colour is usually 50—90 times weaker and the error in the colorimetric determination of C_5H_5N in presence of five times the amount of homologue is 8—10%. Distillation with citrate buffer enables C_5H_5N and its homologues to be separated from NH_3 and nicotine. P. W. C.

Highly sensitive and specific microchemical reactions of sparteine with cobalt and iron salts. A. Martini (Mikrochim. Acta, 1937, **1**, 164—167).—Cryst. ppts. of characteristic habit are formed with NH_4CNS + Co or $Fe^{\cdots}$ salts. J. S. A.

Identification and differentiation of ephedrine and ψ-ephedrine. P. Fourment and H. Roques (Bull. Sci. Pharmacol., 1937, **44**, 372—375).—Ephedrine can be accurately determined by the formation of CHI_3 on adding hypoiodite. It immediately gives with alkaline OsO_4 an orange ppt. which gives a violet coloration with boiling HCl, whereas ψ-ephedrine gives slowly a yellowish ppt. followed by a yellow coloration with HCl. E. M. W.

Reaction of morphine with vanillin and hydrochloric acid. Different action of some aromatic aldehydes on morphine and ψ-morphine. B. Drevon (J. Pharm. Chim., 1937, [viii], **26**, 292—299).—ψ-Morphine (I) with vanillin–HCl at 100° gives a green coloration (cf. this vol., 268). The reaction is given by many aromatic aldehydes in the nucleus of which OH, Me, NO_2, and CH_2O_2 are substituents. Morphine and (I) give different colours. Furfuraldehyde and glucose do not serve as aldehydes. J. L. D.

The biuret reaction. IV. Combination of copper, nickel, and cobalt with proteins. H. Jesserer and F. Lieben. **V. Biuret reaction of organic substances of low mol. wt.** R. Kretschmayer and H. Jesserer (Biochem. Z., 1937, **292**, 403—418, 419—423; cf. A., 1936, 1398).—Alkaline aq. caseinogen (I) combines stoicheiometrically with Cu, Ni, and Co (as hydroxides) to give violet, golden-yellow, and red-brown coloured derivatives, respectively, dialysis of which yields a blue neutral Cu derivative of equal Cu content and a neutral Co derivative of the same colour and Co content, the Ni compound being decomposed to $Ni(OH)_2$. Compounds of Cu, Ni, and Co with zein, edestin, fibrin, gelatin, and Witte's, silk-, and (I)-peptone were investigated. The compounds with peptones are less defined than those with proteins; Ni in the latter is bi- and Co ter-valent. The presence of the metal prevents *N*-methylation, whilst the methylated proteins behave abnormally only with Ni. The metals probably combine at the peptide linking. No reaction occurs between Fe and proteins.

V. The "biuret reaction" is given by arginamide and arginine anhydride but not by histidine, succinimide, serine, colamine, arginine, and α-benzoylarginine. At least two adjacent $CO{\cdot}NH_2$, $CS{\cdot}NH_2$ or $C(:NH){\cdot}NH_2$ groups are essential for the reaction. F. O. H.