BRITISH CHEMICAL
AND
PHYSIOLOGICAL ABSTRACTS

JANUARY, 1944

A II—ORGANIC CHEMISTRY

CONTENTS

Published by the

BUREAU OF CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

(Supported by the Chemical Society, the Society of Chemical Industry, the Physiological Society, the Biochemical Society, the Anatomical Society of Great Britain and Ireland, and the Society for Experimental Biology.)

Offices of the Bureau: 56 VICTORIA STREET, LONDON, S.W.1 *Telephone:* VICTORIA 5215

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A II—Organic Chemistry

JANUARY, 1944.

I.—ALIPHATIC.

Modern methods of preparative organic chemistry. V. Introduction of fluorine into organic compounds. W. Bockemüller. **VI. Use of biochemical oxidations and reductions for preparative purposes.** F. G. Fischer. **VII. Molecular distillation.** F. Wittka (*Angew. Chem.*, 1940, **53**, 419—424, 461—471, 557—568).—Reviews.

Isomerisation and alkylation of [saturated] hydrocarbons.—See B., 1943, II, 366.

Catalytic hydrogenation of carbon monoxide. Methane synthesis from water-gas.—See B., 1943, II, 365.

Alkylation of paraffins with olefines. Identification of the paraffins formed. A. V. Grosse and V. N. Ipatiev (*J. Org. Chem.*, 1943, **8**, 438—447; cf. A., 1935, 1348).—The hexanes formed by the catalytic alkylation of $CHMe_3$ with C_2H_4 in the presence of BF_3 or $AlCl_3$ are $CHMe_2Pr^\beta$ (90—70% of the total hexanes), $Pr^\alpha Pr^\beta$ (10—20%), and traces of $EtBu^\gamma$ (>3%). With both catalysts the relative amounts are approx. the same. Identification is accomplished by the isolation of $(CMe_2Br)_2$ and $NO_2{\cdot}CMe_2{\cdot}CEt(NO_2)_2$, m.p. 96°, and by their Raman spectra. The two other hexanes can be present only in negligible amounts if at all. $Pr^\beta{}_2$ probably arises by isomerisation of the primary $EtBu^\gamma$ but the origin of $Pr^\alpha Pr^\beta$ is obscure. H. W.

Kinetics of vinyl derivative polymerisation.—See A., 1944, I, 20.

End-group structure of polyvinyl alcohol. C. S. Marvel and G. E. Inskeep (*J. Amer. Chem. Soc.*, 1943, **65**, 1710—1714).—Hydrolysis (NaOMe) of polyvinyl acetate and re-esterification (C_5H_5N; Ac_2O; H_2SO_4–AcOH) of the alcohol (**I**) causes irregular increase or decrease in the degree of polymerisation. This is ascribed to the possible existence in (**I**) of a terminal CHO, which in acid can form acetals with the OH of other mols. of (**I**), whereas in alkali aldol or reverse aldol reactions can occur. R. S. C.

Geometrical isomerism of cyclic acetal derivatives from polyhydric nitro-alcohols.—See A., 1944, II, 23.

Preparation and purification of nitrated pentaerythritols.—See B., 1943, II, 367.

Isomeric $\alpha\gamma$- and $\beta\gamma$-benzylidene-*D*-arabitols. W. T. Haskins, R. M. Hann, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1943, **65**, 1663—1667).—*D*-Arabitol (**I**) (1 mol.) and BzCl (2 mols.) in C_5H_5N at 0—5° and then room temp. give the *αε-dibenzoate* (**II**) (51%), m.p. 131—132°, $[\alpha]_D^{20}$ +8·4° in C_5H_5N, and thence the *αε-dibenzoate βγδ-triacetate*, m.p. 102—103°, $[\alpha]_D^{20}$ +31·0° in $CHCl_3$. The structure of (**II**) is proved by consumption of 1·94 and 2·02 mols. of $Pb(OAc)_4$ in AcOH in 30 and 60 min., respectively, with formation of 1 mol. of HCO_2H and 2 mols. of $OBz{\cdot}CH_2{\cdot}CHO$ (1·14 mols. isolated as cryst. semicarbazone). With PhCHO and $ZnCl_2$ at room temp. (**II**) gives *βγ-benzylidene*-D-*arabitol αε-dibenzoate* (**III**) (73%), m.p. 108—109°, $[\alpha]_D^{20}$ +12·6° in $CHCl_3$, and thence the *αε-dibenzoate δ-acetate*, m.p. 73—75°, $[\alpha]_D^{20}$ +2·1° in $CHCl_3$, and *αδε-tribenzoate* (**IV**), m.p. 101—103°, $[\alpha]_D^{20}$ −14·6° in $CHCl_3$. NaOMe–MeOH–$CHCl_3$ converts (**III**) into *βγ-benzylidene*-D-*arabitol* (90%), m.p. 81—83°, $[\alpha]_D^{20}$ +10·8° in EtOH, +18·1° in C_5H_5N, the structure of which (and of its forerunners) is proved by consumption of 1·05 mol. of aq. $NaIO_4$ with formation of CH_2O (0·74 mol. isolated as dimethone derivative) and syrupy 2 : 3-benzylidene-*D*-threose, the structure of which is proved by conversion into 2 : 3-*iso*propylidene-*D*-threose and thence *L*-tartaric acid and by hydrogenation (Raney Ni; EtOH; 25°/110 atm.) to syrupy *βγ*-benzylidene-*D*-threitol and thence *D*-threitol, m.p. 88—89°, $[\alpha]_D^{20}$ +4·6° in H_2O (dibenzylidene derivative, $[\alpha]_D^{20}$ −90·2° in C_5H_5N). Passing HCl into (**I**) and PhCHO at room temp. gives *αγ*-dibenzylidene-*D*-arabitol (**V**) (84%; conc. HCl gives only 10—11%), m.p. 151—152°, $[\alpha]_D^{20}$ −7·6° in C_5H_5N (cf. Fischer, A., 1894, i, 395), converted by BzCl–C_5H_5N into the *βδε-tribenzoate*, m.p. 137—138°, $[\alpha]_D^{20}$ −133·8° in $CHCl_3$, which with H_2SO_4–Ac_2O–AcOH gives D-*arabitol βδε-tribenzoate αγ-diacetate*, m.p. 65—66°, $[\alpha]_D^{20}$ −8·2° in $CHCl_3$. H_2SO_4–Ac_2O–AcOH converts (**IV**) into D-*arabitol αδε-tribenzoate βγ-diacetate*, a syrup, $[\alpha]_D^{20}$ +19·1° in $CHCl_3$. The structure of (**V**) is thus proved (cf. Steifer *et al.*, A., 1934, 1364). M.p. are corr. R. S. C.

New form of crystalline xylitol. J. F. Carson, S. W. Waisbrot, and F. T. Jones (*J. Amer. Chem. Soc.*, 1943, **65**, 1777—1778).—Xylitol is obtained in a more stable *form*, m.p. 93—94·5°. Crystallo-optical data are given for this and the form of m.p. 61—61·5° (A., 1942, II, 389). R. S. C.

Two syntheses of polygalitol (αε-anhydro-*D*-sorbitol). N. K. Richtmyer, C. J. Carr, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1943, **65**, 1477—1478).—Polygalitol (**I**) is a by-product in Zervas' synthesis of styracitol (A., 1930, 1160). Di-*β*-glucosyl disulphide octa-acetate with Raney Ni in EtOH gives slowly the tetra-acetate of (**I**), also obtained in poor yield similarly from *β*-glucothiose tetra-acetate, m.p. 74—75° (lit. 113—114°), $[\alpha]_D^{20}$ −8·3° → +47·0° in 12 weeks in 90% EtOH. R. S. C.

Aliphatic *β*-monoglycerides. B. F. Daubert, H. H. Fricke, and H. E. Longenecker (*J. Amer. Chem. Soc.*, 1943, **65**, 1718—1720).—*αγ*-Benzylideneglycerol with RCOCl in C_5H_5N at 20° gives *αγ-benzylideneglycerylβ-hexoate*, m.p. 34·1°, and *β-octoate*, m.p. 35·0°, converted by H_2–Pd-black–EtOH at 36 lb. into *glycerylβ-n-hexoate*, m.p. −8° to −10°, and *β-n-octoate*, m.p. 29·8°, respectively. R. S. C.

Series of αω-dimercaptans. W. P. Hall and E. E. Reid (*J. Amer. Chem. Soc.*, 1943, **65**, 1466—1468).—$[CH_2]_n(SH)_2$ (*A*) are prepared from the dibromides by $CS(NH_2)_2$ and then KOH in boiling H_2O in 80—85% yield; H_2S–NaOEt–EtOH–Et_2O at the b.p. gives 70—85% yields if $n = >6$, but if $n = 4$ or 5 yields are low owing to cyclisation. (*A*) of low mol. wt. are difficult to isolate because they are sol. in H_2O and tend to polymerise and to form $S([CH_2]_n{\cdot}SH)_2$. $CH_2(SH)_2$ could not be prepared. $[CH_2]_3(SH)_2$, m.p. −79°, b.p. 104·6°/100 mm., 172·9°/760 mm., is obtained in 40—50% yield by K xanthate + KOBz or by $NHPh{\cdot}CS_2M$ (M = Na or NH_4). The following are described: (*A*) in which $n = 2$, m.p. −41·2°, b.p. 146°, 4, m.p. −53·9°, b.p. 74·5°/10 mm., 195·6°/760 mm., 5, m.p. −72·5°, b.p. 90·1°/10 mm., 217·3°/760 mm., and 6, m.p. −21°, b.p. 106°/10 mm., 237·1°/760 mm.; *αη-dithiol-n-heptane*, m.p. −38·1°, b.p. 119·5°/10 mm., 252·2°/760 mm.; *αθ-dithiol-n-octane*, m.p. 0·9°, b.p. 132°/10 mm., 269·3°/760 mm.; *αι*-dithiol-*n*-nonane, m.p. −17·5°, b.p. 145°/10 mm., 284°/760 mm.; *ακ-dithiol-n-decane*, m.p. 17·8°, b.p. 161°/10 mm., 297·1°/760 mm.; *αλ*-dithiol-*n*-undecane, m.p. −5·4°, b.p. 171·5/10 mm., 308·8°/760 mm.; *αμ-dithiol-n-dodecane*, m.p. 28·4°, b.p. 181·5°/10 mm., 319·3°/760 mm.; *αα*-dithiol-*n*-octadecane, m.p. 52°; $[CH_2]_5(OH)_2$, m.p. −18°; $Br{\cdot}[CH_2]_n{\cdot}Br$ in which $n = 6$, m.p. −2·3°, 7, m.p. −41·7°, 9, m.p. −22·5°, and 11, m.p. −10·6°. *d*, *n*, and latent heats of evaporation are also recorded and regularities are noted. Suberic and azelaic acids are prepared by oxidising ricinoleic acid by $HNO_3 + NH_4$ vanadate (trace), removing the monobasic acids in steam, esterifying the dibasic acids, and fractionating the esters. R. S. C.

Sulphonium compounds. III. Reaction of organic sulphides with organic sulphates. F. E. Ray and J. L. Farmer (*J. Org. Chem.*, 1943, **8**, 391—396; cf. A., 1938, II, 135).—It is shown that rearrangements can occur during the formation of sulphonium sulphates and the mechanism proposed (*loc. cit.*) for the formation of sulphonium halides has been extended to these compounds. Me_2SO_4 and Me_2S react vigorously at 0°, giving the extremely deliquescent trimethylsulphonium methosulphate, which could not be isolated pure; it is hydrolysed to the sulphate, which forms a clear solution in H_2O. Addition of $BiCl_3$ to this solution leads to *tristrimethylsulphonium chloride dibismuth chloride*, $3SMe_3Cl,2BiCl_3$, decomp. 245°, also obtained from SMe_3Cl and $BiCl_3$; with a smaller proportion of $BiCl_3$ the product is *trimethylsulphonium chloride bismuth chloride*, m.p. 121—123°. A solution of $(CH_2Ph)_2S$ and Me_2SO_4 (1 : 1) in C_6H_6 is heated for 14 hr. at 100°, then hydrolysed by H_2O and treated with $BiCl_3$ followed by HCl, thereby giving *tribenzyldimethylsulphonium chloride dibismuth chloride*, m.p. 140°, decomp. 145°, whereas $(CH_2Ph)_2S$ and Me_2SO_4 (2 : 1) in hot AcOH afford tribenzylsulphonium sulphate, m.p. 173°, also obtained from $(CH_2Ph)_2S$, MeOH, and conc. H_2SO_4 in hot AcOH. Me_2S, $CH_2Ph{\cdot}OH$, and H_2SO_4 in glacial AcOH at room temp. afford *dibenzyldimethylsulphonium chloride bismuth chloride*, m.p. 138°, no rearrangement having occurred. A modified method for the determination of Bi is given (see C., 1944, Part 1). H. W.

Identification of organic acids by partition between ethyl ether and water. O. C. Dermer and V. H. Dermer (*J. Amer. Chem. Soc.*, 1943, **65**, 1653—1654).—Many org. acids may be identified by shaking

50 ml. of 0·1N. aq. solution with 50 ml. of Et_2O (saturated with H_2O) at 25·0±0·5° and titrating the acid in each layer. Partition coeffs. are recorded for 61 acids. R. S. C.

Methyldiallylcarbinyl acetate. W. G. Young, L. J. Andrews, and S. J. Cristol (*J. Amer. Chem. Soc.*, 1943, **65**, 1657).—Adding $CH_2{:}CH{\cdot}CH_2{\cdot}MgCl$ in Et_2O to AcCl in Et_2O gives *methyldiallylcarbinyl acetate* [*β-allyl-Δ⁵-pentenyl β-acetate*], b.p. 126—129°/192 mm., which is difficult to hydrolyse. R. S. C.

Esters of normal aliphatic alcohols and acids. J. H. Hoback, D. O. Parsons, and J. F. Bartlett (*J. Amer. Chem. Soc.*, 1943, **65**, 1606—1607).—The following are prepared from ROH, $R'CO_2H$, and *p*-$C_6H_4Me{\cdot}SO_3H$ in C_6H_6: Pr, m.p. −68·7°, b.p. 85·28°/20 mm., Bu, m.p. −64·3°, b.p. 99·21°/20 mm., amyl, m.p. −47·0°, b.p. 116·6°/20 mm., *nonyl*, m.p. −22·3°, b.p. 173·3°/20 mm., *undecyl*, m.p. −10·5°, b.p. 198·4°/20 mm., *dodecyl*, m.p. −4·6°, b.p. 221·3°/20 mm., *tridecyl*, m.p. 6·9°, *tetradecyl*, m.p. 2·0°, and *pentadecyl* n-*hexoate*, m.p. 16·3°; Pr, m.p. −63·5°, b.p. 98—100°/20 mm., Bu, m.p. −67·5°, b.p. 112—114°/20 mm., and amyl heptoate, m.p. −49·0°, b.p. 118—119°/20 mm.; Pr, m.p. −45·0°, b.p. 112—113°/20 mm., Bu, m.p. −43·0°, b.p. 121—122°/20 mm., and amyl *n*-octoate, m.p. −34·5°, b.p. 124—126°/20 mm.; *Pr*, m.p. −36·0°, b.p. 120—122°/20 mm., *Bu*, m.p. −38·0°, b.p. 122—124°/20 mm., and *amyl* n-*nonoate*, m.p. −27·0°, b.p. 120—132°/20 mm. Temp. are corr. R. S. C.

Macromolecular compounds. CCXLVII. Constitution of highly polymerised synthetic materials. H. Staudinger and H. Warth (*J. pr. Chem.*, 1940, [ii], **155**, 261—298).—Interconversions of polyvinyl acetates (I) and alcohols (II) establish the macromol. nature of these compounds. A series of fractions of (I) are obtained from $CH_2{:}CH{\cdot}OAc$ polymerised in the cold and in absence of a catalyst; these are hydrolysed by NaOH–EtOH in dioxan in complete absence of air to (II), which are reacetylated by Ac_2O–C_5H_5N. Mol. wts. of (I) and (II) are determined osmometrically in H_2O and $\eta_{sp.}/c$ is observed for (I) in $COMe_2$ at 20° and (II) in H_2O at 20°. The K_m const. falls much below the calc. val. and is progressive. Oxidation of (II) with H_2O_2 lends no support to the hypothesis of the formation of branched chains during polymerisation since AcOH and CO_2 but no $(CH_2{\cdot}CO_2H)_2$ could be detected. Closely similar observations are made with Me polyacrylate and polymethylacrylate. The viscosity law for linear colloids is valid for natural products such as cellulose and its derivatives and the mannans and for relatively simply polymerised synthetic materials; with more highly polymerised compounds divergencies occur as with the polyvinyl substances. Since in these cases the variations in K_m are continuous and there is no evidence that different branching is caused by differing conditions of polymerisation, it is probable that the mols. of polyvinyl compounds are not simply stretched in solution but are bent in a manner which is more pronounced as the complexity of the mol. increases. H. W.

Aluminium stearates. E. Eigenberger and A. Eigenberger-Bittner (*Kolloid-Z.*, 1940, **91**, 287—294).—Pptn. from alcoholic K stearate (acid or neutral) with aq. K alum (acidic, basic, or neutral) gives Al stearate of composition $(C_{18}H_{35}O_2)_{10}Al_8O_7,xH_2O$ (x = 8—12), which is const. on repptn. It is stable up to 110°, decomp. at 120°. All the stearic acid is replaced by alizarin (I) on boiling a PhMe + EtOH solution of Al stearate with (I), to give $(I)_{10}Al_8O_7$. Pseudo-Al stearates of higher Al contents are formed by addition of aq. alkaline K alum to neutral or acid K stearate, or of stearic acid to pptd. $Al(OH)_3$. These stearates show variable composition on repptn., and (I) is adsorbed as well as replacing stearic acid. The pseudo-salts are formed by peptisation of the $Al(OH)_3$ by stearic acid. J. H. Ba.

Preparation of acetoacetic esters of aliphatic alcohols.—See B., 1943, II, 367.

***p*-Nitro-, $[\alpha]_D^{20}$ −58°, and *p*-amino-benzyl ether, $[\alpha]_D$ −65°, −40°, of hyaluronic acid.**—See A., 1943, III, 925.

Activated oxalic acid.—See A., 1944, I, 21.

Conversion of maleic acid into maleic anhydride. Maleic anhydride purification.—See B., 1943, II, 367.

Preparation of nonane- and decane-αω-dicarboxylic acids. W. P. Hall and E. E. Reid (*J. Amer. Chem. Soc.*, 1943, **65**, 1468).—μ-Hydroxystearic acid is boiled with conc. HNO_3 + a little NH_4 vanadate; the monobasic acids are removed in steam, the dibasic acids are esterified, and the esters are fractionated and then hydrolysed. Thus is obtained ~40% each of $CO_2H{\cdot}[CH_2]_n{\cdot}CO_2H$ (n = 11 and 12). R. S. C.

Manufacture of unsaturated aldehydes.—See B., 1943, II, 368.

Oxygenation of crotonaldehyde. L. N. Owen (*J.C.S.*, 1943, 463—468).—$CHMe{:}CH{\cdot}CHO$ (I) in AcOH (equal vol.) containing known amounts of $Mn(OAc)_2$ is shaken in O_2 atm. at room temp.; the optimum amount of $Mn(OAc)_2$ is 2×10^{-6} mol. per l. The reaction products (except those from highest catalyst concns.) contain peroxides or per-acids. $Co(OAc)_2$ behaves similarly, but $Cu(OAc)_2$ has little effect. In absence of solvent Mn is detrimental at all concns., oxidation being most effective without any catalyst. Treatment of (I) with O_2 at 5 atm. resulted in an earlier separation of solid $CHMe{:}CH{\cdot}CO_2H$ (II), yield 70%. The highest yields of (II) are produced by oxygenating pure (I), avoiding undue rise of temp. From the steam-distillate of the reaction product a *bis*-2 : 4-*dinitrophenylhydrazone*, $C_{16}H_{14}O_8N_8$, m.p. 298°, is obtained, possibly a derivative of $COEt{\cdot}CHO$. The part not volatile in steam yields cryst. *dl-erythro-αβ*-dihydroxybutyric acid. *Crotyl crotonate*, an oil, b.p. ~175°/770 mm., is synthesised by adding $CHMe{:}CH{\cdot}CH_2Br$, b.p. 105—110°, to Ag crotonate in Et_2O. (I) gives a *compound*, $CaCl_2,2C_4H_6O$. H. Sch.

Aldol condensation. II. Reaction of *iso*butyraldehyde with its aldol. R. H. Saunders, M. J. Murray, and F. F. Cleveland (*J. Amer. Chem. Soc.*, 1943, **65**, 1714—1717; cf. A., 1943, II, 319).—When 10% KOH is added to $Pr^{\beta}CHO$–Et_2O containing a few drops of $NHBu_2$ at 5—10° and the product is washed with H_2O, distillation then gives ∢80% of the trimeride (I), b.p. 110—111°/8 mm., of $Pr^{\beta}CHO$; if the crude product is washed with 5% H_2SO_4, catalysis during distillation leads to formation of $Pr^{\beta}CHO$ and $OH{\cdot}CHPr^{\beta}{\cdot}CMe_2{\cdot}CHO$ (II). (I) and (II) are differentiated by Raman spectra, (I) having strong lines at 770, 798, and 1722, and (II) at 787 cm.⁻¹ The spectrum of the crude product shows complete absence of (II). The spectrum of (I) shows absence of CO. (I) is also obtained from (II) and $Pr^{\beta}CHO$ at room temp.; with boiling 15% KOH–EtOH it gives $OH{\cdot}CHPr^{\beta}{\cdot}CMe_2{\cdot}CH_2{\cdot}OH$ and $Pr^{\beta}CO_2H$. (I) is the primary product of "aldolisation"; this accounts for the max. yield of (II) being 66·7%. It is probably 4-*hydroxy*-5 : 5-*dimethyl*-2 : 6-*diiso*propyl-1 : 3-*dioxan* and not $Pr^{\beta}CO_2{\cdot}CH_2{\cdot}CMe_2{\cdot}CHPr^{\beta}{\cdot}OH$ as previously supposed. R. S. C.

Termolecular acetone peroxide in *iso*propyl ether. F. Acree, jun., and H. L. Haller (*J. Amer. Chem. Soc.*, 1943, **65**, 1652).—Distilling old Pr^{β}_2O in air gives, as residue, the trimeride, m.p. 98°, of acetone peroxide. R. S. C.

***βββ*-Trifluoro-ethylamine and -diazoethane.** H. Gilman and R. G. Jones (*J. Amer. Chem. Soc.*, 1943, **65**, 1458—1460).—$CF_3{\cdot}CO{\cdot}NH_2$ (prep. in 99% yield from $CF_3{\cdot}CO_2Et$ by dry NH_3–Et_2O at 60—70°) with P_2O_5 at 145—150° gives $CF_3{\cdot}CN$ (74%), b.p. −63·9°/743 mm., hydrogenated (PtO_2; Et_2O; 55—60°/1500 lb.) to *βββ*-trifluoroethylamine (I) (50—80%), b.p. 37—37·3°/737 mm. (I) is a very weak base; its *hydrochloride*, sublimes at >125°, reacts acid to Me-red. With aq. HNO_2–Et_2O, (I) yields *βββ-trifluorodiazoethane* (65—67%), yellow, which is stable in Et_2O for 6 weeks at room temp., is decomposed by acids, and with I–Et_2O gives slowly *αα-di-iodo-βββ-trifluoroethane*, m.p. −15° to −13·5°, b.p. 54°/39 mm. $CF_3{\cdot}CH_2I$ is also prepared (no details). R. S. C.

Contiguously substituted aminodihydroxyalkanes. I. Syntheses of α-amino-βγ-dihydroxy-*n*-hexane and γ-amino-αβ-dihydroxy-*n*-hexane. C. Niemann, A. A. Benson, and J. F. Mead (*J. Org. Chem.*, 1943, **8**, 397—404).—Gradual addition of $CH_2{:}CH{\cdot}CHO$ to $MgPr^{\alpha}Br$ in Et_2O gives $OH{\cdot}CHPr^{\alpha}{\cdot}CH{:}CH_2$, b.p. 90—94°/150 mm., converted by BzO_2H in $CHCl_3$ at 25° for 2 days into *αβ-expoxy-γ-hydroxy*-n-*hexane*, b.p. 87—90°/25 mm., which with conc. aq. NH_3 at 25° for 15 hr. affords *α-amino-βγ-dihydroxy*-n-*hexane* (I), b.p. 91°/0·06 mm., m.p. 53°. Oxidation of (I) by $NaIO_4$ or $Pb(OAc)_4$ follows the normal course but the yield of CH_2O is not even approx. quant. Equimol. amounts of (I), $CH_2Ph{\cdot}O{\cdot}COCl$, and NaOH yield *α-carbobenzyloxy-amino-βγ-dihydroxy*-n-*hexane* (II), m.p. 114—115°. (I) and Ac_2O in dry C_5H_5N at 25° afford *α-acetamido-βγ-diacetoxy*-n-*hexane*, m.p. 95·8—96·5°, hydrolysed by $Ba(OMe)_2$ in dry MeOH at 25° to *α-acetamido-βγ-dihydroxy*-n-*hexane* (III), b.p. 140—145°/0·11 mm. Oxidation of (II) or (III) requires 1 mol. of $NaIO_4$ or $Pb(OAc)_4$. The transformations $OH{\cdot}CHMe{\cdot}CO_2Me \rightarrow CHMeCl{\cdot}CO_2Me \rightarrow OMe{\cdot}CHMe{\cdot}CO_2Me \rightarrow OMe{\cdot}CHMe{\cdot}CO_2H \rightarrow OMe{\cdot}CHMe{\cdot}COCl$ are described in detail; the last substance could not be converted into $OMe{\cdot}CHMe{\cdot}COPr^{\alpha}$ (IV) by $ZnPr^{\alpha}I$. $OMe{\cdot}CHMe{\cdot}CN$, obtained from $CHMeCl{\cdot}OMe$ and dry CuCN, is transformed by $MgPr^{\alpha}Br$ into (IV), b.p. 92—93°/100 mm. (*semicarbazone*, m.p. 168·5—170°), reduced by HCO_2NH_4 and subsequently hydrolysed to γ-amino-β-methoxy-*n*-hexane, b.p. 95—98°/100 mm., which is converted by boiling HBr (*d* 1·5) into γ-amino-β-hydroxy-*n*-hexane, b.p. 95°/20 mm. (*di*-3 : 5-*dinitrobenzoyl* derivative, m.p. 207·2°). Passage of $OEt{\cdot}[CH_2]_2{\cdot}OH$ vapour over Cu at 300—325° gives $OEt{\cdot}CH_2{\cdot}CHO$, b.p. 104—106°/747 mm., converted by HCl in abs. EtOH at 0° into $OEt{\cdot}CHCl{\cdot}CH_2{\cdot}OEt$, b.p. 68·73°/30 mm. This is transformed by $Hg(CN)_2$ in boiling light petroleum (b.p. 60—70°) into *αβ-diethoxypropionitrile*, b.p. 96—98°/34 mm., which is converted by $MgPr^{\alpha}Br$ in dry Et_2O into *αβ-diethoxy*-n-*hexan-γ-one*, b.p. 114—116°/30 mm., hydrogenated at 150°/150 atm. in NH_3–MeOH containing Raney Ni to *γ-amino-αβ-diethoxy*-n-*hexane*, b.p. 85—87°/6 mm., 93—95°/10 mm., which is hydrolysed by HBr (*d* 1·5) to *γ-amino-αβ-dihydroxy*-n-*hexane* (V), b.p. 92—95°/0·1 mm.; the *carbobenzyloxy*-derivative, m.p. 109—110°, is oxidised in the usual manner by $NaIO_4$ or $Pb(OAc)_4$. It thus appears that the *N*-acyl derivatives of (I) and (V) have normal structures and that the stoicheiometry of the oxidation of these compounds by $NaIO_4$ and $Pb(OAc)_4$ is normal and predictable. Additional and substantial evidence in favour of the β-amino-αγ-di-

hydroxy-*n*-octadecane structure for dihydrosphingosine is thus provided although other structures are not definitely excluded. H. W.

Derivatives of *N*-carboxy-α-amino-acid esters. M. Frankel and E. Katchalski (*J. Amer. Chem. Soc.*, 1943, **65**, 1670—1674).—Passing CO_2 into $NH_2{\cdot}CHR{\cdot}CO_2R'$ in dry Et_2O at <0° gives salts, $CO_2R'{\cdot}CHR{\cdot}NH{\cdot}CO_2NH_3{\cdot}CHR{\cdot}CO_2R'$ (cf. A., 1940, II, 7). Thus are prepared *salts* in which (*a*) R = H, R′ = Me (**I**) or Et (**II**), (*b*) R = Me, R′ = Et, (*c*) R = Ph, R′ = Et, and (*d*) R = Bu, R′ = Et. The salts are stable at 0° (dry) or in CO_2 at room temp., in air at room temp. absorb H_2O and evolve CO_2, dissolve unchanged in H_2O at 0° but with liberation of CO_2 at ≮ room temp., and in conc. acid liberate CO_2 quantitatively. Structures are proved as follows. With an aq. suspension of $Ca(OH)_2$, (**I**) gives Siegfried's salt, $\begin{matrix}CH_2\cdot CO\\ NH\text{-}CO\end{matrix}>Ca$ (96%) (A., 1906, i, 324). CH_2N_2 in Et_2O at 0° converts (**II**) into $NH_2{\cdot}CH_2{\cdot}CO_2Et$ and $CO_2Me{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et$, b.p. 127—129°/13 mm.; (**I**) gives similarly $NH_2{\cdot}CH_2{\cdot}CO_2Me$ and N-*carbomethoxyglycine Me* ester, b.p. 130°/20 mm., hydrolysed by conc. H_2SO_4 at room temp. to $CO_2Me{\cdot}NH{\cdot}CH_2{\cdot}CO_2H$, m.p. 95°. CH_2N_2–Et_2O similarly converts NH_4OBz into MeOBz and $EtCO_2NH_4$ into $EtCO_2Me$. R. S. C.

ε-*N*-Acetyl-lysine, m.p. 249—253° (decomp.), $[\alpha]_D$ +3·4±0·2°, and α-*N*-acetyl-*l*-lysine, m.p. 250° (decomp.), $[\alpha]_D$ +4·7°.—See A., 1943, III, 900.

Interaction of amides with amines. General method of acylation. A. Galat and (Miss) G. Elion (*J. Amer. Chem. Soc.*, 1943, **65**, 1566—1567).—The reaction, $NH_2R,HCl + R'CO{\cdot}NH_2 \rightarrow NH_4Cl + R'CO{\cdot}NHR$, is effected in 70—100% yield at 60°—the b.p. Examples are R = Me, Et, Pr, $CH_2{\cdot}CO_2H$, Ph, $C_6H_4{\cdot}OH$, tolyl, CH_2Ph, $Ph{\cdot}[CH_2]_2$, and $C_{10}H_7$ (also benzidine), and R′ = H, Me, Et, Pr$^\beta$, or Ph; $CO(NH_2)_2$ may be used at 250°. Hydrazines, but not guanidines, may be thus acylated. R. S. C.

Kinetics and mechanism of the racemisation of optically active cobalt trisdiguanide complex.—See A., 1944, I, 19.

Pilzcerebrin [cerebrin from lower plants]. II. F. Reindel, A. Weickmann, (Miss) S. Picard, K. Luber, and P. Turula (*Annalen*, 1940, **544**, 116—137).—Cerebrin (**I**), new formula, $C_{46}H_{93}O_5N$, m.p. 143—143·5°, is obtained pure only by way of its tetra-acetate, m.p. 67—68°, which is hydrolysed by KOH–MeOH at 50° (cf. A., 1930, 920). Anhydrocerebrin (**II**), $C_{46}H_{91}O_4N$, m.p. 116·5°, $[\alpha]_D^{22}$ +15·6° in C_5H_5N, best obtained from (**I**) (1 g.) by 0·06 g. of conc. H_2SO_4 in boiling MeOH (100 c.c.), is hydrolysed by conc. H_2SO_4 (3 g.) in boiling Pr$^\alpha$OH (30 c.c.) to $C_{24}H_{49}{\cdot}CH(OH){\cdot}CO_2H$ (**III**), m.p. 103—105°, and a *base* (**IV**), $C_{20}H_{41}O_2N$, m.p. 87—89°, b.p. 245°/12 mm., $[\alpha]_D^{27}$ +31° in $CHCl_3$. (**IV**) is unaffected by H_2SO_4–MeOH and resists hydrogenation, but, when heated at 90°, in boiling C_6H_{14}, or rapidly in NH_3–EtOH, gives an *isomeride* (**V**), m.p. 100—101·5°, $[\alpha]_D^{27}$ +30° in $CHCl_3$. BzCl–C_5H_5N converts (**IV**) or (**V**) into the same Bz_2 derivative, m.p. 117·4—118°, hydrolysed by alcoholic alkali to a Bz_1 derivative, m.p. 105—106·5°, and thence (Pr$^\alpha$OH–KOPr$^\alpha$; with difficulty) to impure (**IV**). A mono-, m.p. 79—80°, and di-acetate, m.p. 69—71°, and picrolonate, m.p. 161—162°, of (**IV**) are also prepared. With $KMnO_4$–$COMe_2$, (**IV**) gives an *acid* (**VI**), $C_{15}H_{31}{\cdot}CO_2H$, m.p. 55·5—56° (*anilide*, m.p. 86·5—87°). Hydrolysis (HCl–MeOH; *loc. cit.*) of (**I**) gives (**III**), (**IV**), and a base (**VII**), now formulated as $C_{20}H_{43}O_3N$; a *product* (**VIII**), m.p. 108—109·5°, $[\alpha]_D^{15}$ +15·5° in $CHCl_3$ (cf. *loc. cit.*), is $C_{43}H_{90}O_6N_2$, formed by loss of H_2O from 2 mols. of (**VII**) and 1 mol. of $COMe_2$ and readily hydrolysed thereinto. With BzCl–C_5H_5N, (**VIII**) gives an oily product, converted by hot KOH–MeOH–H_2O into the N-*Bz* derivative, m.p. 130—131°, $[\alpha]_D^{18}$ +5·0° in C_5H_5N [with CrO_3–AcOH or $Pb(OAc)_4$ gives NH_2Bz], of (**VII**). $Pb(OAc)_4$ converts (**I**) in AcOH + a trace of Ac_2O into the *amide*, m.p. 122·5—124°, of (**III**), an aldehyde (**IX**), probably $C_{15}H_{31}{\cdot}CHO$, m.p. 28—32°, b.p. 155—165°/11 mm. [*polymer* (**X**), m.p. 63—64·5°; *semicarbazone*, m.p. 104—104·5°, hydrolysed by $C_6H_4(CO)_2O$ to (**X**); *thiosemicarbazone*, m.p. 81—83°; 2 : 4-*dinitro*-, m.p. 93·5—95° (corr.), and *p*-nitro-phenylhydrazone, m.p. 80—82°], and a substance (**XI**), $C_4H_8O_3$ [*di*-p-*nitro*-, m.p. 281—283° (decomp.), and *bis*-2 : 4-*dinitro-phenylosazone*, m.p. 295—297° (decomp.)]. (**XI**) is not formed directly by $Pb(OAc)_4$ in C_6H_6, but is obtained when the reaction products therefrom are heated in HCl–MeOH or 50% AcOH. (**III**) has $[\alpha]_D$ +2·1° in C_5H_5N, gives an acetate, m.p. 74—75°, and *anilide*, m.p. 88—89°, and with $Pb(OAc)_4$ in AcOH gives (?) HCO_2H and an aldehyde, m.p. 72—76° (*semicarbazone*, m.p. 115—115·5°; p-*nitrophenylhydrazone*, m.p. 104—105°), oxidised by CrO_3–AcOH to the acid, $C_{25}H_{50}O_2$, m.p. 81°, which is also obtained similarly from (**III**). M.p. show that (**III**), (**IX**), etc. contain a branched chain. For comparison, *n*-palmitaldehyde-2 : 4-dinitro-, m.p. 105—107° (corr.), margaraldehyde-*p*-nitro-, m.p. 96·5—97·5°, and -2 : 4-dinitro-phenylhydrazone, m.p. 103—105° (corr.), and -semicarbazone, m.p. 107—108·5°, are prepared. (**XI**) gives no colour with Schiff's reagent; its structure is uncertain but is not $OH{\cdot}CH_2{\cdot}CMe(OH){\cdot}CHO$ (no osazone) or $OH{\cdot}CHMe{\cdot}CH(OH){\cdot}CHO$ [di-*p*-nitrophenylosazone, m.p. 304° (decomp.)]. Acid hydrolysis of (**I**) leads to (**III**) + (**VII**) or, by way of (**II**), to (**III**) + (**IV**). Structures for (**I**) etc. are suggested. Ruppol's cerebrin, formulated as $C_{46}H_{91}O_4N$ (A., 1937, III, 484), is really (**I**). R. S. C.

Hydrogenation of aliphatic dinitriles. See B., 1943, II, 368.

Catalytic hydrogenation of adipodinitriles to produce hexamethylenediamines.—See B., 1943, II, 368.

Preparation of diazomethane. M. D. Owen (*Current Sci.*, 1943, **12**, 228).—$NH_2{\cdot}CO{\cdot}NMeAc$, m.p. 179—180°, obtained by slowly adding 10% NaOH to NH_2Ac and Br at 0° and then at 100°, is hydrolysed (boiling 3% HCl) and then converted by $NaNO_2$ into $NH_2{\cdot}CO{\cdot}NMe{\cdot}NO$, which can be kept in quantity at 0°. It is converted by aq. KOH in Et_2O into CH_2N_2. J. F. M.

II.—SUGARS AND GLUCOSIDES.

Chemical constitution and the tanning effect. II. Pentagallates of glucose and mannose. A. Russell, W. G. Tebbens, and W. F. Arey (*J. Amer. Chem. Soc.*, 1943, **65**, 1472—1474; cf. A., 1943, II, 61).—β-*d*-Glucose 1 : 2 : 3 : 4 : 6-pentagallate (**I**), softens 133°, sinters 143°, $[\alpha]_D^{23}$ +25·33° in EtOH, is obtained from the acetate by NaOH–NaOAc in aq. $COMe_2$–N_2. *d*-Mannose and 3 : 4 : 5 : 1-$(OAc)_3C_6H_2{\cdot}COCl$ in $CHCl_3$–quinoline at room temp. give d-*mannose penta*(*triacetylgallate*), sinters 121°, $[\alpha]_D^{26}$ −55·5° in $CHCl_3$, and thence, as above, d-*mannose pentagallate* (**II**), sinters 161°, $[\alpha]_D^{23}$ −72·38° in EtOAc. Similarly are obtained d-*glucose Et₂ mercaptal penta*(*triacetylgallate*), sinters 82°, $[\alpha]_D^{22}$ +18·75° in $CHCl_3$, and *pentagallate* (**III**), sinters 167°, $[\alpha]_D^{23}$ +11·13° in EtOAc, and thence (dil. H_2SO_4) aldehydo-d-*glucose pentagallate* (**IV**), sinters 113°, $[\alpha]_D^{20}$ +10·13° in EtOAc. (**I**)—(**IV**) make as good leather as does gallotannin. R. S. C.

Azoyl derivatives of sugars. [Their] separation by chromatographic adsorption. II. G. H. Coleman and C. M. McCloskey (*J. Amer. Chem. Soc.*, 1943, **65**, 1588—1594; cf. A., 1942, II, 395).—Some esters of sugars and $ArN_2{\cdot}C_6H_4{\cdot}CO_2H$ etc. are separated by chromatography on magnesite, dicalite, or SiO_2 gel. It is usually best to separate mixtures first into groups (mono-, di-saccharides etc.) and then to treat these groups on fresh columns. The following are prepared by RCOCl in C_5H_5N at 0°, room temp., or 90°: α-, m.p. 265—266°, [α] +223°, and β-D-*glucose* (**I**), m.p. 252—253°, [α] −50°, α- (**II**), m.p. 275—276°, [α] +436°, and β-D-*galactose* (**III**), m.p. 255—255·5°, [α] +170°, *penta*-p-*benzeneazobenzoate*; β-D-*fructose*, m.p. 124·5—125·5°, [α] −440°, α-D-*xylose*, m.p. 156—157°, [α] +244°, β-D- (**IV**), m.p. 261·5—262°, [α] −755°, and β-L-*arabinose* (**V**), m.p. 262—262·5°, [α] +755°, *tetra*-p-*benzeneazobenzoate*; *sucrose*, m.p. 125—125·5°, [α] +35°, αα- (**VI**), m.p. 134—134·5°, [α] +210°, and ββ-*trehalose* (**VII**), m.p. 328—329°, [α] +17°, α-, sinters 265°, m.p. 287—288°, [α] +320°, and β-*lactose*, m.p. 199—204° [α] +167°, α-*gentiobiose*, m.p. 232—233°, [α] +62°, β-*maltose*, m.p. 274—275°, [α] +2°, β-*cellobiose* (**VIII**), sinters 268°, m.p. 272—273° [α] +105°, β-*melibiose*, m.p. 279·5—280°, [α] +172°, *melezitose*, sinters 127—130°, [α] +188°, and *raffinose*, m.p. 143—145°, [α] +146°, *octa*-(? *hepta*-)p-*benzeneazobenzoate* ([α] above are $[\alpha]_{6438}^{25}$); *diisopropylideneglucose*, m.p. 111—112°, $[\alpha]_{6438}^{22}$ −81·5°, -*galactose*, m.p. 124·5—126°, $[\alpha]_{6438}^{22}$ −57°, and -*mannose* p-*benzeneazobenzoate*, m.p. 190·5—191°, $[\alpha]_{6438}^{23}$ +19°; *isopropylideneglucose tri*-p-*benzeneazobenzoate*, m.p. 166—166·5°, $[\alpha]_{6438}^{23}$ −352°; *methyl*-α-D-*glucoside*, m.p. 214—215°, $[\alpha]_{6438}^{22}$ +74°, and -*cellobioside tetra*-p-*benzeneazobenzoate*, m.p. 282—284°, $[\alpha]_{6438}^{22}$ +209°. Tetra-acetylglucosyl or hepta-acetylcellobiosyl bromide with $p{\text{-}}PhN_2{\cdot}C_6H_4{\cdot}CO_2Ag$ in C_6H_6 gives β-D-*glucose* 2 : 3 : 4 : 6-*tetra-acetate* 1-p-*benzeneazobenzoate* (**IX**), m.p. 214—215°, $[\alpha]_{6438}^{22}$ −63°, and β-*cellobiose hepta-acetate* p-*benzeneazobenzoate* (**X**), m.p. 282—284°, $[\alpha]_{6438}^{23}$ −54·5°. [α] are in $CHCl_3$. M.p. (above) are corr. $p{\text{-}}NH_2{\cdot}C_6H_4{\cdot}CO_2H$ and $p{\text{-}}C_6H_4I{\cdot}NO$ in EtOH–AcOH give p-p′-*iodobenzeneazobenzoic acid*, m.p. 332—334°, the chloride (prep. by $SOCl_2$), m.p. 170—171°, from which in C_5H_5N gives the *Me* ester, *anhydride*, m.p. 199—200°, and D-*glucose penta*-p-p′-*iodobenzeneazobenzoate*. The following groups are separated: (**VIII**)–(**IX**); (**II**)–(**III**); (**VI**)–(**VII**); (**IV**)–(**V**); (**I**)–(**VI**)–(**VIII**); (**V**)–(**I**)–(**VI**)–(**VIII**). R. S. C.

Action of diazomethane on acyclic sugar derivatives. V. Halogen derivatives. M. L. Wolfrom and R. L. Brown (*J. Amer. Chem. Soc.*, 1943, **65**, 1516—1521; cf. A., 1943, II, 294).—1-Diazo-1-deoxy-(**I**) with HCl–$COMe_2$–Et_2O gives 1-*chloro*-keto-D-*galaheptulose penta-acetate, forms*, m.p. 89—90° and 101—102°, $[\alpha]_D^{24}$ −32·8°, and thence (NaI–$COMe_2$) the 1-*I*-compound (**II**), m.p. 144—146°, $[\alpha]_D^{26}$ −44·8°. With the acetate of the appropriate acid in boiling C_6H_6, (**I**) gives keto-D-*galaheptulose* 2 : 3 : 4 : 5 : 6-*penta-acetate* 1-(D-*galactonate penta-acetate*), m.p. 165—167° (soft glass), 171·5—172·5° (Pyrex glass), $[\alpha]_D^{31}$ +13·0°, 1-(D-*gluconate penta-acetate*), m.p. 112—113°, $[\alpha]_D^{30}$ +22·0°, and 1-(D-*arabonate tetra-acetate*), m.p. 153—155° (soft glass), 155·5—156·5° (Pyrex), $[\alpha]_D^{32}$ +22·5°. With I in EtOH in light, (**I**) gives 1 : 1-*di-iodo*keto-D-*galaheptulose penta-acetate* (**III**), m.p. 160—163°, $[\alpha]_D^{19}$ +13°. 47% HI reduces (**I**), (**II**), or (**III**) exothermally to 1-*deoxy*keto-D-*galaheptulose penta-acetate, forms*, m.p. 65·5—67·5° and 78—79°, $[\alpha]_D^{28}$ −14° (*X*-ray diagrams given; *oxime*,

m.p. 125·5—126·5°, $[\alpha]_D^{28}$ +28°). 1-*Iodo*keto-D-*glucoheptulose penta-acetate*, m.p. 79—81°, $[\alpha]_D^{25}$ −9·9°, and -*fructose tetra-acetate*, m.p. 55—56°, $[\alpha]_D^{21\cdot5}$ +63°, 1-deoxy*keto*-D-fructose tetra-acetate, m.p. 81—83° (lit. 77—78°), $[\alpha]_D^{20}$ +56°, and 1-*bromo*keto-D-*galaheptulose penta-acetate*, m.p. 124—125°, $[\alpha]_D^{28}$ −36°, are similarly prepared. COPhMe is obtained from COPh·CHN_2 by 47% HI. The following revised data are recorded (cf. A., 1942, II, 395): 1-chloro-, $[\alpha]_D^{28}$ −2·8°, and 1-bromo-*keto*-*D*-glucoheptulose penta-acetate, m.p. 87—88°, $[\alpha]_D^{28}$ −5·5°, and 1-bromo*keto*-*D*-fructose tetra-acetate, m.p. 67—68°, $[\alpha]_D^{21}$ +65°. [α] are in $CHCl_3$. R. S. C.

Lead tetra-acetate oxidations in the sugar group. IV. Rates of oxidation of trehalose, β-glucosan, α-methyl-*L*-sorbopyranoside, polygalitol, and styracitol in glacial acetic acid. R. C. Hockett, (Miss) M. T. Dienes, and H. E. Ramsden (*J. Amer. Chem. Soc.*, 1943, **65**, 1474—1477; cf. A., 1943, II, 219).—The following rules are postulated: (*a*) ≮2 $Pb(OAc)_4$ are consumed by a vicinal triol; consumption after 2 mols. is often rapid owing to side-reactions, *e.g.*, HCO_2H; (*b*) *cis*-groups are most rapidly oxidised; (*c*) OH·CHR·CHO is attacked, but often slowly; (*d*) OH·CHR·CHO is more rapidly oxidised if a γ- or δ-OH permits formation of a hemiacetal which simulates an αβ-glycol. The oxidation curves of β-methyl-*D*-xylo- and -gluco-pyranoside, β-glucosan, trehalose, α-methyl-*L*-sorbose and -*D*-gluco-pyranoside resemble each other, but differ from those of α-methyl-*D*-mannopyranoside and styracitol (I), which in turn are similar; that of polygalitol is intermediate between the two types. The evidence favours the 1 : 5-mannitan structure for (I). R. S. C.

Preparation of β-primaverose and β-vicianose hepta-acetates. C. M. McLoskey and G. H. Coleman (*J. Amer. Chem. Soc.*, 1943, **65**, 1778—1780).—Passing HBr into xylose tetra-acetate in Ac_2O and keeping at room temp. gives β-*D*-xylosyl bromide 2 : 3 : 4-triacetate (88—90%), m.p. 98—99°, which with β-*D*-glucose 1 : 2 : 3 : 4-tetra-acetate, Ag_2O, "Drierite," and I in $CHCl_3$ gives 57% of β-primaverose hepta-acetate, m.p. 216—217° (corr.), $[\alpha]_D^{24}$ −26·2° in $CHCl_3$. β-*L*-Arabinosyl bromide triacetate gives similarly β-vicianose hepta-acetate (34%), m.p. 158—159° (corr.), $[\alpha]_D^{24}$ +9·4° in $CHCl_3$, and a substance, m.p. 144—149°. R. S. C.

Emulsin. XLIII. Fermentative fission of diglucosides of protocatechualdehyde. B. Helferich and R. Griebel (*Annalen*, 1940, **544**, 191—205; cf. A., 1940, II, 67).—Diglucosides derived from protocatechualdehyde 4-glucoside (I) and 4-β-d-*galactoside* (II) (see below) are relatively very slowly hydrolysed by emulsin from almonds or lucerne. The tetra-acetate of (I) with acetobromo*iso*rhamnose and NaOH in H_2O–$COMe_2$ at room temp. gives *protocatechualdehyde* 4-β-d-*glucoside* 3-β-d-iso*rhamnoside hepta-acetate* (~29%), m.p. 195—196·5°, $[\alpha]_D^{19}$ −56·2° in $CHCl_3$, converted by boiling NaOMe–MeOH into *protocatechualdehyde* 4-β-d-*glucoside* 3-β-d-iso*rhamnoside* (~92%), +EtOH and anhyd., m.p. 158—160°, $[\alpha]_D^{18}$ (anhyd.) −115·3° in H_2O. Similarly are prepared the 4-β-d-*glucoside tetra-acetate* 3-β-d-*glucoside* 2′ : 6′-*diacetate* 3′-*methanesulphonate* (~24%), m.p. 128·5—129°, $[\alpha]_D^{18}$ −80·4° in $CHCl_3$ (converted by Ac_2O–C_5H_5N into the *hepta-acetate*, m.p. 186°, $[\alpha]_D^{18}$ −74·9° in $CHCl_3$), and thence (1% MeOH–NaOMe in $CHCl_3$ at −20°; 90 min.) the 4-β-d-*glucoside* 3-β-d-*glucoside* 2′-*acetate* 3′-*methanesulphonate* (~60%), +4H_2O and anhyd., m.p. 89°, $[\alpha]_D^{19}$ −73·1° in H_2O (complete deacetylation could not be achieved). 3 : 4 : 1-OAc·C_6H_3(OH)·CHO, acetobromogalactose (III), and NaOH in aq. $COMe_2$ at room temp. give *protocatechualdehyde* 3-*acetate* 4-β-d-*galactoside tetra-acetate* (~33%), m.p. 141·5—142·5°, $[\alpha]_D^{21}$ −2·96° in $CHCl_3$, and thence (NaOH–H_2O–MeOH–N_2 at room temp.) (II) (~58%), m.p. 178·5°, $[\alpha]_D^{20}$ −71·4° in H_2O, $[\alpha]_D^{19}$ −122° in 0·5N-NaOH. 3 : 4 : 1-$(OH)_2C_6H_3$·CHO with (III) and NaOH in aq. $COMe_2$ at room temp. gives, according to the relative amounts, the 4-β-*d*-galactoside tetra-acetate (IV), a syrup [hydrolysed to (II)], or the 3 : 4-*di*-β-*galactoside octa-acetate* (~51%), m.p. 149·5°, $[\alpha]_D^{19}$ −37·3° in $CHCl_3$, and thence (NaOMe–MeOH) the 3 : 4-*di*-β-*galactoside* (~61%), m.p. 239—241°, $[\alpha]_D^{19}$ −85·6° in H_2O. (IV) yields, as above, *protocatechualdehyde* 4-β-d-*galactoside tetra-acetate* 3-β-d-*glucoside triacetate* 6″-*methanesulphonate* (~61%), m.p. 187·5—188°, $[\alpha]_D^{21}$ −43·4° in $CHCl_3$, and thence (NaOMe–MeOH–$CHCl_3$) the 4-β-d-*galactoside* 3-β-d-*glucoside* 6″-*methanesulphonate* (~82%), +H_2O and anhyd., m.p. 146—148°, $[\alpha]_D^{20}$ (anhyd.) −99·2° in H_2O. Similarly are prepared *protocatechualdehyde* 4-β-d-*lactoside*, m.p. 215—220° (decomp.), $[\alpha]_D^{21}$ −62·0° in H_2O, $[\alpha]_D^{22}$ −105° in 0·5N-NaOH [*hepta-acetate* (V), m.p. 203—207° (decomp.), $[\alpha]_D^{24}$ −29·8° in $CHCl_3$], 4-β-d-*lactoside* 3-β-d-*glucoside*, +H_2O and anhyd., m.p. 235—237°, $[\alpha]_D^{20}$ (anhyd.) −81·7° in H_2O (undeca-acetate, amorphous, softens 112—114°, $[\alpha]_D^{19}$ −55·4° in $CHCl_3$), and 3 : 4-*di*-β-d-*lactoside*, hygroscopic, m.p. ~200 (decomp.), $[\alpha]_D^{20}$ −60·1° in H_2O (*tetradeca-acetate*, amorphous, softens 126—129°, $[\alpha]_D^{20}$ −52·9° in $CHCl_3$). Vanillin yields similarly *vanillin* 3-β-d-*lactoside*, m.p. 228° (decomp.), $[\alpha]_D^{20}$ −53·2° in H_2O [*hepta-acetate*, m.p. 143·5—145°, $[\alpha]_D^{20}$ −38·9° in $CHCl_3$, also obtained from (V) (proof of structure) by CH_2N_2 or Me_2SO_4]. PhOH gives *Ph* β-d-*lactoside*, m.p. 190·5—191·5°, $[\alpha]_D^{19}$ −36·3° in H_2O (*hepta-acetate*, m.p. 161·5°, $[\alpha]_D^{20}$ −23·2° in $CHCl_3$). M.p. are corr. R. S. C.

Acid hydrolysis of *dl*-alkyl-β-*d*-glucosides.—See A., 1944, I, 19.

Fructose anhydrides. XXIII. Phlein. Ring-structure of polyfructosans. XXIV. Group of natural polyfructosans. H. H. Schlubach and O. K. Sinh (*Annalen*, 1940, **544**, 101—111, 111—116; cf. A., 1940, II, 119).—XXIII. Phlein (I) (prep. described), $[\alpha]_D$ −50·0° in H_2O, has mol. wt. (cryoscopic in H_2O) 2480—2615, has a reduction val. (Bertrand) 0·27%, undergoes 50% hydrolysis in N-H_2SO_4 at 20° in 235 min., and with Ac_2O in warm aq. C_5H_5N gives a triacetate, m.p. 233°, $[\alpha]_D$ +20·7° in $CHCl_3$, which in dil. aq. KOH (not by Zemplén's method) regenerates (I) and with Me_2SO_4–30% aq. NaOH–N_2 at 55° gives a *Me₃ ether* (OMe 45·4%), m.p. 172°, $[\alpha]_D^{20}$ −57·7° in $CHCl_3$, mol. wt. (cryoscopic in C_6H_6) 3280, hydrolysed to 1 : 3 : 4-trimethylfructose containing 1·62% of dimethylfructose as sole impurity. (I) has thus a cyclic structure containing 15—16 fructose units united at positions 2 and 6. Inulin, α-dextrin, and glycogen also contain closed rings. "End-group" determinations are of no val. for determination of mol. wts.

XXIV. Natural polyfructosans fall into groups. The acetates of lævan, (I), poain, and secalin are dextrorotatory; the differences between [α] of these acetates and the respective fructosans decreases in the same order as the yield of 1 : 3 : 4-trimethylfructose, *i.e.*, with increased chain-branching; with increasing chain-branching the mol. wt. decreases and the rate of hydrolysis increases (readier fission of side-chains). The same regularities hold for inulin, asparagosin, sinistrin, and graminin, which yield 3 : 4 : 6-trimethylfructose, except that the differences between [α] of the acetates and fructosans increase with increased branching. The purity of asphodelin is open to doubt. Triticin is abnormal and probably belongs to a third type. Irisin in also abnormal. R. S. C.

Macromolecular compounds. CCXLVI. Constitution of salepmannan. E. Husemann (*J. pr. Chem.*, 1940, [ii], **155**, 246—260).—Salep powder is boiled (1 hr.) with EtOH to inactivate a degrading enzyme and the product is washed with EtOH and Et_2O and dried at 35° vac. The residue is shaken in the dark with H_2O and the somewhat turbid solution is pptd. with MeOH. The ppt. is well pressed and triturated before treatment with Et_2O, which is removed at room temp. before the final desiccation at 35—40°/vac. Salepmannan (I) of various degrees of degradation is obtained by alteration of the conditions of extraction without removal of the enzyme. (I) is a macromol. compound since nitration does not considerably alter the degree of polymerisation. Determinations of the Staudinger K_m const. from observations of η in Schweitzer's reagent or H_2O of (I) of osmotically determined degree of polymerisation proves the validity of the viscosity law for degrees of polymerisation between 46 and 1550 and the similar structure of all samples of (I). K_m of (I) is nearly identical with those of cellulose (II) and pure mannan, thereby indicating an extended, unbranched structure of (I) similar to that of (II). Fractionation proves that (I) is very heterogeneous. (I) loses solubility in H_2O when treated with alkali and acid, which results in elimination of 1 AcOH from 11 mannose mols. Attempts to prepare a sol. (I) by restricted acetylation were unsuccessful. H. W.

Glucan of the yeast membrane. V. C. Barry and T. Dillon (*Proc. Roy. Irish Acad.*, 1943, **49**, B, 177—185).—Yeast glucan (I) is oxidised by HIO_4, then aq. Br, or the latter alone, in similar manner to that described for laminarin (II) (cf. A., 1942, II, 397). and the product is boiled with aq. $H_2C_2O_4$ to give a disaccharide, which affords laminaribiosazone. The mean length of the chain of glucose units in the mol. of (I) is 28 units, viz., 1·75 times that of (II). Configuration of the glucose units is shown to be β, *i.e.*, the same as that of the units in (II). A. T. P.

Limit dextrins and starch. VI. Limit dextrins from potato starch by action of pancreatic amylase. VII. Difficultly hydrolysable glucosidic linkings in starch. K. Myrbäck, B. Örtenblad, and K. Ahlborg. **VIII. Constitution of a limit dextrin. Demonstration of α-glucosidic 1 : 6-linking in dextrin and starch.** K. Myrbäck and K. Ahlborg (*Biochem. Z.*, 1940, **307**, 49—52, 53—68, 69—78; cf. A., 1943, III, 684).—VI. Potato starch was hydrolysed by pancreatin at pH 6·8 and room temp. for 5 months. The product, treated with increasing concns. of EtOH, yielded ten fractions of decreasing P_2O_5 content (11·7—~0·1%) and mol. wt. (~1200—550) and increasing reducing power (~16—32% as glucose). Thus the greater part (probably ~75%) of the limit dextrins (I) consists of tetrasaccharides and the remainder of trisaccharides. Each (I) appears to contain one α-glucosidic 1 : 6-linking in addition to the maltose linkings.

VII. The unimol. coeff. of hydrolysis of maltose by HCl has a const. val., whilst that of sol. starch (II) increases during the reaction excepting towards the end, when it decreases slightly. This indicates the presence of a small no. of difficultly hydrolysable linkings in (II). A variety of limit (I) all show a marked decrease (which is the greater the lower is the mol. wt.) in the reaction const. during hydrolysis. Hence α-glucosidic linkings other than the 1 : 4 are present in (II) and (I) and it is probable that one of these abnormal linkings is present per mol. of (I). The enzymic hydrolysis of (II) and (I) apparently does not involve linkings other than the 1 : 4 and 1 : 6. The possibility of the presence of an *iso*maltose linking is discussed.

VIII. (I), prepared by the action of amylase on maize starch, mol. wt. ~480, [α] +124°, was repeatedly methylated and then distilled in a vac. to give a methylated trisaccharide (OMe 51·5%), [α] +136·5° in $CHCl_3$, which, on hydrolysis, gave 1 mol. of tetramethyl- and 2 mols. of trimethyl-glucose. The trimethylglucose fraction was shown by the Oldham–Rutherford method (A., 1932, 254) to consist of approx. equal parts of 2 : 3 : 4- and 2 : 3 : 6-trimethylglucose. Thus the trisaccharide contains a maltose and an *iso*maltose linking, the latter (α-glucosidic 1 : 6-linking) being present in starch to an extent of ⩽3% of the total glucosidic linkings. The trisaccharide arises from a branching of the starch mol., if Freudenberg's theory of the structure of (II) is accepted. F. O. H.

Starch–iodine complex.—See A., 1944, I, 5.

Viscosity of cellulose acetate solutions. H. Lohmann (*J. pr. Chem.*, 1940, [ii], **155**, 299—309).—Cotton linters is acetylated (Ac_2O–H_2SO_4 in AcOH) so as to give products of differing degree of polymerisation which are then partly hydrolysed (H_2SO_4–H_2O) to the $COMe_2$-sol. stage (~2·4 OAc). Determinations of η of these products (I) which have been washed acid-free by distilled or tap H_2O show a very pronounced influence of slight differences in ash content, which are generally <0·1%. These abnormalities are not observed in AcOH. For the correlation of mechanical properties of acetate silk fibres and η in $COMe_2$ it is essential that the measurements be made in very dil. solution and that dilution must be the greater as the degree of polymerisation increases. The greatest increase of η in $COMe_2$ is caused by $CaCl_2$; $SrCl_2$ has a small effect but other Ca salts, as also Mg, Al, and alkali salts, are ineffective. Increase of [$CaCl_2$] causes increase of η and increased turbidity, the effect being less marked at 40° than at 15°. The associations causing increase of η are due to subsidiary valency activities dependent on temp. The viscosity of (I) in *m*-cresol, CH_2Cl_2–EtOH (8 : 2 by vol.), $CH_2(O{\cdot}[CH_2]_2{\cdot}OH)_2$, dioxan, or COMe–EtOH is not affected by $CaCl_2$ which causes a small increase in NH_2Ph and HCO_2Et and a great increase in COMeEt, MeOAc, and $CHCl_3$–$COMe_2$ (1 : 1). A "salt effect" is not shown by solvents containing OH or OAlk but is very obvious with esters or ketones. H. W.

III.—HOMOCYCLIC.

Formation of *cyclo*propanes from monohalides. IV. Reactions of α-chloro-β-phenyl*iso*butane (neophyl chloride). F. C. Whitmore, C. A. Weisgerber, and A. C. Shabica, jun. (*J. Amer. Chem. Soc.*, 1943, **65**, 1469—1471; A., 1943, II, 21).—$CPhMe_2{\cdot}CH_2Cl$ (I) (prep. from $CH_2{:}CMe{\cdot}CH_2Cl$ by C_6H_6–H_2SO_4 at 20°; 68% yield), b.p. 97°/13 mm., reacts less readily with Na than does $CH_2Bu^{\gamma}Cl$; with 5 Na at <90° it gives $PhBu^{\gamma}$ (34·8%), 1-phenyl-1-methyl*cyclo*propane (11·9%), and $CHPh{:}CMe_2$ (13·7%). With NaEt in C_5H_{12} at −10° to 20°, (I) gives the same products and is thus more reactive than $CH_2Bu^{\gamma}Cl$ towards NaEt. These results confirm Morton's views (A., 1943, II, 114) on the Wurtz reaction. With Na (2 atoms) in liquid NH_3, (I) gives mainly $PhBu^{\gamma}$. (I) decomposes only slowly at 135°, but at the b.p., 222°/741 mm., gives $CHPh{:}CMe_2$, $CH_2{:}CMe{\cdot}CH_2Ph$, and $CH_2Ph{\cdot}CMe_2Cl$. (I) does not react with NaOEt, C_5H_5N, or Na fluorenyl. It readily gives a Grignard reagent and thence $CPhMe_2{\cdot}CH_2{\cdot}CO_2H$ (81·6%) or $CPhMe_2{\cdot}CH_2Cl$ (30·7%). R. S. C.

***cis–trans* Isomerisation and spectral characteristics of carotenoids and related compounds.** L. Zechmeister and A. Polgár (*J. Amer. Chem. Soc.*, 1943, **65**, 1522—1528).—When an all-*trans* natural carotenoid is isomerised by boiling in C_6H_{14} or by I, λ and ε of the main max. progressively decrease, but the chief effect is appearance of a max. at 320—380 mμ., the "*cis*-peak" effect. λ of this peak is 141—144 mμ. below that of the highest max. for the all-*trans*-compound for 12 C_{40}-compounds. Methylbixin and $Ph{\cdot}[CH{:}CH]_4{\cdot}Ph$ show the same phenomenon and adding I increases ε at 240—280 mμ. for vitamin-*A*. R. S. C.

Action of cold concentrated hydriodic acid on carotenes. Structure and *cis–trans* isomerisation of reaction products. A. Polgár and L. Zechmeister (*J. Amer. Chem. Soc.*, 1943, **65**, 1528—1534).—Shaking α- or β-carotene in light petroleum with 55—58% HI (freed from I) and chromatography of the products gives ⩾9% each of 5 : 6-dihydro-β- and -α-carotene, structures of which are indicated by analysis, determination of CMe_2:, spectroscopy, and quant. hydrogenation. The products undergo *cis*-isomerisation when boiled in light petroleum, melted, or treated with I, and six α- and six β-isomerides are characterised by absorption max. R. S. C.

***cis–trans* Isomerisation and spectral characteristics of gazaniaxanthin. Its structure.** L. Zechmeister and W. A. Schroeder (*J. Amer. Chem. Soc.*, 1943, **65**, 1535—1540).—Petals of *Gazania rigens*, R. Br., grown in S. California, yield gazaniaxanthin (I) (0·14%), lycopene (0·0435%), γ- (0·01%) and β-carotene (0·006%), lutein, and cryptoxanthin (cf. Schön, A., 1938, II, 436). (I) is $C_{40}H_{56}O$, contains 11 conjugated C:C, with O_3 gives 1 mol. of $COMe_2$, but may be dihydrorubixanthin. It is fairly stable in light petroleum at room temp., but in boiling C_6H_6 or with I isomerisation occurs and the absorption changes in the manner characteristic of C_{40}-carotenoids. R. S. C.

Preservation and utilisation of styrene. Preparation of styrene.—See B., 1943, II, 369.

Organic reactions with boron fluoride. XXVIII. Isomeric *p*-dibutylbenzenes. G. F. Hennion and L. A. Auspos (*J. Amer. Chem. Soc.*, 1943, **65**, 1603—1606; cf. A., 1943, II, 125).—PhBu with $Pr^{\alpha}COCl$ or $Pr^{\beta}COCl$ and $AlCl_3$ in CS_2 give 76—91% of n-, b.p. 138°/6 mm., sec.-, b.p. 125°/3 mm., iso-, b.p. 116°/3 mm., and tert.-*butyl*-n-*butyrophenone*, b.p. 128°/5 mm., and n-, b.p. 118°/3 mm., sec.-, b.p. 116°/3 mm., iso-, b.p. 121°/7 mm., and tert.-*butyl*-iso-*butyrophenone*, b.p. 140°/4 mm., whence Zn–Hg–H_2O–AcOH–HCl yields p-*di*-n-, m.p. −24°, b.p. 259°/745 mm., 124°/15 mm., and p-*di*-iso-*butylbenzene*, m.p. −21°, b.p. 242°/739 mm., 109°/15 mm., p-n-*butyl*-sec.-, b.p. 250°/739 mm., 117°/15 mm., -iso-, b.p. 251°/743 mm., 118°/15 mm., and -tert.-, m.p. −46°, b.p. 248°/743 mm., 116°/15 mm., p-sec.-*butyl*-iso-, b.p. 241°/739 mm., 113°/15 mm., and -tert.-, b.p. 235°/745 mm., 108°/15 mm., and p-iso*butyl*-tert.-, b.p. 239°/751 mm., 109°/15 mm., -*butylbenzene*. In presence of BF_3–H_3PO_4, $Bu^{\alpha}OH$ or $Bu^{\beta}OH$ introduces *sec.*-Bu and Bu^{γ}, respectively, into PhBu, thus giving the *as*-compounds and p-*di*-sec.-, m.p. −58°, b.p. 239°/739 mm., 108°/15 mm., and -*tert.*-butylbenzene, m.p. 77·7°, b.p. 237°/743 mm., 109°/15 mm. (lit. 225°). *n* and *d* are also given; they are low for the compounds prepared by alkylation, probably owing to presence of small amounts of *o*-isomerides. R. S. C.

Thermal decomposition of the dibromide of αaγγ-tetraphenyl-β-methylpropene. C. F. Koelsch and R. V. White (*J. Amer. Chem. Soc.*, 1943, **65**, 1639—1640).—The product from $CHPh_2{\cdot}CHMe{\cdot}CO_2Me$ and MgPhBr in boiling Et_2O with a trace of H_2SO_4 in boiling AcOH gives αaγγ-*tetraphenyl-β-methyl-*Δ^{α}-*propene* (I) (43%), m.p. 132—133°, which with CrO_3–AcOH gives, by pinacol rearrangement, γγδδ-*tetraphenyl-n-butan-β-one*, m.p. 118—119°. AcOH solutions of the dibromide of (I), when distilled, give 3-*phenyl-2-benzhydrylindene* (II) (72%), m.p. 162—163·5°, oxidised by CrO_3–AcOH at 100° to *benzophenone-2-acetic acid*, m.p. 130—131°. 2-Benzylideneindanone with C_6H_6 and $AlCl_3$ gives 2-*benzhydrylindanone* (74%), m.p. 109—111°, converted into (II) by MgPhBr and then 2% H_2SO_4–AcOH. 2-Phenylindane-1 : 3-dione and MgMeI–Et_2O give 2-*phenyl-3-methylindone* (45%), m.p. 69—71°; *o*-$C_6H_4Ph{\cdot}MgI$ gives an oil. R. S. C.

Preparation of diphenyldimethylpolyenes. K. Bernhauer and I. Skudrzyk (*J. pr. Chem.*, 1940, [ii], **155**, 310—316).—$CHPh{:}CMe{\cdot}CHO$ (p-*nitrophenylhydrazone*, m.p. 203°) and $(CH_2{\cdot}CO_2H)_2$ with PbO_2–Ac_2O at 140°, at the b.p., afford αθ-diphenyl-βη-dimethyl-$\Delta^{\alpha\gamma\epsilon\eta}$-octatetraene, m.p. 174° (cf. Kuhn *et al.*, A., 1938, II, 437). ε-Phenyl-β-methyl-$\Delta^{\beta\delta}$-pentadien-α-al, m.p. 58° [corresponding carboxylic acid, m.p. 160°; *semicarbazone*, m.p. 239° (decomp.); p-*nitrophenylhydrazone*, m.p. 212—213°], similarly yields αμ-*diphenyl-*δι-*dimethyl-*$\Delta^{\alpha\gamma\epsilon\eta\iota\lambda}$-*dodecahexaene*, m.p. 217° (decomp.); the Et_2 analogue has m.p. 206—209·5°. Tiglaldehyde is obtained from MeCHO–EtCHO–1% aq. NaOH (CO_2) at 10°. A. T. P.

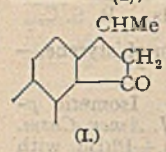
Process of obtaining α- and β-methylnaphthalene and fractions enriched in either of these compounds.—See B., 1943, II, 369.

Aromatic cyclodehydration. XII. Mechanism of the cyclisation of *o*-benzylphenones. C. K. Bradsher and E. S. Smith. **XIII. 1 : 2 : 3 : 4-Dibenzphenanthrene.** C. K. Bradsher and L. Rapoport (*J. Amer. Chem. Soc.*, 1943, **65**, 1643—1645, 1646—1647; cf. A., 1943, II, 265).—XII. α-*o-Chlorophenyliso*propyl *alcohol* (prep. from *o*-$C_6H_4Cl{\cdot}CO_2Me$ and MgMeI in Et_2O; 82·5% yield), b.p. 94°/8 mm., with C_6H_6 and $AlCl_3$ at <10° gives β-*phenyl-β-o-chlorophenylpropane* (61%), b.p. 146°/7 mm. With CuCN–$CH_2Ph{\cdot}CN$–C_5H_5N at 250° this gives β-*phenyl-β-o-cyanophenylpropane* (I) (68%), m.p. 62—63·5° (unaffected by boiling KOH–EtOH), and with CuCN–H_2O–C_5H_5N at 250° gives *o-*αα-*dimethylbenzylbenzamide* (20%), m.p. 132—134°, also obtained similarly (31%) from (I), and resistant to hydrolysis. MgPhBr and (I) in boiling C_6H_6 give *o-*αα-*dimethylbenzylbenzophenoneimine hydrochloride* (60%), unchanged by hot 10% HCl but in boiling 48% HBr giving 10-*phenyl-*9 : 9-*dimethyl-*9 : 10-*dihydroanthracene* (II), m.p. 145—146° (the intermediate ketone cannot enolise). *o*-$CHPh_2{\cdot}C_6H_4{\cdot}CO_2Me$ and MgMeI give a carbinol, cyclised to (II) (proof of structure) by $AlCl_3$ in CS_2 at <10°.

XIII. Adding *o*-C_6H_4PhI and then 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene to Li in Et_2O gives 1-2′-*diphenylyl-*3 : 4-*dihydronaphthalene* (47·5%), m.p. 75·5—76·5°, which with *o*-$CO_2H{\cdot}C_6H_4{\cdot}CO_2H$ in Et_2O gives the 1 : 2-*epoxide*, m.p. 98—99°. With boiling 34% aq. HBr–AcOH this gives resinous 9 : 10-dihydro-1 : 2 : 3 : 4-dibenzphenanthrene (*picrate*, m.p. 135—136°), which with S at 200—220° and then 250° gives 1 : 2 : 3 : 4-dibenzphenanthrene, m.p. 115—116° (picrate, m.p. 139·5—140·5°; quinone, m.p. 238—240°) (cf. Hewett, A., 1938, II, 132). R. S. C.

Synthesis of 3′-alkyl-1 : 2-*cyclo*pentenophenanthrenes. B. Riegel, M. H. Gold, and M. A. Kubico (*J. Amer. Chem. Soc.*, 1943, **65**, 1772—1776).—β-2-Phenanthryl-*n*-butyric acid gives (cf. Bachmann *et al.*, A., 1940, II, 326) I′-keto-3′-methyl-1 : 2-*cyclo*pentenophen-

anthrene (I), m.p. 135—136° [*oxime*, α-, m.p. 169—171° (decomp.), and β-*form*, m.p. 165—170° (decomp.)]. 2-Propionylphenanthrene (II) and $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ give 2-α-*hydroxy*-n-*propylphenanthrene* (73%), m.p. 87·4—88·4°, converted by PBr_3–Et_2O into the *bromide* (87·5%), m.p. 81·5—83°, which with $CHNa(CO_2Et)_2$ in $EtOH$–C_6H_6 gives β-2-*phenanthryl*-n-*valeric acid* (85% crude), m.p. 134·8—136·2°. The derived acid chloride with $AlCl_3$ in $PhNO_2$ at room temp.—80° gives 1′-*keto*-3′-*ethyl*-1 : 2-cyclo*pentenophenanthrene* (78·5%), m.p. 110—111·2° [*oxime*, α-, m.p. 172·5—174·5° (decomp.), and β-*form*, m.p. 169—170·8° (decomp.)], reduced (Clemmensen) to 3′-*ethyl*-1 : 2-cyclo*pentenophenanthrene* (94%), m.p. 85—86°, sublimes 130—140°/2—3 mm. [*picrate*, m.p. 94·8—96·4° (decomp.)]. 2-*iso*Butyrylphenanthrene yields similarly α-2-*phenanthrylisobutyl alcohol*, m.p. 104·4—104·7°, and *bromide*, m.p. 91—94° (decomp.), β-2-*phenanthrylisohexoic acid* (21%), m.p. 148·8—149·6° (and α-2-*phenanthrylisobutyl Et ether*, m.p. 81—83°), 1′-*keto*-3′-iso*propyl*-, m.p. 143·6—144·4° [*oxime*, m.p. 205—211° (decomp.)], and 3′-iso*propyl*-1 : 2-cyclo*pentenophenanthrene*, m.p. 97·6—98·4° [impure picrate, m.p. 108—113° (decomp.), dissociates readily]. $(NH_4)_2S_x$ in dioxan at 160° and then HCl–AcOH converts (II) into β-2-phenanthrylpropionic acid (56·5%), m.p. 177·2—178·4°, and thence 1′-keto-1 : 2-*cyclo*pentenophenanthrene (92%), m.p. 188·6—189·4° (lit. 183—184°) [*oxime*, m.p. 235—236° (decomp.)], and 1 : 2-*cyclo*pentenophenanthrene, m.p. 134·4—135·8° [s-$C_6H_3(NO_2)_3$ compound, m.p. 165—167°]. 9 : 10-Dihydrophenanthrene, $R{\cdot}[CH_2]_2{\cdot}COCl$, and $AlCl_3$ in CS_2 at 0° give 2-β-*bromo*- (III), m.p. 76—77·3°, 2-β-*chloro*- (IV), m.p. 72—73°, and 2-β-*methoxy-propionyl*-9 : 10-*dihydrophenanthrene*, m.p. 87·8—88·7° [also obtained from (III) and (IV) by NaOMe–MeOH], which with chloranil in boiling xylene give only tars, although 9 : 10-dihydrophenanthrene thus gives 65% of phenanthrene (V). $Br{\cdot}[CH_2]_2{\cdot}COCl$, (V), and $AlCl_3$ in CS_2 give 2-β-*bromopropionylphenanthrene* (15%), m.p. 118·7—119·8°, reduced (Clemmensen) to 2-*n*-propylphenanthrene (picrate, m.p. 89—91°) but giving only tars when cyclised. M.p. are corr. R. S. C.

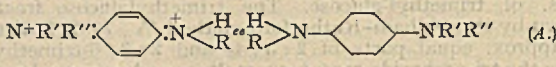

(I.)

Resolutions of enantiomorphs. III. Chromatographic adsorption. H. B. Hass, T. De Vries, and H. H. Jaffé (*J. Amer. Chem. Soc.*, 1943, **65**, 1486—1488; cf. A., 1943, II, 229).—Only slight resolution of dl-α-*phenylethylamine H* d-*tartrate*, m.p. 159—162°, or brucine *dl*-mandelate occurs by adsorption on Al_2O_3, $CaSO_4$, C, fuller's earth, MgO, or glucose. R. S. C.

Selective monoreduction of aromatic dinitro-compounds by alkaline sulphides and by acid stannous chloride. H. H. Hodgson (*J. Soc. Dyers and Col.*, 1943, **59**, 246—247).—In αβ-dinitronaphthalenes, AcOH–HCl–$SnCl_2$ preferentially reduces the α-NO_2 (and ultimately produces diamines) whilst alkaline sulphides (or polysulphides) (I) reduce the β-NO_2 and then practically cease to react. This is explained on the basis of the (−*I*) inductive effect of the second nucleus (cf. A., 1938, II, 316), making the α-NO_2 more electropositive. The less positive β-NO_2 has its O atoms more available for reaction with (I). Anomalous cases are discussed. The reduction of 1 : 2 : 4-$C_6H_3Me(NO_2)_2$ at position 4- by $SnCl_2$, but at 2- by (I), and of picric to picramic acid by (I), is explained as due to the (+*I*) inductive effects of the Me and OH rendering the 2-NO_2 less positive. S. A. M.

Iodinated derivatives of sulphonamido-compounds. C. J. Klemme and E. L. Beals (*J. Org. Chem.*, 1943, **8**, 448—455).—*p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH{\cdot}CH_2{\cdot}CO_2H$ is hydrolysed by 5N-HCl and then added dropwise to ICl in hot 5N-HCl, giving 3 : 5-*di-iodosulphanilylglycine*, m.p. 249·5° (decomp.); this is diazotised and converted by KI into 3 : 4 : 5-*tri-iodobenzenesulphonylglycine*, m.p. 279—280° (decomp.). p-*Iodobenzenesulphonylglycine* has m.p. 189—191° (decomp.). *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH{\cdot}C_6H_4{\cdot}SO_3H$-*p* is converted by ICl in 10% HCl at 40—50° into *N*-3 : 5(?)-di-iodosulphanilylsulphanilic acid, isolated as the *K* salt (anhyd. and $+2H_2O$), which is converted by diazotisation and treatment with KI into N-3 : 4 : 5-*tri-iodobenzenesulphonylsulphanilic acid*, m.p. >310°. p-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2H$, m.p. 201°, in AcOH is transformed by ICl in 10% HCl at 80—90° into p-3′ : 5′(?)-*di-iodosulphanilamidobenzoic acid*, m.p. 261·1° (decomp.), and by diazotisation followed by KI into p-*iodobenzenesulphonamidobenzoic acid*, m.p. 265—267° (decomp.). Addition of ICl in 25% HCl to $NH(SO_2{\cdot}C_6H_4{\cdot}NH_2)_2$ gives 3 : 5 : 3′-*tri-iododisulphanilamide*, m.p. 249·2° (decomp.) (*Na* salt), whereas use of the reagents in the reverse order gives this compound with the 3 : 5 : 3′ : 5′-I_4-derivative, m.p. 259—260° (decomp.; darkens at 230°) (NH_4 salt). *K* 4 : 4′-*diiododibenzenesulphonamide* is described. 2-3′ : 5′-*Di-iodosulphanilamidopyridine* has m.p. 269—272° (decomp.). H. W.

Polymerisation of free radicals of the Wurster dye type. Dimeric resonance bond. L. Michaelis and S. Granick (*J. Amer. Chem. Soc.*, 1943, **65**, 1747—1755).—Prep. of six Wurster dyes, obtainable cryst. only as bromides or perchlorates, is described. Change of colour with temp. is observable with yellow or red, but not with blue, dyes. The dyes exist in equilibrated mono- and di-meric forms in solution, but for solids there is an "all or none" law: crystals are either completely polymerised and diamagnetic with the susceptibility of an ordinary org. mol. or are completely in the free radical state and paramagnetic with the susceptibility of an org. mol. with one odd electron. The latter is so only for Wurster blue. Dimers have the structure (*A*), the two electrons (*e*) being shared between the two


(*A*.)

N, and the H and R forming a square in a plane perpendicular to the plane of the rings; resonance consists in alternation of the two rings between the quinonoid and benzenoid states. Such dimers can exist so long as at least one H is present on a N. Higher polymers can be formed along similar lines. R. S. C.

Evidence for the sulphite and sulphonate structures of Hantzsch's potassium benzene -*syn*- and -*anti*-diazosulphonates. H. H. Hodgson and E. Marsden (*J.C.S.*, 1943, 470—472).—Hantzsch's *syn*-formula for K benzene-*syn*-diazosulphonate is incorrect, and a sulphite structure, viz., $NPh{:}N{\cdot}O{\cdot}SO_2K$ or $\overset{+}{N}_2Ph\}\overset{-}{O}{\cdot}S\vec{O}_2K$, or an equilibrium of both, accounts for all its reactions; the *anti*-form of Hantzsch is valid. The *syn*-form (I) is rapidly converted by moisture into the *anti*-form. Thus, (I) and excess of alkaline β-$C_{10}H_7{\cdot}OH$ give $PhN_2{\cdot}C_{10}H_6{\cdot}OH$-β (II), corresponding to 77·5% of *syn* + 22·5% of *anti*; a delay of 15 min. before coupling causes a decrease in *syn*-form to 33%. Coupling of (I) with *p*-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ (III) yields a complex, converted by alkaline β-$C_{10}H_7{\cdot}OH$ into (II) + *p*-nitrobenzeneazo-β-naphthol (IV); oxidation of the filtrate affords a similar mixture. (III) combines at the S to give a N–S linking, and does not form a diazonium salt. Complexes prepared from both *syn*- and *anti*-isomerides by coupling with ArN_2Cl are unstable, except that from K benzene-*anti*-diazosulphonate (does not couple with β-$C_{10}H_7{\cdot}OH$) and (III); coupling with β-$C_{10}H_7{\cdot}OH$ then gives (IV). The complex from Na *p*-nitrobenzene-*anti*-diazosulphonate and PhN_2Cl at 0°, couples with β-$C_{10}H_7{\cdot}OH$ to give (II), whereas (IV) is obtained from the filtrate after air oxidation. The *syn*-isomeride (V), prepared from neutral (III) and Na_2SO_3 at 0°, similarly yields (II) + (IV), also obtained from the filtrate after oxidation. (V) and (III) afford a complex, and thence almost pure (IV). A. T. P.

Diphenyl series. III. Attempted chlorination of the acetate, benzoate, and benzenesulphonate of 4-chloro-4′-hydroxydiphenyl. 3 : 4′-Dichloro-4-hydroxydiphenyl. (Miss) C. M. S. Savoy and J. L. Abernethy (*J. Amer. Chem. Soc.*, 1943, **65**, 1464—1465; cf. A., 1943, II, 88).—*p*-$C_6H_4Cl{\cdot}C_6H_4{\cdot}OH$-*p* (I) and Cl_2 in CCl_4 give 3 : 4′-*dichloro*-4-*hydroxydiphenyl* (92%), m.p. 71—72° (*acetate*, m.p. 74·5—75°; *benzoate*, m.p. 125—126°; *benzenesulphonate*, m.p. 100—101°), converted by more Cl_2 in CCl_4 into 4 : 3 : 5-$OH{\cdot}C_6H_2Cl_2{\cdot}C_6H_4Cl$-*p*, which is also obtained directly from (I). Esters of (I) are unaffected by Cl_2–I (trace) in CCl_4. R. S. C.

Preparation of 4-halogeno- and 4-nitro-2-naphthols; resonance structure of the internal diazo-oxides (diazonaphthols). H. H. Hodgson and S. Birtwell (*J.C.S.*, 1943, 468—469).—Decomp. of 4-halogenonaphthalene-1 : 2-diazo-oxides (I) by Al powder in boiling EtOH (cf. Morgan *et al.*, *J.C.S.*, 1919, **115**, 1126) gives 4 : 2-$C_{10}H_6Hal{\cdot}OH$ (II). Thus prepared are 4-*chloro*-2-*naphthol* (84%), m.p. 100° (*Me ether*, m.p. 44—45°; *acetate*, m.p. 56°; 1-*benzeneazo*-derivative, m.p. 165°), 4 : 2-$C_{10}H_6Br{\cdot}OH$ (77%) (*Me ether*, m.p. 64°; *acetate*, m.p. 61°; 1-*benzeneazo*-derivative, m.p. 160°), and 4-*iodo*-2-*naphthol* (60%), m.p. 128·5° (*Me ether*, m.p. 67°; *acetate*, m.p. 59°; 1-*benzeneazo*-derivative, m.p. 176°). (I) with $SnCl_2$–aq. NaOH at 80—90° gives variable yields of (II). Attempts to prepare (II) from 4 : 2-$C_{10}H_6Hal{\cdot}NH_2$ failed. 4-Nitronaphthalene-1 : 2-diazo-oxide and Fe–$CuSO_4$–EtOH–H_2O give 50% of 4 : 2-$NO_2{\cdot}C_{10}H_6{\cdot}OH$. The properties of diazonaphthols indicate that they are resonance hybrids. A. T. P.

Synthetic œstrogenic compounds. I. Monosubstituted derivatives of αγ-di-*p*-hydroxyphenylpropane. A. H. Stuart and R. C. Tallman (*J. Amer. Chem. Soc.*, 1943, **65**, 1579—1581).—The rat unit of œstrogenic activity for $Ar{\cdot}[CH_2]_2{\cdot}CHRAr$ and $CHR(CH_2Ar)_2$ ($Ar = p$-$OH{\cdot}C_6H_4$) is 5—10 mg., a slight max. appearing at R = Pr^{α} and Et, respectively. Introduction of R has little effect. Adding *p*-$OMe{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO{\cdot}C_6H_4{\cdot}OMe$-*p* to MgRHal (3 mols.) in Et_2O at −5° to −10° and keeping at room temp. gives p-*methoxy*-β-p-*anisyl*-n-*butyro*-, m.p. 72° (*semicarbazone*, m.p. 142—143°), -n-*valero*-, m.p. 70° (*semicarbazone*, m.p. 127—128°), -n-, m.p. 78—79° (*semicarbazone*, m.p. 126—127°), and -iso-*hexo*-, m.p. 51—52° (*semicarbazone*, m.p. 166—168°), -n-*hepto*-, m.p. 59° (*semicarbazone*, m.p. 125—127°), and -n-*octo-phenone*, m.p. 70°, p-*methoxy*-β-*phenyl*-β-p-*anisylpropiophenone*, m.p. 88°, p-*methoxy*-γ-*phenyl*-β-p-*anisyl*-n-*butyrophenone*, m.p. 102° (*semicarbazone*, m.p. 146°), and p-*methoxy*-ββ-*di*-p-*anisylpropiophenone*, m.p. 83—84° (*semicarbazone*, m.p. 161—162·5°). Reduction, best by H_2–Cu chromite in EtOH at 200°/~150 atm., gives αγ-*di*-p-*anisyl*-n-*butane*, b.p. 152—154°/1 mm., -n-*pentane*, b.p. 161—163°/1 mm., -n-*hexane*, b.p. 198—200°/3 mm., -δ-*methyl*-n-*pentane*, b.p. 178—179°/2 mm., -n-*heptane*, b.p. 201—203°/3 mm., and -n-*octane*, b.p. 194—195°/2 mm., β-*phenyl*-αγ-*di*-p-*anisylpropane*, m.p. 63°, δ-*phenyl*-αγ-*di*-p-*anisyl*-n-*butane*, m.p. 36—38°, and αβγ-*tri*-p-*anisylpropane*, m.p. 62—63°, demethylated

(AcOH–57% HI or EtOH–KOH) to *αγ-di-*p-*hydroxyphenyl-*n-*butane*, a resin, -n-*pentane*, m.p. 99—100°, -n-*hexane*, m.p. 101°, *-δ-methyl-*n-*pentane*, -n-*heptane*, and -n-*octane*, resins, *β-phenyl-αγ-di-*p-*hydroxyphenylpropane*, m.p. 105—106°, and *δ-phenyl-αγ-di-*p-*hydroxyphenyl-*n-*butane*, m.p. 108—110°. *p*-OMe·C_6H_4·CHO, *p*-OMe·C_6H_4·COR (improved prep. for R = Pr^a and Bu^a), and HCl at ~15° give p-*anisyl α-methyl-*, m.p. 60°, *α-ethyl-*, b.p. 200—203°/1·5 mm., and *α-*n-*propyl-*p-*methoxystyryl ketone*, b.p. 207—208°/2 mm., converted as above into CHR(CH_2·C_6H_4·OMe-*p*)$_2$ in which R = Me, m.p. 68—69°, *Et*, m.p. 43°, and *Pr^a*, b.p. 181°/2 mm., and thence into CHR(CH_2·C_6H_4·OH-*p*)$_2$ in which R = Me, m.p. 130°, *Et*, m.p. 102°, and *Pr^a*, m.p. 118—119°. R. S. C.

Analogues of hexœstrol. B. R. Baker (*J. Amer. Chem. Soc.*, 1943, **65**, 1572—1579).—The $(NH_2)_2$, $(CH_2Ph)_2$, and three steric analogues of hexœstrol are pharmacologically inactive [denoted (*I*) below]. The 3 : 4 : 3′ : 4′-(OH)$_4$-analogue is feebly active. *p*-OMe·C_6H_4·CO·CH:CH·C_6H_4·OMe-*p* and H_2–Raney Ni in EtOH at 55°/2—3 atm. give *p*-OMe·C_6H_4·CO·$[CH_2]_2$·C_6H_4·OMe-*p*, m.p. 40—42°, which with MgPr^{a}Br in boiling Et_2O and then $KHSO_4$ at 100—120° gives *αγ-di-*p-*anisyl-Δβ-*n-*hexene* (88%), b.p. 188—190°/1 mm., reduced as above to *αγ-di-p*-anisyl-*n*-hexane, b.p. 178—180°/1 mm.; 48% HBr in boiling AcOH then yields *αγ-*di-*p*-hydroxyphenyl-*n*-hexane (*I*) (61%), m.p. 101·5—103° (*di-*p-*nitrobenzoate*, m.p. 114—116°). Reduction of RCO·$[CH_2]_4$·COR to R·$[CH_2]_6$·R (R = anisyl) is best (82%) effected by N_2H_4 in boiling EtOH followed by KOH on the product at 140° and finally 200°. 3 : 4-*Dimethoxypropiophenoneazine*, m.p. 151—153°, with H_2–$PdCl_2$–AcOH–MeOH gives the oily H_4-azine, which with $CuSO_4$, NaOH, and air gives the H_2-azine, converted in boiling xylene into *γδ-di-*3 : 4-*dimethoxy-* (19·5%), *forms*, m.p. 102—105° and 133—133·5°, and thence *γδ-di-*3 : 4-*dihydroxy-phenyl-*n-*hexane* (I) m.p. 231—235°. 50-μg. doses of (I) cause 100% response in ovariectomised rats, 20-μg. doses cause 29% response. p-*Propionamidopropiophenoneazine*, m.p. 276—280°, gives similarly the *H_2-azine* (18%), m.p. >160° (decomp.), which at 180° and then 240° gives *γδ-di-*p-*propionamidophenyl-*n-*hexane*, meso-, m.p. 261—264°, and dl-, m.p. 207—215°, *-forms*. Boiling conc. HCl then gives *γδ-di-*p-*aminophenyl-*n-*hexane*, meso-, m.p. 132—134°, and dl-, m.p. 63—65°, *-forms*, respectively, the configuration of which is determined by converting the former by HNO_2 into *meso*-hexœstrol. *m*-C_6H_4Et·OR (R = H or Me) with HCl–Zn$(CN)_2$–$AlCl_3$–C_6H_6 gives 4-*hydroxy-* (II), m.p. 51—53°, b.p. 140—145°/1 mm., and 4-*methoxy-*2-*ethylbenzaldehyde*, b.p. 133—134°/12 mm., and the derived *azines*, m.p. 204·5—206° and (III) 117—118° [also obtained from (II) by Me_2SO_4–KOH–H_2O–MeOH followed by N_2H_4], respectively. (III) yields the *H_2-azine*, m.p. 70—73°, and thence *αβ-di-*4-*methoxy-* (8%), m.p. 60—62°, and -4-*hydroxy-*2-*ethylphenylethane* (*I*), m.p. 131—133°. *β-Nitro-α-*p-*anisyl-Δ^α-butene* (prep. from ArCHO, Pr^aNO_2, and OH·$[CH_2]_2$·NH_2 at room temp.; 64%), m.p. 55—57°, with $FeCl_3$–Fe in boiling HCl–EtOH–H_2O gives *p*-OMe·C_6H_4·CH_2·COEt (IV), b.p. 142—147°/13 mm. [semicarbazone, m.p. 153—154° (lit. 156—157°)], and thence the *dihydroazine*, m.p. 89—90°, pyrolysis of which was unsuccessful. CN·CH_2·CO_2Et, (IV), NH_4OAc, and AcOH in boiling C_6H_6 with removal of H_2O give *Et α-cyano-β-*p-*methoxybenzyl-Δ^α-pentenoate*, b.p. 167—168°/1 mm., reduced (H_2–PtO_2–MeOH; 2—3 atm.) to *Et α-cyano-β-*p-*methoxybenzyl-*n-*valerate* (V), b.p. 158—159°/1 mm. NaOEt–EtBr in EtOH–C_6H_6 then gives *Et α-cyano-β-*p-*methoxybenzyl-α-ethyl-*n-*valerate*, b.p. 176—178°/2 mm., converted by KOH in diethylene glycol at 135—140° and then decarboxylation by a trace of CuO at 200° into *γ-cyano-δ-*p-*methoxybenzyl-*n-*hexane* (94%), b.p. 135—136°/1 mm., which resists hydrolysis by acid or alkali but with *p*-OMe·C_6H_4·MgBr in Et_2O–C_6H_6 gives 57—76% of *γ-*p-*anisoyl-δ-*p-*methoxybenzyl-*n-*hexane*, b.p. 208—211°/1 mm. Clemmensen reduction then yields *γδ-di-*p-*methoxy-* (VI) (78%), *form*, m.p. 71—72°, b.p. 190—195°/1 mm., and thence (HI–AcOH) *γδ-di-*p-*hydroxybenzyl-*n-*hexane* (*I*), (? meso-)*form*, m.p. 156—157° [gives (VI)]. *p*-OMe·C_6H_4·CH_2Cl, (V), and NaOEt in EtOH–C_6H_6 give *Et α-cyano-αβ-di-*p-*methoxybenzyl-*n-*valerate* (77%), b.p. 225—230°/1 mm., and thence, successively, (by KOH) *αβ-di-*p-*methoxybenzyl-*n-*valeronitrile*, b.p. 214—216°/1 mm. (*dl*-form, m.p. 136—137°), (by MgMeI–Et_2O) *γδ-di-*p-*methoxybenzyl-*n-*hexan-β-one* (89%), b.p. 213—216°/1 mm. (form, m.p. 86—88°), and (by N_2H_4–CH_2Ph·ONa–CH_2Ph·OH) (VI). CN·CHNa·CO_2Et and OH·CHEt·CN in EtOH at 0° and later with EtBr at the b.p. give *Et γδ-dicyano-*n-*hexane-γ-carboxylate* (52%), b.p. 135—136°/3 mm., converted by boiling 18% HCl and then AcCl into (CHEt·CO)$_2$O, b.p. 100—102°/1 mm., which with PhOMe–$AlCl_2$–C_6H_6 at 15—20° and then H_2SO_4–MeOH–C_6H_6 gives *Me β-*p-*anisoyl-α-ethyl-*n-*valerate* (91%), b.p. 150—152°/1 mm. (enol *lactone*, b.p. ~170°/1 mm.), reduced by Zn–Hg–conc. HCl–H_2O–PhMe to *γ-*p-*anisyl-αβ-diethyl-γ-butyrolactone* (70%), b.p. 143—146°/2 mm. R. S. C.

Effect of reducing agents on the autoxidation of photographic developing agents.—See A., 1944, I, 20.

Chlorination of anisole. C. Weygand [with K. Vogel] (*J. pr. Chem.*, 1940, [ii], **155**, 342—346).—PhOMe (I) and Cl_2 at 150—160° give products of variable Cl content; a H_2O-insol. residue is obtained consisting of (*m*-$C_6H_4Cl)_2CO_3$, formed from *m*-C_6H_4Cl·OH and *m*-C_6H_4Cl·O·CCl_3. Better results are obtained with (I) as vapour; thus, chlorination at 220—225° yields PhO·CH_2Cl and PhO·$CHCl_2$. In a vac. at ~122°, a low yield of product containing 8·7% Cl results. A. T. P.

Higher homologues of azo- and azoxy-phenol ethers, and *p*-alkoxybenzylideneaniline derivatives. C. Weygand and R. Gabler (*J. pr. Chem.*, 1940, [ii], **155**, 332—341).—*p*-NO_2·C_6H_4·OK and AlkBr in COMeEt (or, for higher members, *cyclo*pentanone) give *p-NO_2·C_6H_4 Bu^a*, b.p. 160—163°/7 mm., m.p. 32°, n-C_5H_{11}, b.p. 162—163°/5 mm., n-C_6H_{13}, b.p. 172—174°/5 mm., m.p. 26°, n-C_7H_{15}, b.p. 184—185°/5 mm., n-C_8H_{17}, b.p. 196—197°/5 mm., m.p. 24°, n-C_9H_{19}, b.p. 206—207°/7 mm., m.p. 20°, n-$C_{10}H_{21}$, m.p. 41°, n-$C_{11}H_{23}$, m.p. 30°, and n-$C_{12}H_{25}$ *ether*, m.p. 53°. Electrolytic reduction (Pb anode; Pb or Ni cathode) then affords the following p-*azoxyphenol dialkyl ethers* [the occurrence of cryst.-liquid phases is observed (cf. A., 1938, II, 493; 1939, II, 16), and the clarification temp. or transition points are given in parentheses]: *Bu^a*$_2$, m.p. 107° (134°, Pl form), *di-*n-*amyl*, m.p. 82° (119°, Pl), -n-*hexyl*, m.p. 81° (127°, Pl, and 72°, Bz form), -n-*heptyl*, m.p. 74° (122·5°, Pl, and 92°, Bz form), -n-*octyl*, m.p. 76° (124·5°, Pl; 106°, Bz), -n-*nonyl*, m.p. 77° (121°, Pl; 113°, Bz), -n-*decyl*, m.p. 78° (123°, Pl; 119·5°, Bz), -n-*undecyl*, m.p. 78° (120·5°, Bz), and -n-*dodecyl*, m.p. 82° (122°, Bz). (*p*-OH·C_6H_4·N:)$_2$ and aq. AlkI–KOH–MeOH afford the Et_2, m.p. 159° (150°, Pl), *Bu^a*$_2$, m.p. 135° (124°, Pl), *di-*n-*amyl*, m.p. 112° (106°, Pl), -n-*hexyl*, m.p. 102° (114°, Pl), -n-*heptyl*, m.p. 102° (109°, Pl; 97°, Bz), -n-*octyl*, m.p. 98°, -n-*nonyl*, m.p. 103° (107°, Pl; 99°, Bz), and -n-*dodecyl ether*, m.p. 106° (107°, Pl). *p*-OH·C_6H_4·CHO affords p-*OAlk·C_6H_4·CHO* (I); Alk = *Bu^a*, b.p. 148—149°/10 mm., n-C_5H_{11}, b.p. 145—146°/5 mm., n-C_6H_{13}, b.p. 154—155°/6 mm., n-C_7H_{15}, b.p. 162—164°/7 mm., n-C_8H_{17}, b.p. 162—163°/4 mm., n-C_9H_{19}, b.p. 181—183°/4 mm., *$Pr^β$*, b.p. 135—136°/16 mm., iso*amyl*, b.p. 136—137°/15 mm., and iso*hexyl*, b.p. 175—176°/15 mm. *p*-OEt·C_6H_4·NH_2 in EtOH then yields p-n-*propoxy-*, m.p. 125° (123·5°, Pl), -n-*butoxy-*, m.p. 105·5° (129·5°, Pl), -n-*amyloxy-*, m.p. 102·5° (119°, Pl), *-hexyloxy-*, m.p. 97·5° (122·5°, Pl), *-heptyloxy-*, m.p. 100·5° (118°, Pl), -n-*octyloxy-*, m.p. 99° (119° Pl), *-nonyloxy-*, m.p. 101·5° (115°, Pl; 84°, 104°, Bz I; 79°, Bz II), and *-hexadecyloxy-benzylidenephenetidine*, m.p. 106·5° (105·5°, Pl). Similarly prepared are pp′-n-*propoxybenzylidene-*n-*propoxy-*, m.p. 133° (calc. 107°, Pl), -n-*butoxybenzylidene-*n-*butoxy-*, m.p. 125° (121°, Pl), and -n-*amyloxybenzylidene-*n-*amyloxy-aniline*, m.p. 113° (103°, Pl), and -n-*nonyloxybenzylideneanisidine*, m.p. 108° (96°, Pl); pp′-n-*nonyloxybenzylidine-toluidine*, m.p. 73° (76°, Pl; 74°, Bz I, 70°, Bz II), *-ethylaniline*, m.p. 65° (77°, Bz I; 74°, Bz II), and -n-*propylaniline*, m.p. 51° (83°, Bz I; 79°, Bz II), and -n-*octyloxybenzylidenetoluidine*, m.p. 70° (75°, Pl; 67°, Bz I; 59°, Bz II). (I) and *p*-NH_2·C_6H_4·CH:CH·CO_2Et in EtOH afford *Et* p-n-*propoxy-*, m.p. 64° (159°, Bz I; 131°, Bz II), -n-*butoxy-*, m.p. 66° (162°, Bz I; 134°, Bz II), -n-*amyloxy-*, m.p. 62° (158°, Bz I; 128°, Bz II), -n-*hexyloxy-*, m.p. 49° (156°, Bz I, 126°, Bz II), and -n-*nonyloxy-benzylidene-*p-*aminocinnamate*, m.p. 74° (154°, Bz I; 116°, Bz II). A. T. P.

Condensation of *o*-cresol with formaldehyde in alkaline solution. F. Hanus (*J. pr. Chem.*, 1940, [ii], **155**, 317—331).—*o*-Cresol (1 mol.) in 10% aq. NaOH and 40% CH_2O (1 mol.) at 10—15° for 2 days give a mixture (*A*) from which 2-*hydroxy-* (I), m.p. 32·8—33·8°, and 4-*hydroxy-*3-*methylbenzyl alcohol*, m.p. 81—84°, are isolable. 2 Mols. of CH_2O yield 2 : 1 : 3 : 5-OH·C_6H_2Me(CH_2·OH)$_2$ (II) and/or di-(4-hydroxy-5-hydroxymethyl-3-methylphenyl)methane (III), according to conditions used. Oxidation (aq. NaOH–*m*-NO_2·C_6H_4·SO_3Na) of (*A*) gives, through the $NaHSO_3$ compounds, 2 : 1 : 3- and 2 : 1 : 5-OH·C_6H_3Me·CHO, and o-*cresol-*3 : 5-*dialdehyde* (IV), m.p. 122—122·6° [*dioxime*, m.p. 182—183° (sinters from 174°); also obtained by CrO_3–AcOH oxidation of (II)]. (III), also prepared from (II) and the calc. amount of aq. NaOH at 40°, or from (I) + (II) in 10% aq. NaOH at 15°, is oxidised by $Na_2Cr_2O_7$–AcOH to (IV). A. T. P.

Reaction of epichlorohydrin with the Grignard reagent. Derivatives of *cyclo*propanol. G. W. Stahl and D. L. Cottle (*J. Amer. Chem. Soc.*, 1943, **65**, 1782—1783).—Epichlorohydrin with $MgBr_2$ (1 mol.) and a trace of $FeCl_3$ and then MgEtBr (3 mols.) gives rapidly 43% of *cyclo*propanol (cf. Magrane *et al.*, A., 1942, II, 214), b.p. 100—103°, which could not be purified but is characterised as *phenyl-*, m.p. 101·5—102°, *α-naphthyl-*, m.p. 100·5—101·5°, and p-*nitrophenyl-urethane*, m.p. 159—160°, p-*nitro-*, m.p. 72—72·5°, and 3 : 5-*dinitro-benzoate*, m.p. 108—109°, and *allophanate*, m.p. 179—181° (decomp.). When kept over K_2CO_3 it gives CHEt:CMe·CHO (semicarbazone, m.p. 187—188°). R. S. C.

Lignin. XLII. [Hydrogenation of methoxyphenols.]—See A., 1943, II, 402.

Antispasmodics. V. F. F. Blicke and N. Grier (*J. Amer. Chem. Soc.*, 1943, **65**, 1725—1728).—*p*-C_6H_4Ph·CO·CO_2Et (I) (prep. from Ph_2 by CO_2Et·COCl and $AlCl_3$ in CS_2) with boiling Na_2CO_3–H_2O–EtOH gives *p*-C_6H_4Ph·CO·CO_2H (II), m.p. 105—107° (lit. decomp. 170°), and with H_2–Pt (? Pd)–C in EtOH at 3 atm. and then 10% KOH–EtOH gives *p*-C_6H_4Ph·CH(OH)·CO_2H, m.p. 201—203° (lit. 192°), reduced by red P–I–AcOH to *p*-C_6H_4Ph·CH_2·CO_2H. Adding MgRBr to (I) in Et_2O–N_2 and then hydrolysing by 10% KOH–

EtOH gives *α-hydroxy-α-phenyl-α-p-xenyl-*, m.p. 168—170°, and *α-hydroxy-α-*cyclo*hexyl-α-p-xenyl-acetic acid*, m.p. 202—203°, and *α-hydroxy-α-p-xenylpropionic acid*, m.p. 168—169°. MgRBr and (II) in Et_2O give *α-hydroxy-α-p-xenyl-butyric*, m.p. 175—177°, -n-*valeric*, m.p. 142—143°, and -n-*hexoic acid*, m.p. 178—179°. Red P–I–AcOH then gives *α-phenyl-α-p-xenyl-*, m.p. 141—142°, and *α-*cyclo*hexyl-α-p-xenyl-acetic acid*, m.p. 204—205°, *α-p-xenyl-propionic* (III), m.p. 145—147°, -n-*butyric*, m.p. 123—125°, -n-*valeric*, m.p. 116—117°, and -n-*hexoic acid*, m.p. 99—101°. The following are prepared by heating the appropriate acid and aminoalkyl chloride in $Pr^{\beta}OH$ or the appropriate acid chloride and NH_2-alcohol in C_6H_6: *β-dimethylaminoethyl*, m.p. 158—159°, *β-piperidinoethyl*, m.p. 163—164°, and *γ-diethylaminopropyl α-p-xenylacetate hydrochloride*, m.p. 113—115°; *β-diethylamino-*, m.p. 139—141°, *β-dibutylamino-*, m.p. 128—130°, and *β-piperidino-ethyl*, m.p. 147—149°, *γ-diethylamino-*, m.p. 117—119°, and *γ-piperidino-*n*-propyl α-p-phenyl-α-p-xenylacetate hydrochloride*, m.p. 103—105°; *β-diethylamino-*, m.p. 170—172°, and *β-piperidino-ethyl*, m.p. 179—181°, and *γ-diethylamino-*n*-propyl α-*cyclo*hexyl-α-p-xenylacetate hydrochloride*, m.p. 149—151°; *β-diethylamino-*, m.p. 141—143°, and *β-piperidino-ethyl*, m.p. 162—164°, *γ-diethylamino-*, m.p. 112—114°, and *γ-piperidino-*n*-propyl α-p-xenylpropionate hydrochloride*, m.p. 142—144°; *β-diethylamino-*, m.p. 154—156°, and *β-piperidino-ethyl*, m.p. 146—148°, and *γ-diethylamino-*n*-propyl α-p-xenyl-*n*-butyrate hydrochloride*, m.p. 97—99°; *β-diethylamino-*, m.p. 122—124°, and *β-piperidino-ethyl*, m.p. 127—129°, and *γ-diethylamino-*n*-propyl α-p-xenyl-*n*-valerate hydrochloride*, m.p. 100—102°. Of the esters, those of (III) are the most potent antispasmodics on the untreated, isolated intestinal strip. R. S. C.

Preparation of iodine-containing *X*-ray contrast substances. II. α-Phenyl-β-3 : 5-di-iodo-4-hydroxyphenylpropionic acid ("biliselectan"). W. Baker and (in part) H. Sansbury (*J.S.C.I.*, 1943, **63**, 191—192).—*p*-OH·C_6H_4·CHO, anhyd. $CH_2Ph·CO_2Na$, and Ac_2O at 170—180° (bath; 17 hr.) and hydrolysis (aq. EtOH–NaOH) of the product give *p*-OH·C_6H_4·CH:CPh·CO_2H (83%) (and some *p*-OH·C_6H_4·CH:CHPh), reduced in aq. NaOH–EtOH by Raney Ni and H_2 (2—3 atm.) to *p*-OH·C_6H_4·CH_2·CHPh·CO_2H (I) (93%). With ICl in hot aq. AcOH–HCl, this gives 4 : 3 : 5 : 1-OH·$C_6H_2I_2$·CH_2·CHPh·CO_2H (II), m.p. 159—160° (corr.; shrinks from ~153°), purified by pptn. of the Na salt from hot 10% NaOH by NaCl, followed by crystallisation of the acid successively from $CHCl_3$, 45% (vol.) EtOH, and 55% EtOH; overall yield 52%. It is also prepared (42% overall yield) from *p*-OMe·C_6H_4·CHO (could not be demethylated satisfactorily), which is converted into *p*-OMe·C_6H_4·CH_2·CHPh·CO_2H as above, and then demethylated with aq. HBr–AcOH to (I). (II) titrates as a dibasic acid; it is an orally-administered *X*-ray contrast substance for the gall-bladder. S. A. M.

Fluorinated compounds of possible chemotherapeutic interest. E. Bograchov (*J. Amer. Chem. Soc.*, 1943, **65**, 1652—1653). $C_6H_4F·COCl$ and 4 : 1-$PhN_2·C_{10}H_6·NH_2$ in $C_5H_5N–CHCl_3$ at 0° give 1-o-, m.p. 154°, and 1-p-*fluorobenzamido-4-benzeneazonaphthalene*, m.p. 201°. N^4-o-*Fluorobenzoylsulphanilamide*, m.p. 264°, is prepared from *o*-$C_6H_4F·COCl$ and *p*-$NH_2·C_6H_4·SO_2·NH_2$ in AcOH at 0°. R. S. C.

2′-Hydroxydiphenylphthalide. M. H. Hubacher (*J. Amer. Chem. Soc.*, 1943, **65**, 1655—1656).—4′-Hydroxydiphenylphthalide, new m.p. 170·1—170·4°, obtained from *o*-C_6H_4Bz·COCl and PhOH in C_6H_6 at 40°, is accompanied by a little of the 2′-*OH*-isomeride, m.p. 240·5—241·3° [separated by sublimation; *acetate*, m.p. 136·6—137·7°; Me ether, m.p. 126·1—126·7° (lit. 127—128°); with KOH at 240—245° gives 9-phenylxanthene and BzOH]. R. S. C.

Optically active acyl peroxides. Preparation, decomposition, and use as catalysts for vinyl polymerisation. C. S. Marvel, R. L. Frank, and E. Prill (*J. Amer. Chem. Soc.*, 1943, **65**, 1647—1652).—*p*-C_6H_4BrBu-*sec.* (I) with CuCN gives dl-p-sec.-*butylbenzonitrile* (84%), b.p. 78—80°/4 mm., hydrolysed by 75% H_2SO_4 at 150° to dl-, m.p. 93·5—94° (91—92° by Grignard method), resolved by quinine to l-p-sec.-*butylbenzoic acid* (I), m.p. 88·5—89°, $[\alpha]_D^{26}$ −23·5° in MeOH (*quinine* salt, m.p. 184—185°, $[\alpha]_D^{26}$ −138·4° in MeOH; impure *d*-form, $[\alpha]_D^{30}$ +18·2° in MeOH). The derived ($SOCl_2–C_5H_5N$) dl-, b.p. 135—137°/15 mm., and l-*chloride*, b.p. 143—144°/20 mm., in C_6H_6 with aq. Na_2O_2 at 0° give dl-, m.p. 49—50°, and 1-p-sec.-*butylbenzoyl peroxide* (II), m.p. 45·5—47°, $[\alpha]_D^{27}$ −29·0° in dioxan. In dioxan at 55°, *dl-* or *l-*(II) decompose to give *dl-* or *l-*(I), respectively, but changes in [α] for *l-*(II) are too small for calculation of kinetics. *l*-Menthyl H phthalate, m.p. 108·5—110°, gives similarly 1-o-*carbomenthoxybenzoyl peroxide*, m.p. 117—118° (decomp.), $[\alpha]_D^{27}$ −91·6° in dioxan, decomp. of which in dioxan at 55° is unimol. (k 1·15 × 10^{-4} sec.$^{-1}$; half-life 1·75 hr.). Polymerisation of styrene, CH_2:CMe·CO_2Me, or CH_2:CH·CN in presence of *l-*(II) discloses no peculiarity. R. S. C.

Antispasmodics. II. Basic esters of polynuclear carboxylic acids. R. R. Burtner and J. W. Cusic (*J. Amer. Chem. Soc.*, 1943, **65**, 1582—1585; cf. A., 1943, II, 161).—Of the esters described below, (I) and (II) are much the most potent antispasmodics. The following are usually prepared by LiBu$^{\alpha}$ and then CO_2 : 9 : 10-dihydroanthracene-9-, xanthene-9-, *thioxanthene*-10-, m.p. 227°, 10-*methyl*-5 : 10-*dihydroacridine*-5-, m.p. 184° (decomp.), 9-, m.p. 194—196°, and 10-*methyl*-9 : 10-*dihydroanthracene*-9-, m.p. 204—207°, and 9-cyclo*hexylfluorene*-9-*carboxylic acid*, m.p. 220—222°. The following are prepared, m.p. being those of the *hydrochlorides*: β-diethylaminoethyl (I), m.p. 170—171°, β-, m.p. 185°, and γ-diethylamino-*n*-propyl, m.p. 136°, β-di-*n*-butylaminoethyl, m.p. 130°, and β-morpholinoethyl 9 : 10-dihydroanthracene-9-carboxylate, m.p. 142°; di-β-diethylaminoethyl 9 : 10-dihydroanthracene-9 : 10-dicarboxylate, m.p. 192—193°; β-diethylaminoethyl 10-, m.p. 202°, and 9-methyl-9 : 10-dihydroanthracene-9-carboxylate, m.p. 157—159°, xanthene-9-carboxylate (II), m.p. 159—160°, thioxanthene-10-carboxylate, m.p. 195°, acridan-5-carboxylate, m.p. 201°, 10-methylacridan-5-carboxylate, m.p. 157—158°, acridine-5-carboxylate, m.p. 190° (lit. 179—180°), 9-ethyl-, m.p. 168—169°, and 9-cyclohexyl-fluorene-9-carboxylate, m.p. 184°, indene-1-carboxylate, m.p. 141—143°, 1-naphthoate, m.p. 159—161°, 1 : 4-dihydro-, m.p. 152°, and 1 : 2 : 3 : 4-tetrahydro-1-naphthoate, m.p. 137—138°, diphenylyl-2-acetate, m.p. 108—109°, and phenanthrene-9-carboxylate, m.p. 169—170° (lit. 171—171·5°). R. S. C.

Pentagallates of glucose and mannose.—See A., 1944, II, 6.

4 : 4′-Dicyanobenzaldazine. H. J. Barber and R. Slack (*J. Amer. Chem. Soc.*, 1943, **65**, 1776—1777).—Contrary to Sah (A., 1942, II, 313), *p*-CN·C_6H_4·CHO (prep. from the alcohol by N_2O_4) with N_2H_4,H_2O in EtOH gives the azine, m.p. 318—320°, which yields no (*p*-CN·C_6H_4·CH:)$_2$ but when repeatedly sublimed at 300—320° gives a small amount of *p*-$C_6H_4(CN)_2$. R. S. C.

Gattermann reaction with monomethoxydiphenyl ethers. H. E. Ungnade and E. F. Orwoll (*J. Amer. Chem. Soc.*, 1943, **65**, 1736—1739).—*o*-OMe·C_6H_4·OPh with $AlCl_3$–HCN in C_6H_6 at 0° and then 40—50° gives 40—50% of mixed aldehydes (*A*), whence $KMnO_4$–$COMe_2$ gives 4 : 3 : 1-OMe·C_6H_3(OPh)·CO_2H (I), m.p. 186—186·5°. 1 : 3 : 4-$C_6H_3MeBr·N_2·HSO_4$ with boiling aq. Na_2SO_4–H_2SO_4 gives 1 : 3 : 4-$C_6H_3MeBr·OH$ (93—96%), b.p. 102—104°/20 mm., the Me ether, b.p. 126—127°/25 mm., of which with KOPh and Cu powder at 160—200° gives *Ph* 4-*methoxy*-m-*tolyl ether*, m.p. 38·5—39°. With HI–AcOH this gives *Ph* 4-*hydroxy*-m-*tolyl ether*, m.p. 69·5—70°, and with $KMnO_4$ in aq. C_5H_5N gives (I), converted by $AlCl_3$ in C_6H_6 or HBr–AcOH at 150° (not HI–Ac_2O) into 4-*hydroxy-3-phenoxybenzoic acid*, m.p. 187·6—188°, $AlCl_3$ in C_6H_6 converts (*A*) into 4-*hydroxy-3-phenoxybenzaldehyde* (II), m.p. 121·5—122°, and *o*-OH·C_6H_4·OPh (III). Me_2SO_4 converts (II) into 3-*phenoxy-4-methoxybenzaldehyde*, m.p. 49—50° [*semicarbazone*, m.p. 172·4—173°; oxidised to (I)]. *o*-OMe·C_6H_4·O·C_6H_4·CHO-*p* (*semicarbazone*, m.p. 207—208°) with $AlCl_3$ in C_6H_6 gives (III), whence its formation from (*A*) is explained. By successive treatment with HI–Ac_2O–AcOH, esterification (Ag salts), and extraction with NaOH, the acids from (*A*) give *o*-OH·C_6H_4·O·C_6H_4·CO_2H-*p* (IV), which is also obtained by KOH–$(CH_2·OH)_2$. With KOH–$(CH_2·OH)_2$ *o*-OMe·C_6H_4·O·C_6H_4·CO_2H-*p* gives (IV) (53%), but (I) gives (III) (75%). The *oxazolone*, m.p. 183·5—184°, from (II) gives m-*phenoxytyrosine*, m.p. 236° (block; preheated at 200°) [absorption max. at 2970 A. (log ε 3·62), min. at 2750 A. (log ε 3·4)]. The aldehyde mixture (*B*) obtained in 40—45% yield from *m*-OPh·C_6H_4·OMe (V) gives acids (*C*), whence H_2SO_4 gives 16·7% and AcCl gives 23% of 3-methoxyxanthone (VI); 2 : 4 : 1-OPh·C_6H_3(OMe)·CO_2H (VII) gives 84% of (VI). 3-Hydroxyxanthone, prepared from (VI) by $AlCl_3$, has m.p. 249—250° (lit. 243°). (VII) gives similarly 4-*hydroxy-2-phenoxybenzoic acid*, m.p. 163—164°. 1 : 4 : 2-$C_6H_3MeCl·NH_2$ (prep. from the NO_2-compound by H_2–Raney Ni in MeOH at 60°/2000 lb.), b.p. 120—125°/40 mm., gives 1 : 4 : 2-$C_6H_3MeCl·OH$ (85%), m.p. 67—68°, the Me ether, b.p. 104—106°/25 mm., of which with KOPh and Cu powder at 250—270° gives 4 : 1 : 2-OPh·C_6H_3Me·OMe (10%), b.p. 275—276°, oxidised and then demethylated (AcOH–HI) to 2-*hydroxy-4-phenoxybenzoic acid* (VIII), m.p. 182·4—183°. (VIII) is obtained (m.p. 180·8—181·4°) from (*C*) by $AlCl_3$. (V) with KOH–$(CH_2·OH)_2$ or HI–AcOH gives *m*-OPh·C_6H_4·OH (oxyacetic acid *derivative*, m.p. 67—67·4°), also obtained from (*B*) by $AlCl_3$–C_6H_6. By the Gattermann synthesis *p*-OPh·C_6H_4·OMe gives 6% of *p*-OMe·C_6H_4·O·C_6H_4·CHO. R. S. C.

Formation and structure of organic molecular compounds. II. Molecular compounds of *s*-trinitrobenzene with unsaturated ketones. J. Weiss (*J.C.S.*, 1943, 462—463).—*s*-$C_6H_3(NO_2)_3$ (I) and unsaturated ketones with the CO forming part of the conjugated system form mol. compounds. *Compounds* with the following ketones have been prepared in EtOH, the ratio ketone : (I) and m.p. being indicated: $(CHPh:CH)_2CO$, 1 : 2, 127°; 2 : 1, 115°; *p*-OMe·C_6H_4·CH:CH·CO·CH:CHPh, 1 : 1, 114°, 1 : 2, 124°; (*p*-OMe·C_6H_4·CH:CH)$_2$CO, 1 : 1, 115°; 2 : 1, 122°; $(CHPh:CH·CH:CH)_2CO$, 1 : 1, 113°; 1 : 2, 110°. Compounds are not formed by ketones of the type RCOMe (R = CHAr:CH); hence it is not the isolated group R but the conjugate system as a whole that is responsible for compound formation, the link being provided by the CO. The structure of the compounds and its relation to their colour are discussed. C. R. H.

Properties of *m*-nitrodibenzoylmethane. R. P. Barnes and L. B. Dodson (*J. Amer. Chem. Soc.*, 1943, **65**, 1585—1588).—*m*-$NO_2{\cdot}C_6H_4{\cdot}COMe$, PhCHO, and NaOH in MeOH–H_2O give *m-nitrophenyl styryl ketone*, m.p. 125—127°, the *dibromide* (I), m.p. 162—162·3°, of which with NaOMe–MeOH and then HCl–MeOH gives an enol (II), $OH{\cdot}CPh{:}CH{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2$, m.p. 131—134° (cf. Bodforss, A., 1917, i, 223). With NH_2OH,HCl and KOH in EtOH, (I) gives 5-*phenyl*-3-*m-nitrophenyl*isoo*xazole*, m.p. 169·5—170°, also obtained from (II) by NH_2OH,HCl in MeOH. Similar treatment of $COPh{\cdot}[CHBr]_2{\cdot}C_6H_4{\cdot}NO_2$ gives 3-*phenyl*-5-*m-nitrophenyl*isoo*xazole*, m.p. 180°. Warming (I) with $NHPh{\cdot}NH_2$ in MeOH and later warming with KOH gives 1 : 5-diphenyl-3-*m*-nitrophenylpyrazole (III), m.p. 131°. N_2H_4 leads similarly to 5-phenyl-3-*m*-nitrophenylpyrazole (IV), m.p. 206°. Incorrect configurations were previously (*loc. cit.*) assigned to (III) and (IV). R. S. C.

Condensation of ethyl methylacetoacetate with ethyl chlorofumarate. R. B. Woodward and W. A. Reed (*J. Amer. Chem. Soc.*, 1943, **65**, 1569—1572).—Contrary to Ruhemann *et al.* (*J.C.S.*, 1896, **69**, 1386; 1897, **71**, 325), Et_2 chlorofumarate and $CHMeAc{\cdot}CO_2Et$ give an enolic form of *Et_2 4-methyl-Δ^5-cyclohexene-1 : 3-dione-4 : 5-dicarboxylate* [absorption max. at 326 (log ε 3·68) and ~250 mμ.], converted by hot, conc. HCl into 4 : 6 : 1 : 2-$(OH)_2C_6H_2Me{\cdot}CO_2H$ and thence by conc. H_2SO_4 at 100° into 2 : 4 : 6 : 8-tetrahydroxy-1 : 5-dimethylanthraquinone (tetra-acetate, m.p. 231—232°). R. S. C.

β-Alkylation of certain cationoid systems by means of Grignard reagents. A. J. Birch and (Sir) R. Robinson (*J.C.S.*, 1943, 501—502; cf. A., 1942, II, 345).—Carvone and MgMeI–Et_2O in presence of a little CuBr, followed by heating the product with a trace of I at 180°, afford 6-methylcarvomenthone, b.p. 235—240°, with some diene, b.p. ~200°. 2-Keto-$\Delta^{1:9}$-octohydronaphthalene and MgMeI (+ CuBr) give *cis*-2-keto-9-methyldecahydronaphthalene, m.p. ~14·5°, b.p. 250—254° (2 : 4-*dinitrophenylhydrazone*, m.p. 106°; *CHPh:* derivative, m.p. 85—86°; the oxime separates as a mixture of isomerides, converted by NH_2OH,HCl–aq. EtOH in 1 week into the form, m.p. 109°), oxidised to *cis*-1-methyl*cyclo*hexane-1 : 2-diacetic acid (cf. Linstead *et al.*, A., 1937, II, 406). 2-Keto-10-methyl-$\Delta^{1:9}$-octahydronaphthalene similarly gives (?) trans-2-*keto*-9 : 10-*dimethyldecahydronaphthalene*, m.p. 90—95° (*semicarbazone*, m.p. 202—203°). Et *cyclo*hexylidenecyanoacetate and *n*-$C_{10}H_{21}{\cdot}MgBr$ or MgMeI yield *Et* 1-n-*decyl*- (14%), b.p. 230—235°/15 mm. (and some $C_{20}H_{42}$), or (after previous extraction of the product with aq. EtOH–NaCN) *Et* 1-*methyl*-cyclo*hexane*-1-*cyanoacetate* (45%), b.p. 155—160°/12 mm., respectively. The latter and 15% aq. NaOH give 1-*methyl*cyclo*hexane*-1-*malonamic acid*, m.p. 151°, converted at 180° into the -1-*acetamide*, m.p. 112—113°. 2-β-Carbethoxyethyl*cyclo*hexanone, $CN{\cdot}CH_2{\cdot}CO_2Et$, and piperidine at 100° (bath; 10 hr.) yield *Et* 2-β-*carbethoxyethyl*-Δ^1-cyclo*hexene*-1-*cyanoacetate*, b.p. 150—153°/0·1 mm., which is not alkylated by MgMeI (+CuBr). A. T. P.

Structure of diketen.—See A., 1944, I, 4.

Reactions and enolisation of cyclic diketones. VII. 1 : 2-Diketo-3-*tert.*-butylhydrindene. C. F. Koelsch (*J. Amer. Chem. Soc.*, 1943, **65**, 1640—1643; cf. A., 1942, II, 23).—Enolisation of 1 : 2-*diketo*-3-tert.-*butylhydrindene* (I) (see below) is entirely suppressed by the Bu^{γ}. $CO(CH{:}CHPh)_2$ and $MgBu^{\gamma}Cl$ in boiling Et_2O–C_6H_6 give αε-*diphenyl*-ζζ-*dimethyl*-Δ^{α}-*hepten*-γ-*one* (II), m.p. 146—148°, oxidised by $KMnO_4$–$COMe_2$ or, less well, CrO_3–AcOH to β-*phenyl*-γγ-*dimethyl*-n-*valeric acid* (III), m.p. 114—116° (*anilide*, m.p. 123—125°), the chloride ($SOCl_2$) of which with $AlCl_3$ in C_6H_6 gives 3-tert.-*butyl*-1-*hydrindone*, b.p. 150—153°/20 mm. (*oxime*, m.p. 135—137°). With OBu·NO–conc. HCl–EtOH at 22—65° this gives the 2-*NOH:* derivative, m.p. 182—185°, converted by CH_2O–HCl–AcOH into (I), m.p. 76—78° [$NaHSO_3$ compound; with *o*-$C_6H_4(NH_2)_2$ gives a *quinoxaline*, m.p. 131—132°]. Solid (I) is orange and its solutions in org. solvents are orange-pink; in aq. alkali it is deep blue. It is stable to air and Br–CCl_4. In aq. NaOH, H_2O_2 converts it into α-tert.-*butylhomophthalic acid*, m.p. 176—178° (gas) (*anhydride*, m.p. 106—107°). $CHPh{:}CH{\cdot}COMe$ and $MgBu^{\gamma}Cl$ in Et_2O give δ-*phenyl*-εε-*dimethyl*-n-*hexan*-β-*one* (IV), m.p. 61—62°, b.p. 145—150°/20 mm., and, by 1 : 2-addition, $CHPh{:}CH{\cdot}CMeBu^{\gamma}{\cdot}OH$ (V). (V) could not be purified nor could the dehydration product, $CHPh{:}CH{\cdot}CBu^{\gamma}{:}CH_2$, formed by distillation, but the presence of the latter is proved by condensation with $(CH{\cdot}CO)_2O$ at 100° to give 5-tert.-*butyl*-1 : 2 : 3 : 4-*tetrahydrodiphenyl*-2 : 3-*dicarboxylic anhydride*, m.p. 177—178°, and thence the derived *acid*, sinters 170°, m.p. 190—192° (gas) (Ag_2 salt). With S at 250° this gives 5-tert.-*butyldiphenyl*-2 : 3-*dicarboxylic* [5-tert.-*butyl*-3-*phenylphthalic*] *acid*, sinters 170°, m.p. 190—192° (gas) [*salt*, NaHX,H_2X, m.p. >270°; *anhydride*, m.p. 142—143°], which with conc. H_2SO_4 at 100° yields 3-tert.-*butyl*-9-*fluorenone*-1-*carboxylic acid*, m.p. 184—186°. Only a poor yield of (III) is obtained from (IV) by HOHal; a better yield is obtained by condensing with PhCHO to give (II) which is then oxidised as above. R. S. C.

Synthesis of substances related to the sterols. XLII. R. H. Martin and (Sir) R. Robinson (*J.C.S.*, 1943, 497—501; cf. A., 1941, II, 295).—3-Phenyl-Δ^2-*cyclo*pentenone-2-acetic acid and Ac_2O at 190° give 3′-*keto*-4-*acetoxy*-1 : 2-cyclo*pentenonaphthalene*, m.p. 159—160°; hydrolysis with aq. NaOH–EtOH gives the 4-OH-compound (improved prep.; cf. *loc. cit.*). The *Me ether* (I), m.p. 127·5—128·5° (2 : 4-*dinitrophenylhydrazone*, m.p. 301°), of this is converted by $CH_2Br{\cdot}CO_2Et$–Zn–C_6H_6 into *Et* 4-*methoxy*-1 : 2-cyclo*pentadienonaphthalene*-3′-*acetate*, m.p. 123—123·5° [free *acid*, m.p. 226—228° (decomp.)], which is reduced (H_2, 2% Pd–$SrCO_3$, MeOH at 18°/2 atm.) and then hydrolysed (KOH–MeOH–little H_2O) to 4-*methoxy*-1 : 2-cyclo*pentenonaphthalene*-3′-*acetic acid* (II), m.p. 136—137·5° (previous sintering). With SeO_2 in boiling AcOH (3 min.), (I) gives 2′ : 3′-*diketo*-4-*methoxy*-1 : 2-cyclo*pentenonaphthalene*, m.p. 178—180°. *m*-$OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CHAc{\cdot}CO_2Et$ is hydrolysed (10% aq. NH_3 followed by boiling 10% aq. NaOH) to *m*-$OMe{\cdot}C_6H_4{\cdot}COMe$, which with furfuraldehyde in cold 1% MeOH–NaOMe affords *furfurylidene*-3-*methoxyacetophenone*, b.p. 175°/0·45 mm., m.p. 38·5—39·5° (2 : 4-*dinitrophenylhydrazone*, m.p. 190—191°). The derived γζ-*diketo*-ζ-m-*anisylheptoic acid*, m.p. 87—88°, and 2% aq. NaOH yield 3-m-*anisyl*-Δ^2-cyclo*pentenone*-2-*acetic acid*, m.p. 100—101°; Ac_2O then affords 3′-*keto*-4-*acetoxy*-7-*methoxy*-1 : 2-cyclo*pentenonaphthalene*, m.p. 177·5—178°, and (probably) some 5-*OMe-isomeride*, m.p. 196·5—198°. Reinvestigation (*loc. cit.*) of the hydrogenation of 4 : 6-dimethoxy-1 : 2-*cyclo*pentadienonaphthalene-3′-acetic acid shows that the acid, $C_{17}H_{22}O_4$, m.p. 117—118°, is a mixture (*A*) of stereoisomerides; the main constituent is 4 : 6-*dimethoxy*-5 : 6 : 7 : 8-*tetrahydro*-1 : 2-cyclo*pentenonaphthalene*-3′-*acetic acid*, m.p. 131—132·5°. With boiling HI (*d* 1·7)–AcOH (30 min.), followed by Me_2SO_4–aq. KOH–MeOH, (*A*) yields 4-*methoxy*-7 : 8-*dihydro*-1 : 2-cyclo*pentenonaphthalene*-3′-*acetic acid*, m.p. 154·5—156·5°, the Me ester of which with Pd–C (N_2) at 300°, followed by hydrolysis, gives (II). The non-cryst. acids in the prep. of (*A*) are complex mixtures (deoxygenated) yielding indefinite products on dehydrogenation; their Me esters with Pd–C–N_2 at 220°, followed by hydrolysis, give an *acid*, $C_{15}H_{18}O_2$, m.p. 109·5—111·5°. *o*-Tolyl carbonate (III), m.p. 57—57·5°, and (?) $ClCO_2C_6H_4Me$-*o*, b.p. 84°/15 mm. [convertible by C_5H_5N–C_6H_6 into (III)], are obtained from *o*-cresol and $COCl_2$–aq. NaOH at 70—75°. With HNO_3 (*d* 1·43) in H_2SO_4 at −15° to 0°, followed by boiling aq. K_2CO_3, (III) affords a little 3- + 4-, but mainly 5-nitro-*o*-cresol. 1 : 4 : 2-$C_6H_3MeCl{\cdot}OMe$, obtained from 1 : 4 : 2-$C_6H_4MeCl{\cdot}NH_2$ through the diazo-reaction and subsequent methylation, is converted by AcCl–CS_2–$AlCl_3$ into 6-*chloro*-4-*methoxy*-3-*methylacetophenone*, m.p. 45·5—46°; its *furfurylidene* derivative, m.p. 78—79°, and boiling conc. HCl–EtOH give 2-(4′-*chloro*-6′-*methoxy*-m-*tolyl*)*furan*-5-β-*propionic acid*, m.p. 175—177° (slight sintering) (*Me* ester, m.p. 77—78°) (attempts to open the furan ring failed). 3′-Keto-4 : 6-dimethoxy-1 : 2-*cyclo*pentenonaphthalene and SeO_2–AcOH (b.p.) give 2′ : 3′-*diketo*-4 : 6-*dimethoxy*-1 : 2-cyclo*pentenonaphthalene*, m.p. 243—245° (decomp.) [*quinoxaline* derivative, m.p. 247°, from *o*-$C_6H_4(NH_2)_2$ in AcOH], converted by H_2O_2–aq. NaOH into 2-*carboxy*-4 : 6-*dimethoxy*-1-*naphthylacetic acid*, m.p. 255—257° (decomp.). A. T. P.

Synthesis of substances related to the sterols. XLI. Androstenedione. I. R. H. Martin and (Sir) R. Robinson (*J.C.S.*, 1943, 491—497; cf. A., 1941, II, 295).—A mixture of a max. of eight (probably less) *dl*-stereoisomerides of androstenedione is probably prepared. 2 : 1-$OMe{\cdot}C_{10}H_6{\cdot}CHO$ and H_2–EtOH–Raney Ni at 100°/100 atm. give 6-*methoxy*-5-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (I), m.p. 51·5—52° (HI–AcOH give the 6-*OH*-compound, m.p. 113·5—114·5°), better prepared by a similar hydrogenation of 1 : 2-$C_{10}H_6Me{\cdot}OH$, followed by Me_2SO_4–aq. NaOH at 80°, then at 100°. (I) and CrO_3–aq. AcOH at <20° yield 1-keto-6-methoxy-5-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene (II), m.p. 112—113° (2 : 4-*dinitrophenylhydrazone*, m.p. 249—250°), converted by Et_2O–MgMeI–C_6H_6, followed by S at 215°, into 2-*methoxy*-1 : 5-*dimethylnaphthalene*, m.p. 96—97°; HI–AcOH gives 1 : 5 : 2-$C_{10}H_5Me_2{\cdot}OH$, m.p. 161—162°. $Me_2C_2O_4$–dry NaOMe–C_6H_6 (under N_2) and (II)–C_6H_6 at room temp., then at b.p., afford *Me* 1-*keto*-6-*methoxy*-5-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-2-*naphthylglyoxylate*, m.p. 136—137°, which loses CO at 170—180° to give *Me* 1-*keto*-6-*methoxy*-5-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-2-*carboxylate* (III), m.p. 100—101° (immersed at 93°) (2 : 4-*dinitrophenylhydrazone*, m.p. 223—224° after darkening at 195°). (III) and boiling MeI–NaOMe–C_6H_6 give the 2-*Me* derivative, m.p. 89—90·5°, which with $CH_2Br{\cdot}CO_2Me$–Zn–C_6H_6–Et_2O (+ I) at 70° yields (chromatographic separation) *Me* 1-*hydroxy*-6-*methoxy*-2-*carbomethoxy*-2 : 5-*dimethyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthylacetate* (IV), m.p. 106·5—108°; $SOCl_2$–C_6H_6–C_5H_5N at room temp., followed by boiling aq. KOH–MeOH, gives a mixture of the cis-*anhydride* (V), m.p. 204—205°, of 1-*carboxymethylene*-6-*methoxy*-2 : 5-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-2-*carboxylic acid*, and the *trans*-1 : 2-dicarboxylic acid [in one experiment, 1-*keto*-6-*methoxy*-2 : 5-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 113—114° (2 : 4-*dinitrophenylhydrazone*, m.p. 229°), was also isolated]. (IV) and HCl–C_6H_6–$CaCl_2$ at room temp. give stereoisomeric *Me_2* esters (VI), $C_{18}H_{22}O_5$, b.p. 150°/0·05 mm. and m.p. 105·5—106·5°. (V) (crude) is hydrolysed by KOH–EtOH, and the resulting K salts reduced by 2% Na–Hg to the H_2-acids, and esterified (CH_2N_2) to the α-*Me_2* ester (VII), m.p. 112—113°, of 2-*carboxy*-6-*methoxy*-2 : 5-*dimethyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthylacetic acid*; the β-*Me_2* ester, m.p. 53—54°, also formed is obtained

cryst. through the *β-Me H* ester (**VIII**), m.p. 149—150°, and CH_2N_2. The *α-Me H* ester (**IX**) has m.p. 137—139°. A mixture of α- (main product) and *β-Me*$_2$ esters is obtained by catalytic reduction of (**VI**), using PtO_2 in AcOH or EtOAc, Pd–C or Pd-black in $COMe_2$, or $SrCO_3$–Pd, or Raney Ni at 60°/25 atm. Boiling KOH–MeOH converts the Me_2 esters into the α-, m.p. 217—217·5° (slight sintering), and *β-dicarboxylic acid*, m.p. 198—200°, and thence (Ac_2O) the α-, m.p. 173—174°, and *β-anhydride*, m.p. 168—169°, respectively. Thermodynamic dissociation consts. of the dicarboxylic acids are investigated [by J. C. Speakman], but spatial structure could not be proved. It is probable that CO_2Me and $CH_2{\cdot}CO_2Me$ are *cis*- in the α- and *trans*- in the β-series. Reduction of (**VI**) using Raney Ni (above) is unreliable, and in one experiment, much degradation occurred; after hydrolysis with KOH–EtOH, followed by Ac_2O, (**V**) was isolated; also formed were 1 : 2 : 5 : 6-$C_{10}H_4Me_3{\cdot}OMe$ and (?) 6-*methoxy*-2 : 5-*dimethyl*-3 : 4-*dihydro*-1-*naphthylacetic acid*, m.p. 180—192° (H_2–Pd–$SrCO_3$–EtOAc–$COMe_2$ gives the *H*$_4$-*acid*, m.p. 155·5—159°). (**VII**) with HI (*d* 1·7)–AcOH followed by boiling H_2SO_4–MeOH gives *Me α-2-carboxy-6-hydroxy-2 : 5-dimethyl-1 : 2 : 3 : 4-tetrahydro-1-naphthylacetate*, m.p. 169—170° (+ MeOH), and *α-2-carbomethoxy-6-hydroxy-2 : 5-dimethyl-1 : 2 : 3 : 4-tetrahydro-1-naphthylacetic acid*, m.p. 179·5—180·5°. When the crude demethylation product of (**VII**) or the corresponding dicarboxylic acid is refluxed with MeOH–H_2SO_4, the *Me*$_2$ ester (**X**), m.p. 122—123°, of the phenoldicarboxylic acid is obtained; the β-dicarboxylic acid is demethylated and esterified (HCl–MeOH) to give the *Me*$_2$ ester, m.p. 125—126°, isomeric with (**X**). (**X**) and H_2–dry dioxan–Raney Ni give only a trace of *Me 2-carbomethoxy-6-hydroxy-2 : 5-dimethyldecahydro-2-naphthylacetate*, b.p. 180° (bath)/0·05 mm.; there is considerable deoxygenation. The chloride from (**IX**) and $SOCl_2$–Et_2O (+ C_5H_5N) with Et_2O–CH_2N_2 in C_6H_6 gives the diazo-ketone, which with Ag_2O–MeOH affords *Me α-2-carbomethoxy-6-methoxy-2 : 5-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene-1-β-propionate*, m.p. 84—85°; NaOMe–C_6H_6 (under N_2) then gives *Me 3′-keto-6-methoxy-2 : 5-dimethyl-1 : 2 : 3 : 4-tetrahydro-1 : 2-cyclopentenonaphthalene-2′-carboxylate*, m.p. 107·5—108·5°, converted by boiling HI–AcOH into *6-hydroxy-3′-keto-2 : 5-dimethyl-1 : 2 : 3 : 4-tetrahydro-1 : 2-cyclopentenonaphthalene-α* (**XI**), m.p. 189—191° (vac.). (**VIII**) similarly yields the *OH-ketone-β*, m.p. 230—231° (vac.). The use of 2% Pd–$SrCO_3$ as catalyst for hydrogenations in dioxan is illustrated. Thus PhOH at 20°/113 atm., then 75—140°/125 atm., gives almost quant. yield of *cyclo*hexanol, *p*-$C_6H_4(OMe)_2$ affords 1 : 4-dimethoxy*cyclo*hexane, *p*-OH·C_6H_4·CO_2Et in pure dioxan at 15°/118 mm., then 155°/150 atm. and 157°/90 atm., or in EtOAc at 140—150°/140 atm., yields *trans*-4-carbethoxy*cyclo*hexanol. (**X**) is not similarly reduced, but (**XI**) (in dioxan) at 196°/134 atm., then 202°/133 atm., gives stereoisomeric 6 : 3′-*dihydroxy*-2 : 5-*dimethyldecahydro*cyclo*pentenonaphthalenes*, a colourless glass, oxidised by CrO_3–AcOH at 10—15° to a mixture of diketones containing 6 : 3′-*diketo*-2 : 5-*dimethyldecahydro*-1 : 2-cyclo*pentenonaphthalene*-x-α, m.p. 116—117°. The mixed diketones (not cryst.) with $NaNH_2$ in boiling Et_2O (N_2) for 6 hr., followed by COMe·$[CH_2]_2$·$NMeEt_2I$ in EtOH (N_2), give mixed (?) *androstenediones* (absorption in EtOH confirms C:C·CO).

A. T. P.

Crystalline bisulphite additive compounds of menadione [2-methyl-1 : 4-naphthaquinone]. F. Ablondi, R. W. Price, B. R. Baker, and G. H. Carlson (*J. Amer. Chem. Soc.*, 1943, **65**, 1776).—Cryst. *LiHSO*$_3$, *NH*$_4$*HSO*$_3$, and *Ca*$(HSO_3)_2$, m.p. (air-dried) 97—98°, (anhyd.) 115—117° (decomp.), derivatives of 1 : 2 : 4-O:$C_{10}H_5$·Me:O are prepared.

R. S. C.

Synthesis of 2-methyl-1 : 4-naphthaquinone-8-sulphonic acid. A. Bendich and E. Chargaff (*J. Amer. Chem. Soc.*, 1943, **65**, 1568—1569).—2-$C_{10}H_7Me$ and $ClSO_3H$ in CCl_4 at −10° to room temp. give 2 : 8- (49% isolated as Ba salt) and 2 : 1-$C_{10}H_6Me{\cdot}SO_3H$ (cf. Veselý *et al.*, A., 1930, 1173). 2 : 8-$C_{10}H_6Me{\cdot}SO_3K$ and PCl_5 at 100° give the sulphonyl chloride, m.p. 94—95°, and thence (conc. aq. NH_3) the sulphonamide, m.p. 197°, which with CrO_3–AcOH at 80°—the b.p. gives *2-methyl-1 : 4-naphthaquinone-8-sulphonamide*, m.p. 231—232° (decomp.). $NaNO_2$–H_2SO_4–AcOH then gives 2-methyl-1 : 4-naphthaquinone-8-sulphonic acid [*Ba*, *K*, and *Tl*, m.p. 263—264° (decomp.), salts], which has little or no vitamin-*K* activity.

R. S. C.

Synthesis of the pentacene ring system. C. F. H. Allen and J. W. Gates, jun. (*J. Amer. Chem. Soc.*, 1943, **65**, 1502—1503).—1 : 3-Diphenyl*iso*benzfuran and *p*-O:C_6H_4:O in boiling EtOH give 7 : 12 : 5 : 14-*diepoxy*-5 : 7 : 12 : 14-*tetraphenyl*-5 : 5a : 6a : 7 : 12 : 12a : 13a : 14-*octahydropentacene*-6 : 13-*quinone*, m.p. 197—198°, converted by conc. H_2SO_4 at −10° into 5 : 7 : 12 : 14-tetraphenylpentacene-6 : 13-quinone (A., 1942, II, 320). 7 : 12 : 5 : 14-*Diepoxy*-5 : 7 : 12 : 14-*tetraphenyl*-2 : 3 : 9 : 10-*tetramethyl*-5 : 5a : 6a : 7 : 12 : 12a : 13a : 14-*octahydropentacene*-6 : 13-*quinone* is similarly prepared.

R. S. C.

IV.—STEROLS AND STEROID SAPOGENINS.

17-Amino-10 : 13-dimethyl*cyclo*pentanopolyhydrophenanthrene compounds.—See B., 1943, III, 303.

Steroids with ethylenic linkings between quaternary carbon atoms. III. Structure of α-spinasterol. H. E. Stavely and G. N. Bollenback (*J. Amer. Chem. Soc.*, 1943, **65**, 1600—1603; cf. A., 1943, II, 332).—γ-Cholestenyl acetate (**I**) is unchanged by PtO_2, Pt- or Pd-black unless the catalyst has been treated with H_2 (cf. Wieland *et al.*, A., 1943, II, 268). In presence of H_2 all three catalysts isomerise (**I**). When Pd-black is first shaken in EtOAc with H_2, it then isomerises (**I**) under N_2, but this treatment fails with PtO_2 or Pt-black. α-Spinasterol is proved to be the $\Delta^{8(9)}$-compound. Its acetate with CrO_3–AcOH at room temp. gives a mixture (cf. Simpson, A., 1937, II, 339), resolved by chromatography into 8 : 9- (**II**), m.p. 229—230°, $[\alpha]_D$ −32±1·5°, and 8 : 14-*epoxy*-3-*acetoxy*-Δ^{22}-*stigmasten*-7-*one* (**III**), m.p. 171—173°, $[\alpha]_D^{24}$ −77±3°, both having no selective adsorption at >230 mμ., and a residue which by hydrolysis (HCl–EtOH), treatment with Girard's reagent *T*, acetylation, and chromatography yields 3-*acetoxy*-$\Delta^{8(9):22(23)}$-*stigmastadien*-7-*one* (3%), m.p. 202—204°, $[\alpha]_D^{23}$ −36±2° (absorption max. at 252 mμ., ε 8300), 3-*acetoxy*-$\Delta^{9(11):8(14):22(23)}$-*stigmastatrien*-3-*one*, m.p. 190—192°, $[\alpha]_D^{23}$ −24±2° [absorption max. at 299 mμ., ε 5300; also obtained from (**II**) or (**III**) by HCl–EtOH and then Ac_2O–C_5H_5N], and 3-*acetoxy*-$\Delta^{8(14)}$-*stigmasten*-7-*one*, m.p. 140—141°, $[\alpha]_D$ −53±1·5° (absorption max. at 260 mμ., ε 7800; reduced by H_2–Pd-black or –PtO_2 in AcOH to *α-spinastenyl acetate*, m.p. 117°, $[\alpha]_D$ +13±1°). [α] are in $CHCl_3$.

R. S. C.

Preparation and properties of the 7-epimeric cholestane-3(β) : 7-diols. O. Wintersteiner and (Miss) M. Moore (*J. Amer. Chem. Soc.*, 1943, **65**, 1503—1507).—H_2–PtO_2 converts 7-ketocholesteryl acetate (**I**) in AcOH into 3(β)-*acetoxycholestan*-7(α)- (**II**), m.p. 71—75°, $[\alpha]_D^{23}$ +35·3°, and -7(β)-*ol* (**III**), *forms*, m.p. 116—117° and 124°, $[\alpha]_D^{23}$ 0, with small amounts of β-cholestanyl acetate and 7-ketocholestanyl acetate (**IV**), m.p. 149—149·5°, $[\alpha]_D^{22}$ −36·0° (cf. Marker *et al.*, A., 1940, II, 17); with H_2–PtO_2 in EtOAc, (**I**) gives (**IV**), which in AcOH yields only (**II**) and (**III**). CrO_3 oxidises (**II**) or (**III**) to (**IV**). Boiling 5% KOH–MeOH hydrolyses (**II**) and (**III**) to *cholestane*-3(β) : 7(α)- (**V**), *forms*, m.p. 156—158° and 167—168°, $[\alpha]_D^{24}$ +52·9° {*diacetate* [prep. from (**II**)], *forms*, m.p. 64—69°, 74—78°, and 81—87°, $[\alpha]_D^{24}$ +54·7°; *dibenzoate*, m.p. 151—152°, $[\alpha]_D^{23}$ +67·6°}, and -3(β) : 7(β)-*diol*, m.p. 152—153°, $[\alpha]_D$ +8·1° (*diacetate*, m.p. 138—139°, $[\alpha]_D^{23}$ −17·2°; *dibenzoate*, m.p. 153—154°, $[\alpha]_D^{24}$ +23·0°), respectively. In C_5H_5N at room temp., (**II**) gives 7(α)-*p-toluenesulphonyloxy*-3(β)-*acetoxycholestane*, m.p. 152·5—153°, $[\alpha]_D^{24}$ +11·6°. With PCl_5–$CaCO_3$–$CHCl_3$ at 0°, (**II**) gives 3(β)-*acetoxy*-7-*cholestanyl chloride*, m.p. 118—119°, $[\alpha]_D^{23}$ −21·7°, and thence (20% KOH–MeOH) 7-*chlorocholestan*-3(β)-*ol*, m.p. 170·5—171·5°, $[\alpha]_D^{23}$ −19·8°; Walden inversion may have occurred. With $SOCl_2$–$CaCO_3$–Et_2O, (**II**) gives *di*-3(β)-*acetoxy*-7(α)-*cholestanyl sulphite*, m.p. 131·5—133·5°, hydrolysed by 5% KOH–MeOH to (**V**). [α] are in $CHCl_3$.

R. S. C.

Dehydration of the 7-epimeric 3(β)-acetoxycholestan-7-ols. Transformation products of γ-cholestenol. O. Wintersteiner and (Miss) M. Moore (*J. Amer. Chem. Soc.*, 1943, **65**, 1507—1513).—Dehydration of 3(β)-acetoxycholestan-7(β)-ol by $CuSO_4$ in boiling xylene, *p*-$C_6H_4Me{\cdot}SO_2Cl$ in boiling C_5H_5N, or PCl_5 in $CHCl_3$ at 0°, by elimination of $ArSO_3H$ from the 7-*p*-toluenesulphonate by NaI and C_5H_5N, or of HCl from the 7(α)-chloride by KOAc–AcOH at 130° gives an inseparable mixture (*A*), containing mostly γ- ($\Delta^{7(8)}$-)cholestenyl acetate. Pd–H_2 isomerises (*A*) in AcOH to give a good yield of α-($\Delta^{8(14)}$-)cholestenyl acetate. With OsO_4 in Et_2O at room temp. (6 days) and then Na_2SO_3 in hot aq. EtOH and acetylation, (*A*) gives 3(β) : 7-*diacetoxycholestan*-8-*ol*, m.p. 168—169°, $[\alpha]_D$ −39·8°, and thence by hot 5% KOH–MeOH *cholestane*-3(β) : 7 : 8-*triol*, m.p. 176—178°, $[\alpha]_D^{21}$ −12·9° (no digitonide). (*A*) consumes 2 BzO_2H in $CHCl_3$ in 8 days (cf. Schenck *et al.*, A., 1937, II, 59), giving 8 : 14-*epoxy*-3(β)-*acetoxycholestan*-7-*ol* (**I**), m.p. 122—123°, $[\alpha]_D^{23}$ +6·1°, converted by Ac_2O–C_5H_5N at room temp. into the 3(β) : 7-*diacetate* (**II**), m.p. 162—163°, $[\alpha]_D^{23}$ −11·9°. 5% hot KOH–MeOH hydrolyses (**I**) or (**II**) to 8 : 14-*epoxycholestane*-3(β) : 7-*diol*, m.p. 186—187°, $[\alpha]_D^{21}$ +81° (digitonide, decomp. 225°). Some samples of (*A*) give, besides (**I**), an *isomeride* thereof, m.p. 145·5—146°, $[\alpha]_D^{23}$ +27·6° (derived *diacetate*, sinters 59°, m.p. 63—64°). CrO_3–AcOH at room temp. converts (**I**) into 8 : 14-*epoxy*-3(β)-*acetoxycholestan*-7-*one* (**III**), m.p. 139·5—140°, $[\alpha]_D^{22}$ −75·7° (slight absorption at <240 mμ.; no semicarbazone), converted by conc. HCl in boiling EtOH into 3(β)-*acetoxy*-$\Delta^{8(9):14(15)}$- or -$\Delta^{9(11):8(14)}$-*cholestadien*-7-*one*, sinters 163°, m.p. 166°, $[\alpha]_D^{21}$ −17·6° [absorption max. at 297 (ε 4800), min. at 257 (ε 1500), end at <240 mμ. in EtOH; 2 : 4-*dinitrophenylhydrazone*, m.p. 225—228°, obtained also from (**III**)]. This is reduced by H_2–Pd in EtOH to 3(β)-*acetoxy*-$\Delta^{8(14)}$-*cholesten*-7-*one*, m.p. 141·5—142·5°, $[\alpha]_D^{21}$ −62·2° [absorption max. at 262·5 mμ. (ε 9500); 2 : 4-dinitrophenylhydrazone, m.p. 210—211°], further reduced in AcOH to α-cholestenyl + 7-ketocholestanyl acetates. [α] are in $CHCl_3$.

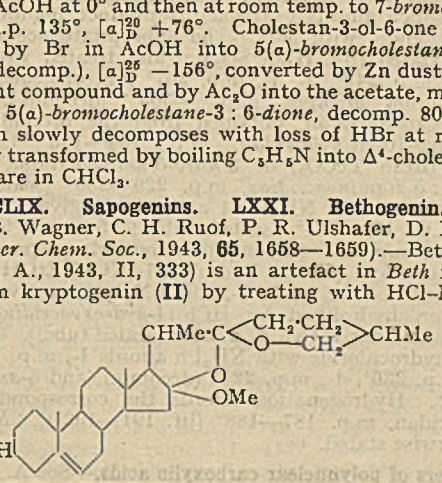
R. S. C.

Oxidation products of α-cholestenyl acetate. O. Wintersteiner and (Miss) M. Moore (*J. Amer. Chem. Soc.*, 1943, **65**, 1513—1516).—Neutral products obtained from α-cholestenyl acetate (**I**) by CrO_3–AcOH–C_6H_6 give, by chromatography, 8 : 14-epoxy-3(β)-acetoxycholestan-7-one with smaller amounts of 3(β)-*acetoxy*-$\Delta^{8(14)}$-*chole-*

sten-15-one, m.p. 134—135°, $[\alpha]_D$ −118° [absorption max. at 259 mμ. (ε 12,750) in EtOH; 2 : 4-*dinitrophenylhydrazone*, m.p. 208—209°; derived 3-*OH-ketone*, m.p. 145—146° (digitonide); slowly hydrogenated to (I)], 8 : 14-*epoxy*-3(β)-*acetoxycholestan*-15-*one*, m.p. 180—181°, $[\alpha]_D^{22}$ +4·7° (in conc. HCl–EtOH gives mixed dienones), (?)8 : 14-*dihydroxy*-3(β)-*acetoxycholestane*-7 : 15-*dione*, m.p. 184—185°, $[\alpha]_D^{22}$ +73·5°, and (?)14-*hydroxy*-3(β)-*acetoxy*-$\Delta^{8(9)}$-*cholestene*-7 : 15-*dione*, m.p. 218—219° (decomp.), $[\alpha]_D^{21}$ +143·5° [absorption max. at 254 mμ. (ε 10,400)]. [α] are in $CHCl_3$. R. S. C.

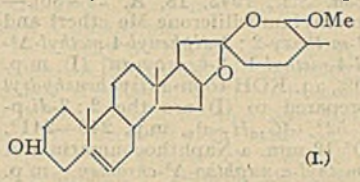
Bromination of steroid ketones. L. H. Sarett, P. N. Chakravorty, and E. S. Wallis (*J. Org. Chem.*, 1943, **8**, 405—416).—Cholestane-3 : 6-dione is converted by Br (9 mols.) in dry $CHCl_3$–AcOH into Δ^4-2 : 4 : 7 : 7-*tetrabromocholestene*-3 : 6-*dione* (I), m.p. 190°, $[\alpha]_D^{20}$ +22°, converted by 15% HBr–AcOH in $CHCl_3$ into Δ^4-4 : 7 : 7-tribromocholestene-3 : 6-dione (II), m.p. 195°, $[\alpha]_D^{20}$ +16°, also obtained if the prep. of (I) is prolonged or if (I) in AcOH–$CHCl_3$ is treated with Br + I. (I) in boiling C_6H_6 containing a little EtOH is reduced by fine Fe powder to Δ^4-4 : 7-dibromocholestene-3 : 6-dione (III), m.p. 175°, $[\alpha]_D^{20}$ +82°, whereas Fe and boiling EtOH reduce (I) to cholestane-3 : 6-dione, m.p. 171°. Fe powder in boiling C_6H_6 containing EtOH reduces (I), (II), or (III) to Δ^4-4-bromocholestene-3 : 6-dione, m.p. 169·5°, $[\alpha]_D^{20}$ −38°, the constitution of which follows from its conversion by o-$C_6H_4(NH_2)_2$ into the same *quinoxaline* derivative, $C_{33}H_{46}ON_2$, m.p. 143° (opaque; clear at 157°), as is obtained from cholestane-3 : 4 : 6-trione. (I) is converted by $AgNO_3$ in C_5H_5N at room temp. into $\Delta^{4:7}$-2 : 4 : 7-*tribromocholestadiene*-3 : 6-*dione*, m.p. 164°, $[\alpha]_D^{20}$ −38°, transformed by HBr–AcOH–$CHCl_3$ into $\Delta^{4:7}$-4 : 7-dibromocholestadiene-3 : 6-dione, m.p. 182°, $[\alpha]_D^{20}$ −18°, and by Fe powder in boiling C_6H_6–EtOH into $\Delta^{4:7}$-7-bromocholestadiene-3 : 6-dione, m.p. 182°, $[\alpha]_D^{20}$ −141°. Attempted hydrolysis of 5(α) : 7-dibromocholestan-3-ol-6-one acetate gives only intractable gels whereas acid hydrolysis of the corresponding 5(β)-derivative leads smoothly to 5(β) : 7-dibromocholestan-3-ol-6-one, decomp. 117—119°, $[\alpha]_D^{20}$ −50°, re-acetylated by boiling Ac_2O to the parent acetate and oxidised by CrO_3 in AcOH to 5(β) : 7-*dibromocholestane*-3 : 6-*dione*, decomp. 100°, $[\alpha]_D^{20}$ −41°, which is converted by KOAc and boiling aq. AcOH into Δ^4-7-bromocholestene-3 : 6-dione (IV), m.p. 130—131°, $[\alpha]_D^{20}$ −41°. (IV) is reduced by Zn dust in boiling EtOH to cholestane-3 : 6-dione, and converted by Br in $CHCl_3$–AcOH containing NaOAc into Δ^4-2 : 7-*dibromocholestene*-3 : 6-*dione* (V), m.p. 119°, $[\alpha]_D^{26}$ +118° (whence a *diquinoxaline* derivative, $C_{39}H_{46}N_4$, m.p. 194°). Further bromination of (V) proceeds very slowly and only initial material is isolated from the product. Cholestane-3(β) : 5(α)-diol-6-one in $CHCl_3$ is converted by Br (1 mol.) in AcOH at 35° into 7-*bromocholestane*-3(β) : 5(α)-*diol*-6-*one*, decomp. 250°, $[\alpha]_D^{26}$ −24° [*acetate* (+ 1MeOH), m.p. 172°], oxidised by CrO_3 in 90% AcOH to 7-bromocholestan-5(α)-ol-3 : 6-dione, m.p. 165—171°, which is reduced by Zn dust and boiling EtOH to cholestan-5(α)-ol-3 : 6-dione, m.p. 232°; attempted dehydration with 95% HCO_2H at room temp. or 100°, with dry HCl or HBr in $CHCl_3$, or with hot Ac_2O gives only uncrystallisable oils. Cholestane-3 : 6-dione in $CHCl_3$ is converted by Br (2 mols.) in AcOH containing NaOAc into 2 : 2-*dibromocholestane*-3 : 6-*dione* (VI), decomp. 175—195° depending principally on the size of the crystals, $[\alpha]_D^{24}$ +65°, which gives an oil when heated with $AgNO_2$–C_5H_5N at room temp., decomposes slowly at room temp., and does not give a quinoxaline derivative. (VI) is transformed by boiling C_5H_5N into Δ^4-2-*bromocholestene*-3 : 6-*dione*, m.p. 204—207°. Acid hydrolysis of 7-bromocholestan-3-ol-6-one acetate gives the parent alcohol, m.p. 113°, $[\alpha]_D^{20}$ +51°, oxidised by CrO_3 in 95% AcOH at 0° and then at room temp. to 7-*bromocholestane*-3 : 6-*dione*, m.p. 135°, $[\alpha]_D^{20}$ +76°. Cholestan-3-ol-6-one in Et_2O is transformed by Br in AcOH into 5(α)-*bromocholestan*-3-*ol*-6-*one*, m.p. ~150° (decomp.), $[\alpha]_D^{25}$ −156°, converted by Zn dust and EtOH into the parent compound and by Ac_2O into the acetate, m.p. 164°; it is oxidised to 5(α)-*bromocholestane*-3 : 6-*dione*, decomp. 80—85°, $[\alpha]_D^{26}$ +140°, which slowly decomposes with loss of HBr at room temp. and is rapidly transformed by boiling C_5H_5N into Δ^4-cholestene-3 : 6-dione. $[\alpha]_D$ are in $CHCl_3$. H. W.

Sterols. CLIX. Sapogenins. LXXI. Bethogenin. R. E. Marker, R. B. Wagner, C. H. Ruof, P. R. Ulshafer, D. P. J. Goldsmith (*J. Amer. Chem. Soc.*, 1943, **65**, 1658—1659).—Bethogenin (I) (Noller *et al.*, A., 1943, II, 333) is an artefact in *Beth* root, being obtained from kryptogenin (II) by treating with HCl–MeOH and



then 2% KOH–MeOH. It has the structure shown. With HBr–AcOH it regenerates (II) or a similar diketone with hydrolysis of the OMe and with NH_2OH in C_5H_5N gives the dioxime of (II). R. S. C.

Saponins and sapogenins. XXIII. Constitution of bethogenin. C. R. Noller and M. R. Barusch (*J. Amer. Chem. Soc.*, 1943, **65**, 1786).—The structure below is suggested for bethogenin (I). (I) or its acetate with HBr–AcOH loses OMe and gives a *diacetate*, $C_{31}H_{46}O_6$, m.p. 148—149°, $[\alpha]_D^{26}$ −161° in dioxan (*dioxime*, m.p. 194—195°), hydrogenated (PtO_2; EtOH) to a *H_2-diacetate*, m.p. 116—117°, $[\alpha]_D^{22}$ −11° in dioxan [CO proved by absorption spectrum; saturated towards $C(NO_2)_4$]. H_2–PtO_2 reduces (I) in EtOH, with removal of OMe, to an unsaturated ketone (*diacetate*, $C_{31}H_{46}O_6$, m.p. 142—144°, $[\alpha]_D^{24}$ −156° in dioxan), and, by exhaustive treatment, a saturated, non-ketonic *substance*, $C_{27}H_{46}O_4$, m.p. 203—208·6°, $[\alpha]_D^{25}$ −57·7° in dioxan, converted by Ac_2O–C_5H_5N into an *acetate*, $C_{29}H_{46}O_4$, m.p. 204—207·5°, $[\alpha]_D^{25}$ −62·2° in dioxan. Kryptogenin may be a keto-aldehyde, since with HBr–AcOH, (I) but not diosgenin, tigogenoic or chlorogenoic acid, or Me chlorogenoate, yields a substance which gives a pink colour with Schiff's reagent and a red colour with 1 : 4-$C_{10}H_6(OH)_2$–HCl–AcOH. R. S. C.



V.—TERPENES AND TRITERPENOID SAPOGENINS.

Triterpene group. X. Continuation of parts II and V. J. C. E. Simpson and R. A. Morton (*J.C.S.*, 1943, 477—486; cf. A., 1938, II, 448; 1939, II, 331).—The previous hypothesis of the presence of an aromatic ring in the hydroxydione, $C_{30}H_{44}O_3$ (obtained originally from β-amyrin by mild S-dehydrogenation and subsequent oxidation), and its congeners is withdrawn, and the results obtained by a study of these compounds are critically considered with reference to recent publications of Ruzicka *et al.* (A., 1942, II, 371) and Kon *et al.* (*ibid.*, 148). It is concluded that neither the Ruzicka nor the Kon formulation for the compound accounts for the properties of certain derivatives of this substance, and this is attributed to incorrect siting of the chromophore. The substances discussed have been examined both chemically and spectrographically, and NO_2-derivatives of the cholesterol series have been included. Generalisations are made respecting the scope and limitation of the Liebermann–Burchard and the $C(NO_2)_4$ reaction for the diagnosis of unsaturation in polycyclic hydroaromatic compounds. Reduction (Na–C_5H_{11}·OH) of the OAc-compound (I), $C_{32}H_{46}O_5$, gives an acid (II), $C_{30}H_{56}O_4$, m.p. 264·5—266·5° [*Ac_2 Me ester* (III), $C_{35}H_{46}O_6$, m.p. 228—229°, $[\alpha]_D^{19}$ +63° in $CHCl_3$], and a neutral fraction, which after acetylation yields a *substance*, $C_{30}H_{48}O_3$, m.p. 195—205°, clear at ~250°. Oxidation of (III) by BzO_2H affords an *oxide*, $C_{35}H_{56}O_7$, m.p. 233·5—234·5°. Acetylation (Ac_2O–C_5H_5N) of (II) leads to the *Ac_2-acid*, m.p. 249—251°, $[\alpha]_D^{19}$ +59° in $CHCl_3$, which is oxidised (CrO_3–AcOH) to an *acid*, $C_{34}H_{52}O_7$, m.p. 285—286°, esterified (CH_2N_2) to the *Ac_2 Me keto-dihydro-ester*, $C_{35}H_{56}O_7$, m.p. 275—277°, also obtained by oxidation (CrO_3) of (III). Oxidation (CrO_3) of (II) gives a *diketo-acid*, $C_{30}H_{46}O_4$, m.p. 192—194°. Reduction of (I) with 2½% C_5H_{11}·ONa–C_5H_{11}·OH affords an *acid*, $C_{30}H_{46}O_5$, m.p. 240—241° (decomp. on keeping), which is esterified (CH_2N_2) and acetylated to the *Ac Me ester*, $C_{33}H_{50}O_6$, m.p. 179—180·5° (decomp. on keeping). PCl_5 and the OH-compound (IV), $C_{30}H_{44}O_4$, yield a *substance*, $C_{30}H_{42}O_3$, m.p. 295—297° (decomp.). The lactone obtained in small yield from the oxidation products of (IV) is reduced (2½% C_5H_{11}·ONa) to an *acid*, $C_{28}H_{40}O_5$, m.p. 251—253°, which is esterified to the Me ester, also obtained by hydrolysis of the lactone. F. R. S.

Sapogenins.—See B., 1943, III, 280.

VI.—HETEROCYCLIC.

Rubber, polyisoprenes, and allied compounds. V. Chemical linking of rubber and of other olefines with phenol–formaldehyde resins. J. I. Cunneen, E. H. Farmer, and H. P. Koch (*J.C.S.*, 1943, 472—476).—1-Methyl*cyclo*hexene (I) in excess with saligenin (II) at 180° in sealed tubes gives 12-*methyl*-1 : 2 : 3 : 4 : 12 : 13-*hexahydroxanthen*, b.p. 138—139°/10 mm., with a little 5-o-*hydroxybenzyl*-12-*methyl*-1 : 2 : 3 : 4 : 12 : 13-*hexahydroxanthen*. Dihydromyrcene with (II) similarly affords *mono*-, b.p. 118°/0·05 mm. [mainly 2 : 2-*dimethyl*-3-(γ-*methyl*-Δ^γ-*pentenyl*)*chroman*], and *di-saligeninodihydromyrcene*, b.p. 200—205°/0·05 mm. [mainly α-(2 : 2-*dimethylchromanyl*-3)-β-(2 : 3-*dimethylchromanyl*-2)-*ethane*]. When purified rubber (1 mol.) in C_6H_6 is heated with (II) in two different proportions (0·18 and 0·27 mol.) two distinct oxygenated products are formed, containing hydroxylic (presumably phenolic) as well as ethereal O, in the ratios 1 : 2 and 5 : 8, so indicating that most of the O is present in simple chroman units. Sepctrographic measurements confirm the constitutions assigned, and 7 : 12-*dimethyl*-1 : 2 : 3 : 4 : 12 : 13-*hexahydroxanthen*, b.p. 147—150°/10 mm., from (I) and 2 : 5 : 1-OH·C_6H_3Me·CH_2·OH, has been prepared for comparison. The relation of chroman-formation to the formation of PhOH–CH_2O resins is discussed and it is suggested that rubber, isoprenic olefines, and doubtless most olefinic substances combine by virtue of their

unsaturation with the condensation products of PhOH and CH_2O to give chroman derivatives. F. R. S.

Action of Grignard reagents on benzpyrones. I. Preparation of some chromens from 4-substituted coumarins. A. R. S. Kartha and K. N. Menon (*Proc. Indian Acad. Sci.*, 1943, **18, A**, 28—30).—7-Methoxy-4-methylcoumarin (4-methylumbelliferone Me ether) and boiling $MgPhBr–C_6H_6$ give *7-methoxy-2 : 2-diphenyl-4-methyl-Δ³-chromen* [*7-methoxy-2 : 2-diphenyl-4-methyl-1 : 2-benzpyran*] (I), m.p. 60—65°, hydrolysed by boiling 50% aq. KOH to *m-anisyl benzhydryl ether*, m.p. 105·5°. Similarly prepared to (I) are the 2 : 2-*di-p-anisyl*, m.p. 110°, *-dibenzyl*, m.p. 52°, $-(C_{10}H_7\text{-}\alpha)_2$, m.p. 240—241°, and *-Me₂* analogue, b.p. 158—160°/12 mm. α-Naphthocoumarin and MgPhBr give 2 : 2-*diphenyl-4-methyl-α-naphtho-Δ³-chromen*, m.p. 126—127°. A. T. P.

Tetrahydrobenzpyrans.—See A., 1943, II, 342.

Geometrical isomerism of cyclic acetal derivatives from polyhydric nitro-alcohols. M. Senkus (*J. Amer. Chem. Soc.*, 1943, **65**, 1656).—5-Nitro-2-phenyl-5-methyl-1 : 3-dioxan, m.p. 118·3°, obtained from $NO_2·CMe(CH_2·OH)_2$ and PhCHO (A., 1942, II, 111), is accompanied by a *stereoisomeride*, m.p. 78·4°; these are reduced to *amines*, m.p. 84·0° and 48·2°, respectively. $NO_2·CEt(CH_2·OH)_2$ and PrCHO give similarly *5-nitro-, forms*, b.p. 104—106°/5 mm. and 136·0—136·5°/5 mm., reduced to *5-amino-5-ethyl-2-propyl-1 : 3-dioxan, forms*, b.p. 94—95°/10 mm. and 95°/10 mm., respectively. R. S. C.

Vat dyes.—See B., 1943, II, 344.

Preparation of iodine-containing *X*-ray contrast substances. I. 3 : 5-di-iodo-4-pyridone-*N*-acetic acid ("perabrodil"). W. Baker and A. S. Briggs (*J.S.C.I.*, 1943, **63**, 189—191).—C_5H_5N (100 g.), treated with $AlCl_3$ 2 g., $C_2H_2Cl_4$ 100 g., and Br 1 mol. for 48 hr. at 20—25°, gives 4-pyridylpyridinium bromide hydrobromide, the aq. solution of which, after distilling off $C_2H_2Cl_4$, is heated in an autoclave at 150° for 8 hr., made alkaline, and distilled, leaving a solution of 4-pyridone. This solution is boiled with I and made alternately acid and alkaline 6 times during 1 hr., giving 3 : 5-di-iodo-4-pyridone. This is finally pptd. by acid, and heated with aq. NaOH and $CH_2Cl·CO_2H$, giving 3 : 5-di-iodo-4-pyridone-*N*-acetic acid, m.p. ~247° (decomp.) (lit. 246°); yield 107 g. S. A. M.

Indole synthesis from a *m*-carboxyphenylhydrazone. C. F. Koelsch (*J. Org. Chem.*, 1943, **8**, 295—299).—*m*-$NH_2·C_6H_4·CO_2H$, prepared from the NO_2-acid by $(NH_4)_2S$, is best isolated as hydrochloride (I). *m*-$CO_2H·C_6H_4·N_2Cl$ and Et *cyclo*pentanone-2-carboxylate (II) in aq. NaOH give a (?) formazyl compound. Treating (I) in HCl at 0° with, successively, $NaNO_2$, NaOAc, and (II) gives Et 2-*m*-carboxybenzeneazo*cyclo*pentanone-2-carboxylate, sinters 105°, m.p. 118—120° (decomp.), converted by boiling 7% Na_2CO_3 (2 min.) into the *hydrazone*, *m*-$CO_2H·C_6H_4·NH·N{:}C(CO_2Et)·[CH_2]_3·CO_2H$ (≮70%), m.p. 165—167°. In boiling 10% NaOH this gives *α-ketoadipic acid* m-*carboxyphenylhydrazone*, m.p. 215—218° (gas), and in boiling 1 : 10 (vol.) H_2SO_4–EtOH gives *Et₂ α-ketoadipate*-m-*carbethoxyphenylhydrazone*, m.p. 125—127°, which in boiling 1 : 5 (vol.) H_2SO_4–EtOH gives *Et β-2 : 4-* (III), m.p. 105—106°, and *β-2 : 6-dicarbethoxyindole-3-propionate* (IV), m.p. 113°. Structures are proved as follows. CrO_3 in AcOH + a little H_2O at 25—30° oxidises (III) and (IV) to *Et γ-keto-γ-2-(ethyl oxalamido)-6-* (V), m.p. 84—86°, and *-4-carbethoxyphenyl-n-butyrate* (VI), m.p. 97—99°, hydrolysed by H_2SO_4–EtOH to Et γ-keto-γ-2-amino-4- (VII), a colourless oil, and *-6-carbethoxyphenyl-n-butyrate* (VIII), yellow, m.p. 87—88° [Bz derivative, m.p. 86—88°, hydrolysed by alkali to a (?) quinoline derivative, sinters and darkens at 210°], respectively. Hot 10% aq. KOH hydrolyses (VIII) to *γ-keto-γ-2-amino-4-carboxyphenyl-n-butyric acid*, yellow, m.p. 250° (block) or partially in a bath at 215° (resolidifies), but converts (VII) into the corresponding 6-CO_2H-*acid*, sinters 168°, m.p. 180° (gas), with some 1 : 3-*diketo-4-aminohydrindene-2-acetic acid*, sinters 192°, m.p. 202° (decomp.). Alkali converts (VI) into (?) 4-hydroxy-2 : 7-dicarboxyquinoline-3-acetic acid, sinters and darkens at >255°. Alcoholysis of (VI), diazotisation (OBu·NO), and then boiling gives *Et 4-hydroxy-7-carbethoxycinnoline-3-acetate*, m.p. 168–171°; similar treatment of (V) gives *γ-keto-γ-2-ethoxy-6-carboxyphenyl-n-butyric acid*, m.p. 166—168°. Attempted Dieckmann reactions with (III) failed. R. S. C.

Antimalarials. I. Veratrole group. K. C. Frisch and M. T. Bogert (*J. Org. Chem.*, 1943, **8**, 331—337).—3 : 4 : 5 : 1 : 2-$(NO_2)_3C_6H(OMe)_2$, m.p. 143° (lit. 144—145°), obtained from veratrole (room temp.; slowly; then 100°) or 6 : 3 : 4 : 1-$NO_2·C_6H_2(OMe)_2·CHO$ (room temp.) by 1 : 1 conc. HNO_3–conc. H_2SO_4, gives with Sn–conc. HCl at 100° 3 : 4 : 5 : 1 : 2-$(NH_2)_3C_6H(OMe)_2$ (70%), m.p. 150—152° (*picrate*, m.p. 86°). 4 : 5 : 1 : 2-$(NO_2)_2C_6H_2(OMe)_2$ with H_2–Pd-black in EtOH at 3 atm. gives 5 : 1 : 2 : 4-$NO_2·C_6H_2(OMe)_2·NH_2$ (70—75%), but both NO_2 of *o*- and *m*-$C_6H_4(NO_2)_2$ and 2 : 4 : 1-$(NO_2)_2C_6H_3·NH_2$ are reduced. 1 : 2 : 4-$(OMe)_2C_6H_3·NH_2$, similarly obtained from the NO_2-compound, gives by a Skraup reaction 6 : 7-dimethoxyquinoline, b.p. 164°/2·3 mm. [*hydrochloride*, m.p. 222° (uncorr.); *methylmethosulphate*, $+H_2O$, m.p. 232° (decomp.); *methiodide*, m.p. 242° (decomp.)], which with fuming HNO_3 in oleum at 0—10° gives 5 : 8-*dinitro-*, m.p. 155°, reduced by, best, $SnCl_2$–HCl at room temp., to 5 : 8-*diamino-6 : 7-dimethoxyquinoline* (85%), b.p. 170°/0·2 mm. (picrate, m.p. 185—186°; *dihydrochloride*, m.p. 186—187°). With $(CH_2·CO)_2O$, $(CH·CO)_2O$, or *o*-$C_6H_4(CO)_2O$ in boiling $COMe_2$ this gives 5 : 8-*di-succin-*, m.p. 159—160° (decomp.), *-malein-*, m.p. 219—220° (decomp.), or *-phthal-amido-6 : 7-dimethoxyquinoline* (I), m.p. 173—175°, respectively; with $(CH_2·CO)_2O$ at 120° or *o*-$C_6H_4(CO)_2O$ in boiling dioxan it gives 5 : 8-*di-succin-*, m.p. >310° (block; sublimes), and *-phthal-imido-6 : 7-dimethoxyquinoline*, m.p. 236—238° (decomp.; block) [also obtained from (I) in boiling EtOH], respectively, but no dimaleinimide can be obtained. M.p. are corr. R. S. C.

Preparation of iodine-containing contrast substances. III. Structure of "choloselectan." W. Baker, H. Sansbury, and (in part) W. H. C. Simmonds (*J.C.S.I.*, 1943, **63**, 193—194).—*p*-$OH·C_6H_4Ac$ (I) (from PhOAc and $AlCl_3$ in $PhNO_2$), treated with ICl in dil. HCl, gives 4 : 3 : 5 : 1-$OH·C_6H_2I_2·COMe$ (II), which with 5-iodoisatin (III) (from isatin and ICl in boiling AcOH) gives 6 : 3′ : 5′-tri-iodo-4′-hydroxy-2-phenylquinoline-4-carboxylic acid (IV), m.p. 271° (lit., decomp. 215—226°). Refluxing the K salt of (II) with $Cl·[CH_2]_2·OH$ in COMeEt gives 3 : 5 : 4 : 1-$C_6H_2I_2(O·[CH_2]_2·OH)·COMe$ (V), which with (III) gives (IV), m.p. 274°. Reduction of (IV) by 1½ atm. H_2 and Raney Ni gives 4′-hydroxy-2-phenylquinoline-4-carboxylic acid [Ac derivative, m.p. 212—213°, identical with a specimen prepared from isatin and (I)]. (V) is hydrolysed to (II) by KOH–EtOH. Choloselectan (VI) is believed to be very impure (IV), prepared from (V). Since (IV) gives no *X*-ray visualisation of the gall bladder, the reputed effect of (VI) must be due to an impurity. S. A. M.

Nature of the amino-group in aminoacridines. I. Evidence from electrometric studies. A. Albert and R. Goldacre. **II. Evidence from chemical reactions.** A. Albert and B. Ritchie (*J.C.S.*, 1943, 454—458, 458—462).—I. The relative basicities of acridine, 1-, 2-, 3-, 4, and 5-hydroxy-, 1-, 2-, 3-, 4-, and 5-amino-, 1-, 2-, 3-, 4-, and 5-*acetamido-acridine*, m.p. 276° (corr.), 2-, 3-, 4-, and 5-amino-10-methylacridinium hydroxide, 2-*aminoacridine-7-carboxylic acid* (I), decomp. 200°, -7-sulphonic acid, and -7-sulphonamide, are examined, and it is found that the structure of 2- and 5-aminoacridines permits a greater degree of resonance in the ion than occurs in the non-ionised base. Hence, these isomerides show an abnormally high degree of ionisation, an effect that parallels their high biological activity. The properties of the other isomerides suggest that they are fairly normal NH_2-derivatives of acridine. Condensation of 4 : 2 : 1-$NO_2·C_6H_3Cl·CO_2H$ and *p*-$NH_2·C_6H_4·CO_2H$ (Cu–NaOAc) gives *5-nitrodiphenylamine-2 : 4′-dicarboxylic acid*, m.p. 281°, which with $POCl_3$ affords *2-nitroacridone-7-carboxylic acid*, m.p. >360°. Reduction (Al–Hg) of this acid yields the 2-aminoacridan acid, which is oxidised ($FeCl_3$) to (I).

II. Examination of the chemical reactions of the five monoaminoacridines reveals no correlation as striking as that between ionisation and antisepsis. The biologically outstanding isomerides (5-, 2-, and 1-) show the greatest chemical individuality, particularly the first, which behaves distinctively on diazotisation, alkaline hydrolysis, hydrogenation, and reaction with aldehydes and with MeI. Because of the highly electrophilic nature of the acridine nucleus, the NH_2 is readily detached from the salts of all the isomerides by NH_2Ph and by acid at 160°. Condensation with aldehydes gives 1-, m.p. 151°, 3-, m.p. 148° (uncorr.), and 4-*benzylidene-*, m.p. 182°, and 2-*salicylidene-aminoacridine*, m.p. 236°, and 2-*nitrodiphenylamine-2′-aldehyde*, m.p. 120° (uncorr.). 5-Aminoacridine (II) is the only compound which affords a satisfactory product, 5-amino-10-methylacridinium iodide, with MeI. The appropriate acetamidoacridine when methylated (*p*-$C_6H_4Me·SO_3Me$) and treated with HBr gives 2- ($+H_2O$), m.p. 243°, 3-, 4-, m.p. 267° (uncorr.), and 5-*amino-10-methylacridinium bromide*, m.p. ~305° (decomp.). 5-*Amino-5-hydroxy-10-methylacridan*, obtained from the bromide, affords at 130° 5-*imino-10-methylacridan*, m.p. 134—136° (sealed tube). Reduction (fresh $FeCO_3$) of 3-*nitro-5-aminoacridine hydrochloride* leads to 3 : 5-*diaminoacridine*, m.p. 229—230° (sealed tube). 5-Phenoxyacridine with NH_3MeCl and PhOH gives 5-*methylaminoacridine*, m.p. 173—174° (sealed tube); 5-*dimethylaminoacridine hydrochloride*, m.p. 275° (decomp.), is similarly prepared. The two foregoing bases and (II) are hydrolysed (KOH–EtOH) to the OH-compound but not the 1-, 2-, 3-, and 4-NH_2-derivatives; the latter are, however, hydrolysed by HCl [4-*hydroxyacridine*, m.p. 250° (decomp.), and 2-derivative, m.p. 285° (sealed tube)]. Treatment of the amine hydrochloride with NH_2Ph affords 1-, m.p. 191°, 2-, m.p. 238°, 3-, m.p. 236°, 4-, m.p. 220° (decomp.), and 5-*anilinoacridine*, m.p. 230·5°. Hydrogenation affords the corresponding acridans [3-aminoacridan, m.p. 187—188° (lit. 191—192°)]. M.p. are corr. unless otherwise stated. F. R. S.

Basic esters of polynuclear carboxylic acids.—See A., 1944, II, 15.

Hydantoins.—See B., 1943, II, 342.

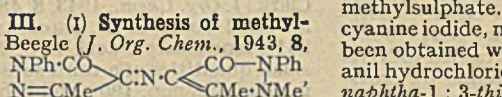
Derivatives of piperazine. XX. Monoalkylation of piperazine by alkylene oxides. L. J. Kitchen and C. B. Pollard (*J. Org. Chem.*, 1943, **8**, 338—341; cf. A., 1941, II, 149).—By use of an excess of piperazine in, *e.g.*, MeOH at 80°, $(CH_2)_2O$, αβ-epoxy-propane and

-*iso*butane give good yields of mono(hydroxyalkyl) compounds. Thus are prepared 1-β-hydroxy-ethyl-, b.p. 119·2°/10 mm. [dihydrochloride, m.p. 188·6—189·6° (lit. 182—183°); picrate, m.p. ~245° (decomp.) (lit. 247—248°); phenylthiocarbamide derivative, m.p. 114·9—115·3°], -*n*-propyl-, b.p. 108·5°/10 mm. [*dihydrochloride*, m.p. ~237·3° (decomp.); picrate, m.p. 174·5—177·5°; phenylthiocarbamide derivative, m.p. 144—144·5°], and -*iso*butyl-, m.p. 80·2—80·5°, b.p. 106°/10 mm. [dihydrochloride, decomp. ~215°, slowly at <215°; picrate, m.p. 257° (decomp.); phenylthiocarbamide derivative, m.p. 129·3—129·5°], and 1 : 4-di-β-hydroxy-ethyl-, m.p. 134·3—150°, -*n*-propyl-, m.p. 116·7—117·9° (lit. 115—116°) [dihydrochloride, m.p. 223·7—224·7° (decomp.)], and -*iso*butyl-piperazine, m.p. 101·5—102·5°, M.p. are corr. R. S. C.

Barbituric acids.—See B., 1943, III, 280.

Cinnolines. II. Influence of substituents on the Widman–Stoermer and the Pschorr reaction. J. C. E. Simpson (*J.C.S.*, 1943, 447—452).—A review of the published evidence respecting cyclisation of diazotised *o*-aminoarylethylenes of type $NH_2{\cdot}C_6H_4{\cdot}\overset{(\alpha)}{C}R{\cdot}CHR'$ leads to the conclusion that the Widman–Stoermer cinnoline synthesis is inhibited when R = H or CO_2H and R′ = aryl or another negative group such as CO_2H, CO_2Et, or CN. It is now shown that the attachment of a Ph group to $C_{(\alpha)}$ is a dominant factor favouring cinnoline formation. The Grignard compound from 1-$C_{10}H_7{\cdot}CH_2Cl$ with *o*-$NH_2{\cdot}C_6H_4{\cdot}COPh$ gives a mixture of $(CH_2{\cdot}C_{10}H_7\text{-}1)_2$, m.p. 161—161·5° (lit. 100°), and *α-phenyl-α-(2-aminophenyl)-β-(1′-naphthyl)-ethylene*, m.p. 182—183°, and its *isomeride* (I), m.p. 144—145°; the intermediate aminocarbinol with Ac_2O affords the *acetamidocarbinol*, m.p. 175—176°. The diazonium solution from (I) with NaOAc and Cu (Pschorr reaction) yields *2-phenylchrysene*, m.p. 192—192·5°, whilst when diluted at room temp. it is cyclised to *4-phenyl-3-(1′-naphthyl)cinnoline*, m.p. 178—179°. $CH_2Ph{\cdot}MgCl$ with *o*-$NH_2{\cdot}C_6H_4{\cdot}COPh$ gives *phenyl-2-aminophenylbenzylcarbinol*, m.p. 150—150·5°, dehydrated (20% H_2SO_4) to *α-(2-aminophenyl)-αβ-diphenylethylenes*, m.p. 113—114° and 102—104° (geometrical isomerides), which are cyclised following diazotisation to 3 : 4-*diphenylcinnoline*, m.p. 149—150°. $Ph{\cdot}[CH_2]_2{\cdot}Br$ similarly affords *phenyl-2-aminophenyl-β-phenylethylcarbinol*, m.p. 97—98° (N-*Ac* derivative, m.p. (68—168·5°), *α-phenyl-α-(2-aminophenyl)-β-benzylethylene*, m.p. 108—109°, and *4-phenyl-3-benzylcinnoline*, m.p. 116·5—118°. Mg allyl bromide with *o*-$NH_2{\cdot}C_6H_4{\cdot}COPh$ gives a mixture of a basic *substance*, $C_{18}H_{17}ON$, m.p. 79—80° [isomerised (5% H_2SO_4) to a *substance*, m.p. 129·5—130·5°], and *phenyl-2-aminophenylallylcarbinol*, m.p. 70—72° (N-*Ac*, m.p. 129—130°, and N-*Bz* derivatives, m.p. 173·5—175°). Condensation ($C_5H_{11}N$) of 1 : 2 : 4-$C_6H_3Me(NO_2)_2$ with furfuraldehyde, piperonal, and vanillin yields *products*, $C_{12}H_8O_5N_2$, m.p. 135—136°, $C_{15}H_{10}O_6N_2$, 179·5—180·5°, and $C_{15}H_{12}O_6N_2$, 191—191·5°, respectively. Reduction of the furfurylidene compound with Fe–AcOH and H_2S–aq. NH_3 affords respectively *α-nitroaminophenyl-β-(2-furyl)ethylenes*, m.p. 130·5—131·5° (N-*Ac* derivative, m.p. 214—215°) and 86—88° (N-*Ac* derivative, m.p. 168·5—169·5°), from the diazo-solutions of which cryst. products could not be obtained. From MgMeI and 5-chloro-2-amino-4′-hydroxy- and -2′-hydroxy-5′-methyl-benzophenone, the corresponding *carbinols*, m.p. 173—174°, and 117—118·5°, have been obtained (cf. Simpson *et al*,. A., 1942, II, 273). F. R. S.

Tetrazole.—See B., 1943, III, 280.

Condensation of aminoantipyrine. III. (I) Synthesis of methylrubazoic acid. E. Emerson and L. C. Beegle (*J. Org. Chem.*, 1943, **8**, 429—432).—*Methylrubazoic acid* (I),  , m.p. 175—176°, is prepared by oxidising an equimol. mixture of aminoantipyrine (II) and 1-phenyl-3-methylpyrazol-5-one or by condensing (I) with 4-keto-1-phenyl-3-methylpyrazol-5-one. The reactions also establish the structures of many of the other coloured products formed in the positive test with (II). Repetition of the work of Pröscher (A., 1902, i, 505) shows that the product described by him as (I) is greatly contaminated by products of high mol. wt. probably due to the nitrosoantipyrine used. H. W.

Properties of *m*-nitrodibenzoylmethane.—See A., 1944, II, 17.

Bacterial chemotherapy. I. Synthesis of N^1-substituted sulphanilamides. II. Synthesis of possible intestinal antiseptics of the sulphanilamide group. III. Synthesis of possible lipophilic chemotherapeuticals of the sulphonamide group. S. Rajagopalan (*Proc. Indian Acad. Sci.*, 1943, **18**, **A**, 100—103, 104—107, 108—112).—I. $NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ is condensed in C_5H_5N with various amines, and the Ac hydrolysed by hot dil. HCl. The following are described, in addition to those mentioned in A., 1942, II, 289: ω-N^4-*acetylsulphanilamidoaceto-phenone*, m.p. 151—152° (decomp.), and -α-*naphthone*, m.p. 202—204° (decomp.); the *hydrochlorides* of ω-*sulphanilamidoaceto-phenone*, m.p. 200—202° (decomp.), and -α-*naphthone*, sinters 185°, m.p. 189° (decomp.); 5-*sulphanilamidobenztriazole*, m.p. 135—137°; 5-N^4-*acetylsulphanilamidoindazole*, m.p. 262° (decomp.); 1-*sulphanilylindole*, m.p. 159° (decomp.) (N^4-*Ac* derivative, m.p. 146—147°); 3-N^4-*acetylsulphanilamidoindotriazine* [-1 : 2 : 4-*triazacarbazole*], m.p. 261—262°. The m.p. of 3-$N^{4'}$-acetylsulphanilamido-1 : 2 : 4-triazole is now given as 210° (decomp.). The following Schiff's bases are prepared by boiling mol. proportions of an aldehyde and a sulphonamide in EtOH until crystals separate: m-*hydroxy-*, m.p. 138°, and o-*nitro-benzylidenesulphanilamide*, m.p. indefinite; o-, m.p. indefinite, and m-*nitrobenzylidenesulphathiazole*, m.p. 220—222° (decomp.); recrystallisation is impossible.

II. Chiefly by the action of alkyl or aralkyl halides or alkyl sulphates on sodio-sulphanilamido-derivatives of heterocyclic compounds, a series of compounds insol. in alkali, therefore not likely to be absorbed in the intestine, and so expected to be particularly useful in infections of the intestinal tract, have been prepared. The following are described: 3-*methyl-*, m.p. 196—198°, and 3-*ethylsulphanilimido*-2 : 3-*dihydrothiazoline*, m.p. 181—182° (decomp.); N^1-*phenyl-*, glassy at 156°, clearing at ~185° (N^4-*Ac* derivative, m.p. 230°), and N^1-*allyl-sulphathiazoline*, softens 187°, m.p. 186—189° (N^4-*Ac* derivative, sinters 176°, m.p. 179—181°); 2-*sulphanilimido-*, m.p. 234° (decomp.) (N^4-*Ac* derivative, m.p. 215—218°), and 2-p-*nitrobenzylaminobenzenesulphonimido*-1-p-*nitrobenzyl*-1 : 2-*dihydropyridine*, m.p. 208—210°; 2-*sulphanilimido*-3-p-*nitrobenzyl-*, m.p. 199—200° (decomp.), and -3-m-*nitrophenacyl*-2 : 3-*dihydrothiazole*, m.p. 238—239° (N^4-*Ac* derivative, m.p. 216—218°).

III. Some members of the sulphonamide group known to be active in coccal infections are acylated, with a view to rendering them lipophilic, and thus useful for mycobacterial infections. By condensing sulphonamides and acyl chlorides in C_5H_5N, the following additional compounds are prepared (cf. A., 1943, II, 144); N^4-n-*octoylsulphapyridine*, m.p. 213—214°; N^4N^1-*diacylsulphapyridines*: acyl = *Ac*, m.p. 194°, n-*butyryl*, m.p. 163°, n-*hexoyl*, m.p. 155—157°, n-*octoyl*, m.p. 135°, *Bz*, m.p. 217°, cyclo*hexoyl*, m.p. 193—195°, *cinnamoyl*, m.p. 196—198°; N^4-*furoylsulphathiazole*, decomp. >240°; N^4-n-*octoylsulphanildimethylamide*, m.p. 79—82°; N^4-n-*hexoyl-*, m.p. 215°. N^4-n-*heptoyl-*, m.p. 173—174°, and N^4-n-*octoyl*-2-*sulphanilimido*-3-*methyl*-2 : 3-*dihydrothiazole*, m.p. 153—154°; N^4-n-*butyryl-*, m.p. 248—250° (decomp.), and N^4-*n*-hexoyl-N^1-*p*-nitrophenylsulphanilamide, m.p. 152° (lit. 225°); N^4-n-*butyryl-*, m.p. 235—236°, and N^4-n-*hexoylsulphanilylsulphanilamide*, m.p. 184—186°; 2-, m.p. 226—228° (decomp.), and 4-$N^{4'}$-*butyrylsulphanilamidobenzoic acid*, m.p. 224—226°. The m.p. of 2-sulphanilamidobenzoic acid is ~215° (decomp.) (lit. 225°), and of its 4-isomeride is 181—182° (lit. 202°, 198—200°). The following are prepared by the action of Me_2SO_4 on aq. alkaline solutions of the corresponding N^1-unsubstituted N^4-acylsulphonamides: 2-N^4-n-*butyryl-*, m.p. 213°, and 2-N^4-n-*hexoyl-sulphanilimido*-1-*methyl*-1 : 2-*dihydropyridine*, m.p. 213—215°; 2-N^4-n-*hexoyl-*, m.p. 201—203°, and 2-N^4-n-*heptoylsulphanilimido*-3-*methyl*-2 : 3-*dihydrolthiazoline*, m.p. 170°. S. A. M.

Photographic products.—See B., 1943, II, 400.

Thiazinocyanines. III. Carbocyanines containing the *peri*-naphtha-1 : 3-thiazine nucleus. (Miss) F. M. Hamer and R. J. Rathbone (*J.C.S.*, 1943, 487—491).—The observations of Joy *et al.* (A., 1937, II, 37) have been confirmed. 2-Methyl*peri*naphtha-1 : 3-thiazine methiodide (I), m.p. 177° (decomp.) [lit. m.p. 222—230° (decomp.)], with $CH(OEt)_3$ in C_5H_5N gives bis-2-(3-methyl-*peri*naphtha-1 : 3-thiazine)trimethincyanine iodide, m.p. 223° (decomp.), without $CHCl_3$ of crystallisation; the *methosulphate*, m.p. 232° (decomp.), is similarly obtained from the corresponding methomethylsulphate. Bis-2-(3-ethyl*peri*naphtha-1 : 3-thiazine)trimethincyanine iodide, m.p. 212° (decomp.) [lit. m.p. 243° (decomp.)], has also been obtained without $CHCl_3$ of crystallation. β-Anilinoacraldehyde anil hydrochloride and (I) with KOAc–Ac_2O give *bis*-2-(3-*methyl*peri-*naphtha*-1 : 3-*thiazine*)*pentamethincyanine iodide*, m.p. 183° (decomp.). 2-Methyl*peri*naphtha-1 : 3-thiazine (II) and 2-β-acetanilidovinylbenzoxazole ethiodide at 125° afford *trimethin*[2-(3-*ethyldihydrobenzoxazole*)][2-(peri*naphtha*-1 : 3-*thiazine*)], m.p. 165—168° (decomp.) [*hydrochloride*, m.p. 200° (decomp.)]. By condensing (II) with the appropriate reagent, the following are obtained: *trimethin*[2-(3-*ethyldihydro*-4 : 5-, m.p. 190° (decomp.), and -6 : 7-*benzbenzoxazole*)]-, m.p. 155° (decomp.), -*benzthiazole*)], m.p. 196° (decomp.), -4 : 5-, m.p. 215° (decomp.), and -6 : 7-*benzbenzthiazole*)]-[2-(peri*naphtha*-1 : 3-*thiazine*)], m.p. 212° (decomp.) [*hydrochloride*, m.p. 218° (decomp.)]. 2-(3-*Ethylbenzoxazole*)][2-(3-*methyl-*, m.p. 202° (decomp.), and -*ethyl*-peri*naphtha*-1 : 3-*thiazine*)]*trimethincyanine iodide*, m.p. 173° (decomp.), are obtained from the carbocyanine with MeI and EtI respectively. 2-p-*Dimethylaminostyrylperinaphtha*-1 : 3-*diazine*, m.p. 213° (decomp.), its *hydriodide*, m.p. 235—240° (decomp.), and *methomethylsulphate*, m.p. 116° (decomp.), are obtained from *p*-$NMe_2{\cdot}C_6H_4{\cdot}CHO$ and (II) or its appropriate derivative. The carbocyanines and dicarbocyanine from (II) are abnormal in being decolorised by alkali. Absorption data for MeOH solutions of the dyes are recorded and comparisons made with the dihydro-1 : 3-thiazine, 2 : 4-benzthiazine, and naphthathiazole series. F. R. S.

VII.—ALKALOIDS.

Senecio **alkaloids. I. Rosmarinine.** (Miss) M. F. Richardson and F. L. Warren (*J.C.S.*, 1943, 452—454).—Rosmarinine (I), isol-

ated originally from *S. rosmarinifolius*, Linn., has now been found in other species. *S. hygrophilus*, R. A. Dyer and C. A. Sm., is con-sp. with "*S. adnatus*," DC., but the alkaloid content varies; (I), platyphylline, and an *alkaloid*, $C_{18}H_{27}O_6N$, m.p. 175—176° (corr.), $[\alpha]_D^{25}$ −62·4° in MeOH, have been isolated as sole constituents or as mixtures, depending on stage of growth, season, and (South African) district. Hydrolysis of (I) gives *rosmarinecine*, $C_8H_{15}O_3N$ (probably 3′ : 4-dihydroxy-3-hydroxymethylpyrrolizidine), m.p. 171—172° (corr.), $[\alpha]_D^{25}$ −118·5° [*methiodide*, m.p. 195° (corr.)], and *senecic acid*, m.p. 151° (corr.), $[\alpha]_D^{25}$ +11·8° in EtOH, neither compound having previously been obtained cryst. Platynecic acid is senecic acid lactone. F. R. S.

Curare alkaloids from *Chondrodendron tomentosum*.—See A., 1944, III, 88.

VIII.—ORGANO-METALLIC COMPOUNDS.

Diazonium borofluorides. IV. Preparation of copper aryl compounds. F. A. Bolth, W. M. Whaley, and E. B. Starkey (*J. Amer. Chem. Soc.*, 1943, **65**, 1456—1457; cf. A., 1942, II, 336).—The reaction, $ArN_2{\cdot}BF_4 + 2Cu \rightarrow CuAr + N_2 + CuF + BF_3$, is realised for Ar = Ph, *p*- and *o*-$NO_2{\cdot}C_6H_4$, and *p*-tolyl in C_6H_6 or PhMe at ~70—85°. For CuPh and $Cu{\cdot}C_6H_4Me$-*p* (I) analysis of the solution shows yields of CuAr to be 4—8% and 30—35%, respectively. CuPh and (I) do not react with Michler's ketone. CuPh, but not (I), reacts with BuBr in C_6H_6 or PhMe. Cu aryls are hydrolysed at once by moisture and with solid CO_2 give amorphous compounds which react at once with air. They are pptd., probably as complexes, by dioxan or Et_2O. C_5H_5N ppts. *Cu Ph* and p-*nitrophenyl tripyridine* (II), which are blue and stable in air, even at 110°, but in boiling H_2O Cu is pptd. from (II). CuPh and $Cu{\cdot}C_6H_4{\cdot}NO_2$-*o* with $CH_2Cl{\cdot}COCl$ give good yields of $CH_2Cl{\cdot}COAr$. The significance of these results for various diazonium reactions is noted. R. S. C.

Solvents in organometallic chemistry. A. H. Haubein (*Iowa State Coll. J. Sci.*, 1943, **18**, 48—50; cf. C., 1944, Part 1).—The orders of stability of LiR compounds in Et_2O and of R_2O compounds in presence of LiBu, $LiBu^{\gamma}$, and Li·CHMeEt were determined by difference between the total and inorg. base formed on hydrolysis. Cleavage by Li compounds of ethers containing $NR_2{\cdot}CH_2{\cdot}$ can be used to introduce this group into a large no. of mols. F. R. G.

Mercurated aliphatic nitriles.—See B., 1943, III, 280.

Selenium compounds.—See B., 1943, II, 343.

Borohydrides of gallium.—See A., 1944, I, 22.

IX.—PROTEINS.

Nature of formaldehyde compounds of proteins. K. H. Gustavson (*Kolloid-Z.*, 1943, **103**, 43—54).—The tanning effect of CH_2O on proteins is discussed. Fibrous proteins, *e.g.*, collagen (I), are more easily studied than H_2O-sol. proteins, since they have measurable properties altered by CH_2O treatment. Properties studied are temp. of contraction, swelling in H_2O, and degradation by trypsin. In dil. CH_2O solutions irreversible CH_2O fixation is due to the ε-NH_2-groups of lysine in the pH range 5—8, and the NH_2-groups of arginine at pH >8. In conc. solutions secondary reactions occur. CH_2O combines with partly deaminated (I) freed from primary NH_2 groups, but does not have a tanning effect. Thus the CH_2O attached to NH_2-groups of arginine residues does not stabilise (I) chains by cross-linking; tanning by CH_2O results from formation of cross-linkings between ε-NH_2-groups of lysine in neighbouring chains. In acid solutions native (I) shows a tanning effect at high CH_2O concn., but deaminated (I) is unchanged. CH_2O fixation is a slow reaction in this case. CH_2O is also taken up by peptide groups, but is not then involved in cross-linking and stabilising the structure. CH_2O is also effective in org. solvents. R. H. F.

Complex formation between synthetic detergents and proteins. F. W. Putnam and H. Neurath (*J. Biol. Chem.*, 1943, **150**, 263—264; cf. Lundgren *et al.*, A., 1943, III, 838).—Cryst. horse serum-albumin is pptd. on the acid side (complex formation but no pptn. occurs on the alkaline side) of the isoelectric point by Na dodecyl sulphate (I) when the ratio of protein to (I) ranges from 5 : 1 to 2·5 : 1, all the (I) being bound by the protein. Excess of (I) causes dissolution of the pptd. complex, but protein recovered from the solution does not differ in solubility and electrophoretic properties from that recovered from the ppt. The max. concn. of (I) required for complete pptn. (144 mols. per g. of protein × 10^5) corresponds closely with the total acid-binding capacity of the protein. Protein recovered from the complex after removal of detergent with $BaCl_2$ is electrophoretically homogeneous but the hydrodynamic vol. is diminished to 75% of the original val. and the mobility at pH 7·6 is increased slightly. Measurements of viscosity show that denaturation occurs on both sides of the isoelectric point. The denaturing power of (I) is ≫ that of $CO(NH_2)_2$ or guanidine. W. McC.

Constitution of proteins. Demonstration [of the presence] of porphyrin complexes, pyridine rings, and elementary [characteristic ?] complexes. N. Troensegaard (5 *Nordiske Kemikermøde*, 1939, 232).—Proteins are acetylated and/or hydrogenated in H_2O-free solvents (no details) to protect them during hydrolysis. The product is hydrolysed in the cold, giving acidic and basic fractions, the latter containing piperazines, pyrroles, and (from some proteins) piperidine. The acid fraction contains complexes characteristic of the original protein: gliadin gives $C_{10}H_{14}O_3N_2$ or $C_{10}H_{12}O_3N_2$. M. H. M. A.

Coloured metallic complexes of keratin and fibroin. B. Nilssen (5 *Nordiske Kemikermøde*, 1939, 234—236).—The coloration given with HNO_3 and keratin or fibroin is due to conversion of tyrosine residues into *o*-quinonemonoxime residues which give lakes with heavy metals. M. H. M. A.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Crystalline barium acid heparinate. M. L. Wolfrom, D. I. Weisblat, R. J. Morris, C. D. DeWalt, J. V. Karabinos, and J. McLean (*Science*, 1943, **97**, 450).—The following molar ratios were established: anhydrohexosamine : anhydrohexuronic acid : SO_3 : Ba = 2·0 : 1·9 : 6·0 : 3·0; N : S : Ba = 2 : 6 : 3. Summation of these data (89%) does not preclude the possible presence of another constituent. *d*-Glucosamine, the NH_2-group of which is not acetylated and not free, was identified in the hydrolysate of the acid Ba salt. Repeated crystallisation from warm, dil. AcOH destroys the anticoagulant power, and is accompanied by the appearance of a free NH_2-group. Prolonged drying and dil. H_2O_2 also inactivate the salt. E. R. R.

Derivatives of lonchocarpic acid. H. A. Jones and H. L. Haller (*J. Org. Chem.*, 1943, **8**, 493—496).—In spite of their closely related origin, no close relationship exists between lonchocarpic acid (I) and rotenone (II). It is quite probable that the characteristic chroman-chromanone system present in (II) is absent from (I). (I), obtained from an unknown species of *Lonchocarpus*, has usually m.p. 203—204° (corr.) when cryst. from EtOAc and 220—221° (corr.) when cryst. from EtOH. It is converted by NaOAc and boiling Ac_2O into *diacetyl-lonchocarpic acid*, m.p. 154°, which is insol. in aq. alkali and when hydrolysed by alkali gives (I), alkali-insol. material, and alkali-sol. resin whereas it affords an unpurified product with KOAc in abs. EtOH. It is indifferent towards CH_2N_2 in MeOH or Et_2O. Methylation of (I) by CH_2N_2 in Et_2O gives *methyl-lonchocarpic acid*, m.p. 210—212°, whereas in MeOH the product is *dimethyl-lonchocarpic acid*, m.p. 150—151°; both products are insol. in alkali and do not yield an alkali-sol. product when hydrolysed by KOH–MeOH. Me_2SO_4 appears to give a mixture of mono- and di-acid. Catalytic hydrogenation (PtO_2 in EtOH) of (I) leads to *tetrahydrolonchocarpic acid*, m.p. 239—240° (*diacetate*, m.p. 192—192·5°; Me_1, m.p. 211—212·5°, and Me_2, m.p. 166—167°, derivatives). Oxidation of (I) by I in EtOH containing KOAc does not give a recognisable product, whereas *p*-$OH{\cdot}C_6H_4{\cdot}CO_2H$ is obtained in ~25% yield by use of H_2O_2 in alkaline solution. PCl_5 and $SOCl_2$ do not react with (I). H. W.

Scandenin, a constituent of the roots of *Derris scandens*. E. P. Clark (*J. Org. Chem.*, 1943, **8**, 489—492).—Extraction of the powdered air-dried roots of *D. scandens* gives *scandenin* (I), $C_{26}H_{28}O_6$, m.p. 231°, lonchocarpic acid, m.p. 223° (corr.), softens at 200—205°, and small quantities of a third substance which by reason of its solubility in alkali, its m.p. 190°, and behaviour in the Durham test is regarded as robustic acid. Rotenone is not observed and the substances isolated do not appear to belong to the rotenone group of fish poisons. (I) contains 1 OMe and 2 OH since it readily gives a *diacetate*, m.p. 150°, and is converted by CH_2N_2 into a *Me_2 ether*, m.p. 129°, in poor yield. Although an oxime or semicarbazone could not be obtained it probably contains a *p*-$OH{\cdot}C_6H_4{\cdot}CO$ since it gives the corresponding acid when oxidised by alkaline H_2O_2. It absorbs ~3 mols. of H_2 when hydrogenated in EtOH containing PtO_2. It is somewhat acidic, dissolving in dil. alkalis. It gives a relatively sparingly sol. Na and K salt. It fails to give the reaction for a 2 : 2-dimethyl-Δ^3-chromene system.

Helvolic acids $C_{32}H_{44}O_8$, m.p. 212°, $[\alpha]_D^{20}$ −49·4° in $CHCl_3$ (Me ester, m.p. 261°).—See A., 1943, III, 917.

Aspergillic acid, $C_{12}H_{20}O_2N_2$.—See A., 1943, III, 916.

***X*-Ray diffraction data on ferritin and *apo*ferritin.**—See A., 1944, I, 5.

XI.—ANALYSIS.

Spectrophotometric analysis of multicomponent mixtures.—See A., 1943, I, 319.

For abstracts on analysis, see C., 1944, Part 1.

INDEX OF AUTHORS' NAMES, A II.

JANUARY, 1944.

ERRATA.

Abstracts A II, 1943.

Column	Line	
353	26	*For* (II) *read* (I).
357	10	*For* (II) *read* (III).
	12	*After* "isohellebrinate" *insert* (IV).
364	25	*After* "-anisyl-" *insert* "Δ".
393		*The formula for "flavazole" should have a double linking between N and* $C_{(3)}$.

Author Index, December, *add* R. R. Davies, 365. Also to H. H. Hodgson *add* 365.

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