BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

AUGUST, 1944

A II—ORGANIC CHEMISTRY

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(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.)

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A II—Organic Chemistry.

AUGUST, 1944.

I.—ALIPHATIC.

Cinchona alkaloids. VI. Configuration of (−)-γ-methyl-δ-ethylhexane. V. Prelog and E. Zalán (*Helv. Chim. Acta*, 1944, **27**, 545—547).—The configuration (*A*) is established for (−)-γ-methyl-δ-ethylhexane (**I**) by its prep. from (−)-CHMeEt·CO_2Me. (−)-CHMeEt·CO_2H, b.p. 71—72°/12 mm., $[\alpha]_D^{17}$ −17·35°±0·05°, is converted by CH_2N_2 into the *Me* ester, b.p. 108—112°/730 mm., $[\alpha]_D^{15}$ −19·42°±0·05°, which with MgEtBr in Et_2O affords (+)-*γ-methyl-δ-ethylhexan-δ-ol*, b.p. 63—65°/11 mm., $[\alpha]_D^{16}$ +17·1°±0·05°. This is dehydrated by anhyd. $H_2C_2O_4$ to the corresponding hexene, which is hydrogenated (PtO_2 in AcOH) to (**I**), b.p. 155—162° (bath), $[\alpha]_D^{19}$ −3·18°±0·05°. H. W.

Et·CH·Et
H·C·Me
Et (*A*.)

Polymerisation of *iso*butene on hydrated silicate catalysts.—See A., 1944, I, 180.

Diolefines from allylic chlorides. II. A. L. Henne and H. H. Chanan (*J. Amer. Chem. Soc.*, 1944, **66**, 392—394; cf. A., 1942, II, 126).—Treating 1 : 1 mixtures of (*a*) CH_2:CH·CH_2Cl, CH_2:CMe·CH_2Cl, or butadiene hydrochloride and (*b*) piperylene hydrochloride or isoprene hydrochloride with Mg in Et_2O gives diolefines in which the *as.* product predominates. Compositions are determined by fractionation. Structures are proved by reduction and ozonolysis. The following are new: *δ-methyl-*$\Delta^{\alpha\epsilon}$*-heptadiene*, b.p. 110·3°; *δε-dimethyl-*$\Delta^{\beta\zeta}$*-octadiene*, m.p. −64·8°, b.p. 153·3°; *βδ-*, b.p. 132·1°, and *γδ-dimethyl-*$\Delta^{\alpha\epsilon}$*-n-heptadiene*, b.p. 129·8°; *γγ-dimethyl-*$\Delta^{\alpha\epsilon}$*-n-hexadiene*, b.p. 101·6°; *β-methyl-*$\Delta^{\beta\zeta}$*-n-heptadiene*, b.p. 119·1°; *γγζ-trimethyl-*$\Delta^{\alpha\epsilon}$*-n-heptadiene*, b.p. 149·7°; *βη-dimethyl-*$\Delta^{\beta\zeta}$*-n-octadiene*, m.p. −74·4°, b.p. 168·6°; *βδδ-trimethyl-*$\Delta^{\alpha\epsilon}$*-n-hexadiene*, b.p. 126·3°; *βζ-dimethyl-*$\Delta^{\alpha\epsilon}$*-n-heptadiene*, m.p. −102·7°, b.p. 141·9°; *βε-dimethyl-*$\Delta^{\beta\zeta}$*-n-heptadiene*, b.p. 134·6°; *δε-dimethyl-n-octane*, b.p. 162·4°; *γδ-dimethyl-*, b.p. 140·1°, and *βεε-trimethyl-n-heptane*, b.p. 152·8°; γ-keto-α-methyl-*n*-valeric acid semicarbazone, m.p. 178° (lit. 191°, 182°). B.p. are corr. R. S. C.

Conjugated diolefines by double bond displacement. II. A. L. Henne and H. H. Chanan (*J. Amer. Chem. Soc.*, 1944, **66**, 395—396; cf. A., 1942, II, 294).—Conversion of unconjugated into conjugated dienes in presence of Al_2O_3 is greatly improved by including 5 mol.-% of Cr_2O_3 in the catalyst (prep.: Grosse *et al.*, B., 1940, II, 260). The optimum temp. is 250°. The catalyst is gradually impaired by deposition of C but is regenerated by heating at 450°, first in air and then in H_2, but repeated treatment impairs the efficiency. $(CH_2$:CH·$CH_2)_2$ gives $(CHMe$:$CH)_2$ (76·7%). $(CH_2$:CMe·$CH_2)_2$ gives $(CMe_2$:$CH)_2$ (85·5%). CH_2:CH·CHMe·CH_2·CH:CHMe gives CHMe:CH·CH:CMeEt (73·1%). CH_2:CH·CH_2·CHMe·CH:CHMe gives CHMe:CH·CMe:CHEt (37·1%), b.p. 135·9°. CH_2:CH·$[CHMe]_2$·CH:CHMe gives CHMe:CH·CMe:CMeEt (22·6%), b.p. 156·5°. CH_2:CH·$[CH_2]_2$·CH:CMe_2 gives CHEt:CH·CH:CMe_2 (54·4%), m.p. −96·4°, b.p. 135·8°. CH_2:CH·CHMe·CH_2·CH:CMe_2 gives CMeEt:CH·CH:CMe_2 (48·9%), m.p. −63·1°, b.p. 156·9°. CH_2:CMe·CH_2·CHMe·CH:CHMe, CHMe:CH·$[CHMe]_2$·CH:CHMe, CH_2:CH·CMe_2·CH_2·CH:CMe_2, CMe_2:CH·$[CH_2]_2$·CH:CMe_2, and CH_2:CMe·$[CH_2]_2$·CH:CMe_2 are not thus rearranged. R. S. C.

Kinetics and mechanism of thermal polymerisation of acetylene and its reaction with nitric oxide. Mercury-photosensitised polymerisation of acetylene.—See A., 1944, I, 179, 180.

Dehydrochlorination of γ-chloro-Δ$^{\beta}$-propen-α-ol. Preparation of propargyl alcohol. L. F. Hatch and A. C. Moore (*J. Amer. Chem. Soc.*, 1944, **66**, 285—287).—The *α-* and *β-*forms of CH$_2$Cl·CH:CHCl in boiling 10% Na_2CO_3 give the *α-* (**I**), b.p. 146·3°/746 mm., and *β-forms* (**II**), b.p. 153·6°/756 mm., respectively, of *γ-chloro-*Δ$^{\beta}$*-propen-α-ol*. Up to 69·3% of CH:C·CH_2·OH is obtained from (**I**) by 10% NaOH, but (**II**) is unaffected except by >10% alkali, which causes resinification. R. S. C.

Optically active phytol. II. P. Karrer, H. Simon, and E. Z. Binden (*Helv. Chim. Acta*, 1944, **27**, 313—316; cf. A., 1944, II, 31).—The conversion of phytols (**I**) into phytadienes is accompanied by marked increase in optical activity and the products derived from (**I**) of differing dextrorotatory power or apparent optical inactivity have approx. the same rotation. Possibly (**I**) in spite of repeated fractionation retains a lævorotatory impurity which more or less compensates the dextrorotation of (**I**) or, more probably, pure natural (**I**) has an immeasurably small optical activity and the dextrorotation of many distilled specimens is due to a difficultly removable, dextrorotatory impurity (unidentified). At any rate it is established that natural (**I**) is not a racemate but an actual or latent optically active compound. Synthetic *l*-phytol (**II**) yields a *l*-phytadiene which has only slightly greater optical activity than the initial material and is much less active than the *d*-compound from natural (**I**). (**II**) and (**I**) are not therefore optical antipodes; (**I**) is probably racemic with respect to $C_{(\eta)}$. Distinction is drawn between: natural *d*-phytol (sterically homogeneous with respect to both asymmetric C atoms and probably having immeasurably small [α]) and *d*-phytadiene; synthetic *l*-phytol, sterically homogeneous with respect to $C_{(\lambda)}$ and racemic at $C_{(\eta)}$ and synthetic *l*-phytadiene; synthetic *dl*-phytol, racemic in respect of both asymmetric C atoms, and optically inactive and synthetic *dl*-phytadiene. H. W.

Lead tetra-acetate oxidations in the sugar group. V. Rates of oxidation of open-chain polyalcohols in dry acetic acid. R. C. Hockett, (Miss) M. T. Dienes, H. G. Fletcher, jun., and H. E. Ramsden. **VI. Structures of di- and tri-benzoates of *D*-sorbitol and *D*-mannitol.** R. C. Hockett and H. G. Fletcher, jun. (*J. Amer. Chem. Soc.*, 1944, **66**, 467—468, 469—472; cf. A., 1944, II, 7).—V. Under standard conditions, the rate of oxidation of polyhydric alcohols, rapid at first and then slower, is independent of configuration but dependent on the no. of CH·OH in unbroken series. An empirical rule enables the no. of *vic.* CH·OH to be determined; reaction is not stoicheiometric as HCO_2H formed reduces more $Pb(OAc)_4$. The diacetamides of *D*-threose, -erythrose, -arabinose, and -lyxose behave similarly.

VI. Oxidation of *D*-sorbitol αζ-dibenzoate by $Pb(OAc)_4$ closely resembles that of erythritol and gives no CH_2O, which proves its structure. The structure of the *αβζ*-tribenzoate is similarly confirmed by consumption of 2 $Pb(OAc)_4$ without formation of HCO_2H. *D*-Sorbitol and BzCl in C_5H_5N at 20° give an *αβ*-dibenzoate and a small amount of *αβζ-tribenzoate* (**I**), m.p. 147·7—148·3° (corr.), $[\alpha]_D^{24\cdot8}$ −11·1° in $CHCl_3$. The structure of (**I**) is proved by consumption of 2 $Pb(OAc)_4$ and formation of *L*-OBz·CH_2·CH(OBz)·CHO and no CH_2O. R. S. C.

Structure of styracitol. R. C. Hockett and (Miss) M. Conley (*J. Amer. Chem. Soc.*, 1944, **66**, 464—466).—The structure of styracitol (**I**) as αε-anhydro-*D*-mannitol (A., 1944, II, 7) is confirmed. Hydroxyglucal tetra-acetate (**II**) with H_2–PtO_2 in AcOH at 23 lb., falling to ~45 lb., and then NaOMe–MeOH at 70° gives (**I**) (57%), m.p. 154—155°, $[\alpha]_D^{20}$ −50·9° in H_2O. Hydrogenation of (**II**) in MeOH and then boiling gives mainly a syrup, $[\alpha]_D^{20}$ +37·1° in EtOH, with only a trace of (**I**). Treating (**I**) with $Pb(OAc)_4$–$CHCl_3$ and then Br–$SrCO_3$–H_2O gives Sr *D*-hydroxymethyldiglycollate (44%). The Me_4 ether, b.p. 88—93°/2 mm., $[\alpha]_D^{20}$ −35·0° (homogeneous), with conc. HNO_3 at 100° gives *l*-(OMe·CH·CO_2H)$_2$ (cf. Asahina *et al.*, A., 1931, 1033), isolated as Me_2 ester and diamide. (**I**) gives a m-*nitrobenzylidene* derivative, m.p. 175—175·5°. R. S. C.

Stereochemistry of methylbixin. L. Zechmeister and R. B. Escue (*J. Amer. Chem. Soc.*, 1944, **66**, 322—330).—The methylbixins (photomicrographs) corresponding sterically to naturally occurring and *β*-bixin are termed "natural" (**I**), m.p. 161—161·5° (corr.), and "all-*trans*"-methylbixin (**II**), m.p. 198° (corr.), respectively. Isomerisation, followed by chromatography, yields also neomethylbixin *A*, m.p. 190—192° (corr.) (photomicrograph), *B*, and *C*, m.p. 150—151° (corr.) (photomicrograph). Light is needed for development of a *cis*-peak. Chromatograms and adsorption data are recorded for products obtained from each isomeride (except *B*) by melting, keeping, refluxing, or irradiating in light petroleum, or treating with I. (**II**) is very stable to light, and (**I**) nearly as stable, but *A* and *C* are more photosensitive. The changes, (**I**) ⇌ *C* and (**II**) ⇌ *A*, are readily achieved, but the interconversion, (**I**) ⇌ (**II**), is very slow. The following configurations are probable: *A* 5-*cis*, (**I**) 2-*cis*, *C* 2 : 5-di-*cis*, and *B* x-*cis*. R. S. C.

Use of trimethyl phosphate as a methylating agent. A. D. F. Toy (*J. Amer. Chem. Soc.*, 1944, **66**, 499).—52·7—69·5% yields of ROMe are obtained by heating Me_3PO_4 with AlkOH at or just below the b.p., provided that this is ⩽160°. $(CH_2$·OH)$_2$ gives 37·2% of the Me_1 ether. An excess of Me_3PO_4 increases the yield. Some olefine

and mixed alkyl H phosphates are formed. *Me β-ethyl*-n-*hexyl*, b.p. 159—160°, and *β-heptyl ether*, b.p. 139—140°, are described. R. S. C.

Preparation of calcium and sodium formate.—See A., 1944, I, 182.

Alkyl exchange of carboxylic esters.—See A., 1944, II, 220.

Unsaturated synthetic glycerides. B. F. Daubert and H. E. Longenecker (*Oil and Soap*, 1944, **21**, 42—46).—Previous literature and recent work by the authors and collaborators (cf. A., 1944, II, 120) on the synthesis, by modern methods, and properties of mixed unsaturated–saturated glycerides of known configuration are reviewed, and graphs are given showing the m.p. and n_D of various series, viz., (*a*) unsymmetrical and (*b*) symmetrical mono-oleyl-disaturated (C_{16-18}) triglycerides; (*c*) unsymmetrical dioleyl-monosaturated triglycerides, (*d*) unsaturated–saturated symmetrical mixed diglycerides. In each series the m.p. of the corresponding products obtained by hydrogenation of the unsaturated glycerides are shown for comparison. All synthetic unsaturated glycerides show anomalous results in cryoscopic determinations (in C_6H_6) of mol. wt., the apparent mol. wt. decreasing with increasing concn., so that extrapolation to zero concn. is necessary in order to obtain true mol. wts. E. L.

Unsaturated synthetic glycerides. IV. Symmetrical mono-oleo-disaturated triglycerides. F. L. Jackson, B. F. Daubert, C. G. King, and H. E. Longenecker. **V. Unsymmetrical monoelaidyl-disaturated and monosaturated-dielaidyl triglycerides.** B. F. Daubert (*J. Amer. Chem. Soc.*, 1944, **66**, 289—290, 290—292; cf. A., 1944, II, 120).—IV. OH·CH_2·CH(OH)·CH_2·O·CPh_3 with RCOCl (R = saturated alkyl) in $CHCl_3$–C_5H_5N at 0° and then HCl–light petroleum at 0° gives the αγ-diesters, which with oleyl chloride in $CHCl_3$–quinoline at 100° give *glyceryl αγ-diacylate β-oleate*, in which the acyl is *n*-decoate, m.p. 5—6°, *n*-dodecoate, m.p. 14·5—15°, *n*-tetradecoate, m.p. 26—27°, palmitate, m.p. 35·5—36°, and stearate, m.p. 42·5—43°. Structures are confirmed by hydrogenation to fully saturated glycerides.

V. α-Monoelaidin, *forms*, m.p. 58·5°, 44·0°, and 17·6° (cf. Bömer *et al.*, A., 1937, II, 439), is obtained from *iso*propylideneglycerol by (*a*) *elaidyl chloride* (I) [prep. by $(COCl)_2$ at 70—80°], b.p. 168—170°/1 mm., in $CHCl_3$–quinoline and then HCl–Et_2O or (*b*) HCl–elaidic acid and then Et_2O–conc. aq. HCl. With saturated acyl chlorides in $CHCl_3$–quinoline it gives *glyceryl βγ-diacylate α-elaidate*, in which the acyl is *n*-tetradecoate, m.p. 39·5°, *n*-dodecoate, m.p. 27·0°, *n*-decoate, m.p. 15·0°, and *n*-octoate, m.p. 3·0°. α-Monomyristin and (I) in $CHCl_3$–quinoline give *glyceryl α-acylate βγ-dielaidate*, in which the acyl is *n*-tetradecoate, m.p. 40·0°, *n*-dodecoate, m.p. 35·5°, and *n*-decoate, m.p. 25·0°. Structures are proved by hydrogenation. *Glyceryl βγ-di*-n-*octoate α-stearate*, m.p. 31·5°, is prepared also solely from saturated acids. R. S. C.

Synthesis of cetyl esters.—See A., 1944, II, 228.

Preparation of unsaturated fatty acid chlorides. T. R. Wood, F. L. Jackson, A. R. Baldwin, and H. E. Longenecker (*J. Amer. Chem. Soc.*, 1944, **66**, 287—289).—Oleic, elaidic, linoleic, and linolenic acids are converted by boiling $(COCl)_2$ into their *acid chlorides*, which are shown by their absorption spectra to contain >1% of conjugated material. Use of $SOCl_2$ is unsatisfactory. R. S. C.

Autoxidation reactions in polyisoprenes and allied compounds. VIII. Photo-oxidation of methyl elaidate. D. A. Sutton (*J.C.S.*, 1944, 242—243).—In ultra-violet light Me elaidate at 35° absorbs O_2 (0·2 mol.) to form a hydroperoxide, which on hydrogenation and hydrolysis followed by acetylation and fractional crystallisation gives a monohydroxystearic acid, m.p. 79°, and a OH-acid, m.p. 30—50°. D. G.

Condensations. XXII. Alkylation of *iso*propylmalonic ester using sodium triphenylmethide. J. C. Shivers, B. E. Hudson, jun., and C. R. Hauser (*J. Amer. Chem. Soc.*, 1944, **66**, 309; cf. A., 1944, II, 120).—Adding CPh_3Na and then EtI to $CHPr^{\beta}(CO_2Et)_2$ in Et_2O–N_2, keeping for 7 days, decanting, removing the Et_2O, and boiling the residue with EtI in C_6H_6 gives 73% of $CEtPr^{\beta}(CO_2Et)_2$, b.p. 234—236°/760 mm., 118—120°/15 mm., converted by KOH–EtOH and then decarboxylation into $CHEtPr^{\beta}\cdot CO_2H$ (48%), b.p. 104—105°/15 mm. (*anilide*, m.p. 118—119°). Use of $Pr^{\beta}I$ in C_6H_6–N_2 gives *Et₂ diisopropylmalonate* (23%), b.p. 122—124°/15 mm., converted by boiling KOH–EtOH in 18—24 hr. into the *Et H* ester, m.p. 71—72°, which is slowly decarboxylated by heat to give *Et β-methyl-α-*iso*propyl*-n-*butyrate*, b.p. 71—72°/15 mm. R. S. C.

Colour reactions of ascorbic acid.—See A., 1944, III, 488.

Ketones, ketonic acids, and enol-lactones. III. Enol-lactone fission. New preparation of esters of β-ketonic and ββ′-diketonic acids which are also αδ-diketones. P. Ruggli and A. Maeder (*Helv. Chim. Acta*, 1944, **27**, 436—443; cf. A., 1943, II, 351).—Et_2 butanolidenemalonate, $\begin{matrix}CH_2\cdot CH_2\\ CO\text{——}O\end{matrix}$>C:$C(CO_2Et)_2$ (I), is best obtained (63% yield) by addition of $(CH_2\cdot CO)_2O$ to $CHNa(CO_2Et)_2$ in boiling Et_2O. It is converted by CN·CHNa·CO_2Et in boiling Et_2O into *Et₃ βε-diketo-α-cyanohexane-αζζ-tricarboxylate*, an oil [*Cu* derivative, decomp. (indef.) ~180°], converted by $NHPh\cdot NH_2$ in cold AcOH into *Et* 1-*phenyl*-3-γ-*keto*-δ-*cyano*-δ-*carbethoxy*-n-*butylpyrazol*-5-*one*-4-*carboxylate*, m.p. 106—107° (green *Cu* compound), and in hot solution into α-4-*carbethoxy*-1-*phenyl*-3-*pyrazol*-5-*onyl*-β-4-*cyano*-1-*phenyl*-3-*pyrazol*-5-*onylethane*, m.p. 167—168°. $CHAcNa\cdot CO_2Et$ and $(CH_2\cdot CO)_2O$ in C_6H_6 at room temp. and then at the b.p. afford *Et₂ βδηι-tetraketodecane-γθ-dicarboxylate* (Et_2 succinyldiacetoacetate) (II), m.p. 48° (*Cu* derivative, decomp. 235°), with some Et H β-keto-α-acetyladipate, m.p. 81—82°. (II) and $NHPh\cdot NH_2$ in hot 50% AcOH afford *α-di-αβ-4-carbethoxy*-1-*phenyl*-5-*methyl*-3-*pyrazolylethane* (III), m.p. 156—157°, which does not give a colour with $FeCl_3$. When kept overnight in Et_2O (I) and $CHAcNa\cdot CO_2Et$ give mainly Et_3 β-hydroxy-ε-keto-α-acetyl-Δ^{α}-hexene-αζζ-tricarboxylate with some (II). The latter can be accumulated by the more rapid pptn. of its Cu compound, but separation or identification is best effected through (III) and α-4-*carbethoxy*-1-*phenyl*-3-*pyrazol*-5-*onyl*-β-4-*carbethoxy*-1-*phenyl*-2-*methyl*-3-*pyrazolylethane*, m.p. 114—115°. H. W.

Preparation of calcium *D*-altronate. P. P. Regna and B. P. Caldwell (*J. Amer. Chem. Soc.*, 1944, **66**, 244—246).—Enzymic hydrolysis of citrus pectin yields *D*-galacturonic acid, isolated as *Na Ca* salt, $(C_6H_9O_7)_2NaCa$, $+6H_2O$, $[\alpha]_D^{20}$ +33·0° in H_2O, which in aq. $Ca(OH)_2$–$CaCl_2$ gives completely (owing to insolubility of the product) basic Ca and thence normal *Ca δ-keto*-L-*galactonate*, $+5H_2O$, $[\alpha]_D^{20}$ −14·0° in H_2O, which with H_2–Raney Ni in H_2O at 80°/2300 lb. yields approx. equal amounts of Ca *L*-galactonate, $+5H_2O$, and *D*-altronate, $+3·5H_2O$, $[\alpha]_D^{20}$ +11·8° → 24·8—25·0° in ~90 min. in N-HCl, best separated by way of the derived Cd salts. R. S. C.

Synthesis of uronic acids. II. 2 : 3 : 4-Trimethyl derivatives of mannuronic, glucuronic, and galacturonic acids. F. Smith, M. Stacey, and P. I. Wilson (*J.C.S.*, 1944, 131—134).—α-Methylmannopyranoside in C_5H_5N with CPh_3Br gives 6-triphenylmethyl-α-methylmannoside, which with Me_2SO_4–NaOH in $COMe_2$ affords 6-*triphenylmethyl*-2 : 3 : 4-*trimethyl-α-methylmannoside*, m.p. 149°, $[\alpha]_D^{20}$ +27° in $CHCl_3$, from which the CPh_3 is removed (HCl) to yield 2 : 3 : 4-trimethyl-α-methylmannoside. Oxidation ($KMnO_4$) of this compound gives 2 : 3 : 4-trimethyl-α-methylmannuronoside. Similar oxidation of 2 : 3 : 4-trimethyl-β-methylglucoside and α-methylgalactoside affords respectively 2 : 3 : 4-trimethyl-β-methyl-α-glucuronoside and α-methyl-α-galacturonoside. *αβγ-Trimethyl-mannonolactone*, m.p. 74°, $[\alpha]_D^{20}$ +131° → +80° (equil.) in H_2O, and *-mannonamide*, m.p. 142°, $[\alpha]_D^{20}$ +5° in H_2O, are described. F. R. S.

Lactones of mannosaccharic acid. I. αδ-Dimethyl-Δ$^{\gamma}$-mannosaccharo-βε-lactone methyl ester. W. N. Haworth, (Miss) D. Heslop, (Miss) E. Salt, and F. Smith (*J.C.S.*, 1944, 217—224).—Mannosaccharodilactone (I) (prep. given) shows reducing properties after treatment with alkaline reagents, correlated with an absorption band at λ 2630 A. in alkaline solution, moving to 2290 A. on acidifying. Methylation of (I) gives similar isomerisation. With MeI and Ag_2O (I) gives Me_2 dimethyl*meso*tartrate (II), a trimethylmannosaccharolactone Me ester, and *αδ-dimethyl-Δ$^{\gamma}$-mannosaccharo-βε-lactone Me ester* (III), b.p. 152—158° (bath)/0·04 mm., $[\alpha]_D^{18}$ −25° in H_2O, absorption band at λ 2290 A. in H_2O. (III) is also obtained from (I) with CH_2N_2, or CH_2N_2 followed by MeI and Ag_2O, together with a little 6-carbomethoxy-3-methoxy-α-pyrone, m.p. 212°. The structure of (III) is confirmed by ozonisation, giving as final product mainly Me β-hydroxy-α-methoxyerythrosuccinate (IV), b.p. 105—110° (bath)/0·01 mm., $[\alpha]_D^{18}$ −43° in MeOH. On methylation (MeI and Ag_2O) (IV) gives (II), which with NH_3 in MeOH gives dimethoxyerythrosuccindiamide. With NH_3 in MeOH (IV) yields the *amide* of *β-hydroxy-α-methoxy*-l-*erythrosuccinic acid* (V), m.p. 153°, not optically active in H_2O. (IV) with NH_2Me in MeOH gives the *bismethylamide* of (V), m.p. 136°, $[\alpha]_D^{18}$ +10·7° in H_2O, identical with that prepared from *d*-araboascorbic acid (cf. A., 1944, II, 213). (III) on hydrogenation yields *αδ-dimethyl-γ-deoxymannosaccharo-βε-lactone Me ester*, b.p. 160° (bath)/0·03 mm., $[\alpha]_D^{20}$ −4° in H_2O, which affords *αδ-dimethyl-γ-deoxymannosaccharodiamide* (VI), m.p. 187°, $[\alpha]_D^{19}$ −74° in H_2O (negative Weerman test). The spatial arrangement in (VI) of the OMe and H on C_5 is not yet determined. Absorption curves for (III) and a comparable *l*-ascorbic acid derivative are given. The *diamide* of *αββ*- (or *αγδ*-)trimethylmannosaccharic acid, m.p. 258° (decomp.), $[\alpha]_D^{20}$ −41° in H_2O, and the *half-amide* NH_4 *salt* of (V), m.p. 181° (decomp.), are described. D. G.

Preparation of α-ketopolyhydroxy-acids. P. P. Regna and B. P. Caldwell (*J. Amer. Chem. Soc.*, 1944, **66**, 243—244).—Dissolving *D*-glucono-γ-lactone and a little H_3PO_4 in boiling MeOH, adding $NaClO_3$ and V_2O_5, shaking at 20°, and then keeping at 3° gives Me α-keto-*D*-gluconate, m.p. 175—176°, $[\alpha]_D^{20}$ −76·8° in H_2O, hydrolysed by 2N-H_2SO_4 at 30° to the acid, which is isolated as *Ca* salt, $+3H_2O$, $[\alpha]_D^{20}$ −70·8° in H_2O. Shaking K *D*-galactonate, $KClO_3$, V_2O_5, and H_3PO_4 in H_2O and isolation by way of the *K* salt, $[\alpha]_D^{20}$ −6·7° in H_2O, gives *α-keto*-D-*galactonic acid*, m.p. 170—171°, $[\alpha]_D^{20}$ −6·0° in H_2O (Me ester, m.p. 138—139°, $[\alpha]_D^{20}$ −11·3° in H_2O). α-*D*-Glucohepto-γ-lactone, neutralised with aq. Na_2CO_3, gives similarly *Na α-keto*-D-*glucoheptonate*, $+H_2O$, $[\alpha]_D^{20}$ +45·5° in H_2O. Mixed α- and β-*D*-galactoheptonic acids give similarly *K α-keto*-D-*galactoheptonate*, $[\alpha]_D^{20}$ +67·5° in H_2O. R. S. C.

Condensations. XXIII. Acetylation of unsymmetrical aliphatic ketones with acetic anhydride in presence of boron trifluoride. C. R. Hauser and J. T. Adams (*J. Amer. Chem. Soc.*, 1944, **66**, 345—349; cf. A., 1944, II, 211).—Isomeric ketones are usually obtained at 0° from COMeAlk (1 mol.) by Ac_2O (2 mols.) saturated with BF_3. Thus, COMeEt gives only (100%) $CHMeAc_2$; $COMePr^{\alpha}$, n-C_5H_{11}·COMe, and n-C_6H_{13}·COMe give 90% of $CHEtAc_2$, $CHBu^{\alpha}Ac_2$, and n-C_5H_{11}·$CHAc_2$, respectively, with 10% of COAlk·CH_2Ac. $COMeBu^{\beta}$ gives 45% of *γ-acetyl-δ-methyl*-n-*pentan-β-one*, b.p. 183—185°/750 mm. (gives no enol test or Cu salt), and 59% of CH_2Ac·$COBu^{\beta}$; $COMePr^{\beta}$ gives 68% of *γγ-dimethyl*-n-*pentane-βδ-dione*, b.p. 172—174° (gives no enol or Cu salt), and 32% of CH_2Ac·$COPr^{\beta}$; 2-methyl-*cyclo*hexanone gives 50% each of 6- (purple $FeCl_3$ colour and oily Cu salt) and 2-*acetyl*-2-*methyl*cyclo*hexanone*, b.p. 220—222° (no enol colour or Cu salt). The mixed products are analysed by their ability or inability to dissolve in NaOH or give Cu salts. R. S. C.

***n*-Propyldi-*n*-butylamine.** T. D. Perrine (*J. Amer. Chem. Soc.*, 1944, **66**, 312).—$NHBu^{\alpha}_2$ (2 mols.) and $Pr^{\alpha}I$ (1 mol.) at 120° or NBu^{α}_2·$[CH_2]_3$·MgCl and aq. HCl give $NPr^{\alpha}Bu^{\alpha}_2$, b.p. 193°/754 mm., 73—75°/8 mm. (*picrate*, m.p. 115·8—116·2°). R. S. C.

Anhydrous tetramethylammonium compounds.—See A., 1944, I. 182.

Bismethylamides of α-hydroxy-β-methoxy-*d*- and *l*-erythrosuccinic acid. (Miss) D. Heslop, (Miss) E. Salt, and F. Smith (*J.C.S.*, 1944, 225—229).—*d*-Araboascorbic acid with CH_2N_2 gives *αβ-dimethyl*-d-*araboascorbic acid* (**I**), which with $CClPh_3$ in C_5H_5N yields *ε-triphenylmethyl-αβ-dimethyl*-d-*araboascorbic acid* (**II**), m.p. 174°, $[\alpha]_D^{18}$ −41° in $CHCl_3$ (gives no reaction with NH_3 in MeOH). This with MeI and Ag_2O gives *ε-triphenylmethyl-αβδ-trimethyl*-d-*araboascorbic acid*, $[\alpha]_D^{18}$ −28° in $CHCl_3$, hydrolysed to *αβδ-trimethyl*-d-*araboascorbic acid* (**III**), b.p. 170° (bath)/0·02 mm., m.p. 74°, $[\alpha]_D^{22}$ +10° in H_2O, which gives *αβδε-tetramethyl*-d-*araboascorbic acid* (**IV**), b.p. 130° (bath)/0·02 mm., $[\alpha]_D^{20}$ +9·5° in H_2O. (**I**), (**III**), and (**IV**) all show an absorption band at λ 2350 A. (**III**) on ozonisation and hydrolysis yields $H_2C_2O_4$ and β-methyl-*d*-erythronic acid (**V**), isolated on distillation of the Me ester as the *γ-lactone* (**VI**), m.p. 113°, $[\alpha]_D^{19}$ −108° in H_2O (no change on keeping). With NH_3 and NH_2Me respectively in MeOH (**VI**) gives the *amide*, m.p. 105°, $[\alpha]_D^{18}$ +36° in H_2O, and the *methylamide*, m.p. 82°, $[\alpha]_D^{17}$ +57·5° in MeOH, of (**V**), and with NH_3–MeOH after methylation (MeI, Ag_2O) the *amide*, m.p. 72°, $[\alpha]_D^{21}$ +55·5° in H_2O, of *αβ*-dimethyl-*d*-erythronic acid. On oxidation (HNO_3), esterification, and treatment with NH_2Me–MeOH, (**VI**) yields the bismethylamide of α-hydroxy-β-methoxy-*d*-erythrosuccinic acid, m.p. 136°, $[\alpha]_D^{18}$ +11° in H_2O, identical with that prepared from *αδ*-dimethyl-Δ^{γ}-mannosaccharolactone Me ester.(cf. A., 1944, II, 212). (**I**) with *p*-NO_2·C_6H_4·COCl in C_5H_5N gives *δε-di*-p-*nitrobenzoyl-αβ-dimethyl*-d-*araboascorbic acid*, a glass, which on ozonisation yields *Me βγ-di*-p-*nitrobenzoyl*-d-*erythronate*, m.p. 133°, $[\alpha]_D^{17}$ +29° in $CHCl_3$ (loses acyl groups on attempted methylation). *meso*Tartaric acid on partial methylation (Me_2SO_4 and NaOH) affords *dl*-CO_2H·$CH(OH)$·$CH(OMe)$·CO_2H, which is purified by distillation, b.p. 100—105° (bath)/0·04 mm., and crystallisation of the amide, m.p. 191°, or by distillation of the Me ester, b.p. 96—98° (bath)/0·01 mm., and resolved by brucine, the less sol. salt, $[\alpha]_D^{18}$ −23° in H_2O, giving β-hydroxy-α-methoxy-*d*-erythrosuccinic (α-hydroxy-β-methoxy-*l*-erythrosuccinic) acid, isolated as the *bismethylamide*, m.p. 135°, $[\alpha]_D^{20}$ −10·5° in H_2O.

D. G.

Structure-chemical investigations. IX. Adipdithioamide. H. Erlenmeyer and G. Bischoff (*Helv. Chim. Acta*, 1944, **27**, 412—413).—Addition of CN·$[CH_2]_4$·CN to NaOEt in EtOH saturated with H_2S at −10° followed by heating at 70° affords *adipdithioamide*, m.p. 180°, which is converted by COMe·CH_2Cl into *αδ-di*-4-*methyl*-2-*thiazolylbutane dihydrochloride*, m.p. 251°. H. W.

Cyanoalkylpyruvic esters from aliphatic nitriles. G. S. Skinner, J. H. Taylor, and J. L. Ernst (*J. Amer. Chem. Soc.*, 1944, **66**, 496—497).—In presence of NaOEt, $Bu^{\alpha}CN$ and $Et_2C_2O_4$ give 13%, in presence of KOEt give 55%, and in presence of 1 : 9 KOEt–NaOEt give 31%, of *Et α-keto-β-cyano*-n-*hexoate* (**I**), b.p. 135—137°/15 mm. (cf. A., 1937, II, 134). In presence of KOEt, $Pr^{\alpha}CN$ or n-C_5H_{11}·CN with $Et_2C_2O_4$ gives *Et α-keto-β-cyano*-n-*valerate* (65%), b.p. 127—129°/15 mm., and -n-*heptoate* (58%), b.p. 148—150°/15 mm., respectively. In presence of 1 : 1 NaOEt–KOEt, EtCN and $Et_2C_2O_4$ give 79% of CN·CHMe·CO·CO_2Et. With Et_2SO_4–NaOEt–EtOH, (**I**) give *Et β-cyano-α-ethoxy*-Δ^{α}-n-*hexenoate*, b.p. 114°/1 mm.

R. S. C.

Unsaturated esters of glycollonitrile. D. T. Mowry (*J. Amer. Chem. Soc.*, 1944, **66**, 371—372).—40% of OH·CH_2·CN (**I**), b.p. 99—100°/17 mm., is obtained by adding COMeEt and then NaCN to aq. $NaHSO_3$ at 0°, treating the product with 37% CH_2O + a little NaCN at 30°, and finally distilling with *o*-$C_6H_4(CO)_2O$. Adding RCOCl to CH_2O and NaCN in H_2O at 10° gives *CN·CH₂ acrylate* (17%), b.p. 60°/4 mm., *β-methylacrylate* (58%), b.p. 90—91°/10 mm., *crotonate* (60%), b.p. 103—104°/17 mm., *β-chlorocrotonate* (53%), b.p. 116°/16 mm., *cinnamate* (**II**) (73%), m.p. 63°, b.p. 164—165°/4 mm., and *α-methylcinnamate* (63%), b.p. 162—163°/3 mm. Adding (**I**) to RCOCl and $NPhMe_2$ in Et_2O at 10° gives (**II**) (75%), *CN·CH₂ fumarate* (45%), m.p. 83°, and *mesaconate* (43%), b.p. 192—193°/3 mm. R. S. C.

II.—SUGARS AND GLUCOSIDES.

Lead tetra-acetate oxidations in the sugar group. VII. Oxidation rates of ethyl β-*D*-galactofuranoside, methyl α-*D*-mannofuranoside, and γζ-anhydro-*D*-sorbitol. R. C. Hockett, M. H. Nickerson, and W. H. Reeder, tert. (*J. Amer. Chem. Soc.*, 1944, **66**, 472—474; cf. A., 1944, II, 210).—The OH attached to the ring of methyl-α-*D*-mannofuranoside (**I**) are *cis* and, as expected, the rate of oxidation by $Pb(OAc)_4$ under standard conditions is very rapid until 1 mol. has been consumed and then much slower, only traces of CH_2O being produced. The OH attached to the ring of ethyl-β-*D*-galactofuranoside are *trans*, so that they are not attacked by $Pb(OAc)_4$ faster than are the exocyclic C·OH; thus the rate of oxidation shows no break until >2 mols. have been consumed and CH_2O is formed in quantity (? 1 mol.). γζ-Anhydro-*D*-sorbitol (prep. from methyl-6-deoxy-α-*D*-glucopyranoside 6-iodide triacetate by way of 3 : 6-anhydro-*D*-glucose), m.p. 108—109°, oxidises, as expected, at a rate very similar to that of (**I**). CH_2Ac_2 consumes 3 mols. of $Pb(OAc)_4$ in an unbroken reaction. R. S. C.

3 : 6-Anhydrogalactose. II. 2-Methyl- and 4-methyl-3 : 6-anhydro-α-methylgalactopyranoside. (Mrs.) P. A. Rao and F. Smith (*J.C.S.*, 1944, 229—232; cf. A., 1940, II, 244).—α-Methylgalactopyranoside or its 6-*p*-toluenesulphonate (**I**) with *p*-C_6H_4Me·SO_2Cl–C_5H_5N gives *α-methylgalactopyranoside* 2 : 6-*di*-p-*toluenesulphonate* (**II**), m.p. 148°, $[\alpha]_D^{18}$ +68° in C_5H_5N. This with aq. 3N-NaOH gives 3 : 6-anhydro-α-methylgalactopyranoside, m.p. 139°, but with N-NaOH in aq. EtOH yields 3 : 6-*anhydro-α-methylgalactopyranoside* 2-p-*toluenesulphonate*, m.p. 138°, $[\alpha]_D^{18}$ +56° in $CHCl_3$, which with MeI and Ag_2O gives the 4-*Me* compound, m.p. 126°, $[\alpha]_D^{23}$ +88° in $CHCl_3$, hydrolysed with NaOH in aq. EtOH at 60° to 4-*methyl*-3 : 6-*anhydro-α-methylgalactopyranoside*, b.p. 110° (bath)/0·03 mm., m.p. 55°, $[\alpha]_D^{19}$ +81° in MeOH, $[\alpha]_D^{16}$ +75° in H_2O, yielding 2 : 4-dimethyl-3 : 6-anhydro-α-methylgalactoside, b.p. 100° (bath)/0·02 mm., $[\alpha]_D^{18}$ +75° in H_2O, which isomerises to the β-form, m.p. 83°, on treating with dry HCl. (**II**) with $COMe_2$ and H_2SO_4 gives the 3 : 4-*CMe₂* derivative, m.p. 148°, $[\alpha]_D$ +115° in C_5H_5N, also obtained from (**I**). This on methylation (MeI and Ag_2O) yields 2-*methyl*-3 : 4-iso*propylidene-α-methylgalactopyranoside* p-*toluenesulphonate*, m.p. 88°, $[\alpha]_D^{23}$ +99° in C_5H_5N, which is hydrolysed (1% HCl in MeOH) to 2-*methyl-α-methylgalactopyranoside* 6-p-*toluenesulphonate*, $[\alpha]_D^{23}$ +27° in EtOH, giving with NaOH in aq. EtOH 2-*methyl*-3 : 6-*anhydro-α-methylgalactopyranoside*, m.p. 102°, $[\alpha]_D^{16}$ +88° in H_2O. D. G.

Action of diazomethane on acyclic sugar derivatives. VI. *D*-Sorbose. M. L. Wolfrom, S. M. Olin, and E. F. Evans (*J. Amer. Chem. Soc.*, 1944, **66**, 204—206; cf. A., 1944, II, 6).—*aldehydo-D*-Xylose tetra-acetate (prep. from the Et_2 mercaptal tetra-acetate improved; cf. A., 1932, 146), m.p. 90—91°, $[\alpha]_D^{22}$ −23·3° in $CHCl_3$, by oxidation (cf. Major *et al.*, A., 1937, II, 49) and then treatment with PCl_5 in Et_2O gives D-*xylonyl chloride tetra-acetate*, m.p. 72—73°, $[\alpha]_D^{25}$ −14° in $CHCl_3$, whence CH_2N_2 in Et_2O yields 1-*deoxy*-1-*diazo*-keto-D-*sorbose tetra-acetate* (92%), m.p. 124·5—125·5°, $[\alpha]_D^{25}$ +44·5° in $CHCl_3$. In boiling AcOH this gives keto-D-*sorbose penta-acetate* (73%), m.p. 97·5—98·5°, $[\alpha]_D^{25}$ −2·5° in $CHCl_3$ (*oxime*, m.p. 113—114°, $[\alpha]_D^{23}$ −42° in $CHCl_3$), which, when crystallised with its *L*-isomeride, gives the DL-*form*, m.p. 83—84°. 0·6N-$Ba(OH)_2$ hydrolyses (**I**) to *D*-sorbose (80%), m.p. 158—160°, $[\alpha]_D^{26}$ +40·5° in $CHCl_3$. 1 : 8-Bisdiazomucyldimethane tetra-acetate with 47% HI in $CHCl_3$ gives *mucyldimethane tetra-acetate* (78%), m.p. 204—206°.

R. S. C.

Preparation of ββ-trehalose octa-acetate. C. M. McCloskey, R. E. Pyle, and G. H. Coleman (*J. Amer. Chem. Soc.*, 1944, **66**, 349—350).—*α-D*-Glucosyl bromide 2 : 3 : 4 : 6-tetra-acetate (**I**) (modified prep.) and β-*D*-glucose 2 : 3 : 4 : 6-tetra-acetate [prep. from (**I**) by H_2O and Ag_2CO_3 in $COMe_2$ at 0° and then 50—60°] give, by Schlubach and Schceteling's method (A., 1933, 148), >4% of *ββ*-trehalose octa-acetate, m.p. 180·5—181·5° (corr.), $[\alpha]_D^{25}$ +18·4° in $CHCl_3$, 18·8% condensation being indicated by the reducing val. By use of Ag_2CO_3, I, and $CaSO_4$ in EtOH the yield is raised to 10·5%, the reducing val. indicating 30—40% condensation (cf. A., 1936, 827).

R. S. C.

III.—HOMOCYCLIC.

Action of sulphuric acid on 1-phenyl-2-alkyl*cyclo*propanes. D. Davidson and J. Feldman (*J. Amer. Chem. Soc.*, 1944, **66**, 488—489).—Decomp. of the appropriate pyrazoline by Pt–asbestos and KOH gives 1-phenyl-*cyclo*propane, b.p. 174°, -2-methyl- (**I**), b.p. 184—186°, -2-*ethyl*- (**II**), b.p. 203—205°, and -2-iso*propyl*-cyclo*propane* (**III**), b.p. 213—216°. In 90% H_2SO_4 at 35—40°, (**II**) gives 1 : 1 : 2-trimethylindane, b.p. 208° (identified by oxidation to *o*-CO_2H·C_6H_4·CMe_2·COMe), but (**I**) and (**II**) give polymers. In 85% H_3PO_4 isomerisation to olefines occurs (no details are given). The *cyclo*propanes obey the modern version of Markovnikov's rule.

R. S. C.

Factors determining the course and mechanism of Grignard reactions. XII. Effect of cobaltous chloride on the reaction of magnesium methyl bromide with alicyclic chlorides. M. S. Kharasch, F. Engelmann, and W. H. Urry (*J. Amer. Chem. Soc.*, 1944, **66**, 365—367; cf. A., 1943, II, 284).—With MgMeBr–Et_2O at the b.p. (28 hr.), *trans*- (I) or *cis*-methyl*cyclo*hexane (II) gives methyl*cyclo*hexane (III) 10% and -hexene (IV) 33—34%, and *iso*bornyl chloride (V) gives a mixture (VI) (90%) of camphene and bornylene, but only 5% interaction occurs with bornyl chloride (VII); in all cases pure CH_4 is evolved. In presence of 5 mol.-% of $CoCl_2$, reaction is 86—98% complete in 5 hr.; (I) and (II) give (III) 28—34%, (IV) 23—31%, and di-2-methyl*cyclo*hexyl 22—27%, and the gas contains CH_4 77—83, C_2H_6 9—15, and C_2H_4 8%; *cyclo*hexyl chloride gives *cyclo*hexane 27, *cyclo*hexene 29, and di*cyclo*hexyl 26% with a gas containing CH_4 85, C_2H_6 9, and C_2H_4 6%; (V) gives camphane 19, (VI) 44, and dibornyl 31% with CH_4 77, C_2H_6 15, and C_2H_4 8%; (VII) gives camphane 15, (VI) 20, and dibornyl 63% with CH_4 72, C_2H_6 19, and C_2H_4 9%. The reactions thus differ from those with aliphatic chlorides (*loc. cit.*). The $CoCl_2$ results are explained as a free radical chain reaction, the electronic strength of the radicals playing a major part in determining the nature of the products. R. S. C.

Condensation of *cyclo*hexanol with halogenobenzenes in presence of sulphuric acid. R. Pajeau (*Compt. rend.*, 1942, **215**, 578—580).—*cyclo*Hexanol and PhCl or PhBr in presence of H_2SO_4 at room temp. give ~30% of *p*-chloro- or -bromo-*cyclo*hexylbenzene, respectively. H_2SO_4 + 60% oleum is used to give the corresponding I-derivative, which is oxidised by CrO_3–AcOH to *p*-$C_6H_4I{\cdot}CO_2H$. Similarly prepared are 4-chloro-3-methyl-, b.p. 150°/4 mm., and 5-chloro-2-methyl-*cyclo*hexylbenzene, b.p. 149°/14 mm. Examination of Raman spectra indicates absence of isomerides. A. T. P.

" Cyclisation " of vitamin-*A* and allied compounds. E. G. E. Hawkins and R. F. Hunter (*Biochem. J.*, 1944, **38**, 34—37).—" Cyclised " vitamin-*A* (I), m.p. 77—78°, max. at 372 mμ. ($E^{1\%}_{1\,cm.}$ 3760) has been obtained (cf. Shantz *et al.*, A., 1943, II, 257). Failure to " cyclise " (by HCl–EtOH) *β-apo*-2-carotenal, axerophthylidene-acetone (II) [max. at 395 mμ. ($E^{1\%}_{1\,cm.}$ 1460) and with $SbCl_3$ a max. at 735 mμ.], the C_{20}-aldehyde (III) [max. at 395 and 730 mμ. ($SbCl_3$)] of Haworth *et al.* (A., 1939, II, 114), and the alcohol prepared by Pondorff reduction of (III), suggests that a terminal OH is necessary for the reaction. This is not the only necessary condition, since *β-apo*-2-carotenol does not cyclise. The absence of OH in (I) (cf. Heilbron *et al.*, A., 1932, 1174) is confirmed (Zerevitinov). Axerophthylidene*iso*propyl alcohol [max. at 351 mμ. and 713 mμ. ($SbCl_3$)] [from (II) and $Al(OPr^{\beta})_3$] and 0·04N-HCl–EtOH give a " cyclised " product which shows max. at 420, 395, and 372 mμ. The results are discussed in connexion with the structure of vitamin-A_2, which undergoes " cyclisation " to a substance having max. identical with those of (I), but distinguishable from (I) by the absorption band at 693 mμ. ($SbCl_3$) (cf. Embree *et al.*, A., 1940, III, 321; Shantz *et al.*, A., 1943, II, 261). " Cyclised " subvitamin-*A* (IV) is formed in the product of " cyclisation " of the unsaponifiable matter of acetylated shark-liver oil and of a similar liver oil which is oxidised in stages by aeration. In the latter case, (IV) is present when >80% of the original -*A* alcohol is destroyed, suggesting that (IV) is a primary oxidation product of -*A*, probably formed by attack of the double linking of the *β*-ionone ring in -*A* by O_2. A. T. P.

***spiro*Pentane.** M. J. Murray and E. H. Stevenson (*J. Amer. Chem. Soc.*, 1944, **66**, 314).—$C(CH_2Br)_4$ and Na in molten NH_2Ac containing also NaI and Na_2CO_3 give ~40% of spiro*pentane*, C_5H_8, b.p. 38·3—38·5°; olefines which are also formed are removed by successive treatment with aq. NH_3, aq. $AgClO_3$, and Br. The Raman spectrum and chemical inertness indicate the structure $C\left(<\begin{matrix}CH_2\\CH_2\end{matrix}\right)_2$. The yield is ~1—5% in aq. MeOH. R. S. C.

1 : 2 : 3 : 4-Dibenzphenanthrene and its derivatives. II. Synthetic attempts. F. Bergmann and H. E. Eschinazi (*J. Amer. Chem. Soc.*, 1944, **66**, 183—184; cf. A., 1943, II, 296).—Δ^1-*cyclo*Hexenyl-*cyclo*hexanone (I) and 1-$C_{10}H_7{\cdot}MgBr$ in C_6H_6 give 2-*hydroxy*-2-α-*naphthyl*-$\Delta^{1':2'}$- or -$\Delta^{1:1'}$-*decahydrodiphenyl* (42%), b.p. 225—230°/0·8 mm., cyclised, best by $AlCl_3$ in C_6H_6 at 0° and then room temp., to 9 : 9-*spirocyclo*hexyl-3 : 4-tetrahydrobenzfluorene and an isomeride, b.p. 210—230°/0·1 mm. (*picrate*, m.p. 160—161°), and 250—270°/0·1 mm. (*picrate*, m.p. 169—170°), which with Se at 320° give 9 : 9-spirocyclo*hexyl*-3 : 4-*benzfluorene* (II), b.p. 225—230°/0·05 mm. (*picrate*, m.p. 141—142°). With $K_2Cr_2O_7$–AcOH at the b.p., (II) gives the 1 : 2-*quinone* (? a *p*-quinonoid isomeride), m.p. 228°. The structure of (II) follows from its absorption spectrum (following abstract) and its resistance to further dehydrogenation by Se or Pd–asbestos at 350°. The oily products obtained by Rapson (A., 1941, II, 95) as by-products of triphenylene ring-closures are probably also spirans. Interaction of Mg 9-phenanthryl bromide with (I), followed by cyclisation as above and dehydrogenation by Se at 350°, gives 9 : 9-*spirocyclo*hexyl-1 : 2 : 3 : 4-dibenzfluorene, b.p. 230—260°/0·2 mm. (brown *picrate*, m.p. 157—159°), with a smaller amount of 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-tetrabenznaphthalene [1 : 2 : 7 : 8-dibenzchrysene], b.p. 290—320°/0·1 mm. [reddish-black picrate, m.p. 210—212° (lit. 200°)]. R. S. C.

Spectrographic characterisation of a hydrocarbon synthesised by Bergmann and Eschinazi. R. N. Jones (*J. Amer. Chem. Soc.*, 1944, **66**, 185—186).—The structure of 9 : 9-*spirocyclo*hexyl-3 : 4-benzfluorene (preceding abstract) follows from the resemblance of its absorption spectrum [max. at 3150 (4·45), 3250 (4·43), 3395 (4·55), 3845 (1·38), 4105 (1·61), and 4360 A. (1·69) in EtOH; figures in parentheses are log $E_{mol.}$] to that of 3 : 4-benzfluorene and the difference thereof from those of chrysene and 3 : 4-benzphenanthrene. The absorption of the 1 : 2-quinone [max. at 2470 (4·28), 2680 (4·32), 3330 (3·94), and 4600 A. (3·49)] renders its formula probable but not certain. R. S. C.

Labile union of oxygen to carbon. Influence of supplementary cyclisations. C. Dufraisse and M. T. Mellier (*Compt. rend.*, 1942, **215**, 576—578).—1 : 9-5 : 10-Di-*o*-phenylenanthracene and 5 : 6-11 : 12-di-*o*-phenylenenaphthacene are stable to light in CS_2. The unsymmetrical 5 : 6-diphenyl- and 6-chloro-5-phenyl-11 : 12-*o*-phenylenenaphthacene afford the normal photo-oxides (62 or 20% yield, respectively), which are decomposed at 150° and 90° to give 24% and 5% of O_2, respectively, and CO_2. A. T. P.

Reaction between benzylamine and alkali metals. W. Krabbe and G. Grünwald [with E. Polzin and W. Menzel] (*Ber.*, 1941, **74**, [*B*], 1343—1352).—Bright colours are developed by $NaNH_2$ with NH_2R (R = OH·$CPh_2{\cdot}CH_2$, OH·CHPh·CHPh, OH·$CPh_2{\cdot}CHPh$, CH_2Ph, Ph·$[CH_2]_2$, Ph, *p*-tolyl, *p*-C_6H_4Cl, *o*- and *m*-$NO_2{\cdot}C_6H_4$), $NH(CH_2Ph)_2$, $NHPh_2$, $N(CH_2Ph)_3$, NPh_3, C_5H_5N, or piperidine. $NH_2{\cdot}CH_2Ph$ gives a very similar colour (absorption spectrum) with Li in Et_2O; the absorption and conductivity with different proportions of $NH_2{\cdot}CH_2Ph$ and Li are determined; the solution contains a ~1 : 1 mixture of $LiNH_2$ and $LiNH{\cdot}CH_2Ph$. LiPh (prep. from PhBr) with $NH_2{\cdot}CH_2Ph$ in Et_2O yields a *compound*, $LiBr,2NH_2{\cdot}CH_2Ph$, m.p. 106°. R. S. C.

Theoretical study of the interaction of dimethylaniline and nitric acid. H. H. Hodgson (*J. Soc. Dyers and Col.*, 1944, **60**, 151—153).—With HNO_3 at 0°, $NPhMe_2$ gives 2 : 4 : 6 : 1-$(NO_3)_3C_6H_2{\cdot}NMe{\cdot}NO_2$ (HNO_3, *d* 1·52), or 2 : 4 : 6 : 1-$(NO_2)_3C_6H_2{\cdot}NHMe$ (*d* 1·42), or 2 : 4 : 1-$(NO_2)_2C_6H_3{\cdot}NMe_2$ (I) (*d* 1·34 and 1·254), or 3 : 5 : 3′ : 5′-tetranitrotetramethylbenzidine (II) (40%) + (I) (60%) (*d* 1·12); no reaction occurs with HNO_3 of *d* 1·046 and 1·024. With rise in temp., Me is expelled with HNO_3 of *d* 1·34 and 1·254, but not with acid of *d* 1·12. $NaNO_2$ accelerates, and $CO(NH_2)_2$ delays or inhibits, the reactions. Reactions of (II) with HNO_3 (*d* 1·52 and 1·42) are analogous to similar reactions of $NPhMe_2$ and (I). All the reactions are interpreted on the basis of modern electronic theory. A. T. P.

Preparation of selenocarbamides from carbodi-imides. F. Zetzsche and H. Pinske (*Ber.*, 1941, 74, [*B*], 1022—1024).—Di*cyclo*hexylcarbodi-imide, m.p. (microscope) 29—30°, and H_2Se in Et_2O give *s-dicyclohexylselenocarbamide*, decomp. 194°. Similarly are prepared *s-di*-p-*tolyl*- (I), m.p. 174° (decomp.), *s-di*-p-*dimethylaminophenyl*- (II), m.p. 183—185° (decomp. from 150°), *s-di*-l-*menthyl*-, m.p. 177° (decomp.), [α] −91·8°, and N-p-*dimethylaminophenyl*-N′-l-*menthyl*-, m.p. 147° (decomp.), [α] −38·4°, *-selenocarbamide* and, from the carbodi-imide salts, the *monomethiodide*, m.p. 187—188° (decomp.), and *monomethosulphate*, sinters 165°, m.p. 167—170° (decomp.), of (II). Selenocarbamides are unstable in air or when treated with oxidising agents or heated at 120° in vac. Acidic decomp. of (I) in air or H_2 gives *p*-$C_6H_4Me{\cdot}NC$ and Se, probably by way of *p*-$C_6H_4Me{\cdot}NCSe$. PhNCS decomposes (I) with pptn. of Se. R. S. C.

Sulphanilamide.—See B., 1944, II, 149.

Derivatives of sulphanilamide.—See B., 1944, III, 118.

New class of medicinal; polymethine colouring matters. Buu-Hoï (*Compt. rend.*, 1942, **215**, 580—582).—*p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ (I) and CNBr in aq. C_5H_5N give α-*p*-sulphamylanilino-ε-*p*-sulphamylanilo-$\Delta^{\alpha\gamma}$-pentadiene. Furfuraldehyde (II), (I), and NH_2Ph,HCl in EtOH afford the hydrochloride of α-anilino-ε-*p*-sulphamylanilo-δ-hydroxy-$\Delta^{\alpha\gamma}$-pentadiene. Analogous hydrochlorides are obtained by replacing NH_2Ph with *m*- and *p*-$C_6H_4Cl{\cdot}NH_2$ and -$C_6H_4Br{\cdot}NH_2$, *o*-, *m*-, and *p*-$C_6H_4R{\cdot}NH_2$ (R = NO_2, OMe, and Me), 2 : 4 : 1-$NO_2{\cdot}C_6H_3Me{\cdot}NH_2$, α- and β-$C_{10}H_7{\cdot}NH_2$, 1 : 2-$NO_2{\cdot}C_{10}H_6{\cdot}NH_2$, *p*-$NH_2{\cdot}C_6H_4{\cdot}N{:}NPh$, and 5 : 2 : 1-$NH_2{\cdot}C_6H_3(OH){\cdot}CO_2H$. *m*- and *p*-$C_6H_4(NH_2)_2$ yield compounds, $[p\text{-}NH_2{\cdot}SO_2{\cdot}C_6H_4{\cdot}N{:}CH{\cdot}C(OH){:}CH{\cdot}CH{:}CH{\cdot}NH]_2C_6H_4,2HCl$, and benzidine gives a similar derivative. $(p\text{-}NH_2{\cdot}C_6H_4)_2SO_2$, NH_2Ph,HCl, and (II) give the dihydrochloride, $[NHPh{\cdot}CH{:}CH{\cdot}CH{:}C(OH){\cdot}CH{:}N{\cdot}C_6H_4]_2SO_2,2HCl$; β-$C_{10}H_7{\cdot}NH_2$ reacts similarly to NH_2Ph, and diamines give more complex derivatives. Analogous compounds are obtained from NH_2Ph or β-$C_{10}H_7{\cdot}NH_2$ and $(p\text{-}NH_2{\cdot}C_6H_4)_2SO$. A. T. P.

1 : 4-Diamino*cyclo*hexane.—See B., 1944, II, 155.

Mechanism of the diazo-coupling reaction. III. Unusual coupling phenomena and their interpretation. H. H. Hodgson and E. Marsden (*J. Soc. Dyers and Col.*, 1944, **60**, 120—124).—An extension of views on the mechanism of the coupling reaction (A., 1943, II, 8; 1944,

II, 75) to cover apparently anomalous examples, *e.g.*, the weak and limited coupling of *o*-OH·C_6H_4·CO_2H, 1 : 3-NO_2·$C_{10}H_6$·OH, and 1 : 5-$C_{10}H_6(OH)_2$, and the polycoupling of resorcinol. There are also discussed the coupling of arylamines, the diazoamino- → aminoazo-conversion, the failure of *o*- or *p*-C_6H_4Me·NMe_2 to couple, and the coupling of aminonaphtholsulphonic acids, all from the resonance viewpoint. There is also discussed the effect of C_5H_5N in promoting the activity of weakly-coupling diazo-compounds, the diazo-exchange reaction, and the coupling of phenol ethers.

K. H. S.

Pyrolysis of lactic acid derivatives. Production of phenyl and *o*-tolyl acrylate. E. M. Filachione, J. H. Lengel, and C. H. Fisher (*J. Amer. Chem. Soc.*, 1944, **66**, 494—496).—Heating 80% OH·CHMe·CO_2H with AcOH, C_6H_6, and a trace of conc. H_2SO_4 with removal of H_2O gives OAc·CHMe·CO_2H (77%), converted by $SOCl_2$ into OAc·CHMe·COCl (82%), which with ArOH at 100° gives *Ph* (I) (86—88%), b.p. 143°/12 mm., and *o-tolyl α-acetoxypropionate* (II), b.p. 112—113°/<1 mm. Pyrolysis of (I) at 440—600° gives up to 80% of CH_2:CH·CO_2Ph, b.p. 63—64°/1—2 mm., and of (II) at 500—591° gives up to 75% of CH_2:CH·CO_2·C_6H_4Me-*o*, b.p. 55—57°/0·5 mm., with larger yields of AcOH and, from (I), up to 20% of styrene and some CO_2 and CO. The acrylates are stable unless washed with alkali; polymerisation yields relatively hard resins.

R. S. C.

Halogenophenols.—See B., 1944, II, 197.

Diphenyl series. IV. Iodination of the acetate, benzoate, and benzenesulphonate of 4-hydroxydiphenyl. H. R. Schmidt, (Miss) C. M. Savoy, and J. L. Abernethy (*J. Amer. Chem. Soc.*, 1944, **66**, 491—494; cf. A., 1944, II, 12).—*p*-C_6H_4Ph·OAc with I and conc. HNO_3 in hot CCl_4 (38·3% yield) or AcOH (13·8% yield), or with ICl in AcOH (10·5% yield), gives *p*-C_6H_4I·C_6H_4·OAc-*p*, m.p. 155—156°, hydrolysed by KOH–EtOH–H_2O to *p*-C_6H_4I·C_6H_4·OH-*p* (I) (also obtained from benzidine) and obtained therefrom by Ac_2O and a little syrupy H_3PO_4. *p*-C_6H_4Ph·OR (R = Bz or $PhSO_2$) with I–HNO_3–AcOH or ICl–AcOH similarly gives *p*-C_6H_4I·C_6H_4·OR-*p* [R = *Bz*, m.p. 207°; *p*-C_6H_4Me·SO_2, m.p. 93·5° (corr.)], hydrolysed to and obtained from (I).

R. S. C.

Preparation of phenolic esters. E. Baumgarten, H. G. Walker, and C. R. Hauser (*J. Amer. Chem. Soc.*, 1944, **66**, 303—304).—RCOCl and ArOH in C_5H_5N give 4-*diphenylyl* (82%), m.p. 74·2—74·8°, and *Ph* isobutyrate (87%), b.p. 111—112·2°/25·5 mm., and 4-*diphenylyl Et carbonate* (60%), m.p. 73·9—75·0°.

R. S. C.

Nitrogenous derivatives of *dl*-γδ-di-*p*-hydroxyphenylhexane. L. Spitzer (*Gazzetta*, 1942, **72**, 445—450).—*dl*-(*p*-OH·C_6H_4·$CHEt)_2$ (Dodds *et al.*, A., 1939, II, 312) in C_6H_6 with dil. HNO_3 gives *dl*-γδ-di-(3-nitro-4-hydroxyphenyl)hexane (I), m.p. 114—115°, with ~5% of, probably, the *meso*-isomeride, m.p. 226—228°, also obtained by nitrating *meso*-(*p*-OH·C_6H_4·$CHEt)_2$. With Me_2SO_4–MeOH–KOH, (I) gives the aci-*form* (II), m.p. 106·5°, yellow, of *dl*-γδ-di-(3-nitro-4-methoxyphenyl)hexane, of which the normal *form* (III), m.p. 107—109°, almost colourless, is obtained by nitrating *dl*-γδ-di-(3-nitro-4-methoxyphenyl)hexane. Hydrogenation (Pd–C) of (II) or (III) gives dl-γδ-*di*-(3-*amino*-4-*methoxyphenyl*)*hexane*, m.p. 113—115° [picrate, m.p. 130—131°; $(COEt)_2$ derivative, m.p. 106—108°], the Ac_2 derivative, m.p. 152—153°, of which is oxidised by $KMnO_4$–$MgSO_4$ to 3 : 4 : 1-NHAc·C_6H_3(OMe)·CO_2H.

E. W. W.

Synthesis of substances with very high œstrogenic activity. C. Mentzer and G. Urbain (*Compt. rend.*, 1942, **215**, 554—556).—*p*-OMe·C_6H_4·CH_2·CN (I) and EtBr–$NaNH_2$ give α-p-*anisylbutyronitrile*, (?) m.p. 130° (corresponding *acid*, m.p. 68°, and *amide*, m.p. 101—102°). (I) and *m*-OMe·C_6H_4·$[CH_2]_2$·Br similarly afford α-p-*anisyl*-γ-m-*anisylbutyronitrile*, b.p. 205—210°/3 mm., hydrolysed to the corresponding acid, which is cyclised ($POCl_3$) to 1-keto-6-methoxy-2-*p*-anisyl-1 : 2 : 3 : 4-tetrahydronaphthalene, convertible by MgMeI, followed by demethylation, into 6-hydroxy-2-*p*-hydroxyphenyl-1-methyl-3 : 4-dihydronaphthalene (cf. Salzer, A., 1943, II, 8), which shows œstrogenic activity in doses of 0·3—0·5 μg.

A. T. P.

Cleavage of phenol ethers by pyridine hydrochloride. V. Prey (*Ber.*, 1941, **74**, [*B*], 1219—1225).—C_5H_5N,HCl (I), m.p. 144°, boils undecomposed at 218° and, acting as a strong acid, is very effective for dealkylation of ArOAlk, even for PhOMe. Heating with 3 parts of (I) at ~200° for 5—6 hr. usually gives 70—100% yields. Unstable substituents, *e.g.*, in anethole or *iso*eugenol, reduce the yield to 15—20%. Ph_2O is unaffected. All OAlk of polyhydric phenol ethers are hydrolysed, but conditions can be found for partial dealkylation; *e.g.*, for *o*- or *m*-$C_6H_4(OMe)_2$ use of 1·3 mols. of (I) and 5—15% of AcOH at 180—190° gives 6—75% of OMe_1-ether.

R. S. C.

Dissociation of hexa-arylethanes. XV. Methoxyl substituents. C. S. Marvel, J. Whitson, and H. W. Johnston (*J. Amer. Chem. Soc.*, 1944, **66**, 415—417; cf. A., 1943, II, 27).—Dissociation into free radicals, indicated by magnetic susceptibility, of OMe-substituted hexa-arylethanes is ≪ is indicated by cryoscopy (cf. Gomberg *et al.*, A., 1923, i, 211; Lund, A., 1927, 661). This is because the ethanes are unstable, giving low " mol. wts." by disproportionation. The following are reported: *m*-OMe·C_6H_4·CO_2Et (prep. by distilling the acid with H_2SO_4–EtOH–C_6H_6), b.p. 130—135°/15 mm.; *p*-OMe·CPh_2·OH, m.p. 60° (lit. 58—61°, 84°, 82°); *diphenyl*-m-*anisyl*-, m.p. 89—90°, and *tri*-m-*anisyl-methyl chloride*, m.p. 123—124°; *o*-, *D* (=dissociation for 0·1M. solutions in C_6H_6) 3·8%, *m*-, *D* 2·1—3·1%, and *p*-$(OMe·C_6H_4·CPh_2)_2$, *D* 3·8—5·2%; $[(o\text{-}OMe·C_6H_4)_3CPh]_2$, *D* 6·8—8·0%; $C_2(C_6H_4·OMe\text{-}o)_6$, *D* 52% (0·05M. solution); $C_2(C_6H_4·OMe\text{-}m)_6$, *D* 10%.

R. S. C.

***o*-Phenylenedioxyacetic acid and its ethyl ester.** W. G. Christiansen and M. A. Dolliver (*J. Amer. Chem. Soc.*, 1944, **66**, 312).—*o*-$C_6H_4(OH)_2$ (I), $CHCl_2$·CO_2Et, and NaOEt (2 mols.) in EtOH–N_2 give *Et o-phenylenedioxyacetate*, b.p. 115—117°/12·5 mm., and thence (N-NaOH) the derived *acid*, m.p. 107—108°. $CHCl_2$·CO_2H does not condense with (I).

R. S. C.

Salts of phenolsulphonic acids.—See A., 1944, I, 182, 183.

Mechanism of the reaction of (−)-phenylalkylcarbinols with hydrogen bromide. C. L. Arcus (*J.C.S.*, 1944, 236—239).—The view of Levene *et al.* (A., 1939, II, 155) that the three mechanisms of substitution (S_Ni; S_N2; S_N1) do not suffice to explain the rotation–temp. curves for the reactions between HBr and CHPhR·OH (R = Me, Et, Pr^a) is modified. If the part played by each mechanism in the total reaction is represented by a distribution curve about a max. at a certain temp., it is found that the algebraic sum of the optical results of the three mechanisms reproduces the experimental curves. The " domain " of each mechanism, represented by the area between its distribution curve and the temp. axis, is calc. for the three reactions.

A. T. P.

Reaction of citronellal with magnesium benzyl chloride. W. G. Young and S. Siegel (*J. Amer. Chem. Soc.*, 1944, **66**, 354—358).—Citronellal (I) and an excess of CH_2Ph·MgCl in Et_2O give 80% of α-benzylcitronellol (II), b.p. 153—156°/3 mm., but use of an excess of (I) leads to 70—80% of o-α-*hydroxy*-β[ζ]-*dimethyl*-Δ^{ϵ}- (or -Δ^{ζ}-)n-*heptenyl*-β′-*hydroxy*-γ′η′-*dimethyl*-$\Delta^{\zeta'}$- (or -$\Delta^{\eta'}$-)*octenylbenzene* (III), b.p. 234—235°/3 mm. (cf. Rupe, A., 1914, i, 131; Gilman *et al.*, A., 1930, 1409). The structure of (III) is proved by its mol. wt. in camphor or C_6H_6, possession of 2 active H (MgMeI) (and no CO), 2 OH (quant. interaction with Ac_2O), 2 C:C (Br; H_2–Pd–$BaSO_4$), 2 citronellyl radicals [with CrO_3 gives 2·61—2·66 AcOH, whereas (II) gives 1·14—1·16 AcOH], oxidation by $KMnO_4$–C_5H_5N to *o*-$C_6H_4(CO_2H)_2$ (IV) (but no BzOH), dehydration by $KHSO_4$ at 160°/<1 atm. to 2 : 6-*di*-α[ε]-*dimethyl*-Δ^{δ}- (or -Δ^{ϵ}-)n-*hexenyl*-3 : 4-*benz*-Δ^3-*dihydro*-1 : 2-*pyran*, b.p. 215—217°/3 mm. [which is probably the substance isolated by Rupe (*loc. cit.*)], and by the different course of the following reaction. The aldol (prep. by KOH in 95% EtOH), b.p. 170·5—173°/5 mm., of (I) with CH_2Ph·MgCl gives the " normal " addition product, oxidised to BzOH with only traces of (IV), and dehydrated to a partly cyclised *hydrocarbon*, $C_{27}H_{40}$, b.p. 204—206°/3 mm.

R. S. C.

Vinyl polymers. XVIII. Optically active styrene derivative and its polymer. C. S. Marvel and C. C. Overberger (*J. Amer. Chem. Soc.*, 1944, **66**, 475—477; cf. A., 1944, II, 123).—*d-sec.*-BuOH, $[\alpha]_D^{23}$ +11·5°, with Na and then *p*-C_6H_4Br·CH_2Br in boiling C_6H_6 gives p-*bromobenzyl* d-sec.-*Bu ether* (I) (49·1%), b.p. 109—110°/8 mm., $[\alpha]_D^{23}$ +10·2° in 95% EtOH. *p*-C_6H_4Br·CH_2·OMe, CuCN, and some C_5H_5N at 215—225° give 68% of *p*-CN·C_6H_4·CH_2·OMe (II), b.p. 108—110°/9 mm. Similarly, but with addition of a little $CuSO_4$ and *p*-C_6H_4Me·CN, (I) gives impure p-*cyanobenzyl* d-sec.-*Bu ether* (III) (90%), b.p. 134—137°/9 mm., $[\alpha]_D^{23}$ +10·9° (the *dl-sec.*-Bu ether also could not be completely purified), hydrolysed by KOH in boiling 95% EtOH to (? dl-)p-sec.-*butoxymethylbenzoic acid*, m.p. 77—78°. With an excess of MgMeI in Et_2O, (II) or (III) gives *p*-methoxymethylacetophenone (52%), b.p. 104—105°/9 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 170—171°), or p-d-sec.-*butoxymethylacetophenone* (IV) (65%), b.p. 129—130°/10 mm., $[\alpha]_D^{20}$ +10·8° in 95% EtOH (2 : 4-*dinitrophenylhydrazone*, m.p. 158—159°), respectively. Slow distillation of (IV) with $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ then yields α-p-d-sec.-*butoxymethylphenylethyl alcohol* (60%), b.p. 144—149°/9 mm., $[\alpha]_D^{23}$ +11·2° in 95% EtOH, converted by $KHSO_4$ and a trace of quinol at 200—220°/60—100 mm. (N_2) into p-*vinylbenzyl* d-sec.-*Bu ether* (V) (47%), b.p. 111—113°/8 mm., $[\alpha]_D^{25}$ +12·8° in dry dioxan. (V) and some Bz_2O_2 in dioxan at 55° give a solid *polymer*, OBz·$[(C_{13}H_{18}O)_8O_{11}]_n$; during 27 hr. α_D^{55} changes from +0·917° to +0·722°; measurement (±0·01°) is sufficiently accurate to indicate a first-order reaction.

R. S. C.

Electrolytic reduction of acetophenone in alkaline solution. S. Swann, jun., P. E. Ambrose, R. C. Dale, R. C. Rowe, H. M. Ward, H. D. Kerfman, and S. Axelrod (*Trans. Electrochem. Soc.*, 1944, **85**, *Preprint* 9, 93—99).—Of many metal cathodes examined in connexion with the alkaline electrolytic reduction of COPhMe in presence of EtOH and KOAc, Sn gave the highest yield of pinacol isomerides; 77% yield was obtained at 85° with c.d. 0·005 amp. per sq. cm. Yields at Cr, Mo, W, Bi, Pb, Zn, Cd, Hg, and Cu cathodes were good, at Fe moderate, and at Ni, Co, and Mg poor.

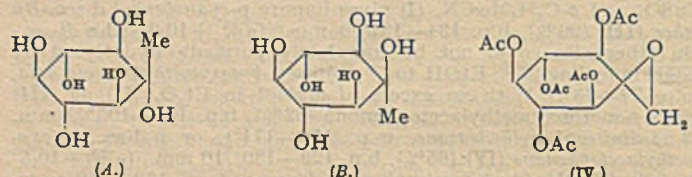
C. R. H.

1-*n*-Alkyl*cyclo*pentanols and their derivatives. C. R. McLellan and W. R. Edwards, jun. (*J. Amer. Chem. Soc.*, 1944, **66**, 409—

412).—*cyclo*Pentanone and MgRBr give 1-methyl-, m.p. 36°, b.p. 81°/100 mm. (p-*nitro*-, m.p. 83°, and 3 : 5-*dinitro-benzoate*, m.p. 115·5°), 1-ethyl-, m.p. −10°, b.p. 74·5°/20 mm. (p-*nitro*-, m.p. 52·5°, and 3 : 5-*dinitro-benzoate*, m.p. 108·3°), 1-*n*-propyl-, m.p. −37·5°, b.p. 83°/20 mm. (p-*nitro*-, m.p. 59·5°, and 3 : 5-*dinitro-benzoate*, m.p. 82°), 1-*n*-butyl-, b.p. 99°/20 mm. (p-*nitro*-, m.p. 31°, and 3 : 5-*dinitro-benzoate*, m.p. 75·3°), 1-*n*-hexyl-, b.p. 124°/20 mm. (3 : 5-*dinitrobenzoate*, m.p. 86·5°), 1-*n*-heptyl-, b.p. 136·5°/20 mm. (p-*nitro*-, m.p. 26°, and 3 : 5-*dinitro-benzoate*, m.p. 76·8°), 1-n-*octyl*-, m.p. −17·5°, b.p. 135·5°/9 mm. (3 : 5-*dinitrobenzoate*, m.p. 77°), 1-n-*decyl*-, m.p. −18°, b.p. 133°/7 mm. (slight decomp.) (3 : 5-*dinitrobenzoate*. m.p. 78°), 1-n-*dodecyl*-, m.p. 2°, b.p. 142·5°/3 mm. (decomp.) (3 : 5-*dinitrobenzoate*, m.p. 81·3°), and 1-n-*tetradecyl*-cyclo*pentanol*, m.p. 16·2°, b.p. 164·5°/2 mm. (decomp.) (3 : 5-*dinitro-benzoate*, m.p. 81·5°). Condensation with PhOH (methods: Huston *et al.*, A., 1937, II, 494; Welsh *et al.*, A., 1938, II, 94) gives 1-p-*hydroxyphenyl*-1-*methyl*-, m.p. 95·5°, *-ethyl*-, m.p. 96·3°, b.p. 137°/2·5 mm. (2′ : 6′-Br_2-derivative, m.p. 97°), -n-*propyl*-, m.p. 67·5°, b.p. 135°/1 mm. (2′ : 6′-Br_2-derivative, m.p. 104·5°), -n-*butyl*-, m.p. 57·5°, b.p. 151°/2 mm. (2′ : 6′-Br_2-derivative, m.p. 69°), -n-*hexyl*-, m.p. 61·8°, b.p. 163°/2·1 mm., -n-*heptyl*-, m.p. 53·5°, b.p. 174°/2·5 mm., and -n-*octyl*-cyclo*pentane*, m.p. 42·8°. B.p. at various pressures (apparatus : C, 1944, Part 3), d_4^0, d_0^{26}, n_D^{25}, and parachors are given for the *cyclo*pentanols; plotting *d* against the no. of C shows an abrupt change at alkyl = C_7, and the same break is shown by *d* of the alkyl*cyclo*pentanes; this is due to the packing being governed for the lower alkyl derivatives by the size of the *cyclo*pentane ring but for the higher alkyl by the size of the alkyl. The phenols in which alkyl = Me—Bu are approx. equally bacteriostatic (*Staph. aureus*), but the higher alkyl derivatives are ineffective. R. S. C.

Stereochemistry of cryptoxanthin and zeaxanthin. L. Zechmeister and R. M. Lemmon (*J. Amer. Chem. Soc.*, 1944, **66**, 317—322).—Irradiation (sunlight) of dil. solutions (1—10 mg. per 100 ml.) of cryptoxanthin (I) or zeaxanthin (II) in light petroleum causes bleaching due to stereoisomerisation, structural conversion into other pigments, and cleavage to colourless or almost colourless substances; these changes occur in the order stated but overlap; they are faster for (II) than for (I). I in light petroleum (also melting or keeping or refluxing in solution in the dark) causes isomerisation, but light (even for a few sec.) is needed for development of a *cis*-peak. Adsorption orders and absorption max. are detailed. The following structures are probable : neocryptoxanthin B 6-*cis*, U 3- or 9-*cis*, and A 6 : *x*-di-*cis*-cryptoxanthin; neozeaxanthin A 6-*cis*, B 5-*cis*, and C (? 6 : *x*-)di-*cis*-zeaxanthin. R. S. C.

Cyclitol series. VII. Cyclitol (mytilitol) of mussels and related substances. T. Posternak (*Helv. Chim. Acta*, 1944, **27**, 457—468; cf. Jansen, A., 1931, 791; Ackermann, A., 1921, i, 764).—Mytilitol (I) is (*A*) and iso*mytilitol* (II) is (*B*). (I), m.p. 266—268° (slight decomp.) (hexa-acetate, two forms, m.p. 181° and ~170° and 181° after re-solidification), gives 1 mol. of AcOH when oxidised by CrO_3, showing it to be a *C*-methylinositol; under like conditions quercitol does not afford AcOH appreciably. (I) is obtained synthetically by the action of a large excess of MgMeI followed by $Ba(OH)_2$ on either form of the penta-acetate of scyllo*meso*inosose (III); it is accompanied by a small proportion of (II). Either penta-acetate and CH_2N_2 in well-cooled $CHCl_3$–Et_2O affords *penta-acetoxymethylene*cyclo*hexane oxide* (IV), m.p. 213°, hydrogenated



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

(PtO$_2$ in glacial AcOH) to iso*mytilitol penta-acetate*, m.p. 226—228°. This is resistant towards CrO_3–AcOH and Ac_2O–C_5H_5N at room temp. and is hydrolysed [$Ba(OH)_2$–MeOH] to (II), rhombs or occasionally long needles, m.p. 225—226° [*hexa-acetate* (boiling Ac_2O containing conc. H_2SO_4 or, preferably, $ZnCl_2$), m.p. 188—189°]. (III) and CH_2N_2 give *pentahydroxymethylene*cyclo*hexane oxide* (V), gradual decomp. >250° in a capillary, m.p. 244—247° (block), hydrogenated to (II). Boiling Ac_2O containing anhyd. $FeCl_3$ or $ZnCl_2$ converts (IV) or (V) into the *hepta-acetate*, m.p. 158—159°, of *hydroxymytilitol* (VI) (also +0·5H_2O), m.p. 247° after softening. With boiling Ac_2O–NaOAc or –KOAc, (IV) gives the *hexa-acetate* (VII), m.p. 185—186°, of *hydroxy*iso*mytilitol* (VIII), m.p. 223°, transformed by boiling Ac_2O–$ZnCl_2$ into the *hepta-acetate*, m.p. 191—192°. (IV) and HBr–AcOH at room temp. give *bromo*-iso*mytilitol penta-acetate*, m.p. 219—220°, which with Ac_2O–H_2SO_4 yields a peracetate, m.p. 191°, and with KOAc gives (VII). *Hydroxy*iso*mytilitol penta-acetate mono*-p-*toluenesulphonate*, m.p. 187—188° (decomp.; rapid heating) [from (IV) and anhyd. *p*-C_6H_4Me·SO_3H in $CHCl_3$], NaI, and $COMe_2$ at 110° afford *iodo*iso*mytilitol penta-acetate*, m.p. 227—231°. (I) is oxidised by HIO_4 less rapidly than (II), thus proving that all the successive OH groups in (I) are *trans*-to one another. Similar differences in the rate of oxidation are found for scyllitol and *meso*-inositol and for (VI) and (VIII), respectively. H. W.

Organic sulphur compounds. New sulphide and its derivatives. A. Cabra Fernández and M. Cabanzón Martínez (*Anal. Fís. Quím.*, 1942, **38**, 400—404).—CHPhPr^{n}Cl with K_2S–EtOH gives *di-α-phenyl-n-butyl sulphide*, b.p. 160—165°/40 mm. (*sulphoxide*, m.p. 50°; *sulphone*, m.p. 56—57°). F. R. G.

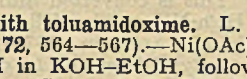
Coupling αβ-unsaturated compounds with diazonium salts. C. F. Koelsch and V. Boekelheide (*J. Amer. Chem. Soc.*, 1944, **66**, 412—415).—When ArN_2Cl reacts with CHR:CHR′ in presence of the aq. NaOAc and $CuCl_2$, the first reaction is reversible formation of Ar·N:N·OAc, followed by irreversible dissociation into Ar·, AcO·, and N_2. Then follow the reactions, (i) Ar· + CHR:CHR′ → CHArR·CHR′· (*A*), (ii) Cu^{++} + (*A*) → Cu^+ + CHArR·CHR′$^+$ (*B*), and (iii) Cu^+ + AcO· → Cu^{++} + OAc^-. The direction of addition of Ar· in (i) is governed by the natures of R and R′. The final reaction is (*B*) + Cl^- → CHArR·CHR′Cl (*C*) or (*B*) → H^+ + CArR:CHR′, according to the natures of R and R′. If R′ = CO_2H, (*C*) is formed; if R = CO_2H, (*B*) is decarboxylated. Since the rate of evolution of N_2 varies for different olefines, formation of a complex must precede formation of Ar·N:N·OAc. Yields are poor and much tar is formed. CHMe:CH·CO_2Et (I) and *p*-C_6H_4Cl·N_2Cl (II) etc. (in $COMe_2$ at 20°) give *Et α-chloro-β*-p-*chlorophenyl*-n-*butyrate* (34%), b.p. 125—140°/2—3 mm., converted by KOH–MeOH into *p*-C_6H_4Cl·CMe:CH·CO_2H (II), m.p. 134° (turbid; clear at 138·5°) [also obtained from *p*-C_6H_4Cl·CMe(OH)·CH_2·CO_2Et, b.p. 160—162°/11 mm], partly converted by warm conc. H_2SO_4 into a stereoisomeride, m.p. 92—99° (lit. 94°). Non-formation of CHMeCl·CH(*p*-C_6H_4Cl)·CO_2Et in the condensation is proved by boiling the crude product in $NPhEt_2$, hydrolysing the resulting ester, hydrogenating (H_2–Raney Ni; NaOH; 40 lb.), and treating with PCl_5 and then with $AlCl_3$ in C_6H_6, which gives mainly (40%) 3-methyl-indanone. PhN_2Cl and (I) etc. at 20—35° give CHPhMe·CHCl·CO_2Et (7·5%), b.p. 100—104° (some decomp.)/4 mm., recognised by conversion into the known CPhMe:CH·CO_2H. CHMe:CH·CO_2Me and 2 : 4 : 1-$C_6H_3Cl_2$·N_2Cl etc. in aq. $COMe_2$ at 5° give 2 : 4 : 1-$C_6H_3Cl_2$·CHMe·CHCl·CO_2Me (20%) (cf. A., 1939, II, 262), converted by KOH–MeOH into *β*-2 : 4-*dichlorophenylcrotonic acid*, m.p. 126—127°, which is hydrogenated (Raney Ni; aq. NaOH) to CHPhMe·CH_2·CO_2H. CHMe:CH·CO_2H and *p*-NO_2·C_6H_4·N_2Cl etc. in aq. $COMe_2$ at 0° followed by MeOH–HCl give *Me α-chloro-β*-p-*nitrophenyl*-n-*butyrate*, b.p. 175—180° (some decomp.)/3 mm., whence *p*-NO_2·C_6H_4·CMe:CH·CO_2H is obtained. CHPh:CH·CO_2Me and (II) etc. in aq. $COMe_2$–C_5H_5N at 30° give CHMeCl·CH(*p*-C_6H_4Cl)·CO_2Me (cf. *loc. cit.*). CHPh:CH·CH:CH·CO_2H and PhN_2Cl etc. in aq. $COMe_2$ at 10° give (CHPh:CH)$_2$ (28%). CHPh:CH·CH:CH·CO_2Me with PhN_2Cl etc. at 15° gives CHPh:CH·CH:CPh·CO_2Me (19%) and with (II) etc. gives, after hydrolysis, *δ-phenyl-α*-p-*chlorophenyl-*$\Delta^{\alpha\gamma}$*-pentadienoic acid*, m.p. 233—234°. Sorbic acid and PhN_2Cl give CHMe:CH·CH:CHPh (26%). R. S. C.

Reactions of *tert.*-butyl cinnamate and benzoate with magnesium phenyl bromide. F. Frostick, E. Baumgarten, and C. R. Hauser (*J. Amer. Chem. Soc.*, 1944, **66**, 305).—Adding CHPh:CH·CO_2Bu^γ (0·115) to MgPhBr (0·23 mol.) in Et_2O and then boiling gives only (44%) *Bu$^\gamma$ ββ-diphenylpropionate*, m.p. 55·5—55·6°, identified by hydrolysis. $Bu^\gamma OBz$ (0·3) and MgPhBr (0·5 mol.) in Et_2O at room temp. and then the b.p. give CPh_3·OH (41%) and BzOH (10%), but not CMe_2:CH_2 or $PhBu^\gamma$. R. S. C.

[Alkyl exchange of] carboxylic esters. II. F. Adickes and V. Krawczyk (*Ber.*, 1941, **74**, [*B*], 1389—1394).—Occurrence of the exchange, RCO_2Et + MeOH → RCO_2Me + EtOH, cannot be predicted from the nature of R. It occurs readily (70% in 8 hr. at the b.p. with 10 mols. of anhyd. MeOH) with Et 2-hydroxythionaphthen-1-carboxylate *S*-dioxide (I) (derived *Me* ester, m.p. 177—180°), fairly readily (~5—10%) with $CH(CO_2Et)_3$, CN·CHPh·CO_2Et, $(CO·CO_2Et)_2$, or Et 1-bromo-2-keto-1 : 2-dihydrothionaphthen-1-carboxylate *S*-dioxide (? *Me hemiacetal*, m.p. 90°), slightly (~1—3%) with CN·CPh$(CO_2Et)_2$ or the Me ether of (I), and not with $C(CO_2Et)_4$, Et_2 fumarate and *r*-tartrate, $(CH·CO_2Et)_2$. CO_2Et·CH_2·NH_2,HCl, CN·CH_2·CO_2Et, OH·CPh_2·CO_2Et, CPh_2F·CO_2Et, CN·CPh_2·CO_2Et, $(OPh)_2C(CO_2Et)_2$, *p*-C_6H_4Me·SO_2·CHPh·CO_2Et, Et nicotinate, and 2-hydroxy- or 2-methoxy-coumarone-1-carboxylate. R. S. C.

Hydrogenolysis of benzyl esters in contact with nickel catalysts. Y. R. Naves (*Helv. Chim. Acta*, 1944, **27**, 261—268).—Esters of CH_2Ph·OH suffer rapid hydrogenolysis in contact with Raney Ni at room temp. and < atm. pressure, whereas esters of alcohols and phenols apparently closely related to CH_2Ph·OH are changed slowly or not at all. A possible means is afforded of evaluating CH_2Ph esters in essential oils, natural perfumes, etc. CHPh:CH·CO_2CH_2Ph readily absorbs 2 H_2 at 30° with formation of PhMe and Ph·$[CH_2]_2$·CO_2H; after union with 1 H_2 the product contains PhMe, Ph·$[CH_2]_2$·CO_2CH_2Ph, and Ph·$[CH_2]_2$·CO_2H but no CHPh:CH·CO_2H. The product of the reaction at 135—140°/10 atm. is $(CH_2Ph·CH·CO_2H)_2$. Hydrogenolysis in contact with Raney Ni in presence of EtOH or EtOAc of CH_2Ph acetate, laurate, succinate, benzoate, and salicylate

is rapid and complete at a low temp. $CH_2Ac{\cdot}CO_2Et$ behaves individually on account of the simultaneous decomp. of $CH_2Ac{\cdot}CO_2H$. Dioxan inhibits and $NPhMe_2$ retards hydrogenolysis. There is little hydrogenolysis of anisyl, *p*-tolylcarbinyl, *p*-cuminyl, dl-*phenylmethyl*-, b.p. 72—73°/4 mm. [not identical with the product thus described by Kenyon *et al.* (A., 1933, 604)], or phenylethyl-carbinyl acetate, and practically no hydrogenolysis with *phenyldimethylcarbinyl acetate*, b.p. 81—82°/2·8 mm., $Ph{\cdot}[CH_2]_2$ acetate or phenylacetate, or $CH_2Ph{\cdot}CO_2{\cdot}C_6H_4Me$-*p*. Cinnamyl cinnamate, *trans-iso*eugenol acetate, and eugenol benzoate are hydrogenated without appreciable hydrogenolysis. H. W.

Complex of nickel with toluamidoxime. L. Malatesta and R. Pizzotti (*Gazzetta*, 1942, **72**, 564—567).—$Ni(OAc)_2$ and *p*-$C_6H_4Me{\cdot}C(NH_2){:}N{\cdot}OH$ in KOH–EtOH, followed by H_2O_2, give not a Ni^{IV} (Kuras, *Chem. Zentr.*, 1942, **113**, I, 2244), but a Ni^{II} *compound*, $C_6H_4Me{\cdot}C$  $C{\cdot}C_6H_4Me$, which is similar to that obtained by Malatesta (*Gazzetta*, 1940, **70**, 842) from $NH_2{\cdot}CPh{:}N{\cdot}OH$; with HCl it evolves N_2. E. W. W.

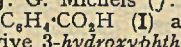
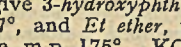
Action of formaldehyde on *m*-hydroxybenzoic acid. I. C. A. Buehler, T. A. Powers, and J. G. Michels (*J. Amer. Chem. Soc.*, 1944, **66**, 417—418).—*m*-$OH{\cdot}C_6H_4{\cdot}CO_2H$ (I) and 40% CH_2O in conc. HCl–H_2SO_4 at 30—40° give *3-hydroxyphthalide* (CO = 1) (II), m.p. 254° [*Me* (III), m.p. 127°, and *Et ether*, m.p. 170°; *acetate*, m.p. 96—97°], and a substance, m.p. 175°. KOH–$KMnO_4$ at 60—75° converts (III) into 3 : 1 : 2-$OMe{\cdot}C_6H_3(CO_2H)_2$ [Me_2 ester, m.p. 73—74° (lit. 71°)]. Br and (I) in AcOH at 50° give 3 : 4 : 6 : 1-$OH{\cdot}C_6H_2Br_2{\cdot}CO_2H$, the Me ether, m.p. 205° (lit. 202—203°), of which with $CH_2(OMe)_2$–conc. HCl–H_2SO_4 at 50—55° gives 4 : 6-*dibromo-3-hydroxyphthalide*, m.p. 146°, reduced to (II) by H_2–Raney Ni at 150—200°/500 lb. R. S. C.

Derivatives of di-iodohydroxybenzoic acids.—See B., 1944, II, 156.

Reactions of *o*-substituents during stilbene syntheses. E. Macovski, J. Georgescu, and C. Bachmeyer (*Ber.*, 1941, **74**, [*B*], 1279—1284).—2 : 1 : 4-$CN{\cdot}C_6H_3Me{\cdot}NO_2$ with 30% H_2O_2 in boiling MeOH–H_2O–KOH gives *4-nitro-o-toluamide* (Me = 1) (I), m.p. 175° (resistant to NaOMe–MeOH at room temp.), which with NaOMe–PhCHO–MeOH at room temp. gives *4-nitrostilbene-2-carboxylamide* (II), m.p. 263° (partial decomp.), and with *o*-$NO_2{\cdot}C_6H_4{\cdot}CHO$ (III)–NaOMe–MeOH gives 4 : 2′-*dinitrostilbene-2-carboxylamide*, m.p. 228°. With (III) at 140—150°, (I) gives *o-nitrobenzylidene-NN′-bis-4′-nitro-o-toluamide*, m.p. 253°, but with RCHO–NaOMe–MeOH at room temp. gives *4-nitro-*, m.p. 206° [with, in one experiment, (II)], and 4 : 2′-*dinitro-stilbene-2-carboxylic acid*, m.p. 210°. R. S. C.

Reaction of γ-anisyl-γ-butyrolactone with potassium cyanide. 6-Methoxy-1 : 2 : 3 : 4-tetrahydro-2-naphthoic acid. C. C. Price and W. Kaplan (*J. Amer. Chem. Soc.*, 1944, **66**, 477—478).—*p*-$OMe{\cdot}C_6H_4{\cdot}CO{\cdot}[CH_2]_2{\cdot}CO_2H$ (prep. modified to give a 95% yield), m.p. 144°, when esterified by boiling with EtOH in a Soxhlet extractor with removal of H_2O by CaC_2 in the thimble and then heated with $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ with very slow removal of $COMe_2$, gives 79% of cryst. γ-*p*-anisyl-γ-*n*-butyrolactone. Interaction thereof with KCN at 210° (N_2) involves rearrangement, yielding *β-cyano-γ-p-anisyl-n-butyric acid* (I), m.p. 116·5° (corr.) (cf. Blaise, A., 1897, i, 323), the structure of which is proved as follows. With HF at 100° (not H_2SO_4 or, as chloride, $AlCl_3$) and then conc. H_2SO_4 at room temp. (1 week), (I) gives *4-keto-6-methoxy-1 : 2 : 3 : 4-tetrahydro-2-naphthoamide*, m.p. 178° (corr.) [*oxime*, m.p. 217—219° (corr.)], reduced by 10% Pd–C–H_2 in EtOH at 41 lb. to *6-methoxy-1 : 2 : 3 : 4-tetrahydro-2-naphthoamide* (II) (68%), m.p. 141° (corr.). Thence HCl–H_2O–AcOH at the b.p. yields the *acid* (III) (85%), m.p. 151° (corr.), not demethylated by KOH–EtOH or HBr–AcOH–H_2O. S at 210—245° converts (II) into a thioamide, which with KOH–EtOH gives 6 : 2-$OMe{\cdot}C_{10}H_5{\cdot}CO_2H$, m.p. 194—196° (lit. sinters 190°, m.p. 209°) [amide, m.p. 220—221° (lit. 219°)]. R. S. C.

Haloform reaction. R. T. Arnold, R. Buckles, and (Miss) J. Stoltenberg (*J. Amer. Chem. Soc.*, 1944, **66**, 209—210).—In aq. MeOH the haloform reaction applied to Ac compounds may lead directly to Me esters owing to the intermediate $CO{\cdot}CCl_3$ reacting faster with MeOH than with H_2O (cf. acid chlorides). 5-Methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene, Ac_2O, and $AlCl_3$ in $PhNO_2$ at 0—5° give 5-acetyl-8-methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene (I), b.p. 164—166°/8 mm. [*oxime*, m.p. 136—139° (decomp.)], which with $Ca(OCl)_2$, KOH, and K_2CO_3 in aq. MeOH gives *Me 8-methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene-5-carboxylate* (II) (80%), m.p. 63—64°, and a small amount of the corresponding *acid* (III), m.p. 215·5—216° [with CH_2N_2 gives (II)]. With $Ca(OCl)_2$ and KOH (excess) in aq. dioxan, (I) gives *7-chloro-8-methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene-5-carboxylic acid*, m.p. 154—156°, which is obtained very rapidly by chlorination of (III) and is not obtained in the haloform reaction if the excess of KOCl is destroyed before acidification. With Br in AcOH, (I) gives *5-bromoacetyl-*, m.p. 73—74°, and thence by KOAc in boiling EtOH *5-acetoxyacetyl-8-methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene*, m.p. 91—92°, hydrolysis of which did not give a pure $OH{\cdot}CH_2{\cdot}CO$ derivative. Structures are proved by conversion of (II) by S at 250° into 4 : 1-$OMe{\cdot}C_{10}H_6{\cdot}CO_2H$. R. S. C.

Phthaleins from phenol and naphthalene-1 : 2-dicarboxylic acid. M. H. Hubacher (*J. Amer. Chem. Soc.*, 1944, **66**, 255—256).—1 : 2-$C_{10}H_6(CO)_2O$, PhOH, and $SnCl_4$ at 113—116° give *phenol-2* : 1- (I), 1 : 2-$C_{10}H_6$  O (22%), m.p. 291·1—292·4° (*diacetate*, m.p. 223·8—225·9°; *dipropionate*, m.p. 162·7—163·7°), and *-1 : 2-naphthalein* (II), 2 : 1-$C_{10}H_6$  O (5%), m.p. 267·5—269·5° (*diacetate*, m.p. 154·5—155·6°; *dipropionate*, m.p. 109·6—110°), converted by KOH at 240—245° into 2- and 1-$C_{10}H_7{\cdot}CO_2H$, respectively; the colour change (to magenta) occurs at pH ~8·6—10·5, but the colour given by (I) is ~4 times as intense as that given by (II); neither colour fades in dil. acid and that of (I) resists H_2O_2. M.p. are corr. R. S. C.

Derivatives of *cis*-3 : 6-*endo*methylene-Δ⁴-tetrahydrophthalic acid. M. S. Morgan, R. S. Tipson, A. Lowy, and W. E. Baldwin (*J. Amer. Chem. Soc.*, 1944, **66**, 404—407).—*cis*-3 : 6-*endo*Methylene-Δ⁴-tetrahydrophthalic anhydride (I) with H_2–Raney Ni in dioxan at 45°/2050 lb. gives 97% of the H_6-anhydride (II), m.p. 167·5—168°. The derived acids show each two well-defined breaks in the titration curve, whereas $(CH_2{\cdot}CO_2H)_2$ shows only one break and *o*-$C_6H_4(CO_2H)_2$ shows only a trace of the first break. In boiling MeOH, (I) and (II) give *Me H* cis-3 : 6-endo*methylene-Δ⁴-tetrahydro-*, m.p. 76—78·5°, and *-hexahydro-phthalate*, m.p. 77—79°, respectively. With a little *p*-$C_6H_4Me{\cdot}SO_3H$ in boiling ROH, (I) gives *Me*$_2$, b.p. 129—130°/9 mm. (indifferent to NH_3 at 0°), *Et*$_2$, b.p. 138—140°/8 mm., and *Bu*$^{\alpha}_2$ cis-3 : 6-endo*methylene-Δ⁴-tetrahydrophthalate*, b.p. 174—176·6°/8 mm. With dry NH_3 at 170° or $(NH_4)_2CO_3$ at 200°, (I) gives the *imide* (III), m.p. 186·5—187°; (II) gives its *imide*, m.p. 174—175·5°, by the former method. With NH_2Ph in warm C_6H_6, (I) gives the *phenylimide*, m.p. 144°; in $CHCl_3$, (II) gives exothermally the anilic acid, m.p. 175—176° (decomp.), readily converted into the *phenylimide*, m.p. 152—153°. With *p*-toluidine in C_6H_6, (I) gives its p-*tolylimide*, m.p. 156·5—157°. With CH_2PhCl and NaOEt in boiling EtOH the imides give the unsaturated, m.p. 82·5—83·5°, and saturated *benzylimide*, m.p. 101—103°. In conc. aq. NH_3 at room temp. (I) or (II) gives *NH*$_4$ cis-3 : 6-endo*methylene-Δ⁴-tetrahydro-*, m.p. 172° (decomp.), and *-hexahydro-phthalamate*, m.p. 177° (decomp.), respectively, converted by aq. HCl at room temp. into the *phthalamic acids*, m.p. 136° (decomp.) and 165—166° (decomp.), respectively, which in boiling H_2O give *NH*$_4$ *H* cis-3 : 6-endo*methylene-Δ⁴-tetrahydro-*, m.p. 148° (decomp.) [derived $(NH_4)_2$ salt, m.p. indefinite], and *-hexahydro-phthalate*, m.p. 149—150°, respectively. An attempt to prepare the diamide from (III) by boiling conc. aq. NH_3 failed. With $AlCl_3$ in C_6H_6 at >45°, (II) gives *3-benzoylnorcamphane-2-carboxylic acid* (87%), m.p. 170—171°, which gives no anthraquinone derivative in H_2SO_4 at 100°. R. S. C.

New synthesis of phenylpropaldehyde and its nuclear homologues. L. Bert (*Compt. rend.*, 1942, **215**, 356—357).—A benzenic hydrocarbon ArH is condensed directly (Friedel–Crafts) or, more generally, indirectly through MgArBr with $CH_2Cl{\cdot}CH{:}CHCl$ to $CH_2Ar{\cdot}CH{:}CHCl$, which is converted by cold Br or heated PCl_5 into $CH_2Ar{\cdot}CHBr{\cdot}CHClBr$ or $CH_2Ar{\cdot}CHCl{\cdot}CHCl_2$, respectively. Either of these when heated with NaOR (R = Me, Et, or Bu$^{\alpha}$) gives $CHAr{:}CH{\cdot}CH(OR)_2$. Hydrogenation then gives $Ar{\cdot}[CH_2]_2{\cdot}CH(OR)_2$, hydrolysed to $Ar{\cdot}[CH_2]_2{\cdot}CHO$. No experimental results are recorded. H. W.

Complex behaviour of potassium permanganate towards an ethylenic function leading to a new mode of formation of *p-iso*propylphenylacetaldehyde. L. Bert (*Compt. rend.*, 1942, **215**, 276—277).—*p*-$C_6H_4Pr^{\beta}{\cdot}CH{:}CH{\cdot}CH_2{\cdot}OR$ (I) (R = Me, Et, Pr$^{\alpha}$, Pr$^{\beta}$, Bu$^{\alpha}$, Bu$^{\beta}$, *iso*-C_5H_{11}) is converted by agitation with a saturated aq. solution of $KMnO_4$ at room temp. into *p*-$C_6H_4Pr^{\beta}{\cdot}CH_2{\cdot}CHO$ (II) with some *p*-$C_6H_4Pr^{\beta}{\cdot}[CH{\cdot}OH]_2{\cdot}CH_2{\cdot}OR$. When R = Bu$^{\alpha}$ or *iso*-C_5H_{11} small amounts of $Pr^{\alpha}CO_2H$ or *iso*-$C_5H_{11}{\cdot}OH$, respectively, are also obtained. The course of the change is (I) + $2O \rightarrow C_6H_4Pr^{\beta}{\cdot}CHO$ (III) + $OR{\cdot}CH_2{\cdot}CHO$ (IV); (III) + (IV) (in presence of KOH from $KMnO_4$) → *p*-$C_6H_4Pr^{\beta}{\cdot}CH{:}C(OR){\cdot}CHO$ (V); (V) + O → *p*-$C_6H_4Pr^{\beta}{\cdot}CH{:}C(OR){\cdot}CO_2H \rightarrow (-CO_2)$ *p*-$C_6H_4Pr^{\beta}{\cdot}CH{:}CH{\cdot}OR \rightarrow (+H_2O)$ *p*-$C_6H_4Pr^{\beta}{\cdot}CH{:}CH{\cdot}OH$ + ROH → (II). No experimental results are recorded. H. W.

Substituted α-amylcinnamaldehydes. A. Weizmann (*J. Amer. Chem. Soc.* 1944, **66**, 310—311).—RCHO, *n*-$C_6H_{13}{\cdot}CHO$ (I), and piperidine in C_5H_5N at 100° give α-p-*anisylidene-*, b.p. 145°/0·3 mm. (*semicarbazone*, m.p. 143—145°), α-3 : 4-*dimethoxybenzylidene-*, b.p. 165°/0·6 mm. (*semicarbazone*, m.p. 175°), and α-3 : 4-methylenedioxybenzylidene-*n*-heptaldehyde, b.p. 158—159°/0·9 mm. (*semicarbazone*, m.p. 155°). PhCHO condenses more readily than do the above aldehydes. Vanillin and (I) do not react. R. S. C.

Reaction of maleic anhydride with aromatic oximes. G. La Parola (*Gazzetta*, 1943, **73**, 94—99; cf. A., 1937, II, 501).—$(CH{\cdot}CO)_2O$ (I) and α-*p*-tolualdoxime in C_6H_6 at the b.p. give N-p-*toluoylaspartic acid*, m.p. 182°. With α-anisaldoxime, (I) gives N-*anisoylaspartic*

acid, m.p. 180°. *α-p*-NMe_2·C_6H_4·CH:N·OH and α-piperonaldoxime give the nitriles, and α-salicaldoxime the aldehyde. E. W. W.

Spectroscopic study in the stereoisomeric capsanthin set. *cis*-Peak effect and configuration. A. Polgár and L. Zechmeister (*J. Amer. Chem. Soc.*, 1944, **66**, 186—190).—The fine structure of the absorption spectrum of capsanthin in hexane is obliterated by adding as little as 2% of EtOH and in abs. EtOH no structure at all is visible. 32 isomerides are possible, 5 of the ethylenic linkings being capable of *trans* → *cis* isomerisation. Isomerisation by I, insolation, and melting is investigated. Light is needed for development of a *cis*-peak. The customary considerations lead to the structures: neocapsanthin *A* 6-*cis*, *B* 5- or 7-*cis*, and *C* di-*cis*. R. S. C.

Isomerisation of aromatic ketones with aluminium chloride. G. Baddeley (*J.C.S.*, 1944, 232—236; cf. A., 1943, II, 264).—The isomerisations are of two types, viz., (*A*) those resembling the isomerisation of *o*-hydroxyaryl alkyl ketones, the mobile alkyl moving intramolecularly into the adjacent position, and (*B*) those involving migration (possibly intramol.) of the CO group. Migrations of alkyl in C_6H_6 homologues, phenols, aryl and hydroxyaryl ketones are related to one another, and to the Jacobson reaction. *o*-C_6H_4Me·COMe (*semicarbazone*, m.p. 212°) and $AlCl_3$ (2 mols.) at 170° for 1·5 hr. give *p*-C_6H_4Me·COMe (**I**) (85%) (type *B*) (*semicarbazone*, m.p. 208°), and no type *A* product. In presence of *m*-5-xylenol (**II**) at 160°, the yield of (**I**) is halved owing to formation of 2 : 4 : 5 : 1-OH·$C_6H_2Me_2$·COMe (**III**); the production of an acylating agent is thus possibly responsible for (**I**). *o*-C_6H_4Me·COEt similarly yields the *p*-isomeride (83%). 2 : 5 : 1-$C_6H_3Me_2$·COMe gives the 3 : 5 : 1-isomeride (77%) (*A*) (*semicarbazone*, m.p. 219°) and 8% of the 3 : 4 : 1-compound (**IV**) (*B*) [no (**IV**) is formed if (**II**) is present in the reaction mixture]. *o*-C_6H_4Et·COMe (*semicarbazone*, m.p. 182°) and $AlCl_3$ yield the *m*-isomeride (70%) (*A*) (*semicarbazone*, m.p. 175°) and a little of the *p*-compound (2 : 4-*dinitrophenylhydrazone*, m.p. 203°; *semicarbazone*, m.p. 191°). 2 : 5 : 1-$C_6H_3Et_2$·COMe (2 : 4-*dinitrophenylhydrazone*, m.p. 105°) yields the 3 : 5 :1-compound (83%) (*A*) (2 : 4-*dinitrophenylhydrazone*, m.p. 185°; *semicarbazone*, m.p. 149°), but no 3 : 4 : 1-isomeride (*semicarbazone*, m.p. 180°), thus showing the great mobility of Et. 2 : 4 : 1-$C_6H_3Me_2$·COMe (*semicarbazone*, m.p. 202°) and $AlCl_3$ or $AlBr_3$ (3 mols. at 150°) give 80% of (**IV**); $AlCl_3$ + (**II**) give (**III**) also. 2 : 4 : 6 : 1-$C_6H_2Me_3$·COMe and $AlCl_3$ afford the 3 : 4 : 5 : 1-isomeride (87%) (*A*) (*semicarbazone*, m.p. 217°) and 2 : 5 : 1-$C_6H_3Me_2$·COPh (at 190°) yields the 3 : 5 : 1-compound (90%) (*A*). *p*-Hydroxyacetophenones undergo isomerisations of type *B* only, and complete isomerisation of 4 : 2 : 1- into 2 : 4 : 1-OH·C_6H_3Me·COMe is achieved with slightly >1 mol. of $AlCl_3$. 2 : 5 : 1-$C_6H_3Me_2$·COMe is converted into the 2 : 4 : 1-isomeride by heating with 1 mol. of 6 : 3 : 4 : 1-OH·$C_6H_2Me_2$·COMe (1 mol.) and $AlCl_3$ (3 mols.); this is type *B* isomerisation occurring under conditions where there is no reagent capable of producing type *A*. 1-Keto-5 : 8-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (**V**), b.p. 164°/20 mm. (*semicarbazone*, m.p. 222°), yields the 5 : 7-Me_2 compound (90%) (*A*) (*semicarbazone*, m.p. 245°), but 4 : 7-dimethyl-α-hydrindone (**VI**), m.p. 77°, is unchanged with $AlCl_3$. Ketones with no alkyl group *o*- to CO do not isomerise. All the *o*-alkylaryl ketones and (**V**), but not (**VI**), are hydrolysed by H_3PO_4 at 180°, CO being detached from the nucleus. The rigid and planar structure of (**VI**) suggests that the isomerisation of an aromatic ketone requires the propulsion of CO out of the plane of the aromatic nucleus. An explanation is given why isomerisation of type *A* is accelerated by alkyl *para* to the one which migrates. $AlBr_3$ (3 mols.) at 150° isomerises 6 : 2 : 4 : 1- to 2 : 4 : 5 : 1-OH·$C_6H_2Me_2$·COMe. $AlCl_3$ does not isomerise homologues of PhCN. The following are new: 3 : 5-*dimethylbenzophenone*, m.p. 70°; *semicarbazones*, m.p. 205°, 226°, and 143°, of *m*-C_6H_4Me·COMe, 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene, and *p*-$C_6H_4Pr^{\alpha}$·COEt (**VII**), respectively; (**VII**) and 2 : 5 : 1-$C_6H_3Pr^{\alpha}_2$·COMe give 2 : 4-*dinitrophenylhydrazones*, m.p. 147° and 75°, respectively. A. T. P.

Factors determining the course and mechanism of Grignard reactions. XIII. Effect of metallic halides on the reaction of sterically hindered acid halides with magnesium methyl iodide. M. S. Kharasch, R. Morrison, and W. H. Urry (*J. Amer. Chem. Soc.*, 1944, **66**, 368—371; cf. A., 1944, II, 215).—Adding MesCOCl (Mes = mesityl) to MgMeI gives good yields of COMeMes, but the reverse addition gives 25% of COMeMes and 50% of $(MesCO)_2$ (cf. Fuson *et al.*, A., 1938, II, 445). Use of very pure Mg or allowing the MgMeI solution to age increases the proportion of COMeMes, as also does addition of 1 atom-% of Cu or, better, 1 mol.-% of $MnCl_2$, $FeCl_3$, or CuCl. MgMeBr gives 87% of COMeMes, but addition of $CoCl_2$ leads to much $(MesCO)_2$, an effect shown less markedly with MgMeI. A free radical chain mechanism is proposed. R. S. C.

Acetylation of 1 : 2-dimethylnaphthalene. P. A. Plattner and A. Ronco (*Helv. Chim. Acta*, 1944, **27**, 400—403).—1 : 2-$C_{10}H_6Me_2$, b.p. 135—137°/13 mm. (picrate, m.p. 129—130°), is obtained homogeneous (76% yield) by the successive action of Li and Me_2SO_4 on 2 : 1-$C_{10}H_6MeBr$ in Et_2O. It is converted by AcCl and $AlCl_3$ in CS_2 or $PhNO_2$ into 3 : 4-*dimethyl*-1-*naphthyl Me ketone* (**I**), b.p. 135—137°/0·3 mm. (*picrate*, m.p. 134—135°; *semicarbazone*, m.p. 225°). The constitution of (**I**) is established by its oxidation (NaOBr) to 3 : 4-*dimethyl*-1-*naphthoic acid*, m.p. 226—227° (*Me* ester, m.p. 49°), also obtained by converting 4 : 1 : 2-$C_{10}H_5BrMe_2$ by CuCN at 260° into 3 : 4-*dimethyl*-1-*naphthonitrile*, m.p. 120—121°, and subsequent hydrolysis with boiling 25% KOH–EtOH. M.p. are corr. H. W.

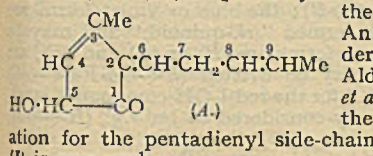
Molecular rearrangements of phenyl styryl ketone oxides. J. Algar and J. McKenna (*Proc. Roy. Irish Acad.*, 1944, **49, B**, 225—249).—COAr·CH:CHAr′ with H_2O_2–aq. EtOH–NaOH gives the oxide, which is rearranged by 50% H_2SO_4 at room temp. into COAr·CHAr′·CHO. This is converted into the corresponding pyrazole by EtOH–NHPh·NH_2. The following are described: *Ph* 3 : 4-*dimethoxystyryl ketone oxide*, m.p. 87—89°; *o*-, m.p. 114—115°, and p-*anisyl* p-*methoxystyryl ketone oxide*, m.p. 119—121°; o-*anisyl* 3 : 4-*methylenedioxystyryl ketone oxide*, m.p. 151°; *α-phenyl-β*-p-*anisylpropane-αγ-dione*, m.p. 115° (uncorr.); *α-phenyl-β*-3 : 4-*methylenedioxyphenylpropane-αγ-dione*, m.p. 108—109°; *α-phenyl-β*-3 : 4-*dimethoxyphenylpropane-αγ-dione*, m.p. 113—114°; *α-phenyl-β*-o-*anisylpropane-αγ-dione* (an oil; Cu salt, m.p. 190—195°, softening at 185°); *β-phenyl-α*-p-*anisylpropane-αγ-dione*, m.p. 82—84° (uncorr.); *αβ-di*-p-*anisylpropane-αγ-dione*, m.p. 135—136°; *β-phenyl-α*-o-*anisylpropane-αγ-dione* (**I**) [an oil; *Cu* salt (+EtOH), m.p. 243° (decomp.), softening at 240°]; *α*-o-*anisyl-β*-p-*anisylpropane-αγ-dione* [an oil; *Cu* salt m.p. 221—222° (decomp.), softening at 214°]; *α*-o-*anisyl-β*-3 : 4-*methylenedioxyphenylpropane-αγ-dione* [an oil; *Cu* salt m.p. 275°)(uncorr.; decomp.)]; *α*-o-*anisyl-β*-3 : 4-*dimethoxyphenylpropane-αγ-dione*; *β-phenyl-α*-2 : 4-*dimethoxyphenylpropane-αγ-dione* (**II**) [an oil; *Cu* salt (+EtOH), m.p. 200—210° after softening]. 1 : 5-*diphenyl*-4-p-*anisyl*-, m.p. 150—151°, -4-3′ : 4′-*methylenedioxyphenyl*-, m.p. 199°, and -4-3′ : 4′-*dimethoxyphenyl*-, m.p. 163°, 1 : 4-*diphenyl*-5-p-*anisyl*-, m.p. 183°, and 1-*phenyl*-4 : 5-*di*-p-*anisyl-pyrazole*, m.p. 173°. Small yields of *iso*flavone and 7-hydroxy*iso*flavone are obtained from (**I**) and (**II**), respectively, by $AlBr_3$ in boiling C_6H_6. Prolonged refluxing of (**I**) gives a *compound*, m.p. 147·5—148·5°, probably *o*-OH·C_6H_4·CO·CPh:CHPh. M.p. are corr. except where stated. J. H. Ba.

Functional aptitude of the methyl group. VIII. Formation of anilides by the action of nitroso-derivatives on compounds with an active methyl group. L. Chardonnens and P. Heinrich (*Helv. Chim. Acta*, 1944, **27**, 321—332; cf. A., 1940, II, 160).—Certain secondary products of the condensation of activated Me groups with NO-compounds are shown to be anilides and not nitrones. 3 : 4 : 1-NO_2·C_6H_3Me·COPh and *p*-NO·C_6H_4·NMe_2 afford 2-nitro-4-benzoylbenzaldehyde-*p′*-dimethylaminoanil, m.p. 174—175°, and 3-*nitrobenzophenone-4-carboxy*-p-*dimethylaminoanilide* (**I**), m.p. 217°. Similarly PhNO yields 3-*nitrobenzophenone-4-carboxyanilide* (**II**), m.p. 169°. 2-Nitro-4-benzoylstilbene is oxidised (CrO_3 in AcOH) to 3-nitrobenzophenone-4-carboxylic acid (*Me* ester, m.p. 82°), the chloride of which with NH_2Ph (or *p*-NMe_2·C_6H_4·NH_2) in C_5H_5N affords (**I**) [or (**II**)]. The minor compound from 3 : 3′-dinitro-4-methylbenzophenone (**III**) and *p*-NO·C_6H_4·NMe_2 is 3 : 3′-*dinitrobenzophenone-4-carboxy*-p-*dimethylaminoanilide* (**IV**), m.p. 234° (cf. A., 1939, II, 428); the *-anilide* (**V**), m.p. 190°, is obtained similarly from PhNO. (**III**) and PhCHO in presence of piperidine afford trans(?)-3 : 3′-*dinitro*-4-*styrylbenzophenone*, m.p. 168°, also obtained from the isomeride, m.p. 155—156°, by the action of a little I in boiling $PhNO_2$; it is oxidised by CrO_3 in AcOH at 70° to 3 : 3′-*dinitrobenzophenone-4-carboxylic acid*, m.p. 193—194°, also obtained from (**III**) and HNO_3 (*d* 1·15) at 155—165°; it is converted through its chloride into the *Me* ester, m.p. 124°, (**IV**), and (**V**). 2-Nitro-4-benzoylbenzaldehyde and NHPh·OH in boiling EtOH afford the N-*Ph* derivative, m.p. 136°, of 2-nitro-4-benzoylbenzaldoxime, isomerised by calcined Na_2CO_3 in boiling EtOH to (**II**). 2-Nitro-4-*m*-nitrobenzoylbenzylidene-*p*-dimethylaminoanil in C_6H_6 is hydrolysed by aq. HCl to 2-*nitro*-4-m-*nitrobenzoylbenzaldehyde*, m.p. 142·5° [*phenylhydrazone*, m.p. 218·5° (decomp.)], converted by NHPh·OH into the N-*Ph* derivative, m.p. 157°, of 2-nitro-4-*m*-nitrobenzoylbenzaldoxime which is isomerised by Na_2CO_3 in boiling EtOH to (**V**). The N-*Ph* derivative, m.p. 147·5°, of 2-nitro-4-benzeneazobenzaldoxime is similarly isomerised to 3-nitroazobenzene-4-carboxyanilide. 5-Nitrobenzophenone-2-carboxylic acid [from 5 : 2 : 1-NO_2·C_6H_3Me·CO_2Ph (**VI**) and HNO_3 (*d* 1·15) at 160—170°] is converted ($SOCl_2$) into the chloride and thence into the *p*-dimethylaminoanilide, m.p. 240°, identical with the substance derived from *p*-NO·C_6H_4·NMe_2 and (**VI**), which, therefore, is not a nitrone. H. W.

Normal and *ψ*-structures of 8-benzoyl-1-naphthoic acid and derivatives. H. E. French and J. E. Kircher (*J. Amer. Chem. Soc.*, 1944, **66**, 298—300).—Crystallisation of 8 : 1-$C_{10}H_6Bz$·CO_2H (*A*) from EtOH, 70% AcOH, or $CHCl_3$ gives a form (**I**), m.p. 110° (Mason, A., 1925, i, 33, 34), but from xylene, *cyclo*hexane, or PhMe gives a form (**II**), m.p. 129—130° (Knapp, A., 1936, 726). After heating at 90°, (**I**) gives a form, m.p. 154°. (**I**) or (**II**) in $CHCl_3$ or (**II**) after boiling in *cyclo*hexane has absorption max. at 3081—3120 and 3252—3297 A., thus resembling 8 : 1-$C_{10}H_6$<$\begin{matrix}CPh_2\\CO\end{matrix}$>O (**III**) (max. at 3092 and 3275 A.) but not 1 : 8-$C_{10}H_6Bz_2$ (max. at 2190 A.). (**III**), its ditolyl analogue, and 1 : 8-$C_{10}H_6(CO)_2O$ show a blue

fluorescence in ultra-violet light, but (**VI**) and (**VII**) (below) appear greyish-white; (*A*), its toluoyl analogue, and (**V**) (below) appear blue. Thus, (*A*) exists in solution largely as 8 : 1-$C_{10}H_6\langle^{CPh(OH)}_{CO}\rangle$O. With $SOCl_2$, (**I**) gives a product which by crystallisation from C_6H_6 gives *α-chloro-α-phenyl*-1 : 8-*naphthalide* (**IV**), m.p. 125—127° (absorption max. at 2961, 3074, and 3251 A.), converted by EtOH into the *α-OEt*-compound (*Et* 8-*benzoyl*-1-*naphthoate ψ*-ester) (**V**), m.p. 166° (absorption max. at 3085 and 3259 A.) (cf. Mason, *loc. cit.*). The Ag salt of (*A*) with EtI gives *Et* 8-*benzoyl*-1-*naphthoate* (normal form) (**VI**), m.p. 134° [absorption max. at 2946 A.; cf. 1 : 8-$C_{10}H_6(CO_2Et)_2$ (**VII**), max. at 2950 A.]. (**V**) and (**VI**) are separated by chromatography (Al_2O_3; C_6H_6–light petroleum), whereby it is proved that crude (**V**), prepared from (**IV**), contains some (**VI**). The crude oily chloride from (**I**) reacts with EtOH more readily than does pure (**IV**) and gives mainly (**VI**); the crude product thus contains much 8 : 1-$C_{10}H_6$Bz·COCl. With C_6H_6–$AlCl_3$, (**IV**) gives 25—50% of (**III**); the oily chloride gives HCl and tars. R. S. C.

Structure of pyrethrolone and related compounds. II. T. F. West (*J.C.S.*, 1944, 239—242; cf. A., 1944, II, 136).—(+)-Pyrethrolone (**I**) with Me_2SO_4–Et_2O–KOH gives a Me ether (**II**), b.p. 87°/0·3 mm., $[\alpha]_D^{20}$ +97·3° in EtOH [regenerated from its semicarbazone (**III**), m.p. 183—184°, $[\alpha]_D^{20}$ −82° in C_5H_5N, by aq. $KHSO_4$–Et_2O], whereas the semicarbazone, m.p. 208°, of (**I**) with MeOH–H_2SO_4 yields *dl*-pyrethrolone Me ether (**IV**), b.p. 85°/0·2 mm. (semicarbazone, m.p. 196—197°, $[\alpha]_D$ ±0° in C_5H_5N). (**III**) with Me_2SO_4–H_2SO_4 gives (**IV**). (**II**) and (**IV**) are probably stereoisomeric; neither is reducible by the Ponndorf–Meerwein method. An explanation for the failure of derivatives of (**I**) to undergo Diels–Alder condensation (cf. LaForge, *et al.*, A., 1938, II, 372) is based on the postulation of a *cis*-configuration for the pentadienyl side-chain. A new formulation (*A*) for (**I**) is proposed.

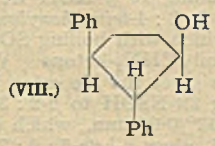


(*A*.)

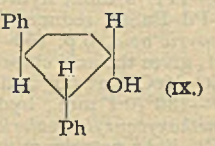
A. T. P.

Preparation of substituted *cyclo*pentanones. Catalytic hydrogenation of (III) αβ-unsaturated carbonyl compounds, (IV) 2 : 3-diphenyl-Δ³-*cyclo*pentenone. H. A. Weidlich and M. Meyer-Delius (*Ber.*, 1941, **74**, [*B*], 1195—1212, 1213—1218).—III. Catalytic hydrogenation of C:C·CO in acid is an ionic reaction, occurring by 1 : 2-addition to the C:C or C:O; in alkaline solution the reaction is at. and occurs by 1 : 4-addition. Hydrogenations listed below are by H_2–PdO_2 in EtOH; "acid" and "alkali" denote addition of a little conc. HCl or KOH–EtOH, respectively. In alkali CHPh:CH·COPh gives Ph·$[CH_2]_2$·COPh (100%) and in acid gives $[CH_2]_3Ph_2$ (100%). Reduction of CHPh:CH·CHO in alkali becomes very slow after absorption of 1 H_2 and a good yield of Ph·$[CH_2]_2$·CHO is obtained (cf. lit.). 4-Hydroxy-3 : 4-diphenyl-Δ³-*cyclo*pentenone (anhydroacetonebenzil), m.p. 146—147°, b.p. 190°/0·4 mm. [2 : 4-*dinitrophenylhydrazone*, m.p. 262° (decomp.)], in alkali absorbs 1 H_2, giving a partly dehydrated mixture, whence by dehydration in boiling AcOH, 3 : 4-diphenyl-Δ³-*cyclo*pentenone (**I**), m.p. 108—109° [*semicarbazone*, m.p. 219° (decomp.); 2 : 4-dinitrophenylhydrazone, m.p. 252° (lit. 259—260°) (decomp.)], is obtained; in acid ~2·5 H_2 are absorbed, yielding (**I**) and 1 : 2-*diphenyl*-Δ¹-cyclo*pentene*, b.p. 119°/0·4 mm., the structure of which is proved by oxidation to *αε-diphenyl*-n-*pentane*-*αε*-*dione*, m.p. 64·5—65°. In alkali or acid (**I**) yields only *cis*-3 : 4-diphenyl-*cyclo*pentanone, m.p. 106°. Dimerisation during hydrogenation occurs by way of C·CH:C·OH which either adds 1 H or dimerises, and will thus occur only when reduction is slow, *i.e.*, in alkaline solution; thus, $CO(CH{:}CHPh)_2$ in acid gives $CO([CH_2]_2{\cdot}Ph)_2$ (2 : 4-*dinitrophenylhydrazone*, m.p. 115—117°) and $OH{\cdot}CH([CH_2]_2{\cdot}Ph)_2$, but in alkali gives Ph·$[CH_2]_2$·CO·CH:CHPh and $(CHPh{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CHPh)_2$. The steric course of reduction may be predicted in simple cases: 1 : 2-addition in acid resembles simple hydrogenation of an isolated C:C and leads to the energy-richer *cis*-form; 1 : 4-addition in alkali leads to CH·C:C·OH, ketonisation of which leads to the energy-poorer *trans*-form. *E.g.*, 3-*β*-naphthyl-Δ²-*cyclo*pentenone-2-acetic acid (as Me ester) in alkali rapidly absorbs 1 H_2 to yield cis-3-*β-naphthyl*cyclo*pentanone*-2-*acetic acid*, m.p. 106°, b.p. 192°/0·3 mm., the *trans*-form of which was obtained by Koebner *et al.* (A., 1939, II, 75) by H_2–Pd–$SrCO_3$; their *x*-norequilenin was similarly a *trans*-form. Cyclisation of $[CH_2]_4Bz_2$ gives 2-benzoyl-1-phenyl*cyclo*pentanol (**II**) and thence 1-benzoyl-2-phenyl-Δ²- (**III**), m.p. 97° (2 : 4-*dinitrophenylhydrazone*, m.p. 132—140°), and -Δ¹-*cyclo*pentene (**IV**), m.p. 42° (2 : 4-*dinitrophenylhydrazone*, m.p. ~165—170°) (cf. Bauer, A., 1914, i, 701). (**II**) is a mixture; *trans*-elimination of H_2O from the *trans*-form gives (**IV**), whereas (**III**) is derived from *cis*-(**II**). In alkali, (**III**) or (**IV**) gives only trans-2-*benzoyl*-1-*phenyl*cyclo*pentane*, m.p. 75—76° (2 : 4-*dinitrophenylhydrazone*, m.p. 129—130°), but in acid gives cis-1-*phenyl*-2-*α-hydroxybenzyl*cyclo*pentane*, m.p. 104—106°, oxidised by CrO_3 to cis-1-*phenyl*-2-*benzoyl*cyclo*pentane*, m.p. 42—43° (2 : 4-*dinitrophenylhydrazone*, m.p. 132—134°).

IV. Hydrogenation of 2 : 3-diphenyl-Δ²-*cyclo*pentenone (**V**) in alkaline EtOH in presence of Pd gives *trans*-2 : 3-diphenyl*cyclo*pentanone (**VI**), m.p. 97° (*semicarbazone*, m.p. 192°) (cf. Burton *et al.*, A., 1939, II, 567), but in EtOH + 1 drop of conc. HCl gives *cis*-1 : 2-diphenyl*cyclo*pentane (**VII**), (**VI**), and, sometimes, trans-trans-2 : 3-*diphenyl*cyclo*pentanol* (**VIII**), m.p. 110—112° [oxidised by CrO_3–AcOH to (**VI**)]. The alkaline reduction and formation of (**VII**) in acid conforms to the rules laid down above; formation of



(VIII.)



(IX.)

(**VI**) and (**VIII**) in acid is due to hindrance by the 2 Ph slowing reaction so that 1 : 4-addition occurs. In presence of $CH(OEt)_3$, addition to the O is largely prevented and hydrogenation in acid gives, by way of the ketal, cis-2 : 3-*diphenyl*cyclo*pentanone*, m.p. 71° (*semicarbazone*, m.p. 189—190°), as well as some (**VI**). In presence of PtO_2 in acid, (**V**) gives trans-cis-2 : 3-*diphenyl*cyclo*pentanol* (**IX**), b.p. 142—144°/0·3 mm., oxidised to (**VI**) by CrO_3–AcOH. R. S. C.

Dehydrogenation of *cyclo*hexanols [to *cyclo*hexanones].—See B., 1944, II, 156.

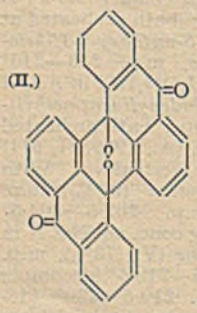
Derivatives of 5-methoxyhydrindene and 6-methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene. Synthesis of β-2-carboxy-5-methoxyphenylpropionic acid. W. S. Johnson, J. M. Anderson, and W. E. Shelberg (*J. Amer. Chem. Soc.*, 1944, **66**, 218—222).—*m*-OH·C_6H_4·CHO, $CH_2(CO_2H)_2$, and a little piperidine in C_5H_5N at 100° give *m*-OH·C_6H_4·CH:CH·CO_2H, m.p. 194—195°, hydrogenated (PtO_2; MeOH) to *m*-OH·C_6H_4·$[CH_2]_2$·CO_2H, m.p. 111·8—112·5°, which in HF gives 5- (85%) (**I**), m.p. 184—185·5° [semicarbazone, m.p. 222—222·5° (decomp.; bath preheated at 215°); *acetate*, m.p. 92·8—93·2°], and 7-hydroxy-1-hydrindone (13%), m.p. 110·5—111·5°. Me_2SO_4–alkali converts (**I**) into the Me ether (**II**), m.p. 110—110·5° [semicarbazone, m.p. 240—241° (decomp.); 2 : 4-*dinitro*-, m.p. 282—284° (decomp.; uncorr.), and *p-nitro-phenylhydrazone*, m.p. 209—211·5° (decomp.; bath preheated at 200°)], which is also obtained in 78% yield from 5-methoxyhydrindene by CrO_3 in AcOH–H_2O at 5—10° and then room temp. With NaOMe and HCO_2Et in C_6H_6–N_2, (**II**) gives 5-*methoxy*-2-*hydroxymethylene*-1-*hydrindone* (**III**) (98%), m.p. 138—138·5° (decomp.) (purple $FeCl_3$ colour) [*bis*-2 : 4-*dinitrophenylhydrazone*, m.p. 223—226° (decomp.; bath preheated at 220°)], which at 140—150° gives HCO_2H and 5-*methoxy*-2-1′-*keto*-5′-*methoxy*-2′-*hydrindenylidenemethyl*-1-*hydrindone*, m.p. 213—215° (decomp.; bath preheated at 205°), and with NH_2OH,HCl in AcOH at room temp. gives *di*-(1-*keto*-5-*methoxy*-2-*hydrindenylidenemethyl*)-*hydroxylamine* (**IV**) (90%), m.p. 216—218° (decomp.; bath preheated at 214°). The supposed nitrile of Robinson *et al.* (A., 1939, II, 511) is probably a similar bimol. hydroxylamine derivative. With Br–Et_2O, (**II**) gives 2-*bromo*-5-*methoxy*-1-*hydrindone* (95%), m.p. 107·8—108·5° [2 : 4-*dinitrophenylhydrazone*, m.p. 202·5—204·5° (decomp.; bath preheated at 195°)], converted by conc. aq. NaCN in boiling EtOH into 2-*cyano*-5-*methoxy*-1-*hydrindone* (**V**) (73%), m.p. 96—96·5° [2 : 4-*dinitrophenylhydrazone*, m.p. 217·5—219·5° (decomp.; bath preheated at 215°); *semicarbazone*, m.p. 219·5—220° (decomp.; bath preheated at 214°)], which could not be obtained from (**III**) or (**IV**). 6-Methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene and $Pb(OAc)_4$ in AcOH at room temp. give exothermally (cooling required) 1-*acetoxy*-6-*methoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (62%), b.p. 118·5°/0·5 mm., which is unstable, particularly in presence of traces of acid, and with a little $KHSO_4$ at 120° rapidly gives AcOH and 7-*methoxy*-1 : 2-*dihydronaphthalene* (**VI**), b.p. 94—95°/2—3 mm. 48% HBr converts (**VI**) into a *dimeride* (? 7-*methoxy*-3-6′-*methoxy*-1′ : 2′ : 3′ : 4′-*tetrahydro*-1′-*naphthyl*-1 : 2-*dihydronaphthalene*), m.p. 75·5—76·5°, supposed by Long *et al.* (A., 1942, II, 96, m.p. 73—74°) to be (**VI**). *β-2-Carboxy*-5-*methoxyphenylpropionic acid*, m.p. 203·5—204°, is obtained from (**IV**) by boiling 2% aq. NaOH (61% yield), from (**V**) by boiling 5% KOH (88% yield), and from (**VI**) by $KMnO_4$ in $COMe_2$ at 0—3° and then room temp. (40% yield), and is cyclised to (**II**) by distilling with BaO. Unless otherwise stated, m.p. are corr. R. S. C.

Introduction of the angular methyl group. II. *cis*- and *trans*-8-Methyl-1-hydrindanone. W. S. Johnson (*J. Amer. Chem. Soc.*, 1944, **66**, 215—217; cf. A., 1943, II, 330).—*cis*-1-Keto-2-benzylidene-9-methyldecahydronaphthalene (**I**) with $KMnO_4$ (excess) in $COMe_2$ at 2—4° and then 0° gives crude *β*-2-carboxy-2-methyl*cyclo*hexylpropionic acid, m.p. 99·5—103°, converted by distillation with BaO at 300—320° into *cis*-8-methyl-1-hydrindanone, m.p. 34·5—36°, b.p. 106°/20 mm. (oxime, m.p. 87—88°; 2 : 4-*dinitrophenylhydrazone*, m.p. 140·5—141°), which only slowly gives the semicarbazone, m.p. 224·5—225·5° (decomp.) (cf. lit.). The *trans*-isomeride of (**I**) gives similarly trans-*β*-2-*carboxy*-2-*methyl*cyclo*hexylpropionic acid*, m.p. 179—180°, and thence *trans*-8-methyl-1-hydrindanone, b.p. 109°/20 mm. (oxime, m.p. 115—115·5°; 2 : 4-*dinitrophenylhydrazone*, m.p. 146·5—147°, resolidifies, remelts 153·5—154°), which readily forms the semicarbazone, m.p. 242—243° (decomp.) (cf. lit.). M.p. are corr. R. S. C.

Synthesis of 5-hydroxy-1-keto-6 : 7-dimethoxy-3-ethyl-1 : 2 : 3 : 4-tetrahydronaphthalene. K. Wallenfels (*Ber.*, 1941, **74**, [*B*], 1428—1433).—2 : 3 : 4 : 1-$(OMe)_3C_6H_2$·CHO (**I**) (improved prep.), b.p. 161—163°/10 mm., $(Pr^{\alpha}CO)_2O$, and $Pr^{\alpha}CO_2K$ at 180° give 2 : 3 : 4-*trimethoxy-α-ethylcinnamic acid* (**II**), m.p. 117°. $CHEtBr{\cdot}CO_2Et$, (**I**), Zn, and a trace of I in boiling C_6H_6 give an Et ester, m.p. 62°, b.p. 176—177°/3 mm., hydrolysed to (**I**) by boiling 10% KOH–EtOH. H_2–Pd–$BaSO_4$ reduces (**II**) in AcOH to *α*-2 : 3 : 4-*trimethoxybenzyl-n-butyric acid*, b.p. 156—157°/0·05 mm., which with boiling $SOCl_2$–C_6H_6 gives the acid chloride and thence the oily CHN_2-ketone. With Ag_2O–MeOH at 50° and then the b.p. this gives the Me ester, b.p. 128—130°/0·1 mm., hydrolysed by boiling 2N-NaOH to *β*-2 : 3 : 4-*trimethoxybenzyl-n-valeric acid*, b.p. 152—153°/0·05 mm., which with $SOCl_2$–light petroleum and then $SnCl_4$–C_6H_6 gives 1-*keto*-5 : 6 : 7-*trimethoxy*-, b.p. 121—122°/0·05 mm., or with $AlCl_3$ in CS_2 at 0° and then the b.p. gives 5-*hydroxy*-1-*keto*-6 : 7-*dimethoxy*-3-*ethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (**III**), m.p. 115°. With SeO_2 in AcOH or EtOH, (**III**) gives a red dye, 1 : 3 : 2 : 5 : 6 : 7 : 4-$O{:}C_{10}HEt(OH)_2(OMe)_2{:}O$ (absorption max. at 553 mμ.), sol. in $NaHCO_3$ with a violet and in NaOH with a blue colour, reduced by $Na_2S_2O_4$ to the colourless quinol and converted by CH_2N_2 into the lighter-coloured $(OMe)_4$-quinone, insol. in $NaHCO_3$ or NaOH, which in boiling, dil. HCl gives 1 : 3 : 5 : 2 : 6 : 7 : 4-$O{:}C_{10}HEt(OH)(OMe)_3{:}O$, insol. in $NaHCO_3$ but sol. in NaOH with a red colour. R. S. C.

Ketones, ketonic acids, and enol-lactones. IV. *cyclo*-**Pentane-1 : 3-diones.** P. Ruggli and J. Schmidlin (*Helv. Chim. Acta*, 1944, **27**, 499—502).—2 : 4-Diphenyl*cyclo*pentane-1 : 3-dione (**I**), m.p. 204—205°, has been obtained by a second method (cf. Eskola, *Diss., Helsinski*, 1937). Like other supposedly *cyclo*pentane-1 : 3-diones, it possesses unusual properties which may be proper to these compounds or indicative of a different structure. $CO(CH_2Ph)_2$ and $Et_2C_2O_4$ give 3 : 5-diphenyl*cyclo*pentane-1 : 2 : 4-trione, m.p. 190—192°, hydrogenated (Raney Ni–EtOH at 50°) to 5-*hydroxy*-2 : 4-*diphenyl*cyclo*pentane*-1 : 3-*dione* (**II**), m.p. 173—175° (decomp.), which dissolves in cold Na_2CO_3 and is converted by Ac_2O–C_5H_5N at room temp. into a *diacetate*, m.p. 114·5—115·5°. Dehydration of (**II**) in anhyd. glycerol at 185—190° leads to 3 : 4-*diphenyl*-Δ^4-cyclo*pentene*-1 : 3-*dione*, m.p. 146—146·5°, which dissolves in warm dil. NaOH, does not give a colour with $FeCl_3$, and is hydrogenated (Raney Ni in C_6H_6 at room temp.) to (**I**). H. W.

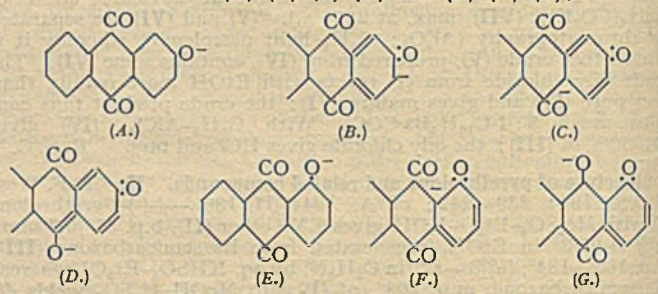
Labile union of oxygen to carbon. Photo-oxidation of *hetero*-coerdianthrone. C. Dufraisse and M. T. Mellier (*Compt. rend.*, 1942, **215**, 541—543).—Irradiation of *hetero*coerdianthrone (7′ : 7″) (**I**) (in CS_2) causes rapid oxidation with disappearance of the violet colour, and formation of the photo-oxide (**II**) (cf. Scholl *et al.*, A., 1932, 617), reconverted into (**I**), with evolution of O_2, at 150°. In C_5H_5N (6 hr.), followed by heating with C, (**I**) yields (**II**) and the 9 : 10-dihydroxy-9 : 10-dihydro-derivative (**III**). Colourless solutions of (**II**) in C_5H_5N in sunlight become similar in colour to that observed with (**I**) in C_5H_5N. Change of solvent and use of C partially transforms (**II**) into (**III**); after irradiation of (**I**) in C_5H_5N for 3 min., (**II**) is formed but is more difficult to purify. A. T. P.



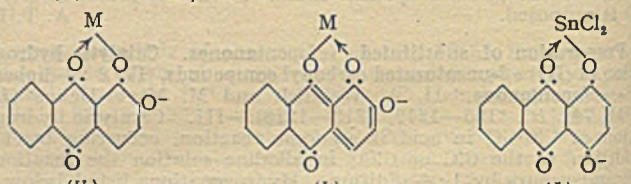
Substituted naphthaquinones.—See B., 1944, II, 197.

Optically active α-phylloquinone (vitamin-K_1). P. Karrer, H. Simon, and E. Zbinden (*Helv. Chim. Acta*, 1944, **27**, 317—319).—α-Phylloquinone (**I**), obtained by condensation of 2 : 1 : 4-$C_{10}H_5Me(OH)_2$ with natural phytol and anhyd. $H_2C_2O_4$ in dioxan followed by Ag_2O in Et_2O + Na_2SO_4, has $[\alpha]_D^{20}$ ~−0·4°±0·04° in C_6H_6. Dihydro-α-phylloquinone diacetate, obtained from (**I**) and Zn dust in Ac_2O–C_5H_5N, has $[\alpha]_D^{20}$ ~+1·5° to +1·65° or ~1·8° in EtOH, when derived from phytol with $[\alpha]_D$ +0·06° or +0·2°. H. W.

(A) Structure of hydroxyanthraquinones in their salts. Homopolar (pseudo-)ammonium salts. Mesomerism. (B) Formation of [substituted] ammonium salts in solution in their basic components and of metal complex salts with ammonia and amines. R. Scholl [(A) with P. J. Dahll]. **(C) Structure of anthraquinol-1-carboxylactones and their salts.** R. Scholl, K. Meyer, and C. Seer (*Ber.*, 1941, **74**, [*B*], 1129—1170, 1171—1181, 1182—1189).—(A) *Salts* are prepared containing: 1-hydroxyanthraquinone and 1 mol. of NH_3, NH_2R (R = Me, Et, and Pr^{α} here and below), $NHMe_2$ and $NHEt_2$; 2-hydroxyanthraquinone and 1 mol. of NH_3, NH_2R, NHR_2, NMe_3, NEt_3, and 1-ethylpiperidine (**I**); alizarin and 1 mol. of NH_3, NH_2Et, NH_2Pr^{α}, NHR_2, NMe_3, NEt_3, (**I**), and C_5H_5N, or 2 mols. of NH_3 and NH_2Me; hystazarin with 2 mols. of NH_3 and piperidine; quinizarin and 1 mol. of NH_3, NH_2Et, NH_2Pr^{α}, $NHMe_2$, or $NHEt_2$, or 2 mols. of NH_2Me; anthrarufin and 1 mol. of NH_3 or 2 mols. of NH_2R; anthraflavin and 1 mol. of $NHPr^{\alpha}_2$, NMe_3, NEt_3, or (**I**), and 2 mols. of NH_3, NH_2R, or NHR_2; purpurin and 1 mol. of NHR_2, NR_3, or (**I**), 2 mols. of NH_3, NH_2Et, or NH_2Pr^{α}, 2·5 mols. of NH_3, or 3 mols. of NH_2Me; when no salt is recorded in these series, none could be obtained. Prep. was by gaseous NH_3 or by an excess of the liquid amine at room temp. or 20° above its b.p. Colours of the salts are of three types, yellow to orange-red or brown, pink to red, or bluish-violet to blue. Colour in solution often differs from that of the solid and light-coloured solids (or base-free anthraquinone) often separate from dark-coloured solutions. The colour of solutions is often reversibly changed by addition of a second solvent. The depth of colour and tendency to salt-formation decrease for any one anthraquinone from primary through *sec.* to *tert.* bases; salt-formation thus involves linkings $R{\cdot}O{\cdot}H{\leftarrow}NR_3$. Differences in colour are due to existence of the separate mesomeric forms, *e.g.*, the series (*A*)–(*B*)–(*C*)–(*D*) and (*E*)–(*F*)–(*G*); these are

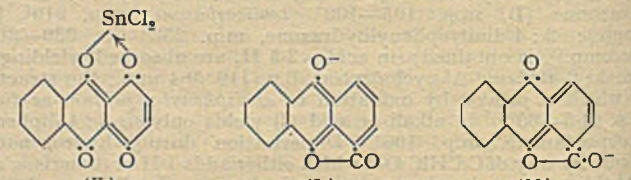


termed electrotropic forms. Salts, solid or in solution, may exist as equilibria with one form largely preponderating. The yellow-orange forms are wholly or mostly the "*el.*-benzoid" form (*A*), (*E*), etc., and may be written, *e.g.*, (*A*⟷*B*); the blue or violet forms are mainly or wholly (*D*), (*G*), etc., termed "*el.*-quinoid," and may be written (*A*⟷*D*) etc.; the red forms are (*B*) or (*C*) and (*F*), are termed "*el.*-carbeniates," and may be written (*E*⟷*F*⟷*G*) etc.; decision between (*B*) and (*C*) for the red 1-OH-compounds is impossible. Metal lakes are similarly considered to be, *e.g.*, (*H*⟷*I*), (*J*⟷*K*) (M = metal) etc.



(B) The colour of solutions of hydroxyanthraquinones in bases or mixed bases is used to determine the "activity" of the bases. These activities are in the same qual. order as the dielectric consts. so long as the latter do not vary greatly.

(C) Salts of anthraquinol-1-carboxylactones which are capable of electropism in the way outlined above are orange, red, or blue according to the nature of the base, solvent, or mixture of solvents; their general colour behaviour resembles that of hydroxyanthraquinones. Thus, red salts of anthraquinol-1-carboxylactone (A., 1930, 1588) are *el.*-lactoid (*L*⟷*M*) and blue salts are *el.*-furoid (*L*⟷*M*). Absorption spectra support this view. R. S. C.



IV.—STEROLS AND STEROID SAPOGENINS.

Water-in-oil emulsifying agents. II. Synthesis of cholesteryl and cetyl esters. E. L. Cataline, L. Worrell, S. F. Jeffries, and S. A. Aronson (*J. Amer. Pharm. Assoc.*, 1944, **33**, 107—108; cf. Powers *et al.*, B., 1940, 402).—The following were prepared from the acid (0·02), alcohol (0·02 or 0·04), and *p*-$C_6H_4Me{\cdot}SO_3H$ (0·0015 mol.) in C_6H_6 (150 ml.) at 130—140° (bath) for 3 hr.: cholesteryl *n*-butyrate, m.p. 102° (clears at 110°), *n*-hexoate, m.p. 98—99°, laurate, m.p. 91—92°, myristate, m.p. 80° (86°), palmitate, m.p. 89—90°, stearate, m.p. 82—83°, and H succinate, m.p. 175—175·5°; dicholesteryl oxalate, m.p. 226—227°, succinate, m.p. 220° (240°), and adipate, m.p. 195° (222°); *cetyl laurate*, m.p. 40—41°, myristate, m.p. 47—48°, palmitate, m.p. 53—54°, stearate, m.p. 56—57°, and λ-hydroxystearate, m.p. 68—69°; dicetyl oxalate, m.p. 56·5—57·5°, succinate, m.p. 58·5—59°, and adipate, m.p. 56·5—57°. The use of these substances for emulsions is discussed. F. O. H.

Bromination of cholesteryl benzoate. H. Bretschneider, Z. Földi, F. Galinovsky, and G. von Fodor (*Ber.*, 1941, **74**, [*B*], 1451—1455).—Cholesteryl benzoate (I) and Br in $CHCl_3$ at 1° give stereoisomeric dibromides (**II**), m.p. 138—140° (after sintering), 136·5—137·5°

(vac.), $[\alpha]_D^{18}$ −40·31° in $CHCl_3$, and **(III)**, m.p. 158—160° (decomp.), $[\alpha]_D^{20}$ +80° in $CHCl_3$ (cf. Obermüller, A., 1891, 298; Dorée *et al.*, A., 1916, i, 261; Petrow, A., 1937, II, 417). The structure of **(II)** is proved by its normal mol. wt. (cryoscopic in C_6H_6), behaviour as a single substance on chromatography (Al_2O_3), reduction to **(I)** by H_2–Pd–C in Et_2O, and by conversion into **(III)** by heating in EtOH. In boiling C_6H_6 or $CHCl_3$, **(II)** or **(III)** gives an equilibrium mixture containing 79—83% of **(III)** as judged by [α]. The 5 : 5′-dibromo-3 : 3′-dibenzoyloxy-6 : 6′-dicholestanyl of Petrov (*loc. cit.*) is **(II)**. R. S. C.

Steroids and sex hormones. XCIV. Introduction of a hydroxyl group in position 5 of the sterol skeleton by hydrogenation of 5 : 6- or 4 : 5-oxido-compounds. P. A. Plattner, T. Petrzilka, and W. Lang (*Helv. Chim. Acta*, 1944, **27**, 513—524).—Hydrogenation of cholesteryl acetate α-oxide **(I)** leads smoothly to the production of 5-OH-compounds, whereas a similar treatment of the β-compounds gives 6-OH-derivatives, whilst the oxido-O and that attached to $C_{(3)}$ are in part removed. Hydrogenation of 4 : 5- or 5 : 6-oxides in the steroid series gives a means of introducing OH at $C_{(5)}$. The course of the change appears to depend considerably on experimental conditions, the configuration of the oxide, and the presence of substituents at vicinal C atoms. **(I)** is hydrogenated homogeneously (PtO_2 in AcOH) to *5-hydroxy-3(β)-acetoxycholestane* **(II)**, m.p. 185—185·5°, $[\alpha]_D$ +12·5°, +10·7° (*c* = 0·83, 0·423) in $CHCl_3$, which gives a very stable chromate with CrO_3 in AcOH, hydrolysed [as is **(II)**] to 3(β) : *5-dihydroxycholestane* **(III)**, m.p. 224—225°, $[\alpha]_D$ +20·6°, +16·9° (*c* = 0·477, 0·860) in $CHCl_3$, converted by boiling Ac_2O (2 hr.) into **(II)** and by AcCl–$NPhMe_2$ in boiling $CHCl_3$ into the 3(β) : *5-diacetate*, m.p. 140—141°, $[\alpha]_D$ +31·8° (*c* = 1·220) in $CHCl_3$. **(III)** is oxidised by CrO_3 in 90% AcOH at room temp. to *5-hydroxy-3-ketocholestane*, m.p. 205—208°, $[\alpha]_D$ +40·0° in $CHCl_3$, dehydrated by boiling Ac_2O to Δ⁴-cholestenone. The product obtained by the action of per-acids on cholesteryl acetate is an additive compound (*A*), m.p. 114—115°, of **(I)** and cholesteryl acetate β-oxide **(IV)**, m.p. 113—114°, $[\alpha]_D$ −1·0° (*c* = 1·004) in $CHCl_3$, separable into its components by chromatography over Al_2O_3. (*A*) is also obtained from cholestane-3 : 5 : 6-triol. **(IV)** is hydrolysed (boiling 0·5N-NaOH–MeOH) to *cholesterol β-oxide*, m.p. 132°, $[\alpha]_D$ +10·3° (*c* = 0·509) in $CHCl_3$, and is hydrogenated (PtO_2 in AcOH) to cholestan-3 : 5-diol **(V)**, m.p. 80—81°, cholestanyl 3(β)-acetate **(VI)**, m.p. 109—110°, and 6-*hydroxy*-3(β)-*acetoxy*- **(VII)**, m.p. 143—144°, $[\alpha]_D$ −6·6° in $CHCl_3$ [oxidised to 6-keto-3(β)-acetoxy-, m.p. 128—129°], acetylated (Ac_2O–C_5H_5N at room temp.) to 3(β) : 6-*diacetoxy*-, m.p. 137·5—138·5°, *-cholestane*. Hydrogenation (PtO_2 in AcOH) of (*A*) with subsequent chromatography leads to **(V)**, **(VI)**, and **(VII)** with a mixture probably of **(VI)** and **(II)**. Absorption of H_2 by (*A*) is not observed in presence of PtO_2–EtOAc, PtO_2–EtOH, Raney Ni in EtOH or EtOH + a little conc. NaOH, Pd–$CaCO_3$ in EtOAc, or PtO_2 in EtOAc containing a little AcOH. 5 : 6-Oxidocholestane, m.p. 79·7—80·5°, $[\alpha]_D$ −55·9° in $CHCl_3$, is hydrogenated to **(V)** and a non-cryst. product, oxidised (CrO_3 in AcOH at room temp.), and then separated into cholestan-6-one, m.p. 98—99°, and *5-hydroxycholestane*, m.p. 109—110°, $[\alpha]_D$ +11·2°, +9·3° (*c* = 0·89, 0·92) in $CHCl_3$. 4 : 5-Oxidocholestane ["coprostene oxide"], m.p. 95—96°, $[\alpha]_D$ +80·3° in $CHCl_3$, is hydrogenated (PtO_2 in AcOH) to 5- and 4-, m.p. 187—187·5°, $[\alpha]_D$ +2·8° in $CHCl_3$, -hydroxycholestane. Cholesterol α-oxide has $[\alpha]_D^{23}$ −43·1° in C_6H_6 (cf. lit.). M.p. are corr. H. W.

Steroids and sex hormones. XCIII. Hydrogenation of the two oxides of *trans*-dehydroandrosterone acetate. L. Ruzicka and A. C. Muhr (*Helv. Chim. Acta*, 1944, **27**, 503—512).—*trans*-Dehydroandrosterone acetate is converted by *o*-$CO_2H{\cdot}C_6H_4{\cdot}CO_3H$ in CCl_4 into α-(I), m.p. 222—224°, $[\alpha]_D^{14}$ −12° in $CHCl_3$, $[\alpha]_D^{16}$ −12·4° in $COMe_2$, and β- **(II)**, m.p. 186—187°, $[\alpha]_D^{15}$ +40·7° in $CHCl_3$, +47° in $COMe_2$, -5 : 6-oxido-3(β)-acetoxyandrostan-17-one. **(I)** is hydrogenated (PtO_2 in AcOH) to 5 : 17-*dihydroxy*-3(β)-*acetoxyandrostane* **(III)**, m.p. 192—197°, oxidised (CrO_3 in AcOH) to *5-hydroxy*-3(β)-*acetoxyandrostan-17-one* **(IV)**, m.p. 152·5—153·5° and 162·5—163·5° after resolidification, $[\alpha]_D^{13}$ +59·3° in $CHCl_3$, which is stable towards Ac_2O–C_5H_5N and BzCl–C_5H_5N in the cold and is hydrolysed (K_2CO_3 in aq. MeOH) to 3(β) : 5-*dihydroxyandrostan*-17-*one*, m.p. 281—282° (vac.; partial sublimation), $[\alpha]_D^{15}$ + 92·8° in MeOH; this is oxidised [$Al(OBu^t)_3$ in abs. $COMe_2$–dioxan] to Δ⁴-androstene-3 : 17-dione, m.p. 171—172·5°, $[\alpha]_D^{16}$ +190·5° in $CHCl_3$. Partial hydrogenation (PtO_2 in AcOH) of **(I)** gives unchanged material, and **(IV)** which is reduced to **(III)**, whereas partial hydrogenation in EtOH affords α-5 : 6-*oxido*-17-*hydroxy*-3(β)-*acetoxyandrostane*, m.p. 146—147° and 152·5—153·5° after resolidification, $[\alpha]_D^{14}$ −66° in $CHCl_3$ [yielding α-5 : 6-*oxido*-3(β) : 17-*diacetoxyandrostane*, m.p. 165—166°, $[\alpha]_D^{14}$ −69·3°, hydrogenated to **(III)**]. Total hydrogenation (PtO_2 in AcOH or, more slowly, in EtOH) of **(II)** leads to 17(α)-hydroxyandrostane **(V)**, m.p. 164—166°, $[\alpha]_D^{20}$ +13·1° in $CHCl_3$, oxidised to androstan-17-one **(VI)**, m.p. 119·5—120·5°, $[\alpha]_D^{16}$ +87·8° in $CHCl_3$; partial hydrogenation (PtO_2 in AcOH) gives unchanged material, **(V)**, **(VI)**, and 6 : 17-*dihydroxy*-3(β)-*acetoxyandrostane*, m.p. 204—207°, oxidised (CrO_3 in AcOH) to 6 : 17-diketo-3(β)-acetoxyandrostane, m.p. 203—205°, $[\alpha]_D^{15}$ +39·2° in $CHCl_3$. H. W.

Steroid ketones.—See B., 1944, III, 119.

Steroids and sex hormones. XCV. Preparation of 2-keto-, 2(α)- and 2(β)-hydroxy-cholestane. L. Ruzicka, P. A. Plattner, and M. Furrer (*Helv. Chim. Acta*, 1944, **27**, 524—530).—3-Keto-2-cholestanylpyridinium bromide is converted by *p*-$NO{\cdot}C_6H_4{\cdot}NMe_2$ and N-NaOH in $CHCl_3$–EtOH at 20° into the corresponding *nitrone*, $C_{35}H_{54}O_2N_2$, m.p. 178—179° (decomp.), converted by 2N-HCl–Et_2O into form *A*, m.p. 135—137°, $[\alpha]_D$ +75° in $CHCl_3$ (cf. Stiller *et al.*, A., 1938, II, 193), of 2 : 3-diketocholestane; this is converted by Ac_2O–C_5H_5N at 100° into the *enol acetate* A, m.p. 138—139°, $[\alpha]_D$ +96° in $CHCl_3$, hydrolysed to homogeneous Δ³-2-ketocholesten-3-ol. This with *p*-$C_6H_4Me{\cdot}SO_2Cl$ in C_5H_5N at 20° gives the 3-*p*-*toluenesulphonate* **(I)**, m.p. 161—162°, $[\alpha]_D$ +83° in $CHCl_3$, which is converted by NaI in anhyd. $COMe_2$ at 160° into Δ³·⁵-*cholestadien*-2-*one*, m.p. 121·5—122·5°, $[\alpha]_D$ −62° in $CHCl_3$ [hydrogenated (PtO_2 in AcOH) and then oxidised (CrO_3) to *cholestan*-2-*one* **(II)**, m.p. 130·5—131·5°, $[\alpha]_D$ +49° in $CHCl_3$, also obtained by hydrogenation (Raney Ni in EtOH at 70°) and subsequent oxidation of (I)]. Oxidation of **(II)** by CrO_3 in 90% AcOH at 60° affords the dicarboxylic acid, $C_{27}H_{46}O_4$, m.p. 194—196° (Me_2 ester, m.p. 59—60°), obtained by Windaus *et al.* (A., 1915, i, 678) by oxidation of cholestanol. **(II)** is hydrogenated (PtO_2 in AcOH) to 2(β)(?)-*hydroxycholestane*, m.p. 154—155°, $[\alpha]_D$ +33° in $CHCl_3$, the configuration assigned to which is based on its precipitability with digitonin. With Na and EtOH **(II)** affords 2(α)(?)-*hydroxycholestane*, m.p. 178—180°, $[\alpha]_D$ +36° in $CHCl_3$ (no ppt. with digitonin). M.p. are corr. H. W.

Lumicœstrone. A. Butenandt, A. Wolff, and P. Karlson (*Ber.*, 1941, **74**, [*B*], 1308—1312).—Irradiating (ultra-violet) œstrone **(I)** in dioxan–N_2 gives *lumicœstrone* **(II)**, m.p. 268—269°, $[\alpha]_D^{21}$ −43°, $[\alpha]_D^{15\cdot5}$ −45·5° in dioxan [*acetate*, m.p. 89—90°; *Me ether* **(III)**, m.p. 129—130°, $[\alpha]_D^{23}$ −28° in $CHCl_3$], which gives an *oxime*, m.p. 200—202°, and *semicarbazone* **(IV)**, m.p. 273° (micro), only with difficulty. NaOEt–EtOH at 190—200° reduces **(IV)** to *deoxolumicœstrone*, m.p. 170—171°, which could not be obtained by irradiating deoxoœstrone. Pd-black at 260° converts **(I)** into *d-iso*equilenin (14-*epi*equilenin), m.p. 257—258°, $[\alpha]_D^{20}$ +152° in dioxan (cf. A., 1939, II, 76), but converts **(II)** into *l-iso*equilenin, m.p. 256—258°, $[\alpha]_D^{20}$ −151° in dioxan (*dl*-compound, m.p. 222—223°) (cf. A., 1940, II, 225). Na–$Pr^{\beta}OH$ reduces **(III)** to *lumicœstradiol Me ether*, m.p. 137—138°, $[\alpha]_D^{20}$ +15·5° in $CHCl_3$. Since Pd-black isomerises $C_{(14)}$, irradiation of **(I)** probably isomerises $C_{(13)}$, so that **(II)** is 13-epicœstrone, but inversion at $C_{(8)}$ may also have occurred. R. S. C.

Conversion of Δ⁴-cholestene-3 : 6-dione into cholestan-3-ol-6-one by partial reduction. H. Bretschneider (*Ber.*, 1941, **74**, [*B*], 1361—1363).—1 mol. of H_2 is rapidly and a second mol. more slowly absorbed by Δ⁴-cholestene-3 : 6-dione. After 2 mols. have been absorbed in presence of Raney Ni in EtOH, cholestan-3-ol-6-one is obtained; partial hydrogenation in presence of 20% Pd–C in AcOH gives cholestane-3 : 6-dione. R. S. C.

Oxidation of cholestenone by oxygen. Formation of progesterone. H. Bretschneider (*Ber.*, 1941, **74**, [*B*], 1360—1361).—O_2 is blown into cholestenone (4 pts.) and V_2O_5 (1 pt.) at 170°; alkali-sol. products are removed. Shaking the Et_2O-solution of the residue repeatedly with conc. HCl removes substances, whence chromatography yields progesterone. R. S. C.

Diginin. III. Degradation of diginigenin to a hydrocarbon diginane. C. W. Shoppee (*Helv. Chim. Acta*, 1944, **27**, 246—260; cf. A., 1943, II, 151).—Direct oxidation of diginigenin (I) gives mixtures of neutral and acid products from which individuals cannot be isolated. Treatment of (I) or its semicarbazone with N_2H_4,H_2O–NaOEt in EtOH at 180° leads to a mixture **(II)** of substances from which *deoxodiginigenin* **(III)**, $C_{21}H_{30}O_3$, m.p. 163—164° (*hydrate*, m.p. 86°), $[\alpha]_D^{15}$ −71·5°±4° in $COMe_2$, is most readily isolated. The presence of a *sec.* OH in **(III)** is established by the isolation of an *acetate*, m.p. 61—62°, hydrolysed to **(III)**, but the functions of the remaining, non-reactive O atoms are not elucidated. **(III)** does not reduce Ag_2O–NH_3 at 20° and gives negative Raudnitz–Puluj, Legal, and Zimmermann tests. Under energetic conditions it does not afford an oxime. **(III)** is readily hydrogenated (PtO_2 in AcOH) to *dihydrodeoxodiginigenin* **(IV)**, m.p. 190—191°, $[\alpha]_D^{16}$ +7·9°±2° in $COMe_2$ (*acetate*, an oil), which does not give a yellow colour with $C(NO_2)_4$. N_2H_4 and alkali yield resinous products or unchanged material from **(IV)**. CrO_3 smoothly oxidises **(IV)** to *dihydrodehydrodeoxodiginigenin* **(V)**, m.p. 178—179°, $[\alpha]_D^{16}$ +21·5°± 2·5° in $COMe_2$ (*oxime*, m.p. 159—160), reduced (Wolff–Kishner) to *dihydrodeoxydeoxodiginigenin*, m.p. 113—115°, becomes opaque at 60—70°, $[\alpha]_D^{13}$ +10°±3° in $COMe_2$, which retains only the two non-reactive O of **(I)** and does not give a cryst. product with Ac_2O at 200°. **(V)** is reduced (Clemmensen) and subsequently hydrogenated (PtO_2 in AcOH) to a liquid *substance*, $C_{21}H_{32(34)}O$, which does not give a yellow colour with $C(NO_2)_4$ and has not been further studied since isomerisations may have occurred in its production. Chromatographic purification of **(II)** leads also to Δ¹-*dihydroxyketodiginene* **(VI)**, $C_{21}H_{32}O_3$, m.p. 147°, $[\alpha]_D^{17}$ −24°±2° in $COMe_2$, which gives a non-cryst. *diacetate*, hydrolysed to **(VI)**. CO does not appear present in **(VI)**, which gives negative Raudnitz–Puluj, Legal, and

Zimmermann tests. (**VI**) gives a marked yellow colour with $C(NO_2)_4$ and is readily hydrogenated to the saturated *dihydroxyketodiginane* (**VII**), m.p. 195—196°, $[\alpha]_D^{17}$ −20°±3° in $COMe_2$, which yields a non-cryst. *diacetate*, hydrolysed to (**VII**). CrO_3 oxidises (**VII**) to (impure) triketodiginane, which gives a 2 : 4-*dinitrophenylhydrazone*, m.p. (indef.) 120°, and a *dioxime*, softens 180—200° (decomp.), and probably contains the non-reactive :CO of (**I**). The residue left after (**II**) has been freed as completely as possible from (**III**) and (**VI**) gives after hydrogenation (PtO_2 in AcOH) *dihydroxydiginane* (**VIII**), plates which become opaque at ~105°, are converted without melting into needles at 140—142° and then have m.p. 153—154°, or, after sublimation, m.p. 155—156°, $[\alpha]_D^{22}$ +25·4°±2° in $CHCl_3$; the non-cryst. *diacetate* is hydrolysed to (**VIII**). CrO_3 oxidises (**VIII**) smoothly to *diketodiginane*, m.p. 140—141°, $[\alpha]_D^{13}$ +39·5°±2° in $COMe_2$ (*bis*-2 : 4-*dinitrophenylhydrazone*, m.p. 185°), reduced (Wolff–Kishner) to *diginane*, $C_{21}H_{36}$, m.p. 75—77°, $[\alpha]_D^{20}$ +24°±4°, $[\alpha]_{5461}^{20}$ +27·5°±4° in $CHCl_3$. M.p. are corr. (block); limit of error ~±2°.

H. W.

Diginin and diginigenin. IV. C. W. Shoppee (*Helv. Chim. Acta*, 1944, **27**, 426—435; cf. preceding abstract).—The experimental results do not justify the consideration of diginigenin (**I**) as a steroid but they can all be brought into harmony with the structure (*A*) (R = H) for (**I**) and (R = $C_7H_{13}O_3$) for diginin. Such a formulation expresses the possible biogenetic relationship with the steroid digitalis saponins and sapogenins. The observation that mild oxidation of (**I**) and its monoacetate does not yield well-defined acids indicates that the CO group is present as ketone in the group :C·CO·CH_2·O·C:. The few substances described in the literature with this arrangement show, like (**I**), strong reducing action and positive reactions with 1 : 4-$C_{10}H_6(OH)_2$ and according to Legal and Zimmermann. The latter reactions are characteristic of activated CH_2 and are not shown by derivatives of (**I**) obtained by hydrogenation or reduction (Wolff–Kishner). The presence of CH_2·CO· in (**I**) is confirmed by the isolation of piperonylidene-diginigenin (*monohydrate*, m.p. 128—131°). Diginigenin monoacetate is hydrogenated (PtO_2 in AcOH at 17°) to tetrahydrodiginigenin monoacetate (**II**), prisms, m.p. 174°, or *needles*, m.p. 156°, slowly converted by Ac_2O in C_5H_5N into the *diacetate*, m.p. 120—121°, $[\alpha]_D^{17}$ +17°±2° in $COMe_2$. (**II**) is oxidised by CrO_3 in AcOH at 15° to the amorphous dihydrodiginigenin monoacetate (*semicarbazone*, m.p. 226°), which has strong reducing power and gives the three colour changes. Energetic acetylation converts it into a non-cryst., unsaturated compound, apparently an enol diacetate, since it is transformed by ozonisation followed by treatment with hot H_2O into a cryst. acid, $C_{23}H_{32}O_7$, m.p. 302—304°, the *Me* ester, m.p. 203—204°, of which does not react with 2 : 4-dinitrophenylhydrazine sulphate and reduces Ag_2O–NH_3 when heated but not appreciably at 20°. Hexahydrodiginigenin diacetate (**III**) is quantitatively hydrolysed to the parent compound, which is converted by short treatment with boiling Ac_2O into the *monoacetate*, m.p. 83°, and with Ac_2O and C_5H_5N at 100° into a non-cryst. diacetate possibly identical with (**III**). The reducing power and colour reactions of many derivatives of (**I**) are described. ω-Methoxyacetophenone, b.p. 122°/15 mm., has been obtained from CH_2Ac·OMe and MgPhBr. M.p. are corr. (block); limits of error ±2°.

H. W.

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Factors determining the course and mechanism of Grignard reactions. XII.—See A., 1944, II, 215.

Triterpene resinols and related acids. XVI. Preliminary examination of a major oxidation product of the β-amyrin group. N. Mower, J. Green, and F. S. Spring (*J.C.S.*, 1944, 256—260).—Oxidation of either β-amyrenonyl acetate, $C_{32}H_{50}O_3$, or β-amyradienonyl acetate (**I**), $C_{32}H_{48}O_3$, with SeO_2 gives an acetate (**II**), $C_{32}H_{46}O_5$ ("O_5-acetate"), m.p. 252—253°, $[\alpha]_D^{23}$ +35° (*c* = 2·1). Similar oxidation of corresponding benzoates gives the *benzoate*, $C_{37}H_{48}O_5$, m.p. 262—263°, $[\alpha]_D^{21}$ +42° (*c* = 2·0). Oxidation (H_2CrO_4) of β-amyradienyl-II acetate yields (**II**) with some (**I**). Treatment of (**II**) with KOH affords, in high yield, a yellow amorphous product, acetylation of which does not regenerate (**II**) but a *diacetate*, $C_{32}H_{42}O_5$ (?), m.p. 249—251°, $[\alpha]_D^{22}$ +149° (*c* = 0·7). Hydrolysis (MeOH–HCl) of (**II**) gives the parent *alcohol*, $C_{30}H_{44}O_4$, m.p. 280·5—281·5°, reacetylated to (**II**). It is shown that (**II**) does not contain either a OH or reactive CO and is resistant to catalytic hydrogenation. This new type of oxidation product is found to be characteristic of the β-amyrin group: SeO_2 treatment of either Me ketoacetyloleanolate or H_2CrO_4 oxidation of Me acetyldehydro-oleanolate affords an *acetate*, $C_{33}H_{46}O_7$, m.p. 253—254°, $[\alpha]_D^{15}$ +15·9° in C_5H_5N (*alcohol*, $C_{31}H_{44}O_6$, m.p. 255—256°, $[\alpha]_D^{16}$ −3·55° in C_5H_5N), which is an exact analogue of (**II**).

F. R. S.

Hydration of camphene to *iso*borneol. L. M. Pesin, E. T. Beljanina, and V. A. Pavlovskaja (*J. Appl. Chem. Russ.*, 1943, **16**, 129—133).—Hydration of camphene (1 part), m.p. 42°, by "Kontakt" (petroleum sulphonic acids) (3 parts) at 50° (12 hr.) yielded up to 90% of crude cryst. *iso*borneol, m.p. 186°. The best results are obtained by freeing the "Kontakt" from mineral oil but not from H_2SO_4.

V. B.

Camphyl compounds.—See B., 1944, II, 198.

4-Camphorylthiosemicarbazide and 4-camphorylsemicarbazide. J. A. McRae and W. H. Stevens (*Canad. J. Res.*, 1944, **22**, B, 45—52).—Camphorylthiocarbimide (**I**) (from camphoryldithiocarbamic acid and BzCl–C_5H_5N, or HNO_2) with N_2H_4,H_2O in EtOH at 0° gives a little dicamphorylthiocarbamide, m.p. 176°, and (80% yield) 4-*camphorylthiosemicarbazide* (**II**), m.p. 168° (corr.), $[\alpha]_D$ +17·34° in $CHCl_3$. (**II**) with dil. HCl or NaOH at room temp. yields the *anhydride*, m.p. 239°, $[\alpha]_D$ +281·5° in $CHCl_3$, which, by conversion into its Ag derivative and treatment with MeI, gives the *monomethylanhydride*, m.p. 107°, $[\alpha]_D$ −57·4°. (**II**) with BzCl in C_5H_5N yields the 1-*benzoate*, m.p. 225°, and with PhNCO N-*anilinoformyl*-N′-*camphorylaminothioformylhydrazine*, m.p. 139—143° (decomp.). (**II**) with the corresponding aldehyde in EtOH gives *benzylidene*-, m.p. 215—216°; $[\alpha]_D$ +68·6° in $CHCl_3$, p-, m.p. 234°, $[\alpha]_D$ +105·2° in $CHCl_3$, and m-*nitrobenzylidene*-, m.p. 140°, *anisylidene*-, m.p. 148—149°, $[\alpha]_D$ +83·8° in $CHCl_3$, and 3 : 4-*diethoxybenzylidene*-, m.p. 111—113°, $[\alpha]_D$ +34·6° in $CHCl_3$, -*camphorylthiosemicarbazone*, but many aldehydes and ketones do not give cryst. products. The possible use of (**II**) as resolving agent for *dl*-carbonyl compounds is thus limited. (**I**) with ArNH·NH_2 in hot EtOH gives the corresponding -4-*camphorylthiosemicarbazides*: 1-o-, m.p. 171°, $[\alpha]_D$ +34·6° in $CHCl_3$, and 1-p-*tolyl*-, m.p. 226°, $[\alpha]_D$ +231·6° in $CHCl_3$, 1-m-*nitrophenyl*-, m.p. 204° (decomp.), $[\alpha]_D$ +313·4° in $CHCl_3$, (decomp. on keeping), 1-p-*bromophenyl*-, m.p. 227° (decomp.), $[\alpha]_D$ +15·2° in EtOH, 1-(2′ : 4′-*dinitrophenyl*)-, m.p. 218°, 1-β-*naphthyl*-, m.p. 191°, $[\alpha]_D$ +51·1° in $CHCl_3$, in all of which the 1-position assigned to the aryl group is tentative. (**I**) with NPh_2·NH_2 gives 1 : 1-*diphenyl*-4-*camphorylthiosemicarbazide*, m.p. 223°, $[\alpha]_D$ −26·9° in $CHCl_3$. Camphorylcarbimide with N_2H_4,H_2O yields 4-*camphorylsemicarbazide* (**III**), m.p. 215°, $[\alpha]_D$ −26·3° in EtOH. With aq. HCl (**III**) gives the *anhydride*, sublimes 325°, $[\alpha]_D$ +115·4° in EtOH, and m-, m.p. 178°, and p-*nitrobenzylidene-semicarbazones*, m.p. 223°, and other non-cryst. semicarbazones.

D. G.

VI.—HETEROCYCLIC.

Action of sodium cyanide on methyl γ-bromo-αα-dimethylacetoacetate. C. F. Koelsch (*J. Amer. Chem. Soc.*, 1944, **66**, 306—307).—Contrary to Lawrence (*J.C.S.*, 1899, **75**, 417) and Conrad *et al.* (A., 1899, i, 258; 1900, i, 475), CH_2Br·CO·CMe_2·CO_2Me and NaCN give *Me* β-*cyano*-βγ-*epoxy*-αα-*dimethyl*-n-*butyrate* (not CN·CH_2·CO·CMe_2·CO_2Me), since hydrolysis yields 4-*hydroxy*-2-*keto*-3 : 3-*dimethyltetrahydrofuran*-4-*carboxylic acid* (**I**) (not the 5-carboxylic acid), m.p. 213—217° (Me ester, m.p. 104—105°), the structure of which is proved by synthesis. OAc·CH_2·CO·CMe_2·CO_2Me (stable when heated with K_2CO_3 or kept; cf. lit.) and boiling HCl–EtOH give 2 : 4-diketo-3 : 3-dimethyltetrahydrofuran (86%), b.p. 200—210°/740 mm., 103—107°/6 mm., which with aq. HCl–NaCN gives an oily cyanohydrin, hydrolysed to (**I**) by boiling 20% HCl.

R. S. C.

Furfurylamines.—See B., 1944, II, 198.

5-Hydroxy- and -methoxy-flavylium salts. L. R. Row and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1944, **19**, A, 141—145).—Condensation of γ-resorcylaldehyde and its Me ether (improved preps.) in EtOAc–HCl with the appropriate substituted COPhMe gives 3 : 5 : 4′-*trihydroxy*-, m.p. >300°, 3 : 4′-*dihydroxy*-5-*methoxy*-, m.p. 258—260°, 3 : 5 : 3′ : 4′-*tetrahydroxy*-, m.p. >300°, and 3 : 5 : 3′ : 4′ : 5′-*pentahydroxy*-*flavylium chloride*, m.p. >300°. These substances exhibit negligible fluorescence even in conc. H_2SO_4. The structural factors which affect fluorescence in flavylium salts are discussed; comparison is made with coumarins.

F. R. S.

Benzopyrylium salts. IV. Nitration of 2 : 3-diphenylbenzopyrylium perchlorate. R. L. Shriner and R. B. Moffett (*J. Amer. Chem. Soc.*, 1944, **66**, 301—302; cf. A., 1942, II, 109).—The position of NO_2 entering 2-phenylflavylium perchlorate (**I**) is governed by electronic considerations on the assumption that the salt has carbenium structure. In fuming HNO_3 at 0°, (**I**) gives crude 3-p-*nitrophenylflavylium perchlorate* (**II**) (53·5%), m.p. ~217° (decomp.), and thence the ferrichloride (**III**), m.p. 136—137°. Pure (**II**) (93·5%), m.p. 235—237° (decomp.), and thence (**III**), m.p. 137—138°, is obtained from *p*-NO_2·C_6H_4·CH_2·COCl, *o*-OH·C_6H_4·CHO (**IV**), HCl (gas), and 72% $HClO_4$ in AcOH. In H_2SO_4–HNO_3 at <0° and then 45°, (**I**) or (**II**) gives 3′-*nitro*-3-p-*nitrophenylpyrylium perchlorate* (**V**) (>90%), m.p. 258—258·5° (decomp.), also obtained from (**IV**), *p*-NO_2·C_6H_4·CH_2·CO·C_6H_4·NO_2-*m*, HCl, and 72% $HClO_4$–AcOH. In boiling MeOH, (**V**) gives 2-*methoxy*-2-m-*nitrophenyl*-3-p-*nitrophenyl*-Δ^3-*chromene*, m.p. 178—179° (177·5—178·5°).

R. S. C.

Santonin series. I. Two new desmotroposantonins and two new desmotroposantonous acids. M. Huang, C. P. Lo, and L. J. Y. Chu (*J. Chinese Chem. Soc.*, 1943, **10**, 126—135).—Santonin (**I**) and

Ac_2O ($+H_2SO_4$) at 100° (bath) or at room temp. (2 weeks) give *l*-α-desmotroposantonin acetate, m.p. 156—157°, hydrolysed by boiling 10% aq. NaOH to *l*-α-desmotroposantonin (**II**), m.p. 194—195°. *d*-β-Desmotroposantonin (**III**), m.p. 260—261°, $[\alpha]_D^{21}$ +106·2° in EtOAc (acetate, m.p. 154—155°), is obtained from (**I**) or (**II**) and boiling aq. H_2SO_4, and *l*-β-*desmotroposantonin* (**IV**), m.p. 260—261°, $[\alpha]_D^{21}$ −106·2° in EtOAc (acetate, m.p. 156—157°), is similarly formed from the *d*-α-form, m.p. 196—196°. (**IV**) is probably identical with the *l*-desmotroposantonin, m.p. 253°, described by Clemo (A., 1934, 1225), and is converted by aq. KOH at 210° (oil-bath) into (**II**). Equal amounts of (**III**) and (**IV**) in boiling EtOAc, on cooling, yield the dl-β-*compound* (**V**), m.p. 231—232° (Ac_2O–NaOAc gives the acetate, m.p. 182—183°, also obtained from the *d*-β- + *l*-β-acetates), converted by aq. KOH at 210° into dl-α-*desmotroposantonin*, m.p. 200—201°, which is formed also from the *d*- + *l*-α-forms, and is reconvertible into (**V**) by boiling aq. H_2SO_4. (**IV**) and Zn dust in boiling aq. AcOH yield d-β-*desmotroposantonous acid*, m.p. 175—176°; the *d*-α-analogue has m.p. 177—178°. dl-β-*Desmotroposantonous acid*, m.p. 180—181°, is obtained from the *d*- + *l*-β-forms or by reducing (**V**). The above nomenclature replaces the system of *iso*desmotropo- by *d*-α-desmotropo-, the *l*- by *l*-α-, and *dl*- by *dl*-α-; the lower-melting series is designated by α; desmotroposantonin is referred to as the *d*-β-form. The isolation of (**IV**) allows the transformation of any known active stereoisomeride of desmotroposantonin into others by acid or alkali treatment, as above. A. T. P.

Dioxan diphosphate. E. Baer (*J. Amer. Chem. Soc.*, 1944, **66**, 303).—Dioxan (**I**) (vapour or liquid) and H_3PO_4 give (exothermally if liquids) *dioxan* 1 : 4-*diphosphate*, sinters 78°, m.p. 83—87° (sealed tube), sol. in many org. solvents, dissociating in H_2O, stable at room temp. or, for a short time, at 150°, giving at 175° (**I**) and a little MeCHO, and with Na_2HPO_4 (2·2 mols.), K_3PO_4, or Na_3PO_4 (1·1 mol.) at 120—130° yielding (**I**) quantitatively. R. S. C.

Aldol condensation. III. Aldol–aldehyde addition products and their derivatives. R. H. Saunders and M. J. Murray (*J. Amer. Chem. Soc.*, 1944, **66**, 206—208).—Aldolisation of CHRR′·CHO leads to 1 : 3-dioxans (cf. A., 1944, II, 4), which with Ac_2O–C_5H_5N at room temp. yield 6-*acetoxy*-2 : 4-*dimethyl*-, b.p. 85·5°/10 mm., -5-*methyl*-2 : 4-*diethyl*-, b.p. 100°/7 mm., -5-ethyl-2 : 4-di-*n*-propyl-, b.p. 114°/3 mm., and -5 : 5-*dimethyl*-2 : 4-*diisopropyl*- (**I**), b.p. 93·5°/2 mm., -1 : 3-*dioxan*. d_4^{25}, $[M]_D^{25}$, and Raman spectra are recorded for these products and for 6-hydroxy-2 : 4-dimethyl-, -5-ethyl-2 : 4-di-*n*-propyl-, and -5-methyl-2 : 4-diethyl-1 : 3-dioxan, b.p. 91·5°/7 mm. The strongest line (at 834 cm.$^{-1}$) is due to the symmetrical breathing of the ring and a line at 1750 cm.$^{-1}$ to the ester-CO of the OAc. Compounds containing a neopentyl group show a strong line between 750 and 800 cm.$^{-1}$ Anhyd. 1% HCl–MeOH at room temp. converts (**I**) into 6-*methoxy*-5 : 5-*dimethyl*-2 : 4-*diisopropyl*-1 : 3-*dioxan*, b.p. 110°/20 mm. Further aldolisation of OH·CHPrβ·CMe$_2$·CHO being impossible, dissociation into PrβCHO occurs, which then yields 6-hydroxy-5 : 5-dimethyl-2 : 4-di*iso*propyl-1 : 3-dioxan and "paraldol" (the derived dimeric aldol), m.p. ~105—107°. R. S. C.

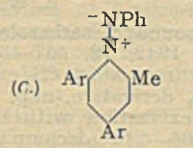
Alkyl exchange of carboxylic esters.—See A., 1944, II, 220.

Compounds of copper sulphate with pyridine. T. L. Chang and P. F. Hu (*J. Chinese Chem. Soc.*, 1943, **10**, 113—115).—$CuSO_4,5H_2O$ in aq. C_5H_5N and hot C_5H_5N–95% EtOH, on cooling, give *Cu*^{II} *sulphate tetrapyridine monohydrate* (**I**), $CuSO_4,4C_5H_5N,H_2O$. The use of relatively more EtOH affords *complexes*, $CuSO_4,3C_5H_5N,3H_2O$ (**II**) and $CuSO_4,2C_5H_5N,2H_2O$ (**III**); excess of 95% EtOH converts (**I**) or (**II**) into (**III**), and all the complexes lose C_5H_5N in air. A. T. P.

Pyridine acids.—See B., 1944, II, 198.

Condensation of 2- and 4-methylpyridine derivatives with cinnamaldehyde. E. Späth, G. Kubiczek, and E. Dubensky (*Ber.*, 1941, **74**, [*B*], 873—879).—In absence of $ZnCl_2$ (cf. Proske, A., 1909, i, 413) this condensation at 150—160° sometimes gives partly the butenol as well as the butadiene. 2-Methylpyridine and CHPh:CH·CHO (**I**) give α-*phenyl*-δ-2-*pyridyl*-Δ$^{\alpha}$-*buten*-γ-*ol* (**II**), m.p. 148°, and -Δ$^{\alpha\gamma}$-*butadiene*, m.p. 123—124° (*picrate*, m.p. 222°), hydrogenated (Pd-black; AcOH) to δ-phenyl-α-2-pyridyl-*n*-butan-β-ol, m.p. 36·5—37° (*picrate*, m.p. 107—109°), and -*n*-butane (*picrate*, m.p. 113—114°), respectively. 4-Methylpyridine and (**I**) give α-*phenyl*-δ-4-*pyridyl*-Δ$^{\alpha}$-*buten*-β-*ol*, m.p. 115—116°, and only traces of α-phenyl-δ-4-pyridylbutadiene, m.p. 157·5—159° [the sole product (m.p. 161—162°) in presence of Ac_2O at 170°]; hydrogenation (Pd-black; MeOH) then gives δ-phenyl-α-4-pyridyl-*n*-butan-β-ol (*picrate*, m.p. 109—110°). 2 : 6-Dimethylpyridine and (**I**) give α-phenyl-δ-6-methyl-2-pyridyl-Δ$^{\alpha}$-buten-γ-ol (*picrate*, m.p. 162°) and -Δ$^{\alpha\gamma}$-butadiene, m.p. 110—111° [*picrate*, m.p. 229° (decomp.)], hydrogenated to δ-phenyl-α-6-methyl-2-pyridyl-*n*-butan-β-ol (*picrate*, m.p. 117—118°) and α-phenyl-δ-6-methyl-2-pyridyl-*n*-butane (*picrate*, m.p. 87—88°); both condensation products are oxidised to BzOH and 6-methylpyridine-2-carboxylic acid, m.p. 128—129°. 2-Methylquinoline and (**I**) give only α-phenyl-δ-2-quinolylbutadiene, m.p. 119° [picrate, m.p. 244° (decomp.)], reduced as above to α-phenyl-δ-2-quinolyl-*n*-butane, an oil (*picrate*, m.p. 123—124°). Pd-black at 150° converts (**II**) into α-*phenyl*-δ-2-*pyridyl*-Δ$^{\alpha}$-*buten*-γ-*one*, m.p. 132—133° (*picrate*, m.p. 110—111°). R. S. C.

1-Arylaminopyridines. III. Influence of substituents [on the] constitution of anhydro-bases. W. Schneider and W. Riedel (*Ber.*, 1941, **74**, [*B*], 1252—1278).—Treating COArMe with H_2SO_4,H_2O and Ac_2O, first cold and then at 50—80°, gives 2 : 4-diaryl-6-methylpyrylium salts, which with NHAr′·NH$_2$ in hot C_6H_6 give 1-arylamino-2 : 4-diaryl-6-methylpyridinium salts (*A*). Heating (*A*) with alcoholic alkali gives highly coloured anhydro-bases which change to brown to red 2 : 4-diaryl-6-*o*-aminobenzylpyridines (*B*). The structure of (*B*) is shown by conversion of (*B*; aryl = Ph) into the *o*-NHBz-derivative, the *o*-NBz·NO-compound from which in boiling C_6H_6 gives an indazole derivative. The time taken for the anhydro-base to pass into (*B*) under standard conditions varies from 1·3 to 320 min., according to the substituents present in Ar and Ar′. It is assumed that the anhydro-bases exist as coloured (*C*) in equilibrium with (*D*) (by way of H-bridged ring intermediates) and that



(*C.*) (*D.*)

only (*D*) isomerises to (*B*). The electronic nature of the substituents is shown to account semi-quantitatively for the variations in the time required for the change (*D*) → (*B*). The colour of the anhydro-base solutions accords approx. with the relative amounts of (*C*) believed to be present. The following are described. 2 : 4-*Di*-p-., m.p. 228° (corresponding sulphoacetate, m.p. 195°), and -m-*tolyl*-, m.p. 209°, 2 : 4-*di*-p-, m.p. 254° (decomp.), and -*m*-bromophenyl-, m.p. 182°, and 2 : 4-*di*-p-, m.p. 225°, and -*m*-chlorophenyl-, m.p. 189°, -6-*methylpyrylium iodide*. 2 : 4-Di-*p*-tolyl-6-ethylpyrylium sulphopropionate, m.p. 195° (decomp.), and iodide, m.p. 232·5°. 1-Anilino-2 : 4-di-*p*-anisyl-, m.p. 155°, -*p*-, m.p. 166°, and -*m*-tolyl-, m.p. 190·5°, -*p*-, m.p. 184·5°, and -m-*bromophenyl*-, m.p. 196·5°, -*p*-, m.p. 150·5°, and -m-*chlorophenyl*-, m.p. 181°, -6-*methylpyridinium iodide*. 1-*p*-Toluidino-2 : 4-di-*p*-anisyl-, m.p. ~134°, -p-, m.p. 172°, and -*m*-tolyl-, m.p. 154·5°, -*p*-bromophenyl-, m.p. 151°, -p-, m.p. 131°, and -*m*-chlorophenyl-, m.p. 153·5°, -6-*m*-ethylpyridinium iodide. 1-*p*-Bromoanilino-2 : 4-di-*p*-anisyl-, m.p. 152°, -*p*-tolyl-, m.p. 192° (decomp.), and -p-*bromophenyl*-, m.p. 180°, -6-*methylpyridinium iodide*. 1-*m*-Toluidino-2 : 4-di-*p*-tolyl-, m.p. 164°, and -2 : 4-di-*p*-chlorophenyl-, m.p. 179°, -pyridinium iodide. 2 : 4-Di-*p*-anisyl-, m.p. 137°, -*p*-, m.p. 126°, and -*m*-tolyl-, m.p. 131°, -p-, m.p. 164°, and -*m*-bromophenyl-, m.p. 139·5°, -*p*-, m.p. 150°, and -*m*-chlorophenyl-, m.p. 134°, -6-*o*-aminobenzylpyridine. 2 : 4-Di-*p*-anisyl-, m.p. 134°, -p-, m.p. 152°, and -*m*-tolyl-, m.p. 140°, -*p*-bromophenyl-, m.p. 165°, -*p*-, m.p. 148°, and -*m*-chlorophenyl-, m.p. 129°, -6-2′-amino-4′-methylbenzylmethylpyridine. 2 : 4-Di-*p*-anisyl-, m.p. 158·5°, -*p*-tolyl-, m.p. 162°, and -*p*-bromophenyl-, m.p. 156°, -6-2′-amino-4′-bromobenzylpyridine. 2 : 4-Di-*p*-tolyl-, m.p. 122°, and -*p*-chlorophenyl-6-2′-amino-3′- or -5′-methylbenzylpyridine, m.p. 160°. 1-Anilino-, 1-*p*-toluidino-, m.p. 145°, and 1-*p*-bromoanilino-2 : 4-diphenyl-6-ethylpyridinium iodide with alkali give blue anhydro-bases which very rapidly yield (?) 2 : 4-diphenyl-6-α-*o*-aminophenylethylpyridine etc. R. S. C.

New case of opening of the isatin ring. G. Jacini (*Gazzetta*, 1942, **72**, 510—514).—Isatin-3-imide with aq. NH_3–H_2O_2 gives o-*carboxylamidophenylcarbamide* (**I**) (picrate, m.p. 340°), which when heated decomposes to give 2 : 4-dihydroxyquinazoline (**II**). (**I**) is also obtained from *o*-NH$_2$·C$_6$H$_4$·CO·NH$_2$ (**III**) and KCNO in AcOH, or from (**II**) and EtOH–NH_3 at 100°. Isatin and aq. NH_3–H_2O_2 give *o*-NH$_2$·C$_6$H$_4$·CO$_2$H. Biuret and (**III**) at >145° give *dianthranylbiuret*, m.p. 315°, easily hydrolysed to (**II**). E. W. W.

Carbon-alkylation with quaternary ammonium salts. Synthesis of compounds containing the β-indolemethylene group. H. R. Snyder, C. W. Smith, and J. M. Stewart (*J. Amer. Chem. Soc.*, 1944, **66**, 200—204).—CH$_2$Ar·NR$_3$Hal reacts with CHXNa·CO$_2$R (X = CN, Ac, or CO$_2$Et) to give CH$_2$Ar·CHX·CO$_2$R, the yield depending largely on the conditions. CH$_2$Ar·NR$_2$ does not react unless X = CO$_2$Et, in which case the yield is poor. CH$_2$Ph·NPhMe$_2$Cl (**I**) with CHNaAc·CO$_2$Et (**II**) in boiling EtOH gives 60% of CH$_2$Ph·CHAc·CO$_2$Et (2 : 4-*dinitrophenylhydrazone*, m.p. 71·5°), and with CHNa(CO$_2$Et)$_2$ (**III**) thus gives 37·6% of CH$_2$Ph·CH(CO$_2$Et)$_2$ (**IV**). With (**III**) in EtOH, 32, 36, 22, 36, 20, and 26% of (**IV**) are obtained from (**I**) at 115° or 130°, benzylmethylpiperidinium iodide (**V**) at 120° or 135°, or benzylmethylpiperidinium chloride at 135° or 130°, respectively, with notable amounts of (CH$_2$Ph)$_2$C(CO$_2$Et)$_2$ (identified by hydrolysis and decarboxylation), but NPhMe$_2$ does not react at 130°. CH$_2$Ph·NPhMe$_2$·OEt and (**III**) at 150° and then 110° give 51·3% of (**IV**). In absence of solvent at 110° and then 140° (**III**) and (**I**) give 79%, (**V**) and (**III**) in Bu$_2$O give 62·5%, and CH$_2$Ph·NMe$_3$Br and (**III**) in Bu$_2$O give 77% of (**IV**). 3-Dimethylaminomethylindole (**VI**) (prep. improved), m.p. 127—128°, and MeI–EtOH at room temp. and then 0° give the methiodide (**VII**),

which with (III) in Bu_2O at 110° and then 145° gives 85% of *Et α-carbethoxy-β-3-indolylpropionate* (85%), m.p. 62°, whence boiling 30% aq. NaOH yields the *dicarboxylic acid* (VIII), m.p. 178° (decomp.) (*diamide*, m.p. 206°), decarboxylated at 180—190° to β-3-indolylpropionic acid (IX), m.p. 132—133°. CN·CHNa·CO_2Et and (VII) give similarly an oil (87%) and thence by hydrolysis (IX). $K_2Ag(CN)_3$ and (VII) in boiling H_2O give an oil, hydrolysed by boiling 20% aq. KOH to 3-indolylacetic acid (46%; 11·4% by KCN), m.p. 164·5—165·5°. (III) and (VI) at 120—150° give, after hydrolysis, 41% of (VIII). R. S. C.

Pyridines and quinolines.—See B., 1944, II, 130.

Doebner reaction. IV. R. Ciusa (*Gazzetta*, 1942, **72**, 567—570).—*p*-NH_2·C_6H_4·SO_2·NH_2 with $AcCO_2H$ and PhCHO in EtOH gives 4-*p''-sulphamylanilo-5-keto-2-phenyl*-1-*p'-sulphamylphenylpyrrolidine*, m.p. 260—263°, and a solution which with Na_2CO_3 gives 6-*sulphamyl*-2-*phenylquinoline*-3-*carboxylic acid* [*Na* salt (+$2H_2O$)]. Using *p*-NH_2·C_6H_4·SO_2·NH·C_5H_4N, the product is a *cinchonic acid*, $C_{22}H_{15}O_4N_3S$, m.p. 157°. E. W. W.

Action of sulphur on heterocyclic compounds: carbazole thio-compounds. (Signa.) L. Raffa (*Gazzetta*, 1942, **72**, 557—563).—Carbazole (I) and S at ~240° give a product from which CS_2 extracts *dicarbazyl disulphide*, m.p. 218—221° (*Bz_2* derivative, m.p. 160—170°); the CS_2-insol. portion yields on extraction with $COMe_2$ *dicarbazyl trisulphide* [*Bz_2* derivative, m.p. 205—210° (decomp.)]; the residue contains a *product*, $C_{24}H_{14}N_2S_5$ (*Bz_2* derivative, m.p. 218—222°), converted by hot 0·5N-NaOH into a *product*, $C_{24}H_{14}N_2S_4$. The product from (I), Mg, and EtBr does not react with S. E. W. W.

Cyclisation in the benzquinoline series. W. S. Johnson and F. J. Mathews (*J. Amer. Chem. Soc.*, 1944, **66**, 210—215).—δ-2-*Naphthylimino*-n-*pentan-β-one* (prep. from β-$C_{10}H_7$·NH_2, CH_2Ac_2, and $CaSO_4$ at 100°), m.p. 98·5—99°, in conc. H_2SO_4 at 100° gives 2 : 4-*dimethyl*-6 : 7-*benzquinoline*-x-*sulphonic acid* (I) (91%) and 2 : 4-dimethyl-5 : 6-benzquinoline (II) (4%), m.p. 128·5—129° (Reed, A., 1887, 681), in conc. H_2SO_4 at 60° gives 2 : 4-*dimethyl*-6 : 7-*benzquinoline* (III) (83%), dimorphic, m.p. 93—93·8° and 74·5—75·5° (Coombes, A., 1888, 968, m.p. 66—67°), and 2% of (I), and in HF at room temp. gives only (90%) (II). (II) is obtained in 70% yield by hydrolysis of (I) by 10% (vol.) H_2SO_4 at 220°. Structures are proved by the following reactions. With aq. $K_2Cr_2O_7$ in boiling AcOH, (II) gives 5 : 6-*phthaloyl*-2 : 4-*dimethylquinoline* (IV) (48%), m.p. 215—216°, photosensitive, which in $Na_2S_2O_4$ gives a deep purple vat, with Zn dust, Ac_2O, and H_2SO_4 gives the *quinol diacetate* (37%), m.p. 198—199°, and is very readily converted by $KMnO_4$ in 20% (vol.) H_2SO_4 into *o*-$C_6H_4(CO_2H)_2$. 1 : 2-$C_{10}H_6$Me·NH_2 (improved prep.), m.p. 49—50°, gives similarly δ-1-*methyl*-2-*naphthylimino*-n-*pentan-β-one*, m.p. 93—94·8°, which in HF gives 2 : 4 : 8-*trimethyl*-6 : 7-*benzquinoline* (V), m.p. 126·2—127°, oxidised as above to (IV). (II) and (V) are readily sulphonated [the SO_3H derivative of (V) is described], give yellow *hydrochlorides*, m.p. 324—325° (decomp.; uncorr.) and 295—296° (decomp.; uncorr.), respectively, and *picrates*, m.p. ~271—273° (decomp.; bath preheated at 250°) after darkening and 253—255° (decomp.; bath preheated at 240°) after darkening, respectively, and in C_6H_6 at room temp. or the b.p., respectively, give 5 : 8-maleic anhydride *adducts*, m.p. ~110—130° (decomp.) (impure) and 203·5—204·5°, respectively. 5 : 6-Benzquinoline (VI) and (III) give colourless anhydrides, are less readily sulphonated, and give tars with (CH·CO)$_2$O. The reactivity of (IV) towards $KMnO_4$ is paralleled by that of 6 : 7-phthaloylquinoline. Structures are supported by absorption spectra (detailed), there being close resemblance between those of (*a*) (III), (V), and anthracene, and (*b*) (II), (VI), and 2 : 4-dimethyl-7 : 8-benzquinoline (prep. in 80—90% yield from the anil by H_2SO_4) (cf. also phenanthrene). Unless otherwise stated, m.p. are corr. R. S. C.

Thiobarbituric acids.—See B., 1944, III, 119.

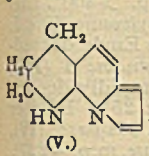
Preparation of *N*-mono- and unsymmetrically di-substituted piperazines. R. Baltzly, J. S. Buck, E. Lorz, and W. Schön (*J. Amer. Chem. Soc.*, 1944, **66**, 263—266).—Monosubstituted piperazine derivatives are obtained in good yield by the appropriate reagent (unless otherwise stated, 1 mol. in 50—100% MeOH or EtOH). CH_2ArCl gives 1-benzyl- (I), b.p. 127—130°/2 mm. (*dihydrochloride*, m.p. 253°), 1-*p*-anisylmethyl-, b.p. 150°/2·5 mm. [*dihydrochloride*, m.p. 263° (decomp.)], and 1-*p*-chlorobenzyl-piperazine, b.p. 140—142°/2·5 mm. [*dihydrochloride*, m.p. 296° (decomp.)]. Ph·[CH_2]$_3$·Br or *n*-$C_{12}H_{25}$Br (0·7 mol.) gives 1-β-phenylethyl-, b.p. 150—152°/8 mm. (*dihydrochloride*, m.p. 252°), or 1-*n*-dodecyl-piperazine, b.p. 140°/0·25 mm. (*dihydrochloride*, decomp. >220°). $(CH_2)_2O$ (0·5—0·66 mol.) gives 1-β-hydroxyethylpiperazine, b.p. 122—123°/10 mm. (*dihydrochloride*, m.p. 189·5°). $ClCO_2$Et in 95% EtOH at >50° (cooling) gives 1-carbethoxy- (hydrochloride, m.p. 145°) and 1 : 4-dicarbethoxy-piperazine, m.p. 49°. Ac_2O in AcOH at 48—54° gives 1-acetylpiperazine (hydrochloride, m.p. 183°). These products yield, by further reaction: 1-*benzoyl*-4-*phenyl*-, m.p. 245°, -4-β-*phenylethyl*-, m.p. 246°, -4-p-*chlorobenzyl*-, m.p. 265°, and -4-p-*anisylmethyl*-, m.p. 234°, 1-*phenylacetyl*-4-p-*anisylmethyl*-, m.p. 225°, and -p-*chlorobenzyl*-, m.p. 241°, -*piperazine hydrochloride*; 1-*benzyl*-4-*methyl*- (II), m.p. 250° (decomp.), -4-*ethyl*- (III), m.p. 250° (decomp.), -4-n-*dodecyl*-, decomp. >250° [*dimethiodide*, m.p. 225° (decomp.), of the derived base], -4-β-*hydroxyethyl*-, m.p. 225°, -4-3′ : 4′-*dimethoxyphenacyl*-, decomp. 250—270°, and -4-3′ : 4′-*dihydroxyphenacyl*- (IV), decomp. 255°, 1-p-*chlorobenzyl*-4-3′ : 4′-*dihydroxyphenacyl*-, decomp. >200°, and 1-p-*anisyl*-4-3′ : 4′-*dihydroxyphenacyl*- (V), m.p. 230—231°, -*piperazine dihydrochloride*; 1 : 4-*di*-n-*dodecylpiperazine dihydrochloride*; 1-β-*benzoyloxyethyl*-*piperazine dihydrochloride*, m.p. 208—210°, and -4-*ethylpiperazine dihydrochloride*, m.p. 245° (decomp.); 1-*benzyl*-4-β-*benzoyloxy*-, m.p. 245°, -4-β-p-*acetamidobenzoyloxy*-, m.p. 229° (decomp.), -4-β-p-*chlorobenzoyloxy*-, m.p. 242°, -4-β-p-*nitrobenzoyloxy*-, m.p. 236—237°, -*ethylpiperazine dihydrochloride*; 1-*benzyl*-4-β-p-*aminobenzoyloxyethylpiperazine trihydrochloride*, m.p. 258—260° (decomp.); (by means of PhNCO) 4-p-*chlorobenzylpiperazine*-1-*carboxylanilide hydrochloride*, m.p. 258° (decomp.); (by means of NH_2·CO·NH·NO_2) 4-p-*chlorobenzyl*-, m.p. 265°, 4-*benzyl*-, m.p. 238·5—239°, 4-β-*hydroxyethyl*-, m.p. 177°, and 4-β-*benzoyloxyethyl*-, m.p. 205° (decomp.), -*piperazine*-1-*carboxylamide hydrochloride*. SMe·C(NH_2):NH,HX and (I) in 65% EtOH give 1-*guanyl*-4-*benzylpiperazine sulphate*, m.p. 200° (decomp.), and (in EtOH, followed by MeI–MeOH) 4-*methiodide hydriodide*, m.p. 219—220° (decomp.). BrCN (1 mol.) and (I) (2 mols.) in Et_2O and then alone at 150—160° give 4 : 4′-*dibenzyl*-1 : 1′-*dipiperazinylcarbimide hydrobromide*, m.p. 229°. Heating (Cl·[CH_2]$_2$)$_2$O and (I) gives 4-*benzylmorpholine*-4′ : 1-spiro-*piperazinium* 1-*chloride* 4-*hydrochloride*, m.p. >280°. Hydrogenation (Pd–C) of (II) and (III) gives 1-*methyl*-, +H_2O, m.p. 110°, and 1-*ethyl*-*piperazine dihydrochloride*, m.p. 203—205°, respectively, and (PtO_2) of (IV) and (V) gives 1-*benzyl*-, decomp. >210°, and 1-p-*anisylmethyl*-4-β-*hydroxy*-3′ : 4′-*dihydroxyphenylethylpiperazine dihydrochloride*, m.p. 175°. R. S. C.

Piperazines.—See B., 1944, II, 147.

Pyrazole synthesis. VII. Reactivity of carbonyl groups in asymmetric β-diketones. R. Fusco [with (Signa.) R. Pizzotti] (*Gazzetta*, 1942, **72**, 411—423).—Hexane-ββδ-dione in NaOMe–MeOH–Et_2O with *p*-NO_2·C_6H_4·NH·N:CBr·CO_2Et gives the *Et* ester (I), m.p. 174°, of 4-*propionyl*-1-p-*nitrophenyl*-5-*methylpyrazole*-3-*carboxylic acid* (II), m.p. 230° (decomp.). With HNO_3 (*d* 1·41), (I) or (II) gives 1-*p*-nitrophenyl-5-methylpyrazole-3 : 4-dicarboxylic acid (III) (A., 1939, II, 451). The expected isomeride of (I), Et 4-acetyl-1-*p*-nitrophenyl-5-ethylpyrazole-3-carboxylate, was not isolated; the mother-liquor in which it should be contained was, however, oxidised by HNO_3 to 1-p-*nitrophenyl*-5-*ethylpyrazole*-3 : 4-*dicarboxylic acid* (IV), m.p. 250°. Heptane-γε-dione, treated as above, gives the *Et* ester (V), m.p. 124°, of 4-*propionyl*-1-p-*nitrophenyl*-5-*ethylpyrazole*-3-*carboxylic acid* (VI), m.p. 169° (decomp.); either (V) or (VI) with HNO_3 gives (IV). Similarly heptane-ββδ-dione gives *Et* 4-n-*butyryl*-1-p-*nitrophenyl*-5-*methylpyrazole*-3-*carboxylate*, m.p. 114°, oxidised to (III), with a product, containing Et 4-acetyl-1-*p*-nitrophenyl-5-propylpyrazole-3-carboxylate, oxidised to 1-p-*nitrophenyl*-5-*propylpyrazole*-3 : 4-*dicarboxylic acid* (VII), m.p. 228°. Similarly nonane-δζ-dione gives *Et* 4-*butyryl*-1-p-*nitrophenyl*-5-*propylpyrazole*-3-*carboxylate*, m.p. 94°, oxidised to (VII). Octane-γε-dione (prepared either from $EtCO_2$Et and COMePr or from $PrCO_2$Et and COMeEt) gives a mixture of Et 4-propionyl-1-*p*-nitrophenyl-5-propyl- and 4-butyryl-1-*p*-nitrophenyl-5-ethyl-pyrazole-3-carboxylate, oxidised to (IV) + (VII). Phenoxyacetylacetone similarly treated gives a mixture of the *Et* ester, m.p. 144°, of 4-*acetyl*-1-p-*nitrophenyl*-5-*phenoxymethylpyrazole*-3-*carboxylic acid* (VIII), m.p. 147—148°, and Et 4-phenoxyacetyl-1-*p*-nitrophenyl-5-methylpyrazole-3-carboxylate (not isolated). With NaOBr, (VIII) gives 1-p-*nitrophenyl*-5-*phenoxymethylpyrazole*-3 : 4-*dicarboxylic acid*, m.p. 233° (with decomp. to the 4-*carboxylic acid*, m.p. 193—194°). The results suggest that the reactivity of ketonic groups is in the order CO·CH_2·OPh > Ac > COEt > COPr. The reaction between CH_2Ac·CO·CO_2R and $2NH_2OH$,HCl, if carried out in alkaline media, followed by heating with conc. HCl, gives mainly 3-methyl*iso*oxazole-5-carboxylic acid (through the dioxime?); in acid media the product is mainly 5-methyl*iso*oxazole-3-carboxylic acid. E. W. W.

Synthesis and hydrogenation of 1 : 8-naphthyridine homologues. E. Ochiai and K. Miyaki (*Ber.*, 1941, **74**, [*B*], 1115—1126).—Substitution of one ring of 1 : 8-naphthyridine by Me reduces the susceptibility of that ring to catalytic hydrogenation (cf. A., 1939, II, 452). 2 : 6-Diaminopyridine, CH_2Ac_2, and $ZnCl_2$ at 120—130° give 7-amino-, m.p. 220° (*Ac* derivative, m.p. 300°), and thence ($NaNO_2$–40% H_2SO_4) 7-hydroxy- (I), m.p. 251°, and ($POCl_3$; 140°) 7-chloro-2 : 4-dimethyl-1 : 8-naphthyridine (II), m.p. 146—147°. Boiling 20% NaOMe–MeOH converts (II) into 7-*methoxy*-2 : 4-*dimethyl*-1 : 8-*naphthyridine*, m.p. 65° (picrate, m.p. 188—189°). With H_2–Ni–kieselguhr in EtOH at 170—180°/110 atm., (I) yields 2 : 4-*dimethyl*-3 : 4-*dihydro*-1 : 8-*naphthyrid*-2-*one*, m.p. 175—180°. With H_2–Pd–C in 10% MeOH–KOH, (II) yields, first, 2 : 4-*dimethyl*- (III), m.p. 85—86° (*hydrochloride*, decomp. 240°; *picrate*, decomp. 204—206°; *methiodide*, +H_2O, m.p. 93—94°; *platinichloride*, decomp. 242—244°; *aurichloride*, decomp. 166—167°), and then 2 : 4-*dimethyl*-5 : 6 : 7 : 8-*tetrahydro*- (IV), m.p. 118° (picrate, m.p. 207°; *Ac* derivative, m.p. 42—43°), -1 : 8-*naphthyridine*, but with H_2–PdO–$CaCO_3$ and a trace of Pd–C in 5% KOH–MeOH gives only

(III) and with H_2–PtO_2 in AcOH or H_2–Raney Ni in *cyclo*hexane–EtOH at 120—190°/70 atm. gives only (IV). (IV) is unaffected by H_2–PtO_2 in AcOH at 110 atm. but with Na–EtOH gives dl-2 : 4-*dimethyldecahydro*-1 : 8-*naphthyridine*, m.p. 92—93° (*Ac*$_2$ derivative, b.p. 135—145°/0·02 mm.). CH_2Cl·COMe and (IV) in a little EtOH give an *adduct*, $C_{15}H_{22}O_2N_2Cl$, m.p. 181—182°, converted by aq. Na_2CO_3 into (IV) and the indolizine (V), a resin (blue Ehrlich test). 2 : 7-Dichloro-4-methyl-1 : 8-naphthyridine with H_2–PdO–$CaCO_3$ and a trace of Pd–C in 10% KOH–MeOH gives 4-*methyl*-1 : 8-*naphthyridine* (VI) (~70%), b.p. 147—148°/0·05 mm. (*picrate*, decomp. 204—205°; *perchlorate*, m.p. 180—181°), and some 2- or 7-*chloro*-4-*methyl*-1 : 8-*naphthyridine*, m.p. 104°.



(V.)

H_2–PtO_2 in AcOH reduces (VI) to 4-methyl-5 : 6 : 7 : 8- (VII) (4 parts), m.p. 102—103° (picrate, decomp. 248°; *Bz*, m.p. 105—106°, and *NO*$_2$-derivative, m.p. 217—218°; ? nitrate, m.p. 124—125°) (cf. Seide, A., 1927, 62), and -1 : 2 : 3 : 4-*tetrahydro*-1 : 8-*naphthyridine* (VIII) (1 part), m.p. 62—63° (*Bz* derivative, m.p. 86—87°). (VII) is unaffected by H_2–PtO_2 in AcOH at 65 atm., but with Na–C_5H_{11}·OH (not Na–EtOH) (VII) or (VIII) gives 4-*methyldecahydro*-1 : 8-*naphthyridine*, m.p. 87° (*picrate*, decomp. 210°). R. S. C.

Ketones, ketonic acids, and enol-lactones. III.—See A., 1944, II, 211.

Fission of indolacylpyridinium salts by alkalis. I. G. Sanna (*Gazzetta*, 1942, **72**, 357—363; cf. Babcock *et al.*, A., 1933, 74; Kröhnke, *ibid.*, 591).—With PhCHO and 25% NaOH, 2′-indolacylpyridinium bromide in aq. EtOH gives indole-2-carboxylic acid and phenacylpyridinium bromide (I). 3-*Methyl*-2-*indolacyl bromide*, m.p. 210° (Ag salt) (obtained from CH_2Br·COBr and the MgBr derivative of indole), with C_5H_5N gives 3′-*methyl*-2′-*indolacylpyridinium bromide*, m.p. 245°, which with NaOH and PhCHO gives 3-methylindole-2-carboxylic acid and (I). 2′-*Pyrrolacylpyridinium bromide*, m.p. 215°, similarly gives pyrrole-2-carboxylic acid and (I). E. W. W.

Indole α-ketoaldonitrones. I. Preparation of ketoaldehydes of the pyrrole and indole series. G. Sanna (*Gazzetta*, 1942, **72**, 363—370):—Indolacylpyridinium bromide (I) with PhNO in EtOH at −5° and N-NaOH gives 2-*aniloacetylindole* N′-*oxide* (I), m.p. 215°, converted by 10% NaOH into 2-indolylglyoxylic acid. With 0·1N-H_2SO_4, (II) gives 2-*phenylhydroxylaminoglycollylindole*, m.p. 93°, reconverted into (II) by keeping over P_2O_5. With NHPh·NH_2 in EtOH, (II) gives a mixture, m.p. 223°, of the α- and β-phenylhydrazones of indolylglyoxal (III). With NH_2Ph in EtOH, (II) gives the *bisaniline derivative*, m.p. 132°, of (III). With *p*-NO·C_6H_4·NMe_2 (IV), (I) gives 2-p-*dimethylaminoaniloacetylindole* N′-*oxide*, m.p. 228°, which with 25% H_2SO_4 (V) gives the hydrate of (III). 2′-Methyl-3′-indolacylpyridinium bromide and (IV) [PhNO ?] give 3-*aniloacetyl*-2-*methylindole* N′-*oxide*, m.p. 140°, which with (V) gives 3-*phenylhydroxylaminoglycollyl*-2-*methylindole*, which gives a mixture, m.p. 115°, of methylindolylglyoxalphenylhydrazones (additive product, m.p. 138°, with H_2SO_4), and a bisaniline derivative. 3′-Methyl-2′-indolacylpyridinium bromide and (IV) [PhNO ?] give 3-*aniloacetyl*-3-*methylindole* N′-*oxide*, m.p. 238°, which readily decomposes to 3-methylindole-2-carboxylic acid, and with (V) gives 3-*phenylhydroxylaminoglycollyl*-3-*methylindole*, m.p. 137°. E. W. W.

Synthesis of optical sensitisers. *iso*Cyanines substituted in position 4. III. V. A. Alexeeva (*J. Appl. Chem. Russ.*, 1943, **16**, 95—104; cf. B., 1938, 141).—11 *dyes* of the general formula 1 : 1′-dimethyl-4-X-*iso*cyanine iodide were prepared. Groups at X and respective m.p. are: Me (α), 233°; Me (γ), 255°; Et, 258° (decomp.); Ph, 246°; OH, 230°; OMe, 323° (decomp.); OEt, 233° (decomp.); NHPh, 281° (decomp.); Cl, 268° (decomp.) [6-Me derivative, 234° (decomp.)]; I, 273—274° (decomp.). Comparison of the methods of prep. described by Kaufmann (A., 1912, i, 503) and Hamer (*J.C.S.*, 1921, **119**, 1440) showed that the method of the former gave better yields. However, the OH-compound is obtainable only by Hamer's method and the OMe-compound only by Kaufmann's. Efforts to introduce the NH_2, NHMe, and NHPh·NH groups in position 4 were unsuccessful. V. B.

Triazines.—See B., 1944, II, 158, 198.

Chemistry of nucleotides. J. M. Gulland (*J.C.S.*, 1944, 208—217).—Tilden lecture, surveying progress over the past five years. Over 100 literature references are given. D. G.

***iso*Oxazole group. XI. Nitrodimethyl*isoo*xazole.** A. Quilico and C. Musante (*Gazzetta*, 1942, **72**, 399—411).—4-Nitro-3 : 5-dimethyl-*iso*oxazole (I) in dil. aq. NaOH with RN_2Cl gives, with ring-opening and -closing, 5-*benzeneazo*-2-*phenyl*- (II), m.p. 135—136°, and 5-p-*tolueneazo*-2-p-*tolyl*-, m.p. 165—166°, -4-*methyl*-2 : 1 : 3-*triazole* 3-*oxide*. In aq. $SnCl_2$–HCl, (II) gives 5-amino-2-phenyl-4-methyl-2 : 1 : 3-triazole, new m.p. 92—93° (*Ac* derivative, m.p. 148—149°; *Bz*$_2$ derivative, m.p. 144—145°; :*CHPh* derivative, m.p. 119—120°; CO·*NHPh* derivative, m.p. 240°). With PhCHO in EtOH, followed by $NHEt_2$, (I) gives 4-*nitro*-5-*styryl*-3-*methylisooxazole* (III), m.p. 153° (*dibromide*, m.p. 167—168°), which on keeping, especially in sunlight, gives a *dimeride*, m.p. 201—202°. Similarly 4-*nitro*-5-p-*methoxy*-, m.p. 163—164°, -5-(3′ : 4′-*methylenedioxy*)-, m.p. 208—209°, -5-m-, m.p. 230—231°, and -p-*nitro*-, m.p. ~220°, and -5-*dimethylamino-styryl*-, m.p. 193—194°, and -5-*cinnamylidenemethyl*-3-*methylisooxazole*, m.p. ~204—205°, are obtained from the corresponding aldehydes. With $SnCl_2$–HCl–EtOH, (III) gives 4-*amino*-5-*styryl*-3-*methylisooxazole* (IV), m.p. 122° [*Bz* derivative (V), m.p. 176°; *Ac*$_2$ derivative, m.p. 111—112°; -*azo*-β-*naphthol*, m.p. 185—186°]. $KMnO_4$–$COMe_2$ oxidises (V) to 4-*benzamido*-3-*methylisooxazole*-5-*carboxylic acid*, m.p. 176—177° (*Me* ester, m.p. 125—127°), which with conc. HCl gives the hydrochloride of 4-amino-3-methyl*iso*oxazole (cf. A., 1943, II, 74). The hydrochloride of (IV) with ice and aq. $NaNO_2$, followed by HCl, gives, after heating, 4-*chloro*-5-*styryl*-3-*methylisooxazole* (VI), m.p. 75° (*dibromide*, m.p. 135°), with PhCHO and a yellow product (CHPh:CH·CO·CHCl·COMe ?), decomposed by NaOH to CHPh:CH·CO_2H. $K_2Cr_2O_7$–H_2SO_4 oxidises (VI) to 4-*chloro*-3-*methylisooxazole*-5-*carboxylic acid*, m.p. 158—159° (Ag salt). E. W. W.

Behaviour of 4-nitro-derivatives of *iso*oxazole. Transformation into pyrazole derivatives. C. Musante (*Gazzetta*, 1942, **72**, 537—548).—4-Nitro-3 : 5-dimethyl*iso*oxazole with NHPh·NH_2 (I) in EtOH at the b.p. gives 4-nitro-1-phenyl-3 : 5-dimethyl- (II) and with N_2H_4 gives 4-nitro-3 : 5-dimethylpyrazole. (II) is reduced by $SnCl_2$–HCl to 4-*amino*-1-*phenyl*-3 : 5-*dimethylpyrazole*, m.p. (anhyd.) 38—40°, (+H_2O) 68° [*Ac*, m.p. 130—131°, and m-NO_2·C_6H_4·*CH*: derivative, m.p. 125—126°; -4-*azo*-β-*naphthol*, m.p. 188—189°; -4-*azoacetylacetone*, m.p. 118—119° (decomp.)]. 4-Nitro-5-methyl-*iso*oxazole (III) and (I) in EtOH give 4-nitro-5-amino-1-phenyl-3-methylpyrazole, which with $SnCl_2$–HCl, followed by NaOH and PhCHO, gives 4 : 5-*bis*(*benzylideneamino*)-1-*phenyl*-3-*methylpyrazole* (?), m.p. 161°, and when heated with 20% NaOH and acidified gives 4-nitro-1-phenyl-3-methylpyrazol-5-one (?). With N_2H_4, (III) gives 4-*nitro*-5-*amino*-3-*methylpyrazole*, m.p. 228° (*Ac* derivative, m.p. 180°; -5-*azo*-β-*naphthol*, darkens from 250°). 5-Methyl*iso*oxazole does not react with (III) or N_2H_4 under the above conditions, but with (III) at the b.p. for 15 hr. gives some 5-amino-1-phenyl-3-methylpyrazole. 4-Nitro-3-phenyl- and -3-methyl-*iso*oxazole give resinous products. 5-Phenyl-3-methyl*iso*oxazole with H_2SO_4–HNO_3 (*d* 1·40) gives 5-p-*nitrophenyl*-, m.p. 180° (oxidised to *p*-NO_2·C_6H_4·CO_2H), reduced to 5-p-*aminophenyl*-3-*methylisooxazole*, m.p. 151—152° (*hydroxchloride*, m.p. 250°; *Ac*, m.p. 241°, *Bz*, m.p. 235°, and *CHPh*:, m.p. 155°, derivatives; -*azo*-β-*naphthol*, m.p. 194°; -*azoacetylacetone*, m.p. 196—197°). E. W. W.

Heterocyclic syntheses. V. L. Panizzi (*Gazzetta*, 1943, **73**, 99—105).—3-Phenyl-5-dichloromethyl*iso*oxazole with NaOEt–EtOH at 140—160° gives 3-*phenylisooxazole*-5-*aldehyde* (I), m.p. 75—76° [*oxime*, m.p. 165—166°; *phenylhydrazone*, m.p. 153—154°; p-*nitrophenylhydrazone*, m.p. 233—234° (decomp.); *anil*, m.p. 133—134°], oxidised by $K_2Cr_2O_7$–H_2SO_4 to the -5-*carboxylic acid*, m.p. 179—180°, also obtained with 3-phenyl*iso*oxazolyl-5-carbinol (*Bz* derivative, m.p. 74—75°) from (I) and hot 20% NaOH. With benzenesulphonhydroxamic acid and NaOH–EtOH, (I) gives 3-*phenylisooxazolyl*-5-*carboxylhydroxamic acid*, m.p. 170° (decomp.); with CH_2N_2 in Et_2O, 5-*acetyl*-3-*phenylisooxazole*, m.p. 103—104° [p-*nitrophenylhydrazone*, m.p. 228—229° (decomp.)]; with $MeNO_2$ and MeOH–NaOMe, α-*nitro*-β-3-*phenyl*-5-*isooxazolylethylene*, m.p. 87—88°. CH(OEt)$_2$·CO_2Et and $COMe_2$, with Na in Et_2O, give α*α*-*diethoxyacetylacetone*, b.p. 90—91°/4 mm. (*Cu* salt, m.p. 124—125°), which with NH_2OH gives 3-methyl*iso*oxazole-5-aldehyde. E. W. W.

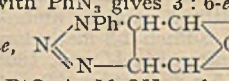
Morpholinomethyl derivatives of carbamide and substituted carbamides. W. I. Weaver, J. K. Simons, and W. E. Baldwin (*J. Amer. Chem. Soc.*, 1944, **66**, 222—225).—OBz·$[CH_2]_2$·NH_2,HCl and CO$(NH_2)_2$ (I) at 130—140° give β-*benzoyloxyethylcarbamide* (36%), m.p. 122—124°. Morpholinomethyl alcohol (II) (1) and (I) (1 mol.) at 80—90° give 92%, morpholine (III), (I), and paraformaldehyde (IV) (equiv. amounts) in boiling dioxan give 84%, and methylenebismorpholine and (I) in boiling dioxan give 33%, of *morpholinomethylcarbamide* (V), m.p. 162—163°. s-*Di*(*morpholinomethyl*)*carbamide* (VI), m.p. 163—164°, is obtained from (I) by 2 mols. of boiling (II) (95%), and from (I) (1 mol.), (III) (2), and (IV) (2 mols.) in boiling dioxan (90% yield). Prep. of (VI) (60% yield) from CO$(CH_2$·$OH)_2$ by (III) (excess) in boiling H_2O and failure of NHR·CO·NHR′ to condense with (II) proves the symmetrical nature of (VI) and the products named below. Hot 10% NaOH hydrolyses (V) or (VI) to (III); Zn–HCl reduces (V) or (VI) to 1-methylmorpholine, which is also obtained with (I) from (V) by H_2–PtO_2 in EtOH. Ac_2O and (V) at 100° give acetylmorpholine (VII) and a *substance*, ? $[\cdot CH_2 \cdot \dot{N} \cdot CO \cdot \dot{N} \cdot CH_2 \cdot]_x$, m.p. 235—236°. In AcOH, (V) and (VI) give *picrates*, m.p. 162—163·3° and 163—164°, respectively, but in EtOH or H_2O give picrates which gradually decompose to regenerate (V) and (VI) when recrystallised. (V) yields, usually in H_2O, N-*morpholinomethyl*-N′-*methyl*-, m.p. 124·4—125·4°, -*ethyl*-, m.p. 109·6—110·8°, -n-, m.p. 89·2—90°, and -iso-*propyl*-, m.p. 126·8—128°, -*allyl*-, m.p. 104—105°, -n-, m.p. 109—109·6°, -iso-, m.p. 112—112·6°, -sec.-, m.p. 111—112°, and -tert.-*butyl*-, m.p. 137·8—138·8°, -sec.-, m.p. 107—108·4°, and -tert.-*amyl*-, m.p. 107·4—109°, -*cyclohexyl*-, m.p. 138—139°, -β-*hydroxyethyl*-, m.p. 118—119·8°, and -β-*benzoyloxy*-

methyl-, m.p. 125·4—127·6°, *-carbamide*, N-*phenyl-*, m.p. 149·4—149·8° (picrate, m.p. 156—158°), N-*benzyl-*, m.p. 149·3—149·8°, and N-*acetyl-* (**VIII**), m.p. 161—161·8° (picrate, m.p. 195°), *-N'-morpholinomethylcarbamide*. Good yields of *morpholinomethylthiocarbamide*, m.p. 141·4—142°, *succin-*, m.p. 109·6—110·4° (picrate, m.p. 188—189°), and *phthal-morpholinomethylimide*, m.p. 117·8—118·8° (picrate, m.p. 205°), *benzene-*, m.p. 81·6—82·6°, and p-*toluene-sulphonmorpholinomethylamide*, m.p. 109·6—111·2°, are obtained. $(RCO)_2O$ and (**VIII**) at 100° give N-*acetyl*-N'-*acetoxy-*, m.p. 144·6—145·2° [and (**VII**)], and *-N'-butyroxy-methylcarbamide*, m.p. 116·8—117°. 1-*Carbamylmorpholine*, m.p. 131·6—133°, is also prepared. R. S. C.

Condensation of xanthhydrol with hydroxyquinolines. (Signa.) L. Monti and M. Delitala (*Gazzetta*, 1942, **72**, 520—524).—4-Hydroxy-2-methylquinoline in AcOH with xanthhydrol (**I**) in EtOH gives 4-*hydroxy*-3-*xanthyl*-2-*methylquinoline*, m.p. 300—305° (decomp.). 4-*Hydroxy*-3-*xanthyl*-2 : 8-*dimethyl-*, decomp. from 290—292°, 4-*hydroxy*-6-*methoxy*-3-*xanthyl*-2-*methyl-*, decomp. from 295—300°, 3-*hydroxy*-4-*xanthyl-*, m.p. 240—242° (Ac derivative, m.p. 190—192°), 5-*hydroxy*-8-*xanthyl-*, decomp. 195—200°), 6-*hydroxy*-5-*xanthyl-*, m.p. 260—262° (Ac derivative, m.p. 214—215°), 8-*hydroxy*-5-*xanthyl-*, m.p. 193—195°, and 2 : 7-*dihydroxy*-8-*xanthyl*-4-*methyl-quinoline* (Ac derivative, decomp. from 205—210°, m.p. 215—220°) are obtained similarly. 2-Hydroxy-4-methyl- and 2-hydroxy-6-methoxy-4-methyl-quinoline do not condense with (**I**), nor do alkyloxy- or acetoxy-quinolines. An improved prep. of 2 : 7-dihydroxy-4-methylquinoline from *m*-$NH_2{\cdot}C_6H_4{\cdot}OH$ and $CH_2Ac{\cdot}CO_2Et$ (C_5H_5N) is described. E. W. W.

Thiazoles.—See B., 1944, II, 131.

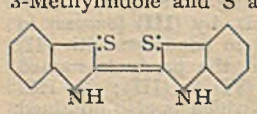
Cyanines etc.—See B., 1944, II, 160.

3 : 6-Epoxy*cyclo*hexene from furan and ethylene. W. Nudenberg and L. W. Butz (*J. Amer. Chem. Soc.*, 1944, **66**, 307—308).—Furan, C_2H_4, and a trace of quinol at 150—155°/1100—1200 lb. (cf. A., 1942, II, 167) give 3 : 6-epoxy-Δ^1-*cyclo*hexene (5—8%), b.p. 118—119°, which with PhN_3 gives 3 : 6-*epoxy*-1'-*phenyl*-1' : 2' : 3'-*triazolino*cyclo*hexane*,  , m.p. 166—167° (corr.), and with H_2–PtO_2 in MeOH and then Ac_2O–$ZnCl_2$ yields 1 : 4-diacetoxy*cyclo*hexane. R. S. C.

Condensation reactions of xanthhydrol [with heterocyclic compounds containing active NH groups]. (Signa.) L. Monti (*Gazzetta*, 1942, **72**, 515—520).—Xanthhydrol (**I**) and 4-hydroxyquinazoline in AcOH give 3-*xanthyl*-4-*quinazolone*, m.p. 198—200°. 2-Hydroxybenziminazole with (**I**) in AcOH–EtOH gives 1-*xanthyl-*, m.p. 268—283—285°. 2-Thiolbenziminazole and (**I**) in AcOH–EtOH give 270°, or with excess of (**I**) gives 1 : 3-*dixanthyl-benziminazolone*, m.p. (1 : 1) 1-*xanthyl-*, m.p. 252—254°, or (1 : 2) 1 : 3-*dixanthyl-benziminazolthione*, m.p. 260—262°. Rhodanine and (**I**) give 3-*xanthylrhodanine*, m.p. 190—192°. E. W. W.

Synthesis of vitamin-B_1. A. I. Gravin (*J. Appl. Chem. Russ.*, 1943, **16**, 105—117).—From a survey of the literature it is concluded that a suitable industrially applicable method for the synthesis of vitamin-B_1 is the condensation (in $CHBr_3$) of 4-amino-2-methyl-5-bromomethylpyrimidine hydrobromide (**I**) with 4-methyl-5-β-hydroxyethylthiazole (**II**). (**I**) is obtained by condensing acetamidine with Et formylsuccinate, and converting the product by P_2O_5 into the chloride and then, by NH_3, into 4-amino-2-methylpyrimidyl-5-acetamide. This is converted (Hofmann) into the amine and then (HNO_2) the OH-derivative; HBr then gives (**I**). (**II**) is obtained by condensing γ-chloro-α-acetoxypentan-δ-one with $(NH_4)_2COS_2$, yielding 2-thiol-4-methyl-5-β-acetoxyethylthiazole, which is oxidised by H_2O_2 to (**II**). The entire synthesis is divided into 17 stages, for each of which yields and experimental details are given. V. B.

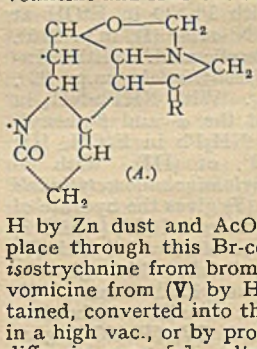
Action of sulphur on heterocyclic compounds : indole and pyrrole thio-compounds. (Signa.) L. Raffa (*Gazzetta*, 1942, **72**, 549—557).—3-Methylindole and S at 115—125° give a *substance*, $C_{27}H_{23}N_3S_2$, probably 2 : 3-*di*-(2' : 2''-*indolylsulphido*)-3 : 3' : 3''-*trimethylindole*, m.p. 215—217° (decomp.) (Ag_2 derivative; *hydrochloride*, decomp. 188°). Indole and S at 190—200° give a green *compound* [regarded as 3 : 3'-(dithio)indigo (*A*), 2 : 2'-(dithio)*iso*-indigo, or 3 : 2'-(dithio)indirubin] (Bz_2 derivative), which on alkali-fusion gives *o*-$NH_2{\cdot}C_6H_4{\cdot}CO_2H$. Pyrrole and S at 115—125° give a *sulphurised pyrrole-black*, $(C_{12}H_{12}N_2S)_x$. E. W. W.

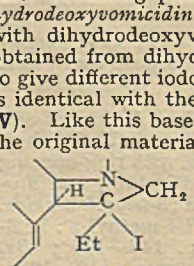

(*A.*)

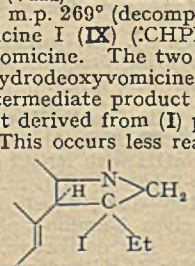
VII.—ALKALOIDS.

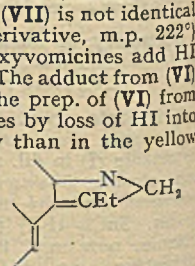
***Strychnos* alkaloids. XXVIII. Emde degradation of vomicine.** H. Wieland and W. Weisskopf [with, in part, R. Huisgen] (*Annalen*, 1943, **555**, 1—9).—Treatment of vomicinium methosulphate in 3N-AcOH containing NaOAc with Na–Hg at 60—70° leads to methylvomicine I (**I**), m.p. 232·5°, $[\alpha]_D$ +156·5°, and *methylvomicine* II (**II**), m.p. 240°, $[\alpha]_D$ +126° [*methiodide*, m.p. 206° (decomp.)], which gives a violet colour with $FeCl_3$ and suffers opening of the lactam ring when boiled with 20% KOH–MeOH. (**II**) contains 1 OMe and 1 NMe and is hydrogenated (PtO_2 in 4N-AcOH) to a H_4-derivative (*picrate*, m.p. 142—144°). (**II**) is demethylated by boiling 40% HBr to a *substance*, $C_{22}H_{27}O_4N_2Br$, m.p. >300°. (**I**) in 60% H_2SO_4 is reduced at a Pb cathode to *methylvomicidine* I, m.p. 230° (decomp.), becomes brown at >225°. The Emde degradation of the methiodide of (**I**) leads to *dimethylvomicine* I (**III**), m.p. 92° [*perchlorate*, m.p. 250° (decomp.)], which is rapidly decomposed without yielding a cryst. product by boiling 25% HBr or HCl. Boiling 40% HBr transforms (**I**) into the OH-*base* (**IV**), $C_{22}H_{26}O_4N_2$, m.p. 272° (*methiodide*, m.p. ~215°; *benzoate*, m.p. ~227°, sinters at 218°; *CHPh* derivative, m.p. 208—210°), in which OH is not *tert.* since (**IV**) is converted by Ac_2O at 180° into a non-cryst. acetate which regenerates (**IV**) when hydrolysed, can be distilled almost unchanged at 290°/high vac., and is indifferent to $SOCl_2$. Demethylated (**I**) is hydrogenated (PtO_2 in 2N-AcOH) to a compound which gives a *picrate*, m.p. 218°. Electrolytic reduction of (**III**) at a Pb cathode leads to *dimethylvomicidine* I, m.p. 236° (slight decomp.). The methiodide of (**III**) is transformed by KOH–MeOH at 110—120° into NMe_3 and an isomeric *dimethylvomicine methiodide*, m.p. 278° (slight decomp.). Emde degradation of the methiodide of (**II**) gives partly (**II**) and partly *dimethylvomicine* II (**V**), m.p. 184°, the lactam ring of which is readily opened by KOH–MeOH. (**V**) is hydrogenated (PtO_2 in 2N-NaOH) to a H_2-derivative, m.p. 165° [*methiodide*, m.p. 290° (decomp.)], and is reduced at a Pb cathode to *dimethylvomicidine* II, m.p. 236°. H. W.

***Strychnos* alkaloids. XXIX. Constitution of deoxyvomicine.** R. Huisgen and H. Wieland (*Annalen*, 1943, **555**, 9—25).—Colourless deoxyvomicine (**I**) is converted by boiling HBr–AcOH containing red P into *tert.*-bromodihydrodeoxyvomicine (**II**), decomp. 235°, becomes discoloured at >165°, re-converted into (**I**) by Zn dust in AcOH but transformed by these reagents in boiling MeOH into *dihydrodeoxyvomicine* (**III**), m.p. 209°, $[\alpha]_D^{22}$ +245° in $CHCl_3$, +221° in EtOH. This is also obtained through a Br-base from dihydrovomicine and HBr but could not be derived by direct hydrogenation of (**II**). (**II**) is re-converted into (**I**) by boiling C_5H_5N or by anhyd. NaOAc in boiling AcOH. (**I**) has therefore the partial formula *A* (R = CHMe) and appears to be the deoxy-derivative of *iso*-vomicine (**IV**), formed from vomicine (**V**) under the influence of HBr and having the structure *A* (R = CH·CH_2·OH). Actually (**IV**) is converted into (**I**) by replacement of OH by Br, which is exchanged for H by Zn dust and AcOH. The formation of (**IV**) from (**V**) takes place through this Br-compound in analogy to the production of *iso*strychnine from bromodeoxystrychnine. In the prep. of deoxyvomicine from (**V**) by HI in AcOH the yellow variety (**VI**) is obtained, converted into the more stable (**I**) by alkalis, by distillation in a high vac., or by protracted heating with solvents. (**VI**) and (**I**) differ in m.p., $[\alpha]_D$, ultra-violet absorption, and reactions but are catalytically hydrogenated to the saturated base $C_{22}H_{30}O_2N_2$ among other products. The isomerism of (**I**) and (**VI**) appears to be caused by differing arrangement of the double linkings, which in (**I**) is as shown in *A* since on ozonisation (**I**) gives >80% of the quantity of MeCHO (as dinitrophenylhydrazone) calc. for 1 mol. (**V**) also gives MeCHO but more slowly and in much lower yield. The double linking in the lactam ring is $\beta\gamma$ to CO (not $\alpha\beta$ as assumed previously) since (**I**) contains a reactive CH_2. Whereas (**V**) and strychnine only condense with PhCHO under the influence of alkali, this condensation occurs with (**I**), (**III**), and (**IV**) in presence of piperidine (*benzylidenedeoxyvomicine* has m.p. 198—199°). (**VI**) is not immediately derived from (**V**) and HI, which directly yield *iododihydrodeoxyvomicine* II *hydriodide*, m.p. 214° (decomp.). Attempts to isolate the free base are accompanied by elimination of HI and formation of (**VI**). Replacement of I by H by use of Zn dust in cold HI affords *dihydrodeoxyvomicine* II (**VII**), m.p. 168°, $[\alpha]_D^{20}$ +345° in $CHCl_3$ [*hydrochloride* (**VIII**), m.p. 235° (decomp.) after becoming pink]. (**VIII**) is reduced at a Pb cathode to *dihydrodeoxyvomicidine* II, m.p. 269° (decomp.). (**VII**) is not identical with dihydrodeoxyvomicine I (**IX**) (*CHPh* derivative, m.p. 222°) obtained from dihydrovomicine. The two deoxyvomicines add HI to give different iododihydrodeoxyvomicines. The adduct from (**VI**) is identical with the intermediate product of the prep. of (**VI**) from (**V**). Like this base that derived from (**I**) passes by loss of HI into the original material. This occurs less readily than in the yellow series but still so easily (with NaOAc) that there can be no doubt about the attachment of I to *tert.* C. The isomerism of the hydr-

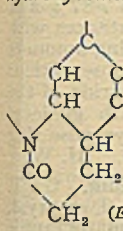

(*A.*)


(*B.*)


(*C.*)


(*D.*)

iodides is epimeric (cf. *B* and *C*). That derived from (**VI**) is *C*, thus leading to *D* from (**VI**). (**III**) is hydrogenated (PtO_2 in 2N-AcOH) to *tetrahydrodeoxyvomicine* (**X**), m.p. 246—247° [*methiodide*, m.p. 222° (decomp.), $[\alpha]_D^{21}$ +210° in $CHCl_3$; *CHPh* derivative, m.p. 247°, obtained by use of 20% NaOH but not of piperidine], and *deoxyvomicine* B (**XI**), m.p. 185—186°, $[\alpha]_D^{20}$ +270° in $CHCl_3$. The change proceeds more rapidly in glacial AcOH but leads exclusively to (**X**), which is also obtained by hydrogenation (PtO_2 in EtOH) of (**II**) and primary bromodihydrodeoxyvomicine. (**X**) and (**XI**) are electrolytically reduced in 60% H_2SO_4 at a Pb cathode to *tetrahydroxyvomicidine-A*, m.p. 250—251° (decomp.), softens at 240°, and *-B*, m.p. (indef.) ~200°. The isomerism of (**X**) and (**XI**) depends on the union of the carbocyclic and heterocyclic 6-membered rings (cf. *E*) in the *cis*- or *trans*-position. Fission of the oxide ring of (**I**) by H halides proceeds similarly with (**V**), strychnine (**XII**), brucine, and their H_2-bases. An apparent exception appears to be afforded by (**XII**), which with HI under drastic conditions gives tetrahydrodeoxystrychnine. Under milder, precisely specified conditions (**XII**) gives deoxystrychnine, m.p. 197—198°, softens at 195—196°. (**XII**) has a semicyclic double linking and when ozonised affords MeCHO (as 2 : 4-dinitrophenylhydrazone) in 90% yield. *apo-Strychnine*, $C_{21}H_{20}ON_2$, m.p. 242—244°, is obtained as by-product of the action of HBr on (**XII**). H. W.



(*E*.)

Physostigmine [eserine] and related substances. IV. Chemical studies on physostigmine breakdown products and related epinephrine derivatives. S. Ellis (*J. Pharm. Exp. Ther.*, 1944, **79**, 364—372).—Methods are described for the prep. of eseroline, rubreserine (**I**), eserine-blue, eserine-brown, and adrenochrome (**II**). Measurements of absorption spectra of (**I**), (**II**), and 2-iodoadrenaochrome indicate that (**I**) contains a substituted 2 : 3-dihydroindole-5 : 6-quinone group and is thus structurally related to (**II**), the oxidation product of adrenaline. F. R. S.

Structure of monocrotaline. XI. Proof of the structure of retronecine. R. Adams and N. J. Leonard (*J. Amer. Chem. Soc.*, 1944, **66**, 257—263; cf. A., 1944, II, 147).—Retronecine is proved to be 7-hydroxy-1-hydroxymethylpyrrolizidine, $CH_2<\begin{matrix}CH(OH)\cdot CH\cdot C(CH_2\cdot OH)\\ CH_2\text{——}N\cdot CH_2\text{——}\end{matrix}>CH$, by synthesis of retronecanone (**II**). Adding molten *m*-$NO_2\cdot C_6H_4\cdot COCl$ to 4-methylpiperidine (prep. from 4-methylpyridine by H_2–Raney Ni at 210°/150—300 atm.), b.p. 126—129°, and aq. NaOH at 35—40° gives 1-*m-nitrobenzoyl-4-methylpiperidine*, m.p. 72—73°, oxidised by boiling aq. $KMnO_4$ to dl-δ-*m-nitrobenzamido-β-methyl*-n-*valeric acid* (**III**) (57%), m.p. 103—105°, which with quinidine in EtOH–Et_2O gives the l- (**IV**) (36%) and d-*acids*, m.p. 113—114°, $[\alpha]_D^{30}$ −5·0±0·2°, +5·3±0·2°, respectively, in EtOH [quinidine salt of (**IV**), m.p. 125—126·5° (corr.), $[\alpha]_D^{28}$ +111·5° in EtOH]. Br and red P at 90° convert (**III**) into the crude, oily α-Br-acid (**V**) with some dl-3 : 3-*dibromo*-1-*m-nitrobenzoyl-4-methyl*-2-*piperidone* (**VI**), m.p. 152—153° (corr.). Boiling Ac_2O cyclises (**III**) to 1-*m-nitrobenzoyl-4-methyl*-2-*piperidone* (**VII**), m.p. 102—103°, which with Br and a trace of PCl_3 in $CHCl_3$ in light yields (**VI**). (**IV**) yields similarly l-(**VII**), m.p. 167—168° (corr.), $[\alpha]_D^{30}$ −20·2±0·2° in C_5H_5N, and oily *l*-(**V**). In N-NaOH at 37°, *dl*- or *l*-(**V**) gives *dl*- and *l*-1-*m*-nitrobenzoyl-3-methylpyrrolidine-2-carboxylic acids, oils, which with boiling 3N-aq. HCl and then boiling HCl–EtOH yield *Et* dl-, b.p. 90—91·5°/17·5 mm. (*picrate*, m.p. 112·5—114°), and l-3-*methylpyrrolidine-2-carboxylate*, b.p. 97—98°/23 mm. $[\alpha]_D^{28}$ ~0° in EtOH, which add CH_2:CH·CO_2Et (in presence of a trace of quinol) at the b.p. to yield *Et* dl- (97%), b.p. 163·5—165·5°/18 mm. (*picrate*, m.p. 98—99°), and l-β-2-*carbethoxy*-3-*methyl*-1-*pyrrolidinopropionate*, b.p. 170—171°/25 mm., $[\alpha]_D^{30}$ −34·9±0·5° in EtOH. Cyclisation by K in xylene–C_6H_6 then affords dl-, b.p. 96·5—98°/18 mm. [*picrate*, m.p. 189—190° (corr.); *methiodide*, m.p. 149·5—150·5° (corr.)], and *l*-7-keto-1-methylpyrrolizidine [=(**II**)] [identified as oxime, m.p. 166—167° (corr.), $[\alpha]_D^{32}$ −77·3±1·5° in EtOH, oxime picrolonate, m.p. 209—211° (corr.), l-*menthhydrazide*, m.p. 175·5—176·5° (corr.), $[\alpha]_D^{28}$ −83·2±0·5° in EtOH, and other derivatives, and by conversion into retronecanol methiodide acetate, m.p. 215—216° (corr.) (lit. 207—208°), $[\alpha]_D^{28}$ −87·4±1·0° in MeOH]. H_2–PtO_2 reduces (**II**) in EtOH to an oily isomeride, $[\alpha]_D^{33}$ −9·5° in EtOH [*picrate*, m.p. 218—219° (corr.; decomp.); *acetate methiodide* (**VIII**), m.p. 210—212° (corr.), $[\alpha]_D^{28}$ +7·5° in EtOH], of retronecanol and in EtOH + a little conc. HCl gives an isomeride {*picrate*, m.p. 230—232° (corr.; decomp.); *acetate picrate*, m.p. 178·5—179·5° (corr.), and methiodide [=(**VIII**)], m.p. 210·5—211·5° (corr.)}. Hydrogenation (PtO_2) of (**VII**) in EtOH yields a *dl*-7-hydroxy-1-methylpyrrolizidine [*picrate*, softens 210°, m.p. 218·5—219·5° (corr.; decomp.); *picrolonate*, m.p. 182·5—183·5° (corr.)]. R. S. C.

VIII.—ORGANO-METALLIC COMPOUNDS.

Amidino-arsenicals. II. Tervalent arsenicals. F. Linsker and M. T. Bogert (*J. Amer. Chem. Soc.*, 1944, **66**, 191—192; cf. A., 1943, II, 284).—*p*-CN·$C_6H_4\cdot AsO_2H_2$ in 2N-NaOH with, successively, KI, H_2SO_4 (excess), and SO_2 at >10° gives p-*cyanophenylarsinous acid* (**I**) (85%), softens 230°, m.p. 234° (decomp.; corr.), also obtained [80%, m.p. 230—240° (decomp.)] from *p*-$NH_2\cdot C_6H_4\cdot AsO,2H_2O$, m.p. 98° (decomp.) [lit. m.p. 100° (decomp.)], by treating the derived diazonium chloride with $CuSO_4$–KCN, purification being by dissolution in N-NaOH and pptn. by NH_4Cl. HCl–EtOH–Et_2O converts (**I**) at 0° into the *imino-ether hydrochloride* (95%), softens 150°, m.p. 152° (decomp.), hydrolysed by ;10% NH_3–EtOH at 60° to p-*amidinophenylarsinous acid hydrochloride*, m.p. 210° (decomp.), whence HCl or HBr at 0° yields *dichloro*-p-*amidinophenylarsine hydrochloride*, sinters 202°, m.p. 208° (decomp.), or the *dibromoarsine hydrobromide*, m.p. 219° (decomp.), respectively. p-*Arsinibenzimino ether hydrochloride*, m.p. 130° (decomp.), is also described. R. S. C.

Preparation of phenylarsinoxides. VI. *p*-Arsinoxidobenzoylcarbamide and related compounds. H. G. Steinman, G. O. Doak, and H. Eagle. **VII. *p*-Arsinoxido-compounds containing amide groups. VIII. Arsonic acids and arsinoxido-compounds containing the azo-linking.** G. O. Doak, H. G. Steinman, and H. Eagle (*J. Amer. Chem. Soc.*, 1944, **66**, 192—194, 194—197, 197—200; cf. A., 1942, II, 337).—VI. *p*-COCl·$C_6H_4\cdot AsCl_2$ (**I**) does not yield *p*-COCl·$C_6H_4\cdot AsO$ by any direct method; with Na urethane in Et_2O (not C_6H_6 or C_5H_5N) it gives *Et* di-p-*arsinoxidobenzoylcarbamate*. p-*Nitrobenzoylisocarbimide* (**II**) [prep. from *p*-$NO_2\cdot C_6H_4\cdot COCl$ (**III**) by AgNCO in boiling C_6H_6], m.p. 209—210°, with $NH_2\cdot[CH_2]_2\cdot OH$ in C_6H_6 gives N-p-*nitrobenzoyl*-N′-*β-hydroxyethylcarbamide* (30%), m.p. 186—187°, hydrogenated (method: Stevinson *et al.*, A., 1935, 1139, in this and similar cases) to the NH_2-derivative, m.p. 230·5—231·5°, which yields (Bart) the p-AsO_3H_2-, m.p. 238—238·5° (decomp.), and thence (SO_2) the amorphous p-*AsO*-derivative (not obtainable from *p*-$AsO_3H_2\cdot C_6H_4\cdot COCl$ by AgNCO etc.). $NH_2\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$ and (**II**) give N-p-*nitrobenzoyl*-N′-*βγ-dihydroxy*-n-*propylcarbamide* (22%), m.p. 197—199°, whence H_2–Raney Ni yields only *p*-$NH_2\cdot C_6H_4\cdot CO\cdot NH_2$. Boiling (**II**) and $CO(NH_2)_2$ in C_6H_6 gives α-p-*nitro*- (50%), m.p. 203—205°, and thence α-p-*amino*- (90%), sinters ~270°, and α-p-*arsono-benzoylbiuret*, m.p. >360°. Boiling $AsCl_2\cdot C_6H_3Me\cdot COCl$ with $CO(NH_2)_2$ and hydrolysing the product gives p-*arsinoxido-*" α "-*toluoylcarbamide*, decomp. >272°. N-p-*Arsinoxyoxidoanilinoacetcarbamide*, amorphous, m.p. 166—168° (decomp.), is obtained by reducing the AsO_3H_2-compound by SO_2. $NH_2\cdot CO\cdot CH_2\cdot NH_2,HCl$ (**IV**) and (**III**) in aq. $NaHCO_3$ give p-*nitrobenzamidoacetamide*, m.p. 239—240° (decomp.), reduced to the p-NH_2-derivative, m.p. 228° (decomp.) (*sulphate*, decomp. >250°), whence the Bart reaction yields the p-AsO_3H_2-derivative, m.p. 211—213° (decomp.); this does not yield the p-*AsO*-derivative, decomp. >285°, which is obtained from (**I**) and (**IV**) in aq. Na_2CO_3. *N*-Glycylglycine and (**I**) in N-KOH give amorphous N-p-*arsinoxidohippurylglycine*, decomp. >220°, which, by way of the *Ag* salt, yields the amorphous *Me* ester, decomp. >240°, and thence the *amide*, decomp. >240°. β-Alanine amide (prep. from $CN\cdot CH_2\cdot CO\cdot NH_2$ by H_2–Raney Ni in EtOH), m.p. 149°, gives similarly β-p-*arsinoxidobenzamidopropionamide*, m.p. 283—285° (decomp.). Glycine amide yields similarly p-*arsenoxido-*" α "-*toluamido-*, m.p. 133° (decomp.), and p-*arsenoxidobenzenesulphonamido-acetamide*, amorphous, m.p. 193—195° (decomp.). Amorphous N-p-*arsono-*, m.p. 326·5°, and N-p-*arsinoxido-benzoylcarbamide*, m.p. 270—271°, are also described.

VII. *m*-5-Xylidine gives (Bart) m-5-*xylylarsonic acid* (18%), m.p. 222—223°, oxidised by $KMnO_4$ to the *salt*, KHX,H_2X [X = $(CO_2H)_2C_6H_3\cdot AsO_3$], decomp. >300°, whence PCl_3–PCl_5 and then cold, aq. NH_3 yields 5-*arsenoxidoisophthalic acid*, $+2H_2O$, amorphous, m.p. 224—225°. The derived Me_2 ester, m.p. 255°, with NH_3 at 100° gives the *diamide*, $+H_2O$, a glass, softens 75°. 5-*Nitro*-o-*tolylarsonic acid* (prep. by Scheller–Bart reaction), m.p. 240°, gives 5-nitro- and thence 5-*amino*-2-*arsonobenzoic acid*, m.p. >360°, which affords (method: Doak *et al.*, A., 1941, II, 272, but using CuCN) impure 5 : 1 : 2-CN·$C_6H_3(CO_2H)\cdot AsO_3H_2$, decomp. >300°, whence 30% H_2O_2 yields 6-*arsono*-, m.p. 347·5°, and thence 6-*arsinoxidoisophthalamic acid*, $+H_2O$, m.p. 236·5—237·5°. Similarly are prepared 4-*nitro*-o-*tolylarsonic acid*, m.p. 235—236°, 4-amino-, $+H_2O$, decomp. 220° [lit., anhyd., m.p. 120° (decomp.)], and 4-*cyano*-2-*arsonobenzoic acid*, decomp. >351°, 4-*arsono*-, m.p. >360°, and 4-*arsinoxido-terephthalamic acid*, m.p. 221·5—222·5°. 2 : 1 : 4-$NO_2\cdot C_6H_3(CO_2H)\cdot AsO_3HK$ gives (PCl_5–$POCl_3$) the acid chloride, converted by cold, aq. NH_3 into 2-*nitro*-4-*arsinoxidobenzamide*, m.p. 162—163° (decomp.), which with 30% H_2O_2 gives 3-*nitro*-4-*carbamylphenylarsonic acid*, decomp. >270°. This is hydrogenated to 4-*carbamyl*-m-*arsanilic acid*, decomp. >230°, reduced by SO_2 to the *AsO*-compound (**V**), $+1·5H_2O$, m.p. 177—178°, which is better obtained from 4 : 2 : 1-$AsO\cdot C_6H_3(NH_2)\cdot CO_2Me$ by aq. NH_3 at 90°. The amorphous *Ac* derivative, $+H_2O$, m.p. 263—264° (decomp.), of (**I**) is obtained therefrom by Ac_2O but not by reduction of the AsO_3H_2-compound. 2 : 4 : 1-$NHAc\cdot C_6H_3(AsO_3H_2)\cdot CO_2H$ could not be converted into the benzamide derivative. 4-*Arsinoxido-*, $+H_2O$, m.p. >360°, is obtained by reducing 4-arsono-salicylamide. *Me* 5-*arsonosalicylate*, softens 193°, suffers fission by NH_3 at 100° but at 0° gives 4-*hydroxy*-3-*carbamylphenylarsonic acid*, decomp. >330°, and thence 5-*arsinoxidosalicylamide*, $+0·5H_2O$, m.p. 222—223°.

4-Hydroxy-5-carbamyl-m-arsanilic acid (similarly prepared) gives an unstable *dichloroarsine hydrochloride*, m.p. 177—178°.
p-$CN{\cdot}C_6H_3{\cdot}AsO_3H_2$ with SO_2–HI–H_2SO_4 gives p-*arsinobenzonitrile*, amorphous, m.p. 195·5—197·5°, whence HCl–Et_2O–95% EtOH at 0° gives p-*dichloroarsinobenzimino Et ether hydrochloride*, $+H_2O$, m.p. 141°, hydrolysed by $NaHCO_3$ to p-*arsinoxidobenzimino Et ether*, $+H_2O$, amorphous, m.p. 184·5—185°. *p*-$AsCl_2{\cdot}C_6H_4{\cdot}COCl$ (**VI**) with 3 : 1 : 2-$NH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$ and Na_2CO_3 in aq. $COMe_2$ gives p-*arsinoxidobenz-βγ-dihydroxypropylamide*, amorphous, decomp. >250°, with N_2H_4,H_2O in C_5H_5N–C_6H_6 gives s-*di*-p-*arsinoxidobenzoyl-hydrazine*, amorphous, decomp. >360°, and with $CN{\cdot}CH_2{\cdot}NH_2,H_2SO_4$ in Na_2CO_3 gives p-*arsinoxidobenzcyanomethylamide*, amorphous, decomp. >265°, oxidised by I to the *arsonic acid*, m.p. 251—252° (decomp.). Similarly (**VI**) with $(CH_2{\cdot}NH_2)_2$ or $NHAc{\cdot}NH_2$ gives s-*di*-p-*arsinoxidobenzethylenediamide*, amorphous, decomp. >320°, or N-p-*arsinoxidobenzoyl-N′-acetethylenediamide*, amorphous, decomp. 270—272° (decomp.), respectively. *Glycylacetanilide*-p-*dichloroarsine hydrochloride* is obtained from the NO_2-compound and is hydrolysed to the AsO-compound. N-p-*Toluoylarsanilic acid* (prep.: Schotten–Baumann), m.p. >360°, with $KMnO_4$–$MgSO_4$–H_2O gives *p*-$C_6H_4(CO_2H)_2$ (100%). *p*-$C_6H_4(COCl)_2$ and *o*-$NH_2{\cdot}C_6H_4{\cdot}AsO_3H_2$ (**VII**) give NN′-*terephthaloyldiarsanilide* (25%), amorphous, decomp. >250°, and p-*arsonoterephthalanilic acid* (5%), m.p. >360° (cf. G.P. 191,548). *p*-$CN{\cdot}C_6H_4{\cdot}COCl$ (prep. from the acid by $SOCl_2$ and C_5H_5N in Et_2O) and (**VII**) give N-p-*cyano-*, amorphous, m.p. >360°, converted by 3% H_2O_2 into N-p-*carbamyl-benzoylarsanilic acid*, m.p. >360°, whence the amorphous *arsine oxide*, m.p. 319°, is obtained. *p*-$NH_2{\cdot}C_6H_4{\cdot}S{\cdot}C_6H_4{\cdot}NO_2$-*p* gives (Scheller–Bart) p-p′-*nitrophenylthiolphenylarsonic acid* (39%), m.p. 291—292°, and thence the NH_2-acid, decomp. >190°, and (Sandmeyer) the *CN-acid* (32%), decomp. >200°, whence H_2O_2 yields p-p′-*carbamylbenzenesulphonylphenylarsonic acid*, m.p. 310·5°.

VIII. ArN_2Cl couples with *o-* and *m*-$OH{\cdot}C_6H_4{\cdot}AsO_3H_2$ in the position *p-* to OH; when the OH is *p-* to the AsO_3H_2, partial replacement of AsO_3H_2 by ArN_2 and then further coupling occur, the amounts of three reactions depending largely on the pH. The Bart and Scheller–Bart reactions can also be used with azobenzene derivatives. *2-Hydroxy-5-*, m.p. 257·3°, and *5-hydroxy-2-benzeneazophenylarsonic acid*, m.p. 237·5°, are obtained by coupling in $NaHCO_3$ or NaOH; they are converted by hydrogenation (Raney Ni) and then reduction in HCl into 4-amino-2-, m.p. 183—183·4°, and *5-amino-4-dichloroarsinophenol hydrochloride*, m.p. 128—128·2°, respectively. *p*-$OH{\cdot}C_6H_4{\cdot}AsO_3H_2$ (**VIII**) at pH 5·8—6·6, 7·3—7·4, or 8·5—9·5 (respective yields in parentheses) gives *p*-$PhN_2{\cdot}C_6H_4{\cdot}OH$ (36·9, 39·4, 9·4), *4-hydroxy-3-benzeneazophenylarsonic acid* (0·5, 5·9, 0), m.p. 290° (obtained in 40% yield by a Scheller–Bart reaction), and 2 : 4 : 1-$(PhN_2)_2C_6H_3{\cdot}OH$ (4·6, 12·2, 27·8%). (**VIII**) does not couple with *p*-$N_2Cl{\cdot}C_6H_4{\cdot}CO_2H$ or *m*-$C_6H_4Me{\cdot}N_2Cl$. 2 : 4 : 1-$(OH)_2C_6H_3{\cdot}AsO_3H_2$ at pH 7·6—7·9 or 8·5—9·5 gives 84 and 5·6%, respectively, of 2 : 4-*dihydroxy*-3 : 5-*dibenzeneazophenylarsonic acid*, m.p. 268°, with, in the latter case, mixed phenols. 4 : 1-$OH{\cdot}C_{10}H_5{\cdot}AsO_3H_2$ (**IX**) at pH 7·1—7·4 gives 4 : 1-$PhN_2{\cdot}C_{10}H_4{\cdot}OH$ (34·4%), $(PhN_2)_2C_{10}H_5{\cdot}OH$ (33·8%), and *4-hydroxy-1-benzeneazonaphthylarsonic acid* (**X**) (20%), m.p. 245°. *4-Amino-1-naphthyl benzoate* (prep. from the NO_2-ester by H_2–Raney Ni in EtOH or from the NH_2-ester hydrochloride by NH_3), m.p. 107·2—107·6°, gives (Scheller–Bart) *4-arsono-1-naphthyl benzoate* (19%), m.p. 199·8—200°, whence cold HCl–MeOH yields (**IX**) (57%) and MeOBz. H_2–Raney Ni reduces the Na_1 salt of (**X**) to *2-amino-1-naphthol-4-arsonic acid*, decomp. when heated, whence *4-hydroxy-1 : 4-α-naphth*-iso*oxazine-6-arsonic acid* is prepared. Bart, or, better, Bart–Scheller, reactions yield *p*-$PhN_2{\cdot}C_6H_4{\cdot}AsO_3H_2$, m.p. 332·5—333·5°, p-*toluene*-p′-*azophenyl-* (**XI**), m.p. >360°, and *4-hydroxy-3-benzeneazophenyl-arsonic acid*, but failed with p-5-*amino*-2-*hydroxyazobenzene-4′-sulphonic acid* (*Na* salt of the Ac derivative) and its *amide* (*Ac* derivative). Oxidising (**XI**) by $KMnO_4$ gives p-p′-*arsonobenzeneazobenzoic acid*, m.p. >360°, converted by PCl_5–$POCl_3$ and then aq. NH_3 R into p-p′-*arsinoxidobenzeneazobenz-amide*, decomp. >260°, and *-β-hydroxyethylamide*, decomp. >275°.
p-$AsO_3H_2{\cdot}C_6H_4{\cdot}N_2Cl$ and *o*-$NHAc{\cdot}C_6H_4{\cdot}OH$ give p-3′-*acetamido-*, m.p. 224·8—225·2°, and thence (HCl–MeOH) p-3′-*amino-4′-hydroxybenzeneazophenylarsonic acid*, decomp. when heated. R. S. C.

Mercuripurine derivatives of phthalimide. G. Carrara and E. Mori (*Gazzetta*, 1943, **73**, 113—116).—Allylphthalimide [new prep. from $C_6H_4(CO)_2O$ and allylamine] and $Hg(OAc)_2$ in MeOH at the b.p. give N-*β-acetatomercuri-γ-methoxypropylphthalimide*, m.p. 139—140°, which with theophylline gives *α-phthalimido-γ-methoxy-β-propylmercuritheophylline*, m.p. 225—226°. E. W. W.

IX.—PROTEINS.

Strometin.—See A., 1944, III, 450.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Formation of " excess material " in the treatment of wood with sodium chlorite and its significance for the chemistry of wood and lignin. G. Jayme, L. Eser, and G. Hanke (*Naturwiss.*, 1943, **31**, 275—276).—Subjection of the solutions obtained by treating wood with $NaClO_2$ to dialysis and electrodialysis yields from pine 10·13% of material with 8·62% OMe and 22·30% lignin residue and from poplar 9·42% of material with 6·84% OMe and 25·05% lignin residue. In these cases the excess material amounts to 7·87% and 7·06% respectively; this consists of a mixture of substances with short chains the individual fractions of which give varying amounts of residue in the customary lignin determination. The observations are explained by assuming the presence of a polysaccharide of the hexose type or its precursor substituted mainly with guaiacyl residues, two aromatic residues being united to each pyranose ring by the loss of 1·5—2 mols. of H_2O or 0·5—2 atoms of O. H. W.

Isolation of euphol and α-euphorbol from euphorbium. G. T. Newbold and F. S. Spring (*J.C.S.*, 1934, 249—252).—Two cryst. monohydric alcohols have been isolated by the chromatographic method from euphorbone, an amorphous solid obtained from euphorbium. One of these is identical with α-euphorbol (cf. Bauer *et al.*, A., 1931, 847), m.p. 126—127°, $[\alpha]_D^{17}$ ±0° in $CHCl_3$ [*acetate*, m.p. 124—125°, $[\alpha]_D^{15\cdot5}$ ±0° in $CHCl_3$; *benzoate*, m.p. 133—135°, $[\alpha]_D^{15}$ + 15° in C_5H_5N; *acetate dibromide*, m.p. 169—171° (decomp.)], which contains at least two double bonds, the acetate being reduced to *dihydro-α-euphorbyl acetate*, m.p. 133—135°, $[\alpha]_D^{15}$ −15° in C_5H_5N. The second component is *euphol*, $C_{30}H_{50}O$ (?), m.p. 116°, $[\alpha]_D^{19\cdot5}$ +32° in $CHCl_3$, containing two double bonds, one of which is relatively inert; it gives an *acetate*, m.p. 109°, $[\alpha]_D^{22}$ +41° in $CHCl_3$, *benzoate*, m.p. 137—139°, $[\alpha]_D^{18\cdot5}$ +59° in C_5H_5N, *acetate dibromide*, m.p. 138·5—139·5°, $[\alpha]_D^{20}$ +23·5° in $CHCl_3$, and *dihydroeuphol*, m.p. 120°, $[\alpha]_D^{18\cdot5}$ +34° in $CHCl_3$ (*acetate*, m.p. 123·5—124°, $[\alpha]_D^{19}$ +34·5° in $CHCl_3$, and *benzoate*, m.p. 160—161°). F. R. S.

Biochemistry of *Eidamella spinosa*.—See A., 1944, III, 502.

Folic acid. I. Concentration from spinach. H. K. Mitchell, E. E. Snell, and R. J. Williams. **II. Adsorption.** E. H. Frieden, H. K. Mitchell, and R. J. Williams. **III. Chemical and physiological properties.** H. K. Mitchell and R. J. Williams. **IV. Absorption spectra.** H. K. Mitchell (*J. Amer. Chem. Soc.*, 1944, **66**, 267—268, 269—271, 271—274, 274—278; cf. A., 1941, III, 1066).—I. The filtrate obtained from pulped spinach (1000 lb.) by H_2O at 30—35° and then the b.p. is adjusted to pH 3·0—3·2, treated with " Super-cel," filtered, and stirred with C. The C is eluted with boiling 2·55% aq. NH_3, which is then stirred with C pretreated with aq. NH_2Ph and then H_2O. Elution by boiling 8% aq. NH_2Ph, extraction with Et_2O, and adjustment of pH to 3·0—3·2 are then followed by a similar adsorption and elution. Finally follow successive pptn. by $Pb(OAc)_2$, elution of the ppt. by boiling aq. $(NH_4)_2SO_4$, pptn. by aq. $AgNO_3$ at pH 6·5, elution by boiling aq. NH_4Cl, pptn. by Lloyd's reagent, elution by 5% aq. NH_3, adsorption on Al_2O_3, fractional elution by NH_3–MeOH–H_2O, pptn. by HCl at 0°, redissolution in aq. NH_3, adsorption on Al_2O_3, and elution and pptn. as above. Thus are obtained 1·2 mg. of amorphous folic acid (I) having a potency 137,000 times as great as Wilson liver fraction *B* when tested as growth stimulant for *Streptococcus lactis R*. Other procedures are less effective.

II. Impure (I) is readily eluted from C on which it has been adsorbed, but pure (I) is tenaciously retained. Retention of pure (I) is rendered less severe by pretreatment of the C by adsorbable substances. Adsorption isotherms confirm the dual nature of the adsorption; equilibrium is reached only slowly. Similar isotherms for riboflavin and thiochrome on C indicate similar phenomena.

III. (I) is readily inactivated by oxidation, reduction, acid, alkali, dry heat, light, acylation, esterification, methylation, benzylation, HNO_2, NaOBr, Br, etc., but the mol. wt. and absorption spectra (and thus chemical structure) are often little affected by these changes. The mol. wt., determined by diffusion, and analyses indicate $C_{15}H_{15}O_8N_5$ as approx. formula. (I) is required for the growth of 4 yeasts, but the relative amounts of different concentrates required for yeasts and bacteria may vary. Thymine (1 μg. per ml.) may replace (I) for *S. lactis R*, as also may 10 μg. per ml. of 9 other pyrimidine derivatives, but numerous other compounds are ineffective. (I), having potency 75,000, has one fifth of the anti-anæmia activity of xanthopterin (II).

IV. Absorption spectra and the effect of pH thereon are very similar for (I) and (II), indicating a similar structure. Results are recorded also for other pyrimidine derivatives. Purification affects the spectra, but inactivation has much less effect. For (I), (II), etc. sudden changes in adsorption at pH ~2·5 and ~9 are due to electronic shifts and tautomerism, respectively. R. S. C.

INDEX OF AUTHORS' NAMES, A II

AUGUST, 1944.

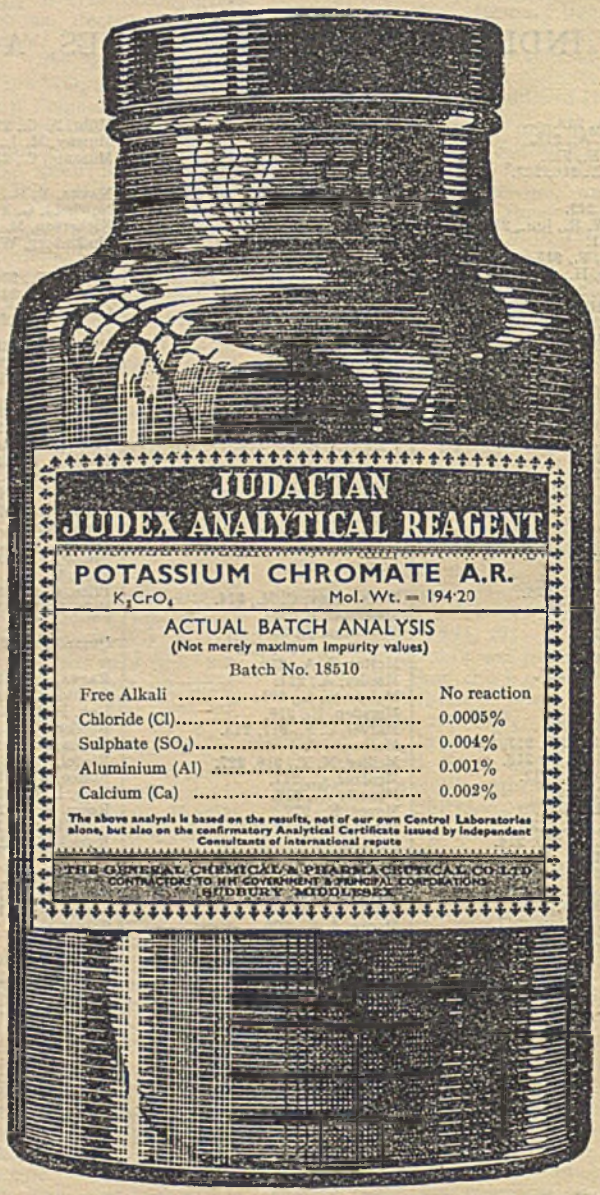
JUDACTAN

ANALYTICAL REAGENTS WITH ACTUAL BATCH ANALYSIS

ACTUAL

BATCH

ANALYSIS



Each Batch subjected to INDEPENDENT ANALYSIS before label is printed

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

THE GENERAL CHEMICAL & PHARMACEUTICAL CO. LTD.

Chemical Manufacturers, Judex Works, Sudbury, Middlesex

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