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BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

NOVEMBER, 1943.

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I.—ALIPHATIC.

Modern methods of preparative organic chemistry. II. Reduction according to Meerwein and Ponndorf and oxidation according to Oppenauer. III. Oxidations with lead tetra-acetate and periodic acid. R. Criegee (*Angew. Chem.*, 1940, **53**, 266—271, 291, 321—326).—Reviews.

Raman spectra of *meso*- and *dl*-disubstituted butanes.—See A., 1943, I, 249.

Addition of hydrogen fluoride to halogeno-olefines. A. L. Henne and E. P. Plueddeman (*J. Amer. Chem. Soc.*, 1943, **65**, 1271—1272).—CHMe:CHCl and HF at 100° give CHMeF·CH_2Cl (20%), b.p. 68·5°, CHMeCl·CH_2Cl (20%), CHEtClF (10%), b.p. 46—49°, $CHEtF_2$ (a trace), and tar. CHEt:CHCl and HF at 65° give CHPr$^{\alpha}$ClF (10%) (identified by its b.p. 73—76°), $C_4H_8Cl_2$ (5%), and tar (60%; more at higher temp.). CHEtClF is distinguished from CHMeF·CH_2Cl by not reacting with Zn and by being obtained also from $CHEtCl_2$ by HgF_2. CMe_2:CHCl and HF at 0° or −23° (much tar formed at higher temp.) readily give *α-chloro-α-fluoro*isobutane (65%), f.p. −69·3°, b.p. 82·5°, also obtained from CH_2:CMe·CH_2Cl owing to the isomerising effect of HF and identified by non-reaction with Zn and synthesis from CHPr$^{\beta}Cl_2$ by HgF_2. Results with CH_2:CEtCl, CH_2:CMeCl, CHMe:CMeCl, and CHMe:CEtCl confirm those of Renoll (A., 1942, II, 294); those with CPhCl:CH_2 are inconclusive, CH_2:CCl_2 and HF at 65° give $CMeCl_2F$ (50%), f.p. −103·5°, b.p. 32·0°, $CMeCl_3$ (5%), and tar (10%). CHEt:CCl_2 and HF at 65° give $CPr^{\alpha}Cl_2F$ (28%) and $CPr^{\alpha}ClF_2$ (15%; more at higher temp.). CMe_2:CCl_2, b.p. 109°, and HF at 100° give mainly $CPr^{\beta}Cl_2F$ (35%), b.p. 105—109°. $(CHCl:)_2$ does not react with HF. *cis*- or *trans*-CMeCl:CHCl and HF at 120° give 7 and 10%, respectively, of $CMeF_2$·CH_2Cl, f.p. −91·7°, b.p. 88·6°, with 5 and 8%, respectively, of CMeClF·CH_2Cl. Similarly, CMeF:CHCl (*trans*- more readily) and HF give $CMeF_2$·CH_2Cl. CHCl:CCl_2, CMeCl:CCl_2, and $(CCl_2:)_2$ do not react with HF. CCl_2:CCl·CCl_3 undergoes substitution in the CCl_3 at high temp. *β-Chloro-β-fluoro*-n-*butane*, f.p. −110°, b.p. 67·7°, gives $CMeEtF_2$. R. S. C.

Acid strengths of aliphatic nitro-compounds.—See A., 1943, I, 278.

Volatile plant substances. XXIII. Presence of *n*-octan-γ-ol and its acetate in oil of pennyroyal (*Mentha pulegium*, L.). Y. R. Naves (*Helv. Chim. Acta*, 1943, **26**, 1034—1036).—The isolation is described of *n*-octan-γ-ol (**I**), b.p. 176—176·5°/732 mm., 52—53°/2·2 mm., $[\alpha]_D^{20}$ +7·93°, further characterised by its conversion into *n*-octan-γ-one (semicarbazone, m.p. 117—117·5°), which is oxidised to *n*-C_5H_{11}·CO_2H. After removal of (**I**) by H_3BO_3 the fraction gives an octyl acetate, b.p. 176—176·5°/ 728 mm., 74°/10 mm., α_D −4·39°. H. W.

Production of acetylmethylcarbinol by the action of *Acetobacter suboxydans* on βγ-butylene glycol.—See A., 1943, III, 848.

βγδε-Dibenzylidene-*D*-mannitol and its derivatives. W. T. Haskins, R. M. Hann, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1943, **65**, 1419—1422).—*D*-Mannitol αζ-dibenzoate, PhCHO, and powdered, fused $ZnCl_2$ at room temp. give *βγδε-dibenzylidene-* (**I**), dimorphic, m.p. 169—170°, resolidifies, remelts 179—180°, $[\alpha]_D^{20}$ +45·2° in $CHCl_3$ (distribution of the CHPh: uncertain), and *γo*-benzylidene-*D*-mannitol αζ-dibenzoate (**II**), m.p. 119—120°, $[\alpha]_D^{20}$ +31·8° in $CHCl_3$ (cf. Brigl *et al.*, A., 1932, 598); according to the conditions, yields of (**I**) are 24—59% and of (**II**) are 20—56%. PhCHO–$ZnCl_2$ at 25° converts (**II**) into (**I**). NaOMe–MeOH–$CHCl_3$ hydrolyses (**II**) at 5° to γδ-benzylidene-*D*-mannitol, m.p. 136—137°, $[\alpha]_D^{20}$ +29·0° in H_2O, the αβεζ-tetrabenzoate, m.p. 126—127°, $[\alpha]_D^{20}$ −27·9° in $CHCl_3$, of which is obtained from (**II**) by BzCl–C_5H_5N at 25°. With H_2SO_4–Ac_2O–AcOH at 25°, (**I**) gives *D*-mannitol βγδε-tetra-acetate αζ-dibenzoate, m.p. 126—127°, $[\alpha]_D^{20}$ +38·9° in $CHCl_3$, and with NaOMe–MeOH–$CHCl_3$ at 5° gives *βγδε-dibenzylidene-D-mannitol*, decomp. 203—205°, $[\alpha]_D^{20}$ +76·7° in C_5H_5N (*αζ-diacetate*, m.p. 185—186°, $[\alpha]_D^{20}$ +100·0° in $CHCl_3$). The *αζ-di-*p-*toluenesulphonate*, m.p. 185—186°, $[\alpha]_D^{20}$ +87·5° in $CHCl_3$, thereof with H_2SO_4–AcOH–Ac_2O gives D-*mannitol βγδε-tetra-acetate αζ-di-*p-*toluenesulphonate* (85%), m.p. 119—120°, $[\alpha]_D^{20}$ +22·9° in $CHCl_3$, and with NaI–$COMe_2$ at 100° gives *βγδε-dibenzylidene-D-mannitol αζ-di-iodide* (98%), m.p. 184—185°, $[\alpha]_D^{20}$ +58·0° in $CHCl_3$, reduced by H_2–Raney Ni in $Ba(OMe)_2$–MeOH to *βγδε-dibenzylidene-αζ-dideoxy-D-mannitol* (96%), m.p. 159—160°, $[\alpha]_D^{20}$ +49·5° in $CHCl_3$, which is hydrolysed by boiling 80% AcOH to the known αζ-dideoxy-*D*-mannitol (65%), m.p. 147—148°, $[\alpha]_D^{20}$ −21·4° in H_2O. M.p. are corr. R. S. C.

Thermal decomposition of vinyl ethyl ether.—See A., 1943, I, 280.

Vitamin-*E*. XLI.—See A., 1943, II, 333.

New Δ^{θ}-undecenoic acid. C. Collaud (*Helv. Chim. Acta*, 1943, **26**, 1064—1069).—Hydrogenation of Δ^{θ}-undecenoic acid in presence of Pt or Pd gives complex mixtures. In presence of Raney Ni, Na Δ^{θ}-undecinenoate in feebly alkaline solution is reduced to *α-Δ^{θ}-undecenoic acid* (**I**), b.p. 156°/4 mm., m.p. 3—3·5°, which is shown to be homogeneous and hence appears to be a geometrical isomeride of the β-acid of Krafft *et al.* (A., 1901, i, 115). The constitution of (**I**) is established by ozonolysis to azelaic acid. Isomerisation of the α- to the β-acid could not be achieved. (**I**) is converted by successive treatments with $SOCl_2$ and NH_3 into *α-Δ^{θ}-undecenoamide*, m.p. 84·5—85°. p-*Phenylphenacyl α-Δ^{θ}-undecenoate* has m.p. 65—66°. H. W.

Ambrettolide and its isomerides. III. Synthesis of ζo-dehydroxyhexadecoic acid. C. Collaud (*Helv. Chim. Acta*, 1943, **26**, 1155—1162).—Δ^{θ}-Undecenoic acid is converted by distillation with Bu$^{\alpha}$OH and C_6H_6 containing H_2SO_4 into its *Bu$^{\alpha}$* ester, b.p. 138°/2 mm., reduced by Na and boiling Bu$^{\alpha}$OH to *α-Δ^{ι}-undecenol*, b.p. 113°/10 mm. (*phenylurethane*, m.p. 51—52°). This is transformed by $SOCl_2$ in CCl_4 containing $NPhMe_2$ into *α-chloro-Δ^{ι}-undecene*, b.p. 80—82°/2 mm., converted by the successive actions of Mg and *cyclo*heptanone in Et_2O into 1-*Δ^{ι}-undecenyl*cyclo*heptan*-1-*ol* (**I**), b.p. 136°/0·06 mm., which is dehydrated by distillation under 3 mm. pressure over $KHSO_4$ to *Δ^{ι}-undecenyl-Δ^{1}*-cyclo*heptene* (**II**), b.p. 113°/0·1 mm. Ozonisation of (**II**) and treatment of the product with aq. H_2O_2 gives *ζ-ketotetradecane-αξ-dicarboxylic acid*, m.p. 113—113·5°. (**I**) is ozonised in AcOH and the product is transformed by Zn powder into a OH-aldehyde which is hydrogenated (Raney Ni) to the non-cryst. 1-*ι-hydroxynonyl*cyclo*heptan*-1-*ol* (**III**), and an isomeric *diol*, m.p. 98—99°, which is not dehydrated by distillation under reduced pressure over $KHSO_4$. Under similar conditions (**III**) is converted into 1-*ι-hydroxynonyl-Δ^{1}*-cyclo*heptene*, b.p. 135—136°/0·2 mm. (*phenylurethane*, m.p. 71—72°). This is ozonised and then treated successively with Zn powder and Ag_2O, thus giving *ζ-keto-o-hydroxyhexadecoic acid*, m.p. 90—91°, reduced (H_2–Raney Ni) to *ζo-dihydroxyhexadecoic acid*, m.p. 97—98°. H. W.

Macro-molecular compounds. CCXLI. Polyesters. H. Staudinger and H. Schmidt [with S. Kautz] (*J. pr. Chem.*, 1940, [ii], **155**, 129—162).—Polyesters obtained by condensing OH·$[CH_2]_2$·OH with succinic or adipic acid or OH·$[CH_2]_6$·OH (**I**) with CO_2H·$[CH_2]_{14}$·CO_2H at high temp. are too insol. for investigation. $CHMe(CH_2·OH)_2$ and sebacic acid (**II**) give viscous polyesters. Polyesters from (**I**) and (**II**) at 200° or 220° contain terminal CO_2H and CH_2·OH, determined by titration and acetylation, respectively. CH_2N_2 then gives Me esters, which can be acetylated by Ac_2O–C_5H_5N, both reactions occurring without change of the degree of polymerisation. Acetylation of the original polyesters leads to further condensation, but esterification of these products by CH_2N_2 causes no further increase in the degree of polymerisation. Me_2 sebacate (**III**) and (**I**) with a trace of NaOMe at ~200° give polyesters, which are acetylated without further condensation. For all these products the same degree of polymerisation is indicated by means of η in C_6H_6 or CCl_4, cryoscopy in 2-$C_{10}H_7$Me, or analyses; these polyesters are straight-chain polymerides containing 95—350 units. Heating (**I**) and (**II**) at 250°/high vac. for 10 days gives a little C_8H_{16} (? C_8H_{18}) and highly polymerised esters, the mol. wt. ranging from 8760 (determined cryoscopically) to 20,700 (determined by osmosis in $CHCl_3$); methylation and then acetylation each causes condensation; in all cases η gives lower vals. for the mol. wt. and determination of CO_2H and CH_2·OH gives still lower vals.; these esters thus have branched chains containing ···CH_2·CH(CO·$[CH_2]_8$·CO_2H)·CO_2·CH···. Adding NaOEt to (**I**) and (**III**) at ~150° gives three-dimensional solid products, insol. in org. solvents and swelling in $CHCl_3$ or C_6H_6; extracting these products with C_6H_6 gives ~4% of mixed products having mol. wt. (osmosis) up to 16,100, which are branched (since

η and analysis give lower "mol. wts.") and have very low OMe contents, so that they probably contain mainly ···CH_2·CH:CH(O·$[CH_2]_6$·OH)$_2$. COCl·$[CH_2]_6$·COCl and (I) at 180° or 200° give branched-chain products, which contain CO_2H and also give low "mol. wts." by η or analysis. $(CH_2·OH)_2$ and (I) give polyesters which are methylated and then acetylated without condensation; mol. wts. determined by cryoscopy exceed (by 18—27%) those determined by η, probably owing to crumpling of the chain (Fuller, A., 1937, I, 172; 1939, I, 601). The extent of ring-crumpling in the other esters is unknown and obscures the results. During determination of OAc in the products by KOH–MeOH air must be rigidly excluded to avoid formation of HCO_2H. R. S. C.

Change of *d*- into *meso*-tartaric acid by pancreas.—See A., 1943, III, 769.

Aldol condensation. I. Detection of carbonyl groups in aldols by means of Raman spectra. R. H. Saunders, M. J. Murray, F. F. Cleveland, and V. I. Komarewsky (*J. Amer. Chem. Soc.*, 1943, **65**, 1309—1311).—Raman spectra are recorded for acet- (I), propion- (II), and butyr-aldol (III) (cf. Hibben, A., 1932, 983; Backés, A., 1938, II, 392). Only (III) shows a CHO line which disappears in a few days. There is no evidence of C:C. The change of (I) and (II) from mobile to viscous liquids is thus not due to gradual disappearance of CO functions. R. S. C.

Essential steps in the catalytic condensation of aldehydes; synthesis of glycol esters. M. S. Kulpinski and F. F. Nord (*J. Org. Chem.*, 1943, **8**, 256—270).—The catalytic condensation of the dissimilar aldehydes, $Pr^{\alpha}CHO$ and CHMe:CH·CHO, to yield an unsaturated glycol ester represents a second form of the "crossed" Cannizzaro reaction, the *cis*- and *trans*-conjugated aldehydes thus obtained representing an interesting example of such isomerides. Co-ordination catalysts permit a trimeric autocondensation of saturated aldehydes; this is generally applicable to α-CH_2 aldehydes and provides a convenient method for the synthesis of glycol esters of this series. Simple alkoxides lead only to dimeric products whereas complex catalysts can bring about trimerisation. Failure to obtain glycol esters as the main products in the case of α-alkylaldehydes with the co-ordination catalysts is due to the limiting factors imposed on the primary stage of the condensation, *i.e.*, aldolisation. The similarity of behaviour in this instance between the simple and the complex alkoxides originates in the bifunctional nature of the latter. The complex alkoxides do not differ qualitatively in their action. $Mg[Al(OEt)_4]_2$ appears to be a better condensing agent than $Mg[Al(OPr^{\beta})_4]_2$ or $Mg[Al(OBu^{\alpha})_4]_2$ but it is more difficult to prepare. $Mg[Al(OEt)_4]_2$ converts a mixture of $Pr^{\alpha}CHO$ and CHMe:CH·CHO into *β-ethyl-Δ$^{\delta}$-hexene-αγ-diol monobutyrate*, b.p. 104·5—105·5°/2 mm. (*acetate*, b.p. 89—90°/1 mm.), hydrogenated to *β-ethylhexane-αγ-diol monobutyrate* (I), b.p. 100—102°/0·5 mm., which is hydrolysed to *β-ethylhexane-αγ-diol* (II), b.p. 88—90°/1 mm., and cis-, b.p. 42—43°/2 mm., and trans-*α-ethyl-Δ$^{\alpha\gamma}$-hexadienal*, b.p. 44—45°/2 mm. (*semicarbazones*, m.p. 185—186° and 201—202°; 2 : 4-*dinitrophenylhydrazones*, m.p. 136—137° and 187·5—188·5°). (I) is also obtained from $Pr^{\alpha}CHO$ alone under the influence of $Mg[Al(OEt)_4]_2$, $Mg[Al(OPr^{\beta})_4]_2$, or $Mg[Al(OBu^{\alpha})_4]_2$ whereas $Pr^{\alpha}CO_2Bu$ is obtained under the influence of $Al(OEt)_3$ or $Al(OPr^{\beta})_3$. (II) gives a *diacetate*, b.p. 87—88°/1 mm. MeCHO and $Mg[Al(OAlk)_4]_2$ afford EtOAc, CHMe:CH·CHO, paracetaldehyde, metaldehyde, and *butane-αγ-diol monoacetate*, b.p. 87—89°/13 mm. (corresponding *diacetate*, b.p. 92—94°/13 mm.). Similarly EtCHO affords α-methyl-Δ$^{\alpha}$-pentenal (2 : 4-dinitrophenylhydrazone, m.p. 159·5°) and *β-methylpentane-αγ-diol monopropionate*, b.p. 92—94°/2 mm. (*acetate*, b.p. 71—72°/0·5 mm.), hydrolysed to the *diol*, b.p. 85—86°/1 mm. $Bu^{\beta}CHO$ yields *ζ-methyl-β-isopropylhexane-αγ-diol monoisovalerate*, b.p. 137—139°/1 mm. (*acetate*, b.p. 126—128°/1 mm.), whence the (impure) diol, b.p. 105—106°/1 mm. In like manner $Bu^{\alpha}CHO$ affords *β-propylheptane-αγ-diol monovalerate*, b.p. 138—139°/1 mm. (*acetate*, b.p. 135—137°/1 mm.), and the *diol*, b.p. 107—108°/1 mm., *n*-C_5H_{11}·CHO gives *β-butyloctane-αγ-diol monohexoate*, b.p. 750—752°/1 mm. (*monoacetate*, b.p. 132—134°/0·5 mm.), and the *diol*, b.p. 128—129°/1 mm., and *n*-C_6H_{13}·CHO gives *β-amylnonane-αγ-diol monoheptoate*, b.p. 167—170°/0·5 mm. (*acetate*, b.p. 160—164°/1 mm.), and the *diol*, b.p. 125—127°/0·5 mm. With $Pr^{\beta}CHO$ the complex alkoxides afford mainly $Pr^{\beta}CO_2Bu^{\beta}$ with small amounts of *ββδ-trimethylpentane-αγ-diol monoisobutyrate*, b.p. 85—86°/0·5 mm. (*acetate*, b.p. 91—93°/2 mm.), hydrolysed to the (impure) diol, b.p. 81—82°/1 mm. $CHEt_2$·CHO gives preponderatingly *β-ethylbutyl α-ethylbutyrate*, b.p. 100—102°/14 mm., identified by hydrolysis to $CHEt_2·CH_2·OH$ (3 : 5-dinitrobenzoate, m.p. 50°) and $CHEt_2·CO_2H$ (amide, m.p. 125°) with small amounts of *ββδ-triethylhexane-αγ-diol monoethylbutyrate*, b.p. 127—130°/1 mm., whence the *diol*. In all cases $CHEtBu^{\alpha}$·CHO gives exclusively *β-ethylhexyl α-ethylhexoate*, b.p. 112—116°/1 mm., hydrolysed to β-ethylhexanol (1-naphthylurethane, m.p. 59—60°) and β-ethylhexoic acid (amide, m.p. 102°). H. W.

Direct reduction of certain carboxylic acids to aldehydes, and preparation of undecaldehyde by a modified Blaise reaction. R. R. Davies and H. H. Hodgson (*J.S.C.I.*, 1943, **62**, 128).—The direct reduction of salicylic, *n*-butyric, nonoic, and lauric acid by Na–Hg produced only poor yields of the corresponding aldehydes, which were hardly improved by the use of dispersing agents. The Blaise reaction has been modified to produce a 62·3% yield of $C_{10}H_{21}$·CHO from lauric acid.

Tertiary alkyl primary amines, CRR′R″·NH$_2$. III. H. R. Henze and T. R. Thompson (*J. Amer. Chem. Soc.*, 1943, **65**, 1422—1425; cf. A., 1943, II, 153).—CH_2:CH·CH_2·MgBr (I) and OEt·CHMe·CN (II) (prep. from CHMeCl·OEt by CuCN–C_6H_6; 51% yield), b.p. 129—130°/751 mm., give *δ-amino-δ-α′-ethoxyethyl-Δ$^{\alpha\zeta}$-n-heptadiene* (35%), b.p. 198—198·5°/751 mm., 70°/5 mm. (*picrate*, m.p. 103°, prepared in SO_2–H_2O), hydrogenated (PtO_2; $COMe_2$) to *δ-amino-δ-α′-ethoxyethyl-n-heptane* (94·5%), b.p. 56°/2 mm. (*picrate*, m.p. 110·5°). OH·$[CH_2]_2$·CN (prep. from OH·$[CH_2]_2$·Cl by NaCN) with $SOCl_2$–$CHCl_3$ gives Cl·$[CH_2]_2$·CN (60%), b.p. 175°/747 mm., converted by NaOEt–EtOH at 0° and then the b.p. into OEt·$[CH_2]_2$·CN (III) (57·5%), b.p. 78°/25 mm., which with (I) yields *δ-amino-δ-β′-ethoxyethyl-Δ$^{\alpha\zeta}$-n-heptadiene* (33%), b.p. 95°/5 mm. (*picrate*, m.p. 91°), and thence *-n-heptane*, b.p. 100°/10 mm. (*picrate*, m.p. 99·5°). Adding (I) to the product from (II) and $MgPr^{\alpha}Br$ gives *δ-amino-δ-α′-ethoxyethyl-Δ$^{\alpha}$-n-heptene* (40%), b.p. 78°/3 mm. (*picrate*, m.p. 103°), and a small amount of OEt·CHMe·$COPr^{\alpha}$ (IV) (*semicarbazone*, m.p. 124·5°); this reaction fails with (III). Adding (II) to $MgPr^{\alpha}Br$ in Et_2O, replacing the Et_2O by $Bu^{\alpha}{}_2O$, and heating gives 28% of (IV), b.p. 163—164°/759 mm., and a smaller amount of *δ-α′-ethoxyethyl-n-heptan-δ-ol*, b.p. 203—205°/759 mm.; in boiling Et_2O, 50% of (IV) is obtained; (III) does not undergo this reaction. Adding (I) to the product from MgMeI and $OPr^{\alpha}·CH_2·CN$ in Et_2O gives *β-amino-α-n-propoxy-β-methyl-Δ$^{\delta}$-n-pentene* (51%), b.p. 100°/100 mm. (*picrate*, m.p. 110°), and some $OPr^{\alpha}·CH_2·COMe$ (*semicarbazone*, m.p. 75°); H_2–PtO_2 in EtOH then yields *β-amino-α-n-propoxy-β-methyl-n-pentane*, b.p. 105—106°/100 mm. (*picrate*, m.p. 95°). Adding *iso*-C_5H_{11}·O·CH_2·CN to MgMeI–Et_2O and then to (I)–Et_2O gives *β-amino-α-isoamyloxy-β-methyl-Δ$^{\delta}$-n-pentene* (65%), b.p. 89—90°/8 mm. (*picrate*, m.p. 104°), *iso*-C_5H_{11}·O·CH_2·COMe (*semicarbazone*, m.p. 60°), and *iso*-C_5H_{11}·OH (3 : 5-*dinitrobenzoate*, m.p. 61°). *β-Amino-α-isoamyloxy-β-methyl-n-pentane*, b.p. 97°/8 mm. (*picrate*, m.p. 86°), is also prepared. M.p. are corr. The amines prepared slightly lower the blood pressure of pithed cats. R. S. C.

Hydroxyalkylamino-acids. W. Cocker (*J.C.S.*, 1943, 373—378).—Allyl bromide, 3N-NaOH, and the appropriate arylsulphonylglycine at 100° afford N-*benzenesulphonyl-* (I), m.p. 107°, and N-p-*toluenesulphonyl-* (II), m.p. 109—110°, -N-*allylglycine* which rapidly decolorise Br–H_2O and alkaline $KMnO_4$. Ozonisation of (II) leads to *N-p*-toluenesulphonyl-*N*-aldehydomethylglycine, identified as the 2 : 4-dinitrophenylhydrazone, m.p. 173—174°. (I) is hydrolysed by 60% H_2SO_4 at 125° to dl-N-*β-hydroxypropylglycine* (III), m.p. 194—195° (decomp.), converted by $PhSO_2Cl$ in alkaline solution followed by acidification into N-*benzenesulphonyl-6-methyl-2-morpholone* (IV), m.p. 128—128·5°. N-p-*Toluenesulphonyl-N-β-hydroxypropylglycene* (V), m.p. 138—139°, passes at 120°/vac. or when treated with Ac_2O, $SOCl_2$, or boiling C_6H_6 into N-p-*toluenesulphonyl-6-methyl-2-morpholone*, m.p. 92—93°. (I) and (II) are converted by conc. H_2SO_4 into (IV) and (V) respectively. OH·CHMe·CH_2·NH_2 [*phenylcarbamyl* derivative, (?) OH·CHMe·CH_2·NH·CO·NHPh, m.p. 108—109°, and its *phenylurethane*, m.p. 180—181°] and $CH_2Br·CO_2Et$ yield (III). Oxidation of (III) by I and Na_2CO_3 gives CHI_3 as sole cryst. compound. $SO_2Ph·NH·CH_2·CO_2H$, methylallyl chloride, and 3N-NaOH at 100° afford N-*benzenesulphonyl-N-β-methylallylglycine* (VI), m.p. 91—92°. N-p-*Toluenesulphonyl-N-β-methylallylglycine* (VII), m.p. 109—110° (also + C_6H_6), is transformed by HCl–EtOH into *Et* N-p-*toluenesulphonyl-N-β-chloroisobutylaminoacetate*, m.p. 67·5—68°. (VI) and conc. H_2SO_4 afford N-*benzenesulphonyl-6 : 6-dimethyl-2-morpholone* (VIII), m.p. 134—135°, and $Pr^{\beta}CHO$; (VII) similarly gives N-p-*toluenesulphonyl-6 : 6-dimethyl-2-morpholone*, m.p. 133—134°. Ozonolysis of (VI) leads to N-*benzenesulphonyl-N-acetonylglycine*, m.p. 123° (2 : 4-*dinitrophenylhydrazone*). $Pr^{\beta}CHO$ is formed by hydrolysis of (VIII) by boiling 60% H_2SO_4. N-*Mesitylenesulphonyl-N-β-methylallylglycine*, m.p. 117—118°, best obtained from *Et mesitylenesulphonamidoacetate*, m.p. 43—44°, is hydrolysed by boiling AcOH–conc. HCl to N-*β-hydroxyisobutylglycine*, m.p. 176° (decomp.), also prepared from OH·CMe_2·CH_2·NH_2 and $CH_2Br·CO_2Et$. $SO_2Ph·NH·CHMe·CO_2H$ and CH_2:CH·CH_2Br give a mixture from which N-*benzenesulphonyl-3 : 6-dimethyl-2-morpholone*; N-*benzenesulphonyl-N-allylalanine*, m.p. 95°, is obtained by hydrolysis of the product from CH_2:CH·CH_2Cl and *Et benzenesulphonyl-α-aminopropionate*, m.p. 61—62°, in NaOEt–EtOH. *β-Hydroxypropylalanine*, m.p. 214°, is derived from CHMeBr·CO_2Et and OH·CHMe·CH_2·NH_2 in EtOH. *Et* p-*toluenesulphonyl-α-aminopropionate*, m.p. 66—67°, and *mesitylenesulphonylalanine*, m.p. 155—156°, are incidentally described. Br in $CHCl_3$ converts the requisite unsaturated compound into N-*benzenesulphonyl-N-βγ-dibromopropylglycine* (IX), m.p. 117—118° (*Me*, m.p. 101—102°, and *Et*, m.p. 72°, ester), and N-p-*toluenesulphonyl-N-βγ-dibromopropylglycine* (X), m.p. 127—128°. (IX) is reduced (H_2–Raney Ni in MeOH) to $SO_2Ph·NHPr·CH_2·CO_2H$ whereas Zn dust and glacial AcOH at 100° reduce (X) to (II). (X) is hydrolysed to CH_2:CH·CHO, *p*-$C_6H_4Me·SO_2·NH·CH_2·CO_2H$, and a compound, m.p. 193°. Glycine, *m*-$NO_2·C_6H_4·COCl$, and N-NaOH afford N-m-*nitrobenzenesulphonylglycine*, m.p. 149—150°;

the *Et* ester, m.p. 122°, is transformed by $CH_2{:}CH{\cdot}CH_2Cl$ and NaOEt in EtOH into *Et* N-m-*nitrobenzenesulphonyl*-N-*allylaminoacetate*, m.p. 57·5—58° (*dibromide*, m.p. 91—91·5°). H. W.

Growth effects of α-methyl homologues of pantothenic acid and β-alanine. M. A. Pollack (*J. Amer. Chem. Soc.*, 1943, **65**, 1335—1339).—$CN{\cdot}CHMe{\cdot}CO_2Et$ (prep. from $CHMeCl{\cdot}CO_2Na$ by aq. NaCN at 85—100°, followed by evaporation and esterification), b.p. 77°/9·5 mm., is hydrogenated (PtO_2–H_2SO_4–AcOH; 530 lb.) and the product is repeatedly evaporated with addition of water. The Na salt of the resulting *α-methyl-β-alanine* (73%), m.p. 181—182°, with *l*-α-hydroxy-ββ-dimethyl-γ-butyrolactone at 108° or in boiling EtOH–Pr$^{\beta}$OH gives *Na α-methylpantothenate*. For biological results see A., 1943, III, 847. R. S. C.

***dl*-Ethylalanine.**—See A., 1943, III, 768.

Effect of *N*-methylation on structure and properties of linear polyamides.—See A., 1943, I, 251.

Higher alkyl thiocyanates. T. Wagner-Jauregg, H. Arnold, and H. Hippchen (*J. pr. Chem.*, 1940, [ii], **155**, 216—224).—The following *thiocyanates* are prepared from the respective alkyl bromide and $NaCNS,2H_2O$ in aq. $COMe_2$ (reflux and then autoclave at 80°) or EtOH (reflux) (cf. Allen, A., 1935, 479): *oleyl*, b.p. 205—210°/0·1 mm., *elaidyl*, b.p. 198—199°/0·1 mm., *linoleyl*, b.p. 202°/0·15 mm., *hydnocarpyl*, b.p. 190—210°/0·5 mm., and its H_2-derivative, b.p. 205—215°/0·3 mm., *cholesteryl*. m.p. 129—130°, *cinnamyl* (**I**), b.p. 140—150°/0·3 mm., cetyl, b.p. 190—195°/0·2 mm., and undecyl, b.p. 140—150°/0·1 mm., thiocyanate. Cinnamyl bromide and (**I**) or $NaCNS,2H_2O$ in boiling 99% EtOH yield *cinnamyl cinnamylaminothioformate*, $SR{\cdot}CO{\cdot}NHR$ ($R = CH_2{\cdot}CH{:}CHPh$), m.p. 111—112°. A. T. P.

II.—SUGARS AND GLUCOSIDES.

Complex mutarotation of *d*-galactose. R. E. Rundle and B. C. Hendricks (*J. Physical Chem.*, 1943, **47**, 364—369).—Published data for the mutarotation of α- and β-*d*-galactoses at 20° and 0° have been used to calculate the course of "thermal mutarotation" which occurs when an equilibrium solution is rapidly cooled. The course of the mutarotation of a pseudo-equilibrium mixture of α- and β-*d*-galactoses at 0° has been similarly calc. The calc. results agree well with published data. The mechanism of mutarotation is discussed. The mechanism of Smith and Lowry (A., 1928, 510) is regarded as of more general application than that of Isbell and Pigman (A., 1937, II, 177, 275; 1938, II, 349). C. R. H.

Behaviour of lactose in alkaline solution. IV. B. Bleyer and A. Schloemer (*Biochem. Z.*, 1940, **306**, 155—160; cf. A., 1923, i, 1180). —[α] of 5 and 10% aq. α-lactose at first increases, then decreases, as a result of addition of aq. NaOH (0·20—20·0%). Subsequent neutralisation increases [α] to an extent ∝ to the conc. of NaOH used to produce the decrease. The changes are explained by supposing concurrent, complete degradation by NaOH and production of substances (*e.g.*, α-galactose, *d*-sorbose) having [α] > that of α-lactose. Neutralisation increases [α] by altering the equilibrium between α- and β-forms of the intermediate products. W. McC.

Enzymes present in highly purified invertase preparations. Fructofuranosidases, galactosidases, glucosidases, and mannosidases.—See A., 1943, III, 844.

Orientation in stretched films of amylose triacetate.—See A., 1943, I, 251.

Sclerotiose, polysaccharide metabolite of *Penicillium sclerotiorum*, van Beyma. V. J. Albericci, T. P. Curtin, and D. Reilly (*Biochem. J.*, 1943, **37**, 243—246).—The metabolic products of *P. sclerotiorum* include a polyglucose, *sclerotiose*, m.p. 290—300°, becomes brown at 260°, $[\alpha]_D^{70}$ +244° in 6% NaOH, $[\alpha]_D^{90}$ +284° in $HCO{\cdot}NH_2$ [*nitrate*, $C_{24}H_{31}O_{11}(NO_3)_9$, m.p. 200° (decomp.); *undecanitrate*, m.p. 132° (decomp.); *diacetate*, $C_6H_8O_3(OAc)_2$; *triacetate*, $C_6H_7O_2(OAc)_3$, m.p. 165—168° (decomp.), $[\alpha]_D$ +205·7° in $CHCl_3$; (?) tribenzoate] (cf. A., 1943, III, 846). P. G. M.

Action of *macerans* amylase on the fractions from starch. E. J. Wilson, jun., T. J. Schoch, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1943, **65**, 1380—1383).—Starch is fractionated by BuOH–*iso*-$C_5H_{11}{\cdot}OH$ by use of an ordinary or super-centrifuge. The pptd. fractions from maize or potato starch with *B. macerans* amylase yield more Schardinger dextrins and less limit dextrins than do the original starches; for the non-pptd. fractions these proportions are reversed. Waxy maize starch resembles the non-pptd. fractions. Formation of insol. "γ-amylose" does not occur under proper conditions; its formation observed by Kerr (A., 1943, II, 156, 157) is due to the conditions used. Alkali-lability increases during the enzymolysis. Schardinger α- and β-dextrins are stable to alkali, but limit dextrins are unstable. R. S. C.

Macro-molecular compounds. CCXXXVIII. Lower and macro-molecular chemistry. H. Staudinger (*J. pr. Chem.*, 1940, [ii], **155**, 1—12).—The scope and general properties of compounds of very high mol. wt. are reviewed. R. S. C.

***X*-Ray studies of reactions of cellulose in non-aqueous systems. II. Interaction of cellulose and primary amines.** W. E. Davis, A. J. Barry, F. C. Peterson, and A. J. King (*J. Amer. Chem. Soc.*, 1943, **65**, 1294—1299; cf. A., 1936, 458).—Ramie cellulose swells in NH_2R if R = Me, Et, or Pr, but only after pre-swelling in NH_3 if R = Bu—C_7H_{15}. *X*-Ray diffraction spectra are recorded for the products. The 101 lines retain their intensity but show a progressive increase in interplanar distance from 14·67 (R = Me) to 28·74 A. ($R = C_7H_{15}$) (cf. 10·6 A. if R = H; *loc. cit.*; also Hess *et al.*, A., 1937, II, 401, and Clark *et al.*, *ibid.*, 447). The other lines are little changed. The structure thus changes to a diamond of progressively increasing length but const. width. The increase in length corresponds to insertion of 2 NH_2R between cellulose units. For higher alkyl this insertion cannot occur for steric reasons; hence the necessity for pre-swelling in NH_3. Swelling occurs by creation of O–H···N bridges between the cellulose and NH_2R. No swelling occurs in $OH{\cdot}[CH_2]_2{\cdot}NH_2$ because this would change the surface of the cellulose; it does, however, occur in $(CH_2{\cdot}NH_2)_2$ as expected on this hypothesis. R. S. C.

Macro-molecular compounds. CCXLII. Native and precipitated celluloses and their nitrates. H. Staudinger and A. W. Sohn (*J. pr. Chem.*, 1940, [ii], **155**, 177—215; cf. A., 1942, II, 353).—Nitration of native fibre cellulose with HNO_3–H_3PO_4 gives nitrates of the same degree of polymerisation (D.P.) whether or not $KClO_3$ is added to the nitration mixture. The effect of dissolution, nitration, oxidation, etc. on D.P. of celluloses and cellulose esters is discussed. The D.P. of cellulose esters is found by dissolving in conc. H_3PO_4, pptg. with H_2O at 0°, dissolving the ppt. in Schweitzer's reagent, and determining η. In this treatment, H_3PO_4 hydrolyses ~50% of the ester groups and, when oxycellulose esters are examined, some of the glucosidic linkings are broken. With normal celluloses, pptn. from Schweitzer's reagent or treatment with H_3PO_4 has no effect on D.P. Ramie is converted into oxycellulose esters by Cr_2O_7'' or $H_2C_2O_4$, the properties of the product being similar to those of oxycellulose ester from cotton. Technical sulphite pulp, which has a high ester val., and ramie oxycellulose ester are converted into normal cellulose by pptn. from solution in Schweitzer's reagent. The average D.P. of oxycellulose esters in Schweitzer's reagent does not change after keeping for 4 months at 20° and 60% R.H., but the ester groups are partly hydrolysed. The nitrates of cellulose esters are more stable than are the oxycellulose esters. Data for the degradation of nitrates of normal cellulose and of oxycellulose ester at 105° are tabulated and discussed. Oxycellulose esters with a high ester val. readily yield sol. acetates on treatment with 90% H_3PO_4 (which reduces the ester val. and produces swelling) followed by treatment with Ac_2O–C_5H_5N at 60°; the product has a higher D.P. than had the initial material. Hydrolysis of these acetates gives oxycellulose esters of D.P. approx. the same as the original oxycellulose ester. When degraded cellulose (D.P. ~1000), which gives a nitrate of considerably higher D.P. (~1400), is treated in 89% H_3PO_4, the product gives a nitrate (or acetate) of approx. equal D.P. (~900). Data are given for the tensile strength of normal celluloses and oxycellulose esters; the quality of fibres of the latter is indicated by the D.P. of the nitrates in $COMe_2$. The tenacity of fibres of oxycellulose esters is approx. the same as that of fibres of normal celluloses of the same D.P., although the former are not stable to, *e.g.*, washing with H_2O. The above results are discussed in relation to previously published data. F. O. H.

Macro-molecular compounds. CCXXXIX. Constitution of wood polyoses. E. Husemann (*J. pr. Chem.*, 1940, [ii], **155**, 13—64).—Treating washed wheat straw with 0·25% aq. ClO_2 containing 2% of C_5H_5N for 18 days and then with 6% aq. NaOH in absence of air and light, filtering, treating the filtrate with MeOH and AcOH, washing the ppt. and purifying it by pptn. from 6% NaOH by MeOH gives xylan-I (**I**), $[\alpha]_D$ −87° in 6% NaOH, sol. in Schweitzer's reagent and NaOH at room temp. and in H_2O and $HCO{\cdot}NH_2$ at 90°; its acetate and nitrate are insol.; with Me_2SO_4–KOH–N_2 it gives a Me ether (**II**) (32% OMe) and thence (Ac_2O–C_5H_5N) a Me ether acetate (**III**). Osmotic measurements of (**I**) in $HCO{\cdot}NH_2$, of (**II**) in $CHCl_3$ or H_2O, and of (**III**) in $COMe_2$ indicate degrees of polymerisation 119, 113, and 123, respectively. Treating the straw directly with 8% NaOH and methylating the crude product gives a Me ether and Me ether acetate (30—31% OMe; 8% Ac); CH_2PhCl–30% NaOH and then acetylation give a CH_2Ph ether acetate (~8·5% Ac); these products have (osmosis) degrees of polymerisation 151—152, 146, and 145, respectively. Thus, ClO_2 causes considerable degradation. All these products obey Staudinger's law for η, showing linear configuration; K_m are 4·2—8·0 × 10^{-4}, indicating absence of much chain-branching. Extracting beech wood with 8% NaOH and purifying the product with 0·2% ClO_2 gives ~6—8% of a xylan, $[\alpha]_D$ −87°; treating the residue for a short time with ClO_2–H_2O–C_5H_5N and then with 8% NaOH gives a further 8% of xylan, $[\alpha]_D$ −83° in 6% NaOH; these products and their CH_2Ph ether acetates have degrees of polymerisation 144—157 and K_m (Staudinger's equation) 4·4—6·8 × 10^{-4}. Fractional pptn. of the xylans and a Me ether shows that ∢94% has homogeneous chain-length; for the CH_2Ph ether acetate 70—80% of homogeneity is indicated. The xylans thus are linear products from uniformly

~150 xylose units; the facts that xylans are more sol. than cellulose although the K_m are similar indicates a regular series of very short side-chains. Treating pine wood with 0·25% aq. $ClO_2 + C_5H_5N$ and then with 8% NaOH, purifying the product by ClO_2, and finally fractionally pptg. from 6% NaOH by MeOH gives two fractions having $[\alpha]_D$ −20° to −25° and then 5 fractions having $[\alpha]_D$ −42° to −44° in NaOH and similar η. These last fractions have (osmosis in 0·1N-$CaCl_2$) a degree of polymerisation 150; they give a CH_2Ph ether acetate for which the degree of polymerisation (osmosis in $CHCl_3$) is 147. K_m (Staudinger's equation) indicates a linear mol., although variation from 3·9 to 7·1 according to the solvent is unexplained. Extracting *Larix occidentalis* with H_2O–N_2 at room temp., pptg. by MeOH, and purifying the product by ClO_2 and repptn. gives an arabogalactan (**IV**) having a degree of polymerisation 222; Ac_2O–C_5H_5N at 60° gives a degraded acetate (**V**) (43·9% Ac; degree of polymerisation 75—81), but at 20° gives an acetate (**VI**) (33·44% Ac) having degree of polymerisation 198—218, reconverted by 0·5N-NaOMe–MeOH–N_2 into a product having a degree of polymerisation 197. Nitration gives a highly degraded nitrate. K_m of (**IV**) and (**V**) is 0·24–0·32, that of (**VI**) is 0·87—1·04 × 10^{-4}. (**IV**) etc. are thus highly branched compounds. Fractional pptn. from 0·1N-$CaCl_2$ by MeOH gives fractions having degrees of polymerisation falling from 267 to 182; the derived acetates vary similarly. (**IV**) is thus not a homogeneous material. The results as a whole show that wood polyoses are of such low degrees of polymerisation that they must be removed from cellulose prior to prep. of fibres or films. R. S. C.

III.—HOMOCYCLIC.

Hydrogen fluoride as a condensing agent. XVII. Addition of an alkyl chloride to the ethylenic linking. J. H. Simons and A. C. Meunier (*J. Amer. Chem. Soc.*, 1943, **65**, 1269–1271; cf. A., 1942, II, 344).—Adding *cyclo*hexene (**I**) (1 mol.) to $Bu^{\gamma}Cl$ (1—2 mols.) in HF (2—6 mols.) at 0—5° and keeping at room temp. gives *cyclo*hexyl chloride (**II**) (65%) and fluoride (11·5%), 3-tert.-*butyl*cyclo*hexyl chloride* (**III**) (11·1%), b.p. 98°/20 mm., aliphatic chlorides, and olefines. The structure of (**III**) is proved by conversion by boiling KOH–EtOH into an unsaturated *hydrocarbon*, $C_{10}H_{18}$ (36%), b.p. 60°/15 mm., which with aq. $KMnO_4$ at 0°—room temp. gives $CO_2H\cdot[CH_2]_3\cdot CHMe\cdot CO_2H$, m.p. 114° (dianilide, m.p. 206°), also obtained from 4-*tert.*-butyl*cyclo*hexanol (**IV**). Further, the Grignard reagent from (**III**) with O_2 and then NH_4Cl–ice gives 3-*tert.*-butyl*cyclo*hexanol, b.p. 119—129°/29 mm. (3 : 5-*dinitrobenzoate*, m.p. 144°). The 3 : 5-*dinitrobenzoate* of (**IV**) has m.p. 157·5°. $Bu^{\gamma}Cl$ and $CMe_2{:}CHMe$ in HF give an inseparable mixture. $Pr^{\beta}Cl$ and (**I**) give much (**II**) and a considerable residue, but no aliphatic fraction. R. S. C.

Derivatives of 1 : 2 : 4 : 5-tetrachlorobenzene. II. *N*-Nitroamino-compounds. A. T. Peters, F. M. Rowe, and D. M. Stead (*J.C.S.*, 1943, 372—373).—2 : 3 : 5 : 6 : 1-$C_6HCl_4\cdot NHAc$ (**I**) with Ac_2O–HNO_3 (*d* 1·5) (warmed gradually to 50°) gives 2 : 3 : 5 : 6-*tetrachloro*-N-*nitroacetanilide* (**II**), m.p. 131° (vigorous decomp.). In boiling xylene, (**II**) gives (**I**), 1 : 2 : 4 : 5-$C_6H_2Cl_4$ (**III**), and a little chloranil (**IV**) but in boiling PhMe affords (**III**), (**IV**), and C_6HCl_5. With boiling aq. AcOH–HCl or –HBr, (**II**) gives C_6Cl_6 or 2 : 3 : 5 : 6 : 1 : 4-$C_6Cl_4Br_2$, respectively, and forms 2 : 3 : 5 : 6 : 1-$C_6HCl_4\cdot NH_2$ (**V**) with aq. HI–AcOH. 3% aq. NaOH and (**II**) afford 2 : 3 : 5 : 6-*tetrachloro*-N-*nitroaniline* (**VI**), m.p. 145—146° (vigorous decomp.), also obtained with 4 : 2 : 3 : 5 : 6 : 1-$NO_2\cdot C_6Cl_4\cdot NH_2$ (**VII**) from (**V**) and AcOH–HNO_3 (*d* 1·5) at 60°. In AcCl, (**VI**) gives C_6Cl_6 and C_6HCl_5, in AcOH affords (**VII**), and in AcOH–HHal behaves as (**II**). Excess of HNO_3 (*d* 1·5) in AcOH at 50° converts (**V**) into 2 : 3 : 5 : 6-*tetrachloro*-4-*nitro*-N-*nitroaniline* (**VIII**), m.p. 88—95° (according to rate of heating). With Me_2SO_4–10% aq. NaOH, 2 : 3 : 5 : 6-*tetrachloro*-N-*nitromethylaniline*, m.p. 138—139°, and its 4-NO_2-derivative, m.p. 171—175° (decomp.), are obtained from (**VI**) and (**VIII**), respectively. HNO_3 partly converts (**VI**) and (**VIII**) into diazonium salts (coupling with 2 : 3-$OH\cdot C_{10}H_6\cdot CO\cdot NHPh$). F. R. S.

Influence of the 6-nitro-group on the halogenation, nitration, mercuration, and diazo-coupling of 6-nitro-1-naphthylamine and related naphthalides. H. H. Hodgson and H. S. Turner (*J.C.S.*, 1943, 391—394).—6 : 1-$NO_2\cdot C_{10}H_6\cdot NH_2$ (**I**) [*picrate*, m.p. 197°; *formyl*, m.p. 193°, *mono*- (**II**), m.p. 205·5°, and *di*-p-*toluenesulphonyl* derivative, m.p. 204·5—205·5°; 6-*nitronaphthyl*-1-*maleamic acid*, m.p. 181°] gives (Sandmeyer) 1-*chloro*-, m.p. 118—120°, 1-*bromo*-, m.p. 130·5—131°, and 1-*iodo*-6-*nitronaphthalene*, m.p. 73°. Cl_2 and 6 : 1-$NO_2\cdot C_{10}H_6\cdot NHAc$ (**III**) in AcOH at 90° afford the *Ac* derivative, m.p. 243° (hydrolysed by H_2SO_4–aq. EtOH), of 2 : 4-*dichloro*-6-*nitro*-1-*naphthylamine*, m.p. 177—178°, whilst Br–$CHCl_3$ and (**I**) at −5° give 4-*bromo*-6-*nitro*-1-*naphthylamine* (**IV**), m.p. 123—124°, converted (diazo-methods) into 1-*bromo*-7-*nitro*-, m.p. 104—105°, and 1 : 4-*dibromo*-6-*nitro*-*naphthalene*, m.p. 110°. 6-*Nitro*-1-*naphthaleneazo*-β-*naphthol* has m.p. 220°. 1 : 2-$C_{10}H_6Br\cdot NH\cdot SO_2\cdot C_6H_4Me$-*p* and HNO_3 (*d* 1·5) in AcOH at 30—40° (later 50—60°) give 1-*bromo*-6-*nitro*-p-*toluenesulphon*-2-*naphthalide*, m.p. 197—198°; the free base affords (Sandmeyer) 1 : 2-*dibromo*-6-*nitronaphthalene*, m.p. 175°, and (diazo-method) 1 : 6-$C_{10}H_6Br\cdot NO_2$. Further bromination [as for (**I**)] of (**IV**) yields 2 : 4-*dibromo*-6-*nitro*-1-*naphthylamine*, m.p. 195°. Nitration of (**III**) followed by hydrolysis gives mainly 4 : 6-, m.p. 178°, and some 2 : 6-*dinitro*-1-*naphthylamine*, m.p. 226·5—228·5°. (**II**) with HNO_3 (*d* 1·5)–AcOH at 90° affords the p-*toluenesulphonyl* derivative, m.p. 172·5° (hydrolysed by H_2SO_4) of 2 : 4 : 6-*trinitro*-1-*naphthylamine*, m.p. 301—304° (decomp.). (**I**) and $Hg(OAc)_2$ in AcOH give the 4-*OAc*·*Hg*-*derivative*, m.p. >400°, which with KI–I forms 4-*iodo*-6-*nitro*-1-*naphthylamine*, m.p. 175°, converted into 1-*bromo*-4-*iodo*-6-*nitronaphthalene*, m.p. 130·5—131·5°. 6 : 1 : 2-$NO_2\cdot C_{10}H_5Br\cdot NH_2$ gives 1-*bromo*-2-*iodo*-6-*nitronaphthalene*, m.p. 193—194°. *p*-$C_6H_4Me\cdot N_2Cl$ with (**I**) affords 6-*nitro*-4-p-*toluneazo*-1-*naphthylamine*, m.p. 242·5° (*Ac* derivative, m.p. 300—301°), which yields 6-*nitro*-4-p-*toluneazo*-1-*naphthaleneazoresorcinol*, m.p. >400°. Hence the 6-NO_2 group favours reaction at the 4-position. M.p. are corr. F. R. S.

Preparation of dithizone (diphenylthiocarbazone). J. H. Billman and (Miss) E. S. Cleland (*J. Amer. Chem. Soc.*, 1943, **65**, 1300—1301).—Adding CS_2 to $NHPh\cdot NH_2$ in cold Et_2O gives $NHPh\cdot NH\cdot CS\cdot S\cdot NH_3\cdot NHPh$ (97%), converted at 96—98° (not >98°) (bath) into H_2S and $CS(NH\cdot NHPh)$ (60—75%), which in boiling KOH–MeOH gives $NHPh\cdot NH\cdot CS\cdot N{:}NPh$ (52—66% overall), $NHPh\cdot NH\cdot CS\cdot NH_2$, and NH_2Ph. R. S. C.

Decomposition of diazo-compounds in neutral solution. The diazo-coupling reaction. H. H. Hodgson and E. Marsden (*J.C.S.*, 1943, 379—380).—Aq. solutions of diazotised NH_2Ar, when maintained neutral by $CaCO_3$, decompose to form bis- (NH_2Ph, *o*-toluidine) or mono-arylazophenols (*p*-toluidine, *o*-, *m*-, and *p*-$NO_2\cdot C_6H_4\cdot NH_2$, α- and β-$C_{10}H_7\cdot NH_2$). An aq. solution of the equilibrium mixture $NPh{:}N\cdot OH$ (**I**) $\rightleftharpoons$ $NPh{:}\overset{\oplus}{N}\}\overset{\ominus}{O}H$ (**II**) decomposes to form nearly equal parts of 2 : 4-bisbenzeneazo- and 4-benzeneazophenol. The results are held to indicate that undissociated (**I**) and not (**II**) is the coupling component. 3-*Nitro*-4-m-, m.p. 202°, and 4-*nitro*-2-p-*nitrobenzeneazophenol*, m.p. 168°, are described. F. R. S.

Recovery of phenols and olefines from alkylated phenols.—See B., 1943, II, 309.

Ambrettolide and isomerides. III.—See A., 1943, II, 318.

Dihydroresorcinols.—See A., 1943, II, 338.

Mechanism of fission of ethers. I. Fission of aromatic ethers in non-aqueous solvents. S. P. Walvekar, N. L. Phalnikar, and B. V. Bhide (*J. Indian Chem. Soc.*, 1943, **20**, 131—136).—Fission of PhOMe, *p*-$C_6H_4R\cdot OMe$ (R = Cl, Br, Me, NO_2), and *o*-$NO_2\cdot C_6H_4\cdot OMe$ by anhyd. HCl and HBr has been studied. In CCl_4 or *n*-C_6H_{14} (PhOMe only) after 50 hr. at 70° or 5 months at room temp. fission is usually <1%. With M-HBr in CCl_4 at 70°, addition of 5% of C_5H_5N produces 1·5—37% fission, 5% of AcOH 2·0—9·3%, of NH_2Ph 65 (PhOMe) or 79% (anisidine), and of $NPhMe_2$ 78% (PhOMe). HBr produces considerable fission in $PhNO_2$, $CHCl_3$, or AcOH alone; addition of C_5H_5N increases the amount. A mechanism for the fission is suggested. A. Li.

Derivatives of creosol. J. H. Fletcher and D. S. Tarbell (*J. Amer. Chem. Soc.*, 1943, **65**, 1431—1432).—Martin–Clemmensen reduction of vanillin gives creosol (63%), b.p. 105—106°/15 mm., the allyl ether (prep. by $CH_2{:}CH\cdot CH_2Br$ and NaOH in aq. $COMe_2$; 86%), b.p. 128—130°/15 mm., of which with aq. $KMnO_4$–Na_2CO_3 gives 3-*methoxy*-p-*tolyloxyacetic acid* (31%), m.p. 115—116°, or at 210° alone gives 5 : 1 : 3 : 4-$CH_2{:}CH\cdot CH_2\cdot C_6H_2Me(OMe)\cdot OH$ (**I**) (84%), b.p. 135—138°/18 mm. (α-*naphthylurethane*, m.p. 132—132·5°). With Me_2SO_4–2N-NaOH, (**I**) gives 3 : 4 : 1 : 5-$(OMe)_2C_6H_2Me\cdot CH_2\cdot CH{:}CH_2$ (**II**) (86%), b.p. 125—135°/12 mm., oxidised ($KMnO_4$) to 4 : 5-*dimethoxy*-m-*toluic acid*, m.p. 91·5—92·5°, which is also obtained from 3 : 4 : 1 : 5-$(OMe)_2C_6H_2Me\cdot CH{:}CHMe$ (**III**). KOH in $O([CH_2]_2\cdot OH)_2$ at 150—170° isomerises (**I**) to 5-*propenylcreosol* [3-*methoxy*-5-*propenyl*-p-*cresol*], m.p. 61—62°; at 175—185° (**II**) similarly gives (**III**) (39%), b.p. 109—111°/1 mm. R. S. C.

Synthetic œstrogens of the diphenylethane series. H. Bretschneider, A. de Jonge-Bretschneider, and N. Ajtai (*Ber.*, 1941, **74**, [B], 571—588).—p-*Hydroxypropiophenoneazine* (**I**), m.p. 170—171° (slight previous sintering), distils unchanged at ~250° (bath)/high vac., is reduced (H_2, Pd–C, EtOH) to the hydrazine, which is oxidised directly (I–KOAc) to a H_2-derivative (**II**), decomp. ~133—150° (sinters 126°), of (**I**). Oxidation by O_2 in presence of $CuSO_4$ and NaOH gives a resin, decomposed at 120—150°/1 mm. to a mixture of dl- (**III**), m.p. 126—128°, and meso- (**IV**), m.p. 185—187°, -$(p\text{-}OH\cdot C_6H_4\cdot CHEt)_2$. (**II**) is methylated (Me_2SO_4) to the dihydro-*p*-methoxypropiophenoneazine (**V**), m.p. 76—78° (Foldi *et al.*, below), is hydrolysed (MeOH–conc. HCl) to (probably) an anol polymeride, and decomposed at 140—160° to (**IV**) (62%). p-*Acetoxypropiophenoneazine*, m.p. 135·5—136·5° [from (**I**) and Ac_2O–C_5H_5N], is similarly reduced and oxidised (O_2–$CuSO_4$) to a H_2-derivative, m.p. 115—116° [at 125—150° gives *meso*-$(p\text{-}OAc\cdot C_6H_4\cdot CHEt)_2$, m.p. 140—141° (**VI**)], and oil [gives (**VI**) also]. $(p\text{-}OMe\cdot C_6H_4\cdot CH{:}N)_2$ and MgEtBr afford a product [from which (**V**) is isolable] which at 130—150° (bath)/high vac. yields *dl*- (**VII**), m.p. 55°, and *meso*- (**VIII**),

m.p. 144°, -(*p*-OMe·C_6H_4·CHEt)$_2$ (cf. Campbell *et al.*, A., 1940, II, 79). (**VII**) and (**VIII**) are unaffected by Pd-black at 250° whereas (**IV**) undergoes fission. With Pd–C at 300° in CO_2 (**VII**) yields (**VIII**) (42%) [and 33% of unchanged (**VII**)]; (**VIII**) similarly gives much oil, (?) a little (**VII**), and 28% of unchanged (**VIII**). Partial methylation (Me_2SO_4 in cold MeOH–N-NaOH) of (**IV**) affords the *Me*$_1$ *ether*, m.p. 120—121° (*propionate*, m.p. 85—87°), also obtained [with (**IV**)] from (**VIII**) and aq. MeOH–NaOH at 250°, and by thermal decomp. of a mixture of (**II**) and (**V**) (m.p. 58—67°). 4-*Hydroxy*-2-*methylacetophenoneazine*, m.p. 251—253° (block) (*diacetate*, m.p. 129—130°, sinters 128°), is reduced (H_2, Pd–C, EtOH–AcOH; not EtOH alone), the mixture treated with $KHCO_3$, then oxidised (O_2–$CuSO_4$), and the resulting oil heated at 140°; 4 : 4′-*dihydroxy*-2 : 2′-*dimethyl*-β*γ*-*diphenylbutane* (**IX**), m.p. 191—192° [*diacetate*, m.p. 164°, sinters 161°; *dipropionate*, m.p. 123—124°; *Me*$_2$ *ether* (**X**), m.p. 141—142°], is thereby obtained in poor yield. (**X**) is similarly prepared starting from 4-*methoxy*-2-*methylacetophenoneazine*, m.p. 110—111°, sinters 109° (*H*$_2$-derivative, m.p. 112—113°, sinters 111°), in 38% yield and is demethylated to (**IX**). The difference in biological activity of (**IV**) and diethylstilbœstrol is shown by using mice (not rats) in the Allen–Doisy test; (**IX**) has a high activity. H. B.

Synthetic œstrogens of the diphenylethane series. Z. Földi and G. von Fodor (*Ber.*, 1941, **74**, [*B*], 589—595).—p-*Methoxypropiophenoneazine* (**I**), m.p. 134°, absorbs 2 H_2 on catalytic reduction (Pd–C, 96% EtOH, room temp.) but evaporation of the resulting solution gives an oil (*A*) and a *H*$_2$-derivative (**II**), m.p. 75—77°, of (**I**). (*A*) and (**II**) show the same behaviour on thermal decomp. Reduction of (**I**) and subsequent atm. oxidation of the product affords (**II**) and an *isomeride* (**III**), m.p. 58—65°, which undergo thermal decomp. to a mixture of *meso*-, m.p. 144°, and *dl*-(*p*-OMe·C_6H_4·CHEt)$_2$, m.p. 55° [demethylated by MeOH–KOH at 200° or AcOH–HBr to *meso*- and *dl*-(*p*-OH·C_6H_4·CHEt)$_2$, respectively]. (**II**) and (**III**) may be stereoisomeric forms of (*p*-OMe·C_6H_4·CHEt·N:)$_2$. H. B.

Preparation of the œstrogen β-bromo-β-phenyl-αα-di-*p*-phenetylethylene. W. Tadros and A. Schönberg (*J.C.S.*, 1943, 394).—(*p*-OEt·C_6H_4)$_2$CO and CH_2Ph·MgCl give *β-phenyl-αα-di*-p-*phenetylethyl alcohol*, m.p. 124°, which on distillation with a little 20% H_2SO_4 in a vac. yields *β-phenyl-αα-di*-p-*phenetylethylene*, m.p. 74°, brominated (Br–AcOH) to the *β-Br*-compound, m.p. 97—98°. F. R. S.

Rapid and practical method of preparation of 4-amino-2-methyl-1-naphthol hydrochloride (vitamin-*K*$_5$) from 2-methyl-1 : 4-naphthaquinone. P. P. T. Sah and W. Brüll (*Ber.*, 1941, **74**, [*B*], 552—554).—1 : 2 : 4-O:$C_{10}H_5$Me:N·OH (from the quinone and NH_2OH,AcOH in EtOH) is treated with aq. NaOH and the resulting 4 : 2 : I-NO·$C_{10}H_5$Me·ONa reduced (Sn, aq. HCl) to 1 : 2 : 4-OH·$C_{10}H_5$Me·NH_2,HCl, m.p. 280° (decomp.) (darkens ~262°). H. B.

Stereoisomeric forms of additive compounds of alcohols and substituted 7-nitrostilbenes. B. Reichert and W. Kuhn (*Ber.*, 1941, **74**, [*B*], 328—337).—(*trans*-)7-Nitro-4′-methoxystilbene [*p*-OMe·C_6H_4·CH:CPh·NO_2] (**I**) and MeOH–KOH give (cf. Meisenheimer *et al.*, A., 1907, i, 858), in addition to the known (α-) form, m.p. 139° (up to 80%), of *p*-OMe·C_6H_4·CH(OMe)·CHPh·NO_2, a *β-form*, m.p. 77° (10—35%; amount increases with rise in temp. of reaction mixture), and some *cis*-(**I**), m.p. 112—113° (cf. Flürscheim *et al.*, A., 1932, 730). *trans*-7-Nitro-3′ : 4′-methylenedioxystilbene (**II**), m.p. 129—129·5° (corr.), similarly affords α-, m.p. 149—150°, and *β-forms*, m.p. 128—129°, of *α-nitro-β-methoxy-α-phenyl-β*-3 : 4-*methylenedioxyphenylethane*, a little of the cis-*form* (**III**), m.p. 123—123·5° (corr.), of (**II**), and some 3 : 5-*diphenyl*-4-3′ : 4′-*methylenedioxyphenyl*isoo*xazole*. 7-Nitro-3′ : 4′ : 5′-trimethoxystilbene and cold MeOH–KOH give 83% of the α-, m.p. 142—143°, and traces of the *β-form* (**IV**), m.p. 138—139°, of *α-nitro-β-methoxy-α-phenyl-β*-3 : 4 : 5-*trimethoxyphenylethane*; at the b.p. (**IV**) and 3 : 5-*diphenyl*-4-3′ : 4′ : 5′-*trimethoxyphenyl*isoo*xazole*, m.p. 162—163°, result. *trans*-7-Nitro-3′ : 4′-dimethoxystilbene (**V**), m.p. 109°, similarly gives one form only of *α-nitro-β-methoxy-α-phenyl-β*-3 : 4-*dimethoxyphenylethane*, m.p. 120—121°; (**VI**) (below) and 3 : 5-*diphenyl*-4-3′ : 4′-*dimethoxyphenyl*isoo*xazole*, m.p. 170—171°, are by-products. Ultraviolet irradiation of (**II**) and (**V**) in MeOH gives (**III**) and cis-7-*nitro*-3′ : 4′-*dimethoxystilbene* (**VI**), m.p. 102—103° (corr.), respectively. 7-*Nitro*-4′-*methoxy*-3′-*chloromethylstilbene*, m.p. 108—109° [from 4 : 3 : 1-OMe·C_6H_3(CH_2Cl)·CHO and CH_2Ph·NO_2 in EtOH–NH_2Me], and α-nitro-α-phenyl-β-2-furylethylene (**VII**) do not add MeOH. (**VII**) is reduced (H_2, Pd–C, C_5H_5N, room temp.) to *Ph furfuryl ketoxime*, m.p. 90°, further reduced (Na–Hg, 50% AcOH) to α-phenyl-β-2-furylethylamine, b.p. 158—160°/30 mm. [*hydrochloride*, m.p. 206—208° (decomp.)]. The above α- and β-forms are racemates. H. B.

Thermal decomposition of polyarylated carbinols. C. F. H. Allen and J. A. VanAllan (*J. Amer. Chem. Soc.*, 1943, **65**, 1384—1389).—2 : 3 : 4 : 5-Tetraphenylcyclopentadienone (**I**) and MgPhBr in Et_2O or C_6H_6 give, by 1 : 2-addition, 1 : 2 : 3 : 4 : 5-pentaphenyl-$\Delta^{2:4}$-cyclopentadienol (**II**) (Ziegler *et al.*, A., 1926, 57), but in boiling (*iso*-C_5H_{11})$_2$O give, by 1 : 4-addition, 2 : 3 : 3 : 4 : 5-*pentaphenyl*-$\Delta^{1:4}$-cyclo*pentadienol* (**III**), m.p. 189° (1 active H; no addition of MgMeI). Formation of (**III**) is direct, since the Mg derivative of (**II**) is unchanged in boiling (*iso*-C_5H_{11})$_2$O. Distilling or heating (**II**) at 290—300° gives (**III**) and 2 : 3 : 3 : 4 : 5-*pentaphenyl*-Δ^4-cyclo*pentenone* (**IV**), m.p. 164° (adds 1 MgMeI; no active H), with small amounts of 1 : 2 : 3 : 4 : 5-*pentaphenyl*cyclo*pentadiene*, m.p. 250°, H_2O, and PhCHO; the main reaction is thus an allylic shift of Ph. (**III**) is converted into (**IV**) by boiling 48% HBr–AcOH, and (**IV**) into (**III**) by $NaNH_2$ in boiling xylene. CrO_3–Ac_2O oxidises (**III**) or (**IV**) to BzOH and $COPh_2$ as sole products. (:CH·CO)$_2$O and (**II**) at the m.p. give 3 : 4 : 5 : 6-*tetraphenyl*-3 : 6-endo-α-*hydroxybenzylidene*-Δ^4-*tetrahydrophthalic anhydride*, m.p. 220°, which, when distilled, regenerates (**II**) and so yields (**III**) and (**IV**). *p*-OMe·C_6H_4·MgBr and (**I**) in C_6H_6 give 2 : 3 : 4 : 5-*tetraphenyl*-1-p-*anisyl*cyclo*pentadienol*, m.p. 203°; 1 : 4-addition could not be effected. The presence of CH·CO in (**IV**) is proved by conversion by MgPhBr into 1 : 2 : 3 : 4 : 4 : 5-*hexaphenyl*-Δ^2-cyclo*pentenol*, m.p. 248° (1 active H; does not add MgMeI), dehydrated by Ac_2O or AcCl to 1 : 2 : 3 : 4 : 5 : 5-*hexaphenyl*-$\Delta^{1:3}$-cyclo*pentadiene*, m.p. 172°; MgMeI gives by addition and simultaneous dehydration 1 : 3 : 4 : 5 : 5-*pentaphenyl*-1-*methyl*-$\Delta^{1:3}$-cyclo*pentadiene* (? 1 : 2 : 3 : 3 : 4-*pentaphenyl*-5-*methylene*-Δ^1-cyclo*pentene*), m.p. 159°. 2 : 3 : 4 : 5-Tetraphenyl-Δ^2-cyclopentenone (**V**) and MgMeI give 1 : 2 : 4 : 5-*tetraphenyl*-3-*methyl*-$\Delta^{1:3}$-cyclo*pentadiene* (or 1 : 2 : 4 : 5-*tetraphenyl*-3-*methylene*-Δ^1-cyclo*pentene*), m.p. 163°. C_6H_6–$AlCl_3$ does not affect (**IV**) or (**V**), but converts (**I**) or the bimol. product from αβ-dimethylanhydroacetonebenzil, by reduction, into 2 : 3 : 4 : 5-*tetraphenyl*- (**VI**), m.p. 328°, and diphenyldimethyl-*cyclo*pentanone, respectively. MgPhBr and (**VI**) give 1 : 2 : 3 : 4 : 5-*pentaphenyl*cyclo*pentanol*, m.p. 254°. Attempts to prepare (**IV**) from CO(CH_2Ph)$_2$ or OH·CPh_2·COPh failed. At 290—300° 2 : 3 : 4 : 5-tetraphenyl-1-benzyl-$\Delta^{2:4}$-*cyclo*pentadienol (**VII**) gives 1 : 2 : 3 : 4-tetraphenyl-5-benzylidene-$\Delta^{1:3}$-*cyclo*pentadiene (47%) with smaller amounts of (CHPh:)$_2$, (by the alternative mode of decomp.) (**I**) + PhMe, and a substance (**VIII**) (1%), m.p. 158°. Styrene and (**I**) in warm C_6H_6 give 3 : 6-endo*keto*-1 : 2 : 3 : 4 : 6-*pentaphenyl*-Δ^1-cyclo*hexene* [1 : 2 : 4 : 5 : 6-*pentaphenyl*-[2 : 2 : 1]-dicyclo-Δ^5-*hepten*-7-*one*] (**IX**), m.p. 191° (adds 1 MgMeI; no active H), converted by MgPhBr into 1 : 2 : 3 : 4 : 6-*pentaphenyl*-3 : 6-endo-α-*hydroxybenzylidene*-Δ^1-cyclo*hexene* (89%), m.p. 258°, which, when heated, gives (**IV**), a *compound* (**X**), $C_{36}H_{28}O$, m.p. 172°, and small amounts of styrene and PhCHO. With CH_2Ph·MgBr in C_6H_6 or MgMeI in (*iso*-C_5H_{11})$_2$O, (**IX**) gives 1 : 2 : 3 : 4 : 6-*pentaphenyl*-3 : 6-endo-α-*hydroxy-β-phenylethylidene*- (**XI**), m.p. 212°, or -α-*hydroxyethylidene*-, m.p. 209° (1 active H; does not add MgMeI), -Δ^1-cyclo*hexene*, respectively, but it does not react with 1-$C_{10}H_7$·MgBr. MgMeI or Ac_2O does not affect (**X**), but 72% $HClO_4$–Ac_2O (not HBr or HI) at the b.p. gives C_6HPh_5. In boiling C_6H_6, (:C·CO_2Me)$_2$ and (**II**) give *Me*$_2$ 3 : 4 : 5 : 6-*tetraphenyl*-3 : 6-endo-α-*hydroxybenzylidene*-3 : 6-*dihydrophthalate*, m.p. 209°, which at 250° gives 3 : 4 : 5 : 6 : 1 : 2-C_6Ph_4(CO_2Me)$_2$ (75%) and PhCHO. Ac_2O or AcCl does not dehydrate (**VII**) but yields the *acetate*, m.p. 195°; (**II**) similarly yields its *acetate*, m.p. 158° [not (**VIII**)], converted by HCl–AcOH into the known 1-chloro-1 : 2 : 3 : 4 : 5-pentaphenyl-$\Delta^{2:4}$-*cyclo*pentadiene. The decomp. of the bridged-ring compounds by heat occurs at the linking C:C·C—C. R. S. C.

Hydrogenolysis of sulphur compounds by Raney nickel catalyst.—See A., 1943, II, 293.

Multiplication process for the separation of racemates.—See A., 1943, I, 275.

Synthesis of pharmacologically important carboxylic acids. III. Control of hydrogenation of *O*-acetylmandelic acid esters. K. Kindler. **IV. Synthesis of substituted β-phenylpropionic acids from aryl ethyl ketones.** K. Kindler and T. Li (*Ber.*, 1941, **74**, [*B*], 315—321, 321—327; cf. A., 1936, 1508).—III. OAc·CHPh·CO_2Et (**I**) is unaffected by H_2 (2·5 atm.)–Pd-black in AcOH at room temp. but at 100° 4 H_2 are rapidly consumed and Et *cyclo*hexylacetate (**II**) results. Interruption of the reaction after absorption of 1 H_2 gives (**I**), CH_2Ph·CO_2Et (65%), and a little (**II**); the 3 : 4-(OMe)$_2$- and -CH_2O_2: derivatives of (**I**) similarly give CH_2Ar·CO_2Et although the use of a highly active catalyst leads to some nuclear hydrogenation. Suppression of nuclear hydrogenation is, however, effected by addition of $HZnCl_3$ or, better, HBr. Thus OAc·CHAr·CO_2Me (*A*) with H_2–Pd-black in AcOH–H_2SO_4–HBr or AcOH–HBr at room temp. give 84—95% of CH_2Ar·CO_2Me [Ar = *p*-anisyl, b.p. 158°/19 mm., 3 : 4-(OMe)$_2$$C_6H_3$, b.p. 175°/15 mm., 3 : 4-(OEt)$_2$$C_6H_3$, b.p. 180—181°/18 mm., 3 : 4-CH_2O_2:C_6H_3, b.p. 170—171°/16 mm. (free acids, m.p. 86°, 99—100°, 79—80°, and 128°, respectively)]. *p*-C_6H_4R·CH(OAc)·CO_2Et (R = Me, Et, Ph, *cyclo*hexyl) are rapidly reduced in AcOH–$HClO_4$ (or –H_2SO_4) at room temp. to *p*-C_6H_4R·CH_2·CO_2Et; reaction does not occur in presence of HBr. The following are prepared (75—85% yield) from OAc·CHAr·CN and HCl in MeOH or EtOH containing a little H_2O: (*A*), Ar = *p*-anisyl, b.p. 166—167°/14 mm., 3 : 4-CH_2O_2:C_6H_3, b.p. 181°/14 mm., 3 : 4-(OMe)$_2$$C_6H_3$, b.p. 195°/16 mm., and 3 : 4-(OEt)$_2$$C_6H_3$, b.p. 192°/14 mm.; OAc·CHAr·CO_2Et, Ar = Ph, b.p. 160°/28 mm., *p*-tolyl, b.p. 150°/14 mm., m.p. 74°, *p*-C_6H_4Et, b.p. 166°/12 mm., *p*-xenyl, b.p. 227°/14 mm., m.p. 67°, *p-cyclo*hexylphenyl, b.p.

211°/11 mm., m.p. 53°, and 3 : 4-$(OMe)_2C_6H_3$, b.p. 195°/14 mm.

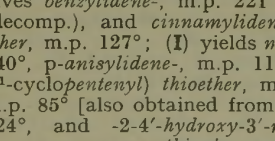
IV. COArEt, $NHMe_2$, and S at 140—150° give $CH_2Ar{\cdot}CH_2{\cdot}CS{\cdot}NMe_2$ (*B*) presumably thus: COArEt + $NHMe_2$ → $NMe_2{\cdot}CArEt{\cdot}OH$ → $S{:}NMe_2{\cdot}CArEt{\cdot}OH$ → $[S{:}NMe_2{\cdot}CAr{:}CHMe]$ → (*B*). The following β-arylthiopropiondimethylamides are described: aryl = *p*-tolyl, b.p. 225°/18 mm., m.p. 48—49°, *p*-C_6H_4Et, b.p. 295—310°/13 mm., *p*-C_6H_4F, b.p. 220°/26 mm., m.p. 57—58°, *p*-C_6H_4Cl, m.p. 64°, *p*-C_6H_4Br, b.p. 243°/17 mm., m.p. 71—72°, *p*-C_6H_4I, m.p. 112—113°, *p*-anisyl, b.p. 240—250°/17 mm., 3 : 4-$(OMe)_2C_6H_3$, m.p. 94°, 4 : 3-$OMe{\cdot}C_6H_3Me$, m.p. 83°, *p*-$SMe{\cdot}C_6H_4$, m.p. 67°, and 4 : 1-$OMe{\cdot}C_{10}H_6$, m.p. 160—170°. Hydrolysis (10% KOH) of (*B*) affords $Ar{\cdot}[CH_2]_2{\cdot}CO_2H$; β-p-*fluoro*-, m.p. 91°, and -p-*methylthiol-phenyl*-, m.p. 101°, -6-*methoxy*-m-*tolyl*-, m.p. 99—100°, and -4-*methoxy*-1-*naphthyl-propionic acid*, m.p. 170—171°, are new. p-*Fluoropropiophenone*, b.p. 105—107°/22 mm., and 4-*methoxy*-1-*naphthyl Et ketone*, b.p. 205°/15 mm., m.p. 57°, are prepared from PhF and α-$C_{10}H_7{\cdot}OMe$ with EtCOCl and $AlCl_3$ in CS_2 at 0°—room temp. and 0°—50—60°, respectively. H. B.

Iodinated organic compounds as contrast media for radiographic diagnoses. II. Ethyl esters of iodinated straight- and branched-chain phenyl-fatty acids. J. T. Plati [with W. H. Strain and S. L. Warren] (*J. Amer. Chem. Soc.*, 1943, **65**, 1273—1276; cf. A., 1942, II, 311).—Adding coarsely crushed, cryst. $NaNO_2$ to $Ph{\cdot}[CH_2]_n{\cdot}CO_2H$ and I in 10 : 1 (vol.) $AcOH–H_2SO_4$ and boiling with stirring gives a mixture whence by crystallisation only the *p*-I-acid is isolated; yields are 39—50% for acids with an odd and 14—45% for acids with an even no. of C. $NaIO_3$, but not HNO_3, may replace the $NaNO_2$. Thus are obtained *p*-$C_6H_4I{\cdot}CH_2{\cdot}CO_2H$, β-p-*iodophenylpropionic*, m.p. 139—141° (*Et* ester, b.p. 140°/2 mm.), γ-p-*iodophenyl*-n-*butyric*, m.p. 89—90·5° (*Et* ester, b.p. 146—148°/0·8 mm.), δ-p-*iodophenyl*-n-*valeric* (**I**), m.p. 109·5—110·5° [*Et* ester (**II**), b.p. 158°/2 mm.], ε-p-*iodophenyl*-n-*hexoic*, m.p. 66—67° (*Et* ester, b.p. 158—160°/2 mm.), and ζ-p-*iodophenyl*-n-*heptoic acid*, m.p. 93—94·5° [*Et* ester (**III**), b.p. 175—177°/2·5 mm.]. $Ph{\cdot}[CH_2]_4{\cdot}CO_2H$ (**IV**), m.p. 59—60°, is obtained from $Ph{\cdot}[CH_2]_3{\cdot}Br$ (**V**) and $CH_2(CO_2Et)_2$ etc. or in 70% over-all yield by successively condensing $CHPh{:}CH{\cdot}CHO$ with $COMe_2$–10% NaOH at room temp., oxidising with aq. NaOCl at 40—50°, rising to 60—65°, and hydrogenating in EtOH in presence of Raney Ni at 110°. HNO_3 at ≯80° (cool to 60°) converts (**IV**) into δ-p-*nitro*- (28%), m.p. 84—85° (oxidised by aq. CrO_3 at 75—120° to *p*-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$), which with $Fe(OH)_2$–aq. NH_3 gives δ-p-*amino-phenyl*-n-*valeric acid* (42%), m.p. 113—113·5°, and thence (Sandmeyer) (**I**) (oxidised by alkaline $KMnO_4$ to *p*-$C_6H_4I{\cdot}CO_2H$). $CHEt(CO_2Et)_2$ with *p*-$C_6H_4I{\cdot}CH_2Br$ or (**V**) gives *Et*$_2$ p-*iodobenzyl*- (64%), b.p. 176—180°/2 mm., or γ-*phenyl*-n-*propyl-ethylmalonate* (58%), b.p. 193—196°/11 mm., and thence *Et* α-p-*iodobenzyl*-n-*butyrate* (52%), b.p. 182—183°/14 mm., or δ-*phenyl*-α-*ethyl*-n-*valeric acid* (**VI**) (80%), b.p. 189—190°/14 mm., respectively. $CHBu^{\alpha}(CO_2Et)_2$ gives similarly *Et*$_2$ p-*iodobenzyl*-n-*butylmalonate* (67%), b.p. 178—182°/2 mm., and thence *Et* α-p-*iodobenzyl*-n-*hexoate* (68%), b.p. 156°/2 mm. $NaNO_2$–I etc. converts (**VI**) into an oily I-acid [*Et* ester (61%), b.p. 162—164°/2 mm.]. (**II**) and (**III**) are the most suitable *X*-ray contrast media but are somewhat toxic in the spinal canal. (**II**) is very suitable in various other body cavities. R. S. C.

1-Naphthylacetic acid.—See B., 1943, II, 310.

Iodination of tyrosine by iodine monochloride. P. Block, jun., and G. Powell (*J. Amer. Chem. Soc.*, 1943, **65**, 1430—1431).—Tyrosine and ICl in AcOH, later $AcOH–H_2O$, at 60° give 85% of the pure I_2-derivative, m.p. 201° (corr.). R. S. C.

Thioketonic esters. X. K. Chandra, N. K. Chakrabarty, and S. K. Mitra (*J. Indian Chem. Soc.*, 1942, **19**, 139—144).—*Et thio*cyclo-*pentanone*- (**I**), b.p. 110°/5·5 mm. [free *acid* (**II**), m.p. 122 °(decomp.)], and -*hexanone*-2-*carboxylate* (**III**), b.p. 112°/6 mm. [free *acid* (**IV**), m.p. 115° (decomp.)] (from the CO-esters in EtOH with anhyd. HCl followed by H_2S at 0°), with mol. Na followed by the appropriate halide in C_6H_6 at 25° yield *Et* 1-*ethyl*-, b.p. 115°/6 mm. (free *acid*, m.p. 177°), and 1-*carbethoxymethyl-thiol*-Δ¹-cyclo*pentene*- (**V**), b.p. 170°/3 mm., and 1-*ethyl*-, b.p. 125°/3 mm. (free *acid*, m.p. 146°), and 1-*acetyl-thiol*-Δ¹-cyclo*hexene*-2-*carboxylate*, b.p. 132°/5 mm. With the appropriate aldehyde in saturated EtOH–HCl at 0°, (**II**) gives *benzylidene*-, m.p. 221° (decomp.), p-*anisylidene*-, m.p. 185° (decomp.), and *cinnamylidene-bis*-(2-*carboxy*-Δ¹-cyclo*pentenyl*) *thioether*, m.p. 127°; (**I**) yields *methylene*-, m.p. 117°, *benzylidene*-, m.p. 140°, p-*anisylidene*-, m.p. 118°, and *vanillylidene-bis*-(2-*carbethoxy*-Δ¹-cyclo*pentenyl*) *thioether*, m.p. 136°; (**IV**) gives 4-*keto*-2-*phenyl*-, m.p. 85° [also obtained from (**III**) and PhCHO], -2-p-*anisyl*-, m.p. 124°, and -2-4′-*hydroxy*-3′-*methoxyphenyl*-5 : 6-*tetramethylene*-1 : 3-*thioxine*, m.p. 178°. (**III**) with mol. Na in C_6H_6 at room temp., then $CH_2Cl{\cdot}CO_2Et$ at the b.p., yields 2-*hydroxy*-6-*carbethoxy*-3 : 4 : 5 : 8-*tetrahydrothionaphthen*, m.p. 59°. (**V**) and Na in C_6H_6 give the *ester* (*A*), b.p. 140°/5 mm., m.p. 54°. Iodometric measurements show that in EtOH at 30° and 60° (**I**) contains 36·6 and 35·1% respectively, while (**III**) contains 77·4 and 75·7% respectively, of the thiol form. A. Li.


(*A*.)

Steric course and mechanism of the diene reaction. F. Bergmann and H. E. Eschinazi (*J. Amer. Chem. Soc.*, 1943, **65**, 1405—1411).—The main product of a Diels–Alder reaction is sometimes accompanied by a small amount of an isomeride. In both products the configuration of the singly unsaturated reactant is retained. The isomerism is not due to stereoisomerism but to a shift of the newly formed ethylenic linking. This postulates simultaneous reaction of both poles of the reactants, $>C^+{\cdot}C{:}C{\cdot}C^-<$ and $>C^-{\cdot}C^+<$; in accordance with this view, dienes which contain large amounts of the resonance form illustrated react readily, and olefines must contain "resonance-producing" groups (CO, CN, CO_2H, etc.). In an open tube di-Δ¹-*cyclo*hexenyl (**I**) and $CHPh{:}CH{\cdot}CO_2H$ at 175° or 250° give only 9-phenyl-Δ¹²-dodecahydrophenanthrene-10-carboxylic acid (**II**), m.p. 231° (A., 1938, II, 330; m.p. 221°), but in a sealed tube give also a small amount of an "ethylenic" *isomeride* (**III**), m.p. 282°. With CH_2N_2, (**II**) gives the *Me* ester (**IV**), m.p. 111—112°, which is unaffected by NaOH– or NaOEt–EtOH and with NaOBu–BuOH regenerates (**II**); hydrolysis of the Et ester also gives (**II**). The *Me* ester (**V**), m.p. 147°, of (**III**) is formed slowly and with NaOBu–BuOH regenerates (**III**). It follows that (**II**) and (**III**) are not stereoisomeric at $C_{(9)}$–$C_{(10)}$. (**II**) is not decarboxylated by basic Cu carbonate in boiling quinoline or by soda–lime at 350°. $CHPh{:}CH{\cdot}COMe$ and (**I**) at 175° in an open flask or sealed tube give only 10-*acetyl*-9-*phenyl*-Δ¹²-*dodecahydrophenanthrene* (**VI**) (27%), m.p. 135°, and condensation products of the ketone. (**VI**) gives no hydrazone or semicarbazone and is unaffected by $Al(OPr^{\beta})_3$–xylene. $CHPh{:}CH{\cdot}COPh$ and (**I**) at 180—185° in an open vessel give 10-*benzoyl*-9-*phenyl*-Δ¹²-*dodecahydrophenanthrene* (**VII**), m.p. 216° (no CO derivative), and a small amount of an "ethylenic" *isomeride* (**VIII**), m.p. 153—154° (no CO derivatives). When *trans*-$(CHBz{:})_2$ and (**I**) are heated for 3 hr. in boiling xylene, 9 : 10-*dibenzoyl*-Δ¹²-*dodecahydrophenanthrene* (**IX**), dimorphic, (*a*) yellow, m.p. 182° (stable), and (*b*) colourless, m.p. 162°, is obtained; these forms are probably not isomerides, since recrystallisation converts (*b*) into (*a*); only (*a*) is obtained if the reactants are heated for 6 hr. in boiling xylene or in $PhNO_2$ at 150° to the b.p. With a little H_3PO_4 in boiling Ac_2O, (**IX**) gives 2′ : 5′-*diphenylfurano*-3′ : 4′-9 : 10-Δ¹²-*dodecahydrophenanthrene*, fluorescent, m.p. 179—180°, which does not add $(CH{\cdot}CO)_2O$ but in H_2SO_4 at ~80° gives non-fluorescent (?) 10-*phenyl*-1 : 2 : 3 : 4-*bistetramethylene*-1 : 4-*dihydro*-9-*anthrone*, m.p. 141°. *trans*-$CHBz{:}CH{\cdot}CO_2H$ and (**I**) at 170—180° or in boiling xylene or EtOH give 22—27% of 9-*benzoyl*-Δ¹²-*dodecahydrophenanthrene*-10-*carboxylic acid* (**X**), m.p. 258—259°, converted by CH_2N_2 (not HCl–MeOH) into the *Me* ester, m.p. 159—160°, and by H_2SO_4 at room temp. into a *substance*, $C_{22}H_{26}O_4$, m.p. 124—125°; (**X**) could not be cyclised. None of the adducts reacts with Grignard reagents under normal conditions. MgMeI (not MgPhBr) reacts [no solvent at 100° (bath)] with (**IV**) [not (**V**)] to give (**VI**). With MgMeI in boiling PhMe, (**VI**) gives 9-*phenyl*-10-α-*hydroxy*iso*propyl*- (60%), b.p. 190—200°/4 mm., but with MgPhBr in boiling xylene (not PhMe) gives (?) 9-*phenyl*-10-α-*phenylethylidene*- or -10-α-*phenylvinyl*- (**XI**), m.p. 106—107°, -Δ¹²-*dodecahydrophenanthrene*. MgMeI and (**VII**) in boiling PhMe give (?) (**XI**), m.p. 156°, but (**VIII**) gives only a trace of a yellow oil. R. S. C.

Friedel–Crafts reactions of 9-phenyldodecahydrophenanthrene-10-carboxylic acid. H. E. Eschinazi and F. Bergmann (*J. Amer. Chem. Soc.*, 1943, **65**, 1411—1412).—9-Phenyl-Δ¹²-dodecahydrophenanthrene-10-carboxylic acid (**I**), m.p. 231°, with $PCl_5–C_6H_6$ gives the acid chloride, which with hot NH_2Ph gives the *anilide*, m.p. 307—308°, with $AlCl_3–C_6H_6$ at the b.p. gives 10-*benzoyl*-9-*phenyl*-Δ*-*dodecahydrophenanthrene*, m.p. 198—199° (at room temp. oils are formed), and with $SnCl_4$ in boiling light petroleum gives 9-*phenyl*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydrophenanthrene* (**II**), m.p. 94°, probably by way of 10-chloro-9-phenyl-Δ¹²-dodecahydrophenanthrene. S at 200—260° or Se at 320—340° converts (**II**) into 9-phenylphenanthrene (**III**). Se and (**I**) give 9-phenylphenanthrene-10-carboxylic acid; S affords (**III**). The isomeride, m.p. 281°, of (**I**) (preceding abstract) gives an *anilide*, m.p. 247—248°, but its acid chloride does not react with $SnCl_4$. R. S. C.

Preparation of organic peracids.—See B., 1943, II, 310.

Condensations by sodium. XXVI.—See A., 1943, II, 345.

Bromine value of aromatic ethylenic ketones. P. Duquénois and Z. Sezer (*Rev. Fac. Sci. Istanbul*, 1942, **7**, 98—106).—The Br val. of these ketones determined according to Volmar *et al.* (B., 1928, 326) in the dark is usually in accordance with or slightly > the theoretical val. $COMe{\cdot}CH{:}CHPh$ affords the dibromide, m.p. 125° (phenylhydrazone, m.p. 205—206°). $COPh{\cdot}CH{:}CHPh$ gives almost exclusively the α-dibromide, m.p. 153—155°. The corresponding tetrabromide, m.p. 208°, is derived from $CO(CH{:}CHPh)_2$. $COMe{\cdot}[CH{:}CH]_2{\cdot}Ph$ gives a somewhat low Br val. Unstable resinous products are obtained from *o*-$OH{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}COR$ (R = Me, Ph). Vanillylideneacetone gives a normal Br val. in the dark but results are high in the light. H. W.

Hydrogen fluoride as a condensing agent. XVIII. Ar[yl] alkyl ketones. J. H. Simons and E. O. Ramler (*J. Amer. Chem. Soc.*, 1943, **65**, 1390—1392; cf. A., 1942, II, 344).—COPhMe is unchanged in HF at 25°, but at 50° gives dypnone (**I**) (23·8), BzOH

(16·2), and resin (20%), and at 99° gives BzOH (34) and resin (46%). Similarly, COPhEt in HF at 55° gives BzOH (59), resin (30), and CPhEt:CMe·COPh (3·5%), but at 99° gives only BzOH (34·4) and resin (60%). In HF at 99° (**I**) gives resin (57) and BzOH (34%), p-$C_6H_4Bu^{\gamma}$·COMe gives resin (43) and p-$C_6H_4Bu^{\gamma}$·CO_2H (33%), and COPhBu$^{\beta}$ gives resin (75%) but no acid. HF does not affect $COPh_2$ at 99° or COPh·CCl_3 at 169°. The resin from COPhMe, when heated to >300°, gives a small amount of an unsaturated liquid, b.p. ~164°, which with cold neutral $KMnO_4$ gives COPhMe, and thus contains units CPhMe:C. O_2 does not increase the yield of BzOH from COPhMe, nor does addition of COPhMe lead to formation of BzOH from $COPh_2$. The reaction mechanism is thus: 2COPh·CH_2R → COPh·CHR·CPh(CH_2R)·OH → COPh·CR:CPh·CH_2R → CH_2R·CPh:CHR + BzF (→ BzOH), resin being formed at each stage. The reaction cannot proceed beyond the first stage for COPh·CHRR′ and not at all for COPh·CRR′R″ or COPhAr. R. S. C.

Photochemical pinacolinisation. F. Bergmann and Y. Hirshberg (*J. Amer. Chem. Soc.*, 1943, **65**, 1429—1430).—The formation of pinacols by illumination of ketones (A., 1938, II, 348) is influenced by the nature of the aryl nucleus, side-chain, and substituents. No pinacol is formed from 1- or 2-$C_{10}H_7$·COMe, 1-$C_{10}H_7$·COPh, (1-$C_{10}H_7$)$_2$CO, or p-C_6H_4Ph·COPh. CH_2Ph·COPh gives the α-pinacol (~80%; no β-form), but Ph·$[CH_2]_2$·COPh is unchanged and Ph·$[CH_2]_3$·COPh (prep. from Ph·$[CH_2]_2$·MgBr and PhCN), b.p. 180°/6 mm., 155°/0·2 mm., gives only a small amount of a (?) *mixture*, b.p. 190°/0·25 mm. 1-Indanone gives only 2-1′-*indanylidene*-1-*indanone*, m.p. 142—143°, or in sunlight a small amount of a substance, $C_{36}H_{26}O$, m.p. 352—353° (? impure bouxene), but 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene gives up to 75% of the pinacol, m.p. 192°. CHPh:CH·COPh and CHPh:CH·COMe are unaffected. p-OR·C_6H_4·COEt (*A*; R = Me) is unchanged; (*A*; R = Ac, COEt, or COPr) suffer partial deacylation, but (*A*; R = Ac) gives also traces of (p-OAc·C_6H_4·CEt·OH)$_2$, m.p. 214° (lit. 200°). Benzoin undergoes a reverse Cannizzaro reaction, giving only PhCHO. R. S. C.

Phenanthrene derivatives. XI. Acetylation and succinoylation of 3-methylphenanthrene. W. E. Bachmann and G. D. Cortes (*J. Amer. Chem. Soc.*, 1943, **65**, 1329—1334; cf. A., 1940, II, 348).—4-Keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (prep. from 2-$C_{10}H_7$·$[CH_2]_3$·CO_2H by PCl_5–C_6H_6 and then $SnCl_4$; 85% yield; cf. Haworth, A., 1932, 608), m.p. 67—68°, with $Me_2C_2O_4$ etc. gives *Me* 4-*keto*-1 : 2 : 3 : 4-*tetrahydro*-3-*phenanthrylglyoxylate* (85%), m.p. 70—71°, converted by heating with powdered glass at 180° into CO and *Me* 4-*keto*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-3-*carboxylate* (92%), m.p. 91—92°, which with hot NaOMe–MeOH–C_6H_6 and then MeI gives *Me* 4-*keto*-3-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-3-*carboxylate* (89%), m.p. 83·5—84°. Boiling HCl–AcOH–H_2O then yields 4-keto-3-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene (88%), m.p. 64—65°, also obtained (89%) from 2-$C_{10}H_7$·$[CH_2]_2$·CHMe·CO_2H by PCl_5–C_6H_6 and then $SnCl_4$, and reduced by boiling Al(OPr$^{\beta}$)$_3$–Pr$^{\beta}$OH to the 4-OH-compound (91·8%), m.p. 89—93°, which with Pd–C–N_2 at 300—310°, gives 3-methylphenanthrene (**I**) (95%), m.p. 61—62° (cf. lit.). 1-$C_{10}H_7$·CH_2·CH:CH_2 and 30% HBr–AcOH at 40—50° and then room temp. give 1-β-*bromo*-n-*propylnaphthalene* (75·3%), b.p. 152—156°/1·5 mm., which, when successively added in C_6H_6 to CHNa(CO_2Et)$_2$–EtOH at 70—80°, boiled, hydrolysed (KOH–EtOH), and decarboxylated (160°), gives γ-1-*naphthylisovaleric acid* (43%), m.p. 92—93°. Cyclisation (PCl_5; $SnCl_4$) then yields 1-*keto*- (91%), m.p. 105—106°, and thence [Al(OPr$^{\beta}$)$_3$–Pr$^{\beta}$OH] 1-*hydroxy*-3-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (85%), m.p. 92—93°, which with Pd–C–N_2 at 300—310° gives (**I**) (89%). 3-Acetylphenanthrene and aq. $(NH_4)_2S_x$ in dioxan at 165—167° give 3-phenanthrylacetamide (40—80%), m.p. 172—176°, hydrolysed by boiling conc. HCl–AcOH to the acid (76%), m.p. 177—178° (lit. 175—177°), the K salt of which, when distilled with soda-lime at 20 mm., gives ≯84% of (**I**). With Ac_2O and $AlCl_3$ in $PhNO_2$ at 0°, (**I**) gives a mixture, whence, by way of the semicarbazones, 6-*acetyl*-3-*methylphenanthrene* (**II**) (40%), m.p. 95—96° (semicarbazone, m.p. 213—215°), is isolated. However, AcCl–$AlCl_3$ in $PhNO_2$ at 0° gives 9-*acetyl*-3-*methylphenanthrene* (**III**), m.p. 90—91°. Structures are proved as follows. Na–Hg–conc. HCl–AcOH–PhMe reduces (**II**) to 3-*methyl*-6-*ethylphenanthrene* (**IV**) (60%), m.p. 47—48° (picrate, m.p. 156—156·5°), which is also obtained as follows: 3-ethylphenanthrene, Ac_2O, and $AlCl_3$ in $PhNO_2$ at 0° give 6-*acetyl*-3-*ethylphenanthrene*, m.p. 86—87° (semicarbazone, m.p. 203—206°), which gives (Willgerodt) 3-*ethyl*-6-*phenanthrylacetamide* (82%), m.p. 182—183°, and thence, as above, the derived *acid* (77%), m.p. 110—111°, and (**IV**) (77%). Similarly (**III**) gives 3-*methyl*-9-*ethylphenanthrene* (**V**) (56%), m.p. 47—48° (picrate, m.p. 121—122°). 1-$C_{10}H_7$Et, EtOCl, and $AlCl_3$ in CS_2 give 4-*propionyl*-1-*ethylnaphthalene* (73%), a liquid, giving in light in Et_2O the oily α-Br-derivative, which with CHNa(CO_2Et)$_2$ etc. gives β-4-*ethyl*-1-*naphthoyl*-n-*butyric acid* (48%), m.p. 127—128°; Clemmensen reduction and cyclisation thereof gives 1-*keto*-3-*methyl*-9-*ethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (52%), m.p. 97·5—98°, and thence [Al(OPr$^{\beta}$)$_3$–Pr$^{\beta}$OH and then Pd–C–N_2 at 310°] (**V**). $(CH_2·CO)_2O$ and $AlCl_3$ in $PhNO_2$ at 0° convert (**I**) into γ-*keto*-γ-6-*methyl*-3-*phenanthryl*-n-*butyric acid* (**VI**), m.p. 184·5—185°. Illuminating (**II**) and Br in Et_2O gives 6-*bromoacetyl*-3-*methylphenanthrene* (82·5%), m.p. 157—158°, which with CHNa(CO_2Et)$_2$ etc. gives (**VI**). (**III**) gives similarly 9-*bromoacetyl*-3-*methylphenanthrene* (83%), m.p. 101—102°, and thence γ-*keto*-γ-3-*methyl*-9-*phenanthryl*-n-*butyric acid* (71%), m.p. 174—175°, which by Clemmensen reduction and subsequent ring-closure [$SOCl_2$–Et_2O–C_5H_5N (a drop); $SnCl_4$–C_6H_6] gives 1-keto-10-methyl-1 : 2 : 3 : 4-tetrahydrotriphenylene (91%), m.p. 80—83°, converted by Al(OPr$^{\beta}$)$_3$ and then Pd–C–N_2 at 220° into 2-methyltriphenylene (65%), m.p. 101—102° (picrate, m.p. 191—192°) (Fieser *et al.*, A., 1939, II, 540). Clemmensen reduction of (**VI**) gives γ-6-methyl-3-phenanthryl-*n*-butyric acid, m.p. (crude) 108—111°, which with PCl_5 and $SnCl_4$ gives 1-keto-2′-methyl-1 : 2 : 3 : 4-tetrahydro-5 : 6-benzanthracene (54%), m.p. 165—168°, and thence, as above, 2′-methyl-1 : 2-benzanthracene (Cook, A., 1932, 374). R. S. C.

2-Methylene*cyclo*hexanone. C. Mannich (*Ber.*, 1941, **74**, [*B*], 554—556; cf. A., 1928, 300).—2-Piperidino- or 2-dimethylaminomethyl*cyclo*hexanone (or mixtures) when heated in a vac. (~0·3 mm.) gives 2-methylene*cyclo*hexanone (**I**) (*semicarbazone*, viscous ~155°, sinters 160°, decomp. ~210°), which can be distilled (high vac.), rapidly dimerises at room temp., and is reduced (H_2, Pd, MeOH) to 2-methyl*cyclo*hexanone. MgMeI and (**I**) afford 1-methyl-2-methylene*cyclo*hexanol, b.p. 58°/10 mm. H. B.

Introduction of the angular methyl group. Preparation of *cis*- and *trans*-1-keto-9-methyldecahydronaphthalene. W. S. Johnson (*J. Amer. Chem. Soc.*, 1943, **65**, 1317—1324).—A three-step process for introducing angular Me into cyclic ketones is described. 2-Benzylidene-6-methyl*cyclo*hexanone (improved prep.) with MeI in KOBu$^{\gamma}$–Bu$^{\gamma}$OH–N_2 at 0° and then 100° gives 2-benzylidene-6 : 6-dimethyl*cyclo*hexanone (**I**) (95%), m.p. 79·5—80°, which with Br–CCl_4 gives the *dibromide*, m.p. 86·5—87·5° [at 140—150° regenerates a little (**I**)], and with Cl_2–CS_2 at <0° gives the *dichloride*, α- (**II**) (75%), m.p. 82—83°, and β-*form* (20%), m.p. 83—84°. Boiling NaOEt–EtOH converts (**II**) into (?) 2-α-ethoxybenzylidene-6 : 6-dimethyl*cyclo*hexanone, an oil, hydrolysed by hot conc. HCl–EtOH to 2-*benzoyl*-6 : 6-*dimethyl*cyclo*hexanone* (**III**), isolated as Cu derivative, m.p. 214—216·5° (decomp.), and obtained in diketo-, m.p. 76—77° (no immediate $FeCl_3$ colour), and enol *forms*, m.p. 65—65·5° (purple $FeCl_3$ colour). Distilling (**III**) (mixed forms) from 1% NaOH by steam gives ζ-*keto*-ζ-*phenyl*-αα-*dimethyl*-n-*heptoic acid* (46%), m.p. 105—105·5°, 2 : 2-dimethyl*cyclo*hexanone (29%), and BzOH. 1-Ketodecahydronaphthalene, PhCHO, and NaOH in aq. EtOH at room temp. give the 2-CHPh: derivative (**IV**) (75%), m.p. 91—92° [*semicarbazone*, m.p. 212·5—214° (decomp.) (bath preheated to 208°)], and some (?) 1-*hydroxy*-2-α-*hydroxybenzyldecahydronaphthalene*, m.p. 139·5—140°. MeI–KOBu$^{\gamma}$–Bu$^{\gamma}$OH–N_2 converts (**IV**) into (?) cis- (**V**), m.p. 104—104·5°, and (?) trans-1-*keto*-2-*benzylidene*-9-*methyldecahydronaphthalene* (**VI**), m.p. 93·5—94°. The *semicarbazone*, m.p. 209—210° (decomp.) (bath preheated to 200°), of (**VI**) is more rapidly formed than is *that*, m.p. 191—192°, of (**V**), and (**V**) and (**VI**) may be thus separated. Cl_2–CS_2 at 0°, then boiling NaOEt–EtOH–N_2, hydrolysis (dil. HCl), and steam distillation from dil. NaOH convert (**V**) into (?) *cis*-1-keto-9-methyldecahydronaphthalene (71%), b.p. 116°/14—15 mm. [semicarbazone, m.p. 226—227° (decomp.) (bath preheated to 220°); oxime, dimorphic, m.p. 109—110° and 114·5—115·5°; 2 : 4-dinitrophenylhydrazone, m.p. 164·5—165·5°; with PhCHO etc. gives (**V**)] (cf. Cook *et al.*, A., 1937, II, 292), and 1-*methyl*-2-δ-*keto*-δ-*phenyl*-n-*butyl*cyclo*hexane*-1-*carboxylic acid* (**VII**) (? *cis*-Me–H), m.p. 131—133°; incomplete hydrolysis gives some (?) *cis*-1-keto-2-benzoyl-9-methyldecahydronaphthalene [amorphous *Cu* derivative, m.p. 150—153° (decomp.)]. (**VI**) yields similarly dichlorides (a *form*, m.p. 160—161°, was isolated) and thence (?) *trans*-1-keto-2-benzoyl-9-methyl- (**VIII**) [amorphous *Cu* derivative, m.p. 235—238° (decomp.)], and (?) trans-1-*keto*-9-*methyl-decahydronaphthalene*, b.p. 119—120°/14—15 mm. [*semicarbazone*, m.p. 219—220° (decomp.) (bath preheated to 215°), formed rapidly; *oxime*, m.p. 141·5—142° (cf. *loc. cit.*); 2 : 4-*dinitrophenylhydrazone*, m.p. 171·5—172°; with PhCHO gives (**VI**)], and the (?) trans-*isomeride* (**IX**), softens at 162°, m.p. 167—168° (oxime, m.p. 166—166·5°; *semicarbazone*, m.p. 184—185°), of (**VII**). The *Me* ester, m.p. 42—43°, resolidifies, remelts 46—47°, of (**IX**) with NaOMe–C_6H_6–N_2 gives (**VIII**). M.p. are corr. R. S. C.

Synthesis of condensed ring compounds. X. *cis*-1-Keto-9-methyl-Δ^6-octahydronaphthalene and *cis*-10-methyl-1-vinyl-$\Delta^{1:7}$-naphthitadiene. W. Nudenberg and L. W. Butz (*J. Amer. Chem. Soc.*, 1943, **65**, 1436; cf. A., 1942, II, 313, 319).—2-Methyl-Δ^2-*cyclo*hexenone and $(CH_2:CH)_2$ give cis-1-*keto*-9-*methyl*-Δ^6-*octahydronaphthalene*, b.p. 67°/0·5 mm. [*semicarbazone*, m.p. 224·8—225° (decomp. from 224°); absorbs 1·88 H], which by way of cis-1-*hydroxy*-9-*methyl*-1-*acetylenyl*-, b.p. 93—94°/0·5 mm., gives -1-*hydroxy*-9-*methyl*-1-*vinyl*-Δ^6-*octahydronaphthalene*, b.p. 92°/0·55 mm. With, best, PBr_3–C_5H_5N this yields 9-*methyl*-1-*vinyl*-3 : 4 : 5 : 8 : 9 : 10-cis-*hexahydronaphthalene* ["cis-10-*methyl*-1-*vinyl*-$\Delta^{1:7}$-*naphthitadiene*"], b.p. 66—67°/0·45 mm. [absorption max. at 2380 A. (ε 9400) in C_6H_{14} or 2380 A. (ε 10,000) in EtOH; absorbs 3 H_2], which with 1 : 4-O:$C_{10}H_6$:O at 110° yields (?) 1 : 2-*phthaloyl*-13-*methyl*-1 : 2 : 3 : 5 : 8 : 9 : 10 : 11 : 13 : 14-*decahydrophenanthrene*, m.p. 191·8—192·8°. No details are given. R. S. C.

Catalytic hydrogenation of alkyl [aryl] halides. II. M. Busch, W. Weber, and H. Zink (*J. pr. Chem.*, 1940, [ii], **155**, 163—176; cf. A., 1936, 1099).—Hydrogenating (1% Pd–$CaCO_3$) 2-bromoanthraquinone in presence of N_2H_4,H_2O in 5% KOH–MeOH at 133°/10 atm. gives di-2-anthraquinonyl (**I**) and anthraquinone (**II**). 2-Chloroanthraquinone behaves similarly, but less (**I**) is formed, or, in presence of an excess of N_2H_4, only (**II**). 1-Chloroanthraquinone gives only (**II**). 9-Chlorobenzanthrone gives *di-9-benzanthronyl* (13·3%), m.p. 371°, but 3-bromobenzanthrone gives violanthrone (46%). 3 : 9-Dibromobenzanthrone gives a mixture. 7-Bromoquinoline gives *di-7-quinolyl* (57·5%), m.p. 171°, and quinoline (36·8%). 9 : 10-Dibromoanthracene gives only anthracene. 2 : 7-Dibromofluorene gives fluorene (31%), di-2-fluorenyl (30%), m.p. 310—312°, and impure higher coupling products (12%), m.p. 355—375°. (p-$C_6H_4Br\cdot CH_2)_2$ [prep. from $(CH_2Ph)_2$ by Br–I–CCl_4 at 0°; 34% yield], m.p. 216°, gives $(CH_2Ph)_2$ (17·8%), 4 : 4′-di-β-phenylethyldiphenyl [bisdibenzyl] (17·4%), m.p. 151°, p-terdibenzyl, $Ph\cdot([CH_2]_2\cdot C_6H_4\cdot C_6H_4)_x\cdot[CH_2]_2\cdot Ph$ (*A*; $x = 2$) (17·0%), m.p. 240—250° (clear at 273°), ? p-quaterdibenzyl (*A*; $x = 3$) (12·8%), softens 305°, m.p. 350°, and ? quinquedibenzyl (*A*; $x = 4$) (7·5%), softens ~340°, m.p. >365° (clear >400°). $CO(C_6H_4Br\text{-}p)_2$ gives similarly $COPh_2$ (16%), $(C_6H_4Bz\text{-}p)_2$ (24%), m.p. 214° (216°), ? terbenzophenone (13%), m.p. 326—327° (amorphous phenylhydrazone), ? quaterbenzophenone (11%), sublimes (? m.p.) 387—394°, and products, (3%) decomp. ~400° and (7%) decomp. 440°.
R. S. C.

Aërobic oxidation of aromatic hydrocarbons in presence of ascorbic acid. Reaction with anthracene and 3 : 4-benzpyrene. F. L. Warren (*Biochem. J.*, 1943, **37**, 338—341).—In presence of ascorbic acid (**I**), O_2 oxidises anthracene in aq. 80% $COMe_2$ in the dark to anthraquinone and 3 : 4-benzpyrene to the corresponding 5 : 8- and 5 : 10-quinones. The reaction is unaffected by $Cu^{\cdot\cdot}$ (trace) or H_2O_2 but is inhibited by KCN or HPO_3. Dihydroxymaleic acid acts like (**I**). Probably the oxidising agent is a product of autoxidation of (**I**) (*e.g.*, dehydroascorbic acid or a peroxide thereof), the mechanism being similar to that which occurs during the inhibition by aromatic hydrocarbons of autoxidation of aldehydes.
W. McC.

IV.—STEROLS AND STEROID SAPOGENINS.

Steric junction of rings C and D in steroids. K. Dimroth and H. Jonsson (*Ber.*, 1941, **74**, [*B*], 520—523).—The semicarbazone, new m.p. 226°, $[\alpha]_D^{18}$ +46° in $CHCl_3$, of 4-keto-8-methyl-1-αδε-trimethyl-Δ^{β}-hexenylhydrindane (**I**) (Windaus *et al.*, A., 1936, 1247; prep. from vitamin-D_2 slightly modified) is hydrolysed (aq. $H_2C_2O_4$) to an isomeride (**II**) (*semicarbazone*, m.p. 202°, $[\alpha]_D^{18}$ +3·6° in $CHCl_3$). Since crude (**I**) is isomerised by H_2SO_4 or $C_5H_{11}\cdot OK$ to (**II**), (**I**) and (**II**) are the *trans*- and *cis*-derivative, respectively. Hydrogenation (Pd-black, MeOH) of (**II**) gives its side-chain H_2-derivative (*semicarbazone*, m.p. 207°, $[\alpha]_D^{15}$ +37° in $CHCl_3$), different from that (Windaus *et al.*, A., 1936, 69) of (**I**). Accordingly rings C and D of the vitamins-*D* and normal steroids are *trans*.
H. B.

Deuterocholesterol. K. Bloch and D. Rittenberg (*J. Biol. Chem.*, 1943, **149**, 505—507).—No exchange occurs when suspensions of cholesterol (**I**) in D_2O, with or without EtOH, are heated up to 200° in presence of active Pt. Se effects slow introduction of D at 110—230°. Addition of AcOH (containing 60 at.-% D) to the system (**I**)–D_2O–Pt at 127° results in D being introduced into the side-chain and ring system of (**I**); simultaneous destruction of (**I**) occurs, and the rate of deuteration is roughly parallel to the extent of decomp. The deuterocholesterol, m.p. 148°, $[\alpha]_D^{26}$ −3·9° in $CHCl_3$, 4·16 at.-% D, is converted into the cholesteryl chloride, and thermally degraded; the H in the resulting mixture of *iso*-octane and -octene shows a higher level of D than that of the hydrocarbon $C_{19}H_{30}$, although more isotope was actually present in an equimol. amount of the latter.
A. T. P.

Marine products. XIII. Sterols from various marine invertebrates. W. Bergmann, M. J. McLean, and D. Lester (*J. Org. Chem.*, 1943, **8**, 271—282).—The broken material is extracted successively with $COMe_2$ and Et_2O, the solutions are evaporated, and the residues are hydrolysed (20% KOH in 70% EtOH). The solution is extracted with Et_2O and the sterols are pptd. with digitonin, the digitonides being subsequently decomposed with C_5H_5N. The amount of 7-dehydrosterols present in the crude sterol mixture is determined spectrographically. The homogeneity of the crude sterol is tested by recrystallisation and the prep. of derivatives. When the presence of a mixture is indicated, attempts are made to bring about a separation of the components by means of solubility differences of their bromides. The staghorn coral, *Madrepora cervicornis*, contains a mixture of sterols which are difficult to separate; one of the components gives an acetate, m.p. 176°. The sterols of *Meandra areolata* (*A*) consist of cholesterol (**I**) and a sterol showing considerable similarity to clionasterol (**II**). The gorgonia, *Xiphogorgia* sp., contains a mixture of sterols similar to that present in (*A*). *Plexaura flexuosa* contains among other unidentified sterols a mono-unsaturated compound, *gorgosterol*, $C_{30(31)}H_{32(34)}O$, m.p. 184—185°, $[\alpha]_D^{26}$ −45° (*acetate*, m.p. 152·6°, becomes opalescent at 140°, $[\alpha]_D^{26}$ −56·3°; 3 : 5-*dinitrobenzoate*, m.p. 227·5—228·5°, $[\alpha]_D^{26}$ −20·3°). The crude sterols of three varieties of sea urchin consist of (**I**) and of a sterol of the order C_{29} which is similar to sterols of the sitosterol or (**II**) type. The sea cucumber, *Holothurio princepo*, contains a mixture of sterols similar to that in starfish. The horseshoe crab, *Limulus polyphemus*, contains (**I**) and a sterol similar to plant sterols or (**II**). The mixture from the tunicate, *Styela plicata*, contains only (**I**) and some 7-dehydrosterol. The singificance of these results is discussed. M.p. are corr. and [α] are in $CHCl_3$.
H. W.

Conversion of sterols into aromatic compounds. V. Aromatisation of ring A by migration of methyl. H. H. Inhoffen and G. Zühlsdorff (*Ber.*, 1941, **74**, [*B*], 604—616).—Partly an account of work previously abstracted (A., 1939, II, 17). $\Delta^{1:4}$-Cholestadien-3-one is converted into the phenol, $C_{27}H_{42}O$ (**I**), m.p. 145—146° (*loc. cit.*), at 300—320°/3 hr. or by Ac_2O–conc. H_2SO_4 at room temp. or Ac_2O–HI (*d* 1·96) at 100° (bath). (**I**) gives a dinitrobenzoate (**II**), m.p. 179—180°, Me ether, m.p. 104—105°, benzeneazo-, m.p. 182—183°, and 2(or 4)-Br_1-derivative (**III**), m.p. 83—84° [*dinitrobenzoate*, m.p. 179—180°, raised to 200—201° when admixed with (**II**)]. (**III**) is reduced (Na, aq. EtOH) to (**I**). Coupling of (**I**) with Na p-nitrophenyl*anti*diazotate in AcOH affords its p-*nitrobenzeneazo*-derivative, m.p. 208—209°, but (**III**) similarly gives the 4 (or 2)-p-*nitrobenzeneazo*-2(or 4)-*acetoxy*-derivative, m.p. 229—230° [acetylated (Ac_2O–C_5H_5N) to the corresponding 2(or 4) : 3-*diacetate*, m.p. 227—228°], of (**I**). $\Delta^{1:4}$-Androstadien-17-ol-3-one with Ac_2O–conc. H_2SO_4 at room temp. affords 1-*methylœstradiol diacetate*, m.p. 135—136°, hydrolysed by AcOH–30% H_2SO_4 at 100° (bath) to the 17-*monoacetate*, m.p. 199—200° (œstradiol 17-monoacetate can be similarly prepared), and by 5% MeOH–KOH to 1-*methylœstradiol* (**IV**), m.p. 231—232°, $[\alpha]_D^{22}$ +179·5° in dioxan [*Me ether*, m.p. 114°; ? *benzeneazo*-derivative, m.p. 196—197° (*diacetate*, m.p. 193—194°)]. Absorption spectra for most of the compounds are given. (**IV**) has no œstrogenic activity.
H. B.

Steroids with ethylenic linkings between quaternary carbon atoms. I. Oxidation of α-ergostenyl acetate. II. Structure of α-dihydroergosterol. H. E. Stavely and G. N. Bollenback (*J. Amer. Chem. Soc.*, 1943, **65**, 1285—1289, 1290—1294).—I. Structures ascribed below are proved by the reactions and absorption spectra in EtOH. They provide proof that α-ergosterol has an ethylenic linking at position 8 : 14 and that α-dihydroergosterol is $\Delta^{8:22}$-ergostadien-3-ol. α-Ergostenyl acetate (**I**) and CrO_3 in AcOH–C_6H_6 at room temp. give (cf. Reindel, A., 1929, 61; Heilbron, A., 1932, 845) acids and a mixture of neutral products, chromatography of which yields 3-*acetoxy*-$\Delta^{8(14)}$-*ergosten*-15-*one* (7%), m.p. 170°, $[\alpha]_D^{23}$ +110±3° [absorption max. at 259 mμ. (ε 13,300); *semicarbazone*, m.p. 199—200°; 2 : 4-dinitrophenylhydrazone, m.p. 220° (decomp.); with Pd–H_2 (2·1 mols.) in AcOH (not EtOH) gives (**I**) (80%)], 8 : 14-*epoxy*-3-*acetoxyergostan*-7-*one* (**II**) (18%), m.p. 134°, $[\alpha]_D^{23}$ −83±3° (gives CO_2 derivatives only after rupture of the epoxy-ring; no absorption at >230 mμ.), 8 : 14-*epoxy*-3-*acetoxyergostan*-15-*one* (**III**) (2%), m.p. 208—210°, $[\alpha]_D^{23}$ −6·0±1·5° (no absorption at >230 mμ. or 2 : 4-dinitrophenylhydrazone), (?) 3-*acetoxyergostane*-8 : 14-*diol*-7 : 15-*dione*, m.p. 201—202°, $[\alpha]_D^{23}$ −69±2°, and a mixture, which, by hydrolysis by boiling conc. HCl–EtOH, acetylation, and then chromatography, yields (?) dehydroergostenyl acetate, m.p. 138°, $[\alpha]_D^{23}$ −29°, 3-*acetoxy*-$\Delta^{8(14)}$-*ergostene*-7 : 15-*dione* (2%), m.p. 149—151°, $[\alpha]_D^{24}$ −24±2° [absorption max. at 255 mμ. (ε 5000); *pyridazine* derivative, m.p. 220—225° (decomp.)], and 3-*acetoxy*-$\Delta^{8(14):9(11)}$-*ergostadien*-7-*one* (**IV**), m.p. 177°, $[\alpha]_D^{24}$ −22±2° [absorption max. at 298 mμ. (ε 5100); 2 : 4-dinitrophenylhydrazone, m.p. 223° (decomp.)]. Conc. HCl–EtOH at 100° hydrolyses (**III**) to 3-*acetoxy*-$\Delta^{8(14)\cdot 9(11)}$-*ergostadien*-15-*one*, m.p. 155° [absorption max. at 307 mμ. (ε 10,700); an oil is also formed], and (**II**) to (**IV**) (m.p. 176—178°), which with H_2–Pd in EtOH gives 3-*acetoxy*-$\Delta^{8(14)}$-*ergosten*-7-*one* (**V**), m.p. 155°, $[\alpha]_D^{22}$ −62±3° [absorption max. at 262 mμ. (ε 9,800)].

II. γ- is not isomerised to α-cholestenol by Pd in N_2, so that the corresponding stability of α-dihydroergosterol is without significance. Chromatography of the neutral products formed from α-dihydroergosteryl acetate by CrO_3 in AcOH–C_6H_6 at room temp. gives 8 : 9- (**VI**) (16%), m.p. 223—225°, $[\alpha]_D^{24}$ −46±2° [no absorption at >230 mμ.; 2 : 4-dinitrophenylhydrazone, m.p. 209° (decomp.)], and 8 : 14-*epoxy*-3-*acetoxy*-Δ^{22}-*ergosten*-7-*one* (**VII**) (18%), m.p. 155°, $[\alpha]_D^{24}$ −99±3° [no absorption at >230 mμ.; 2 : 4-dinitrophenylhydrazone, m.p. 218° (decomp.)], and a mixture, which by hydrolysis by hot conc. HCl–EtOH gives ketones (Girard's reagent *T*), separated by chromatography (after acetylation) into 3-*acetoxy*-$\Delta^{8(14):9(11):22}$-*ergostatrien*-7-*one* (**VIII**), m.p. 187—189°, $[\alpha]_D^{24}$ −47±2·5° [absorption max. at 300 mμ. (ε 5000); 2 : 4-dinitrophenylhydrazone, m.p. 222° (decomp.)], and 3-*acetoxy*-$\Delta^{8(9):22}$-*ergostadien*-7-*one* (**IX**) (4%), m.p. 206—208°, $[\alpha]_D^{24}$ −53±2° [absorption max. at 252 mμ. (ε 10,100)]. Conc. HCl–EtOH converts (**VI**) or (**VII**) into (**VIII**). Hydrogenation (Pd) in EtOH converts (**VI**) into 8 : 9-*epoxy*-3-*acetoxyergostan*-7-*one*, m.p. 211°, $[\alpha]_D^{23}$ −38±3°, (**VII**) into (**II**) (m.p. 132—133°, $[\alpha]_D^{23}$ −77±4°), (**VIII**) into (**V**), and (**VIII**) or (**IX**) (in AcOH) into (**I**) and 3-*acetoxyergostan*-7-*one*, m.p. 183—184°, $[\alpha]_D^{23}$ −36±1·5° [*semicarbazone*, m.p. 225—228°; 2 : 4-dinitrophenyl-

hydrazone, m.p. 216° (decomp.)], hydrolysed to *ergostan-3-ol-7-one*, m.p. 154°. (**V**) is not isomerised by conc. HCl–EtOH. [α] (both parts) are in $CHCl_3$. R. S. C.

Saturated and unsaturated steroid ketones.—See B., 1943, III, 255.

Cyclic ketals of 3-keto-17-hydroxy-17-acetylenyl*cyclo*pentanoperhydrophenanthrenes.—See B., 1943, III, 255.

Compound *C*, $C_{21}H_{32}O_3$, m.p. 268°, $[\alpha]_D$ −48° (±2°) to −39° (±2°) in C_5H_5N [oxime, m.p. 238—239° (decomp.)] (? testalolone), and substance *E*, $C_{13}H_{24}O_2N_2$, m.p. 270—280°, $[\alpha]_D$ +3·5°±3·5° in $CHCl_3$, from swine testis.—See A., 1943, III, 742.

Sterols. CLVIII. Sapogenins. LXX. Structure of lilagenin. R. E. Marker, R. B. Wagner, C. H. Ruof, D. P. J. Goldsmith, and P. R. Ulshafer (*J. Amer. Chem. Soc.*, 1943, **65**, 1434).—*Lilium humboldtii* yields lilagenin, new formula $C_{27}H_{42}O_4$ (cf. A., 1941, II, 50), m.p. 242—246° (diacetate, m.p. 153—155°), which absorbs Br slowly and with 2N-HCl–EtOH gives yuccagenin (A., 1943, II, 304), from which it thus differs only in the configuration of the side-chain. R. S. C.

Saponins and sapogenins. XXII. Composition and constitution of bethogenin. C. R. Noller and M. R. Parusch (*J. Amer. Chem. Soc.*, 1943, **65**, 1435—1436).—Bethogenin (**I**) is shown to be $C_{28}H_{44}O_4$ (cf. A., 1943, II, 99) by analysis of (**I**), its acetate, and benzoate. The additional C is present as Me, possibly as enol Me ether, since, although NH_2OH–EtOH–C_5H_5N introduces 2 N, (**I**) has no CO absorption [rise from 3500 to 2300 A., inflexion at 2850 A. (ε 0·3)] until after treatment with HBr–AcOH [then a max. at 2850 A. (ε 1·77)]. R. S. C.

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Dependence of optical rotatory power on chemical constitution. XXI. Rotatory dispersion of stereoisomeric hydroxyphenylaminomethylenecamphors and their acetylated and benzoylated derivatives. B. K. Singh and S. C. Sen (*J. Indian Chem. Soc.*, 1943, **20**, 1—10).—d- and l-, m.p. 180—182°, $[\alpha]^{25}_{5461}$ ±436·2° in EtOH (*Ac*, m.p. 131—132°, $[\alpha]^{25}_{5461}$ +266·3° and −267·8° in EtOH, and Bz derivative, an oil), and dl-o-, m.p. 164—165° (*Ac* derivative, m.p. 140—142°), d- and l-, m.p. 165°, $[\alpha]^{25}_{5461}$ +417·1° and −415·9° in EtOH (*Ac*, m.p. 140—142°, $[\alpha]^{25}_{5461}$ ±181·1° in EtOH, and Bz derivative, an oil)], and dl-m-, m.p. 165°, and d- and l-, m.p. 158—160°, $[\alpha]^{25}_{5461}$ +450·5° and −450·0° in EtOH (*Ac*, m.p. 220—222°, $[\alpha]^{25}_{5461}$ ±190·3° in EtOH, and *Bz* derivative, m.p. 236—237° $[\alpha]^{25}_{5461}$ ±6·20° in EtOH), and dl-p-*hydroxyanilinomethylenecamphor*, m.p. 150—152° (*Ac* derivative, m.p. 195—197°), are prepared from hydroxymethylenecamphor in MeOH and NH_2·C_6H_4·OH in AcOH at room temp. [α] of these for 6 λλ in 5 solvents have been determined [and can be expressed as $k/(\lambda^2 - \lambda_0^2)$] and compared with vals. for anilino- and methyl-, chloro-, bromo-, and iodo-anilino-methylenecamphor. The influence on [α] of the nature and position of substituents, the nature of the solvent, and of acetylation and benzoylation is discussed. A. LI.

Cardanol derivative.—See B., 1943, II, 212.

VI.—HETEROCYCLIC.

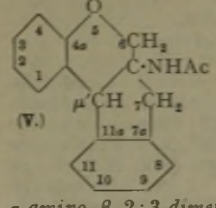
Tetrahydrofurfuryl ethers.—See B., 1943, II, 283.

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

Condensations by sodium. XXVII.—See A., 1943, II, 345.

Vitamin-*E*. XLI. Synthesis of α-chloro-γηλο-tetramethylhexadecan-γ-ol and its condensation with trimethylquinol to form α-tocopherol. L. I. Smith and J. A. Sprung (*J. Amer. Chem. Soc.*, 1943, **65**, 1276—1283; cf. A., 1943, II, 240).—Pure α-tocopherol is synthesised from citral in 4—5% over-all yield. Adding Na and then EtBr to $[CH_2]_3(OH)_2$ in xylene at 115—120° and then heating at 120° gives 58—62% of OEt·$[CH_2]_3$·OH, b.p. 157—163° (38% obtained from Cl·$[CH_2]_3$·OH by NaOEt). Similarly are prepared OMe·$[CH_2]_3$·OH (64% obtained in absence of xylene), b.p. 148—149°, and CH_2Ph·O·$[CH_2]_3$·OH (73%), b.p. 145—150°/13 mm. Thence PBr_3 in Et_2O at >60° gives OR·$[CH_2]_3$·Br, in which R = Et (55—65%), b.p. 147—150°/760 mm., 86—87°/100 mm., and Me (27%), b.p. 131—133°; PBr_3 in $NPhMe_2$ at 0° and then 50° gives *γ-benzyloxy*-n-*propyl bromide* (34%), b.p. 130—132°/8 mm.; PCl_3 in C_5H_5N at 0° and then 75° gives OEt·$[CH_2]_3$·Cl (67%), b.p. 125—128°. Saturating freshly distilled COMe·CH:CH_2 with dry HCl at 0° and keeping at room temp. gives 67% of Cl·$[CH_2]_3$·COMe (**I**), b.p. 48—50°/15 mm., converted by quinoline or KOH–EtOH into impure mixed dienes, b.p. 65—75°, which give no solid product with 2 : 3 : 5 : 1 : 4-$C_6HMe_3(OH)_2$ (**II**). For the following synthesis ψ-ionone (**III**) should be prepared from purified citral and $COMe_2$ (Russell *et al.*, *Org. Syntheses*, 1943, **23**, 78) and purified by way of the $NaHSO_3$ compound (45% yield), otherwise yields drop greatly. Adding OR·$[CH_2]_3$·Br and (**III**) to Mg in Et_2O, the reaction having been started by a trace of I or EtBr, gives *α-ethoxy*- (52%), b.p. 163—165°/3 mm. (the chloride gives 46%), impure α-methoxy- [53·3% from impure (**III**)], b.p. 150—160°/3 mm., and α-benzyloxy-δθμ-trimethyl-$\Delta^{\gamma\epsilon\eta\lambda}$-n-tridecatetraene (49%), b.p. 210—220° (some decomp.)/3 mm. H_2–Raney Ni at 125—150°/2000 lb. then yields *α-ethoxy-δθμ-trimethyl*-n-*tridecane* (82%), b.p. 138—140°/3 mm. (impurities hinder the hydrogenation), converted [best (96%) by dry HBr at 150° in a sealed tube] into *δθμ-trimethyl*-n-*tridecyl bromide* (**IV**), b.p. 138—140°/3 mm. The saturated Me ether (similarly prepared) reacts more readily, the CH_2Ph ether still more so. (**IV**), freed from alcohol by H_2SO_4, yields a Grignard reagent in Et_2O, which with MeCHO at 0° and then the b.p. gives *ζ-ξ-trimethyl*-n-*pentadecan-β-ol* (70%), b.p. 150—155°/3 mm., oxidised by $Na_2Cr_2O_7$–AcOH–H_2SO_4–C_6H_6 at 40°–50° to the corresponding ketone ("phytol ketone") (75%), b.p. 150—152°/3 mm., identical with that derived from natural phytol. *α-Chloro-γ-methyl*-n-*pentan-γ-ol* [prep. by adding (**I**) to MgEtBr–Et_2O at 0°; 51% yield], b.p. 104—105°/50 mm., (**II**), and $ZnCl_2$ in boiling AcOH give 6-hydroxy-2 : 5 : 7 : 8-tetramethyl-2-ethylchroman. n-$C_{12}H_{25}Br$ with CH_2:CH·COMe and Mg gives a gel, but with Mg and (**I**) gives impure α-chloro-γ-methyl-n-pentadecan-γ-ol (34·5%), b.p. 165—170°/3 mm. The Grignard reagent from impure (**IV**) with (**I**) in Et_2O at 0° and then the b.p. gives *α-chloro-γηλο-tetramethyl*-n-*hexadecan-γ-ol* (38%), b.p. 173—175°/2 mm., which with (**II**) and $ZnCl_2$ in AcOH at 115° and then the b.p. gives 70% of α-tocopherol (fully identified). Br·$[CH_2]_3$·OAc (prep. from Br·$[CH_2]_3$·OH by AcCl) reacts sluggishly with (**III**) and Mg in Et_2O and gives only polymerides. R. S. C.

Brazilin and hæmatoxylin. XVII. Synthesis of μ-aminochromindane. P. Pfeiffer and H. Epler (*Annalen*, 1940, **545**, 263—286).—OPh·CH_2·O·CH_2Ph (**I**), b.p. 167°/1·5 mm., m.p. 43°, is not readily obtained from OPh·CH_2·COCl and CH_2Ph·MgCl but is prepared readily from the Grignard reagent and OPh·CH_2·CN. It is not brominated in AcOH or CCl_4 alone but in presence of $CaCO_3$ affords *CHPhBr OPh·CH₂ ketone*, m.p. 83—90° (slight decomp.), which is not converted into an oxazole derivative by NH_2Bz in presence of NaOAc or altered by $AlCl_3$ in Et_2O. (**I**) when heated under CO_2 at 80°/40 atm. with KCN and $(NH_4)_2CO_3$ in aq. EtOH affords 5-benzyl-5-phenoxymethylhydantoin, m.p. 197°, slowly hydrolysed by 40% KOH at 175° to *α-amino-β-phenoxy-β′-phenyl*iso*butyric acid* (**II**) (+AcOH), m.p. ~210° (decomp.) (*hydrochloride*, decomp. 240°), purified through the *Cu* salt, $C_{32}H_{32}O_6N_2Cu$. The *Ac* derivative (**III**), m.p. 201·5°, of (**II**) is transformed by short treatment with $AlCl_3$–NaCl at 160° into 3-*acetamido*-3-*benzylchromanone* (**IV**), m.p. 148°, in very poor yield. Much better results are obtained by controlled treatment of (**III**) with syrupy H_3PO_4 whereby also an unidentified *substance*, m.p. 183°, and a *fulvene* derivative, $C_{16}H_{10}O$, m.p. 198°, are formed. (**IV**) does not give an oxime. (**IV**) cannot be reduced by AcOH–HI but is converted by Na–Hg in an aq. alcoholic phosphate buffer under polarographic control into 3-*acetamido*-3-*benzylchromanol*, *α-form*, m.p. 146·5° (also +1Et_2O), *β-form*, m.p. 219°. Either alcohol is transformed by syrupy H_3PO_4 at >140° into *μ-acetamidochromindane* (**V**), m.p. 193°. Hydrolysis of (**V**) is difficult and best effected with HCl in aq. EtOH at 120°, thereby yielding *μ-aminochromindane hydrochloride*. 3 : 4-Dimethoxybenzyl 2 : 3-dimethoxyphenoxymethyl ketone is transformed by KCN and $(NH_4)_2CO_3$ in aq. EtOH under CO_2 at 97°/8 atm. into 5-3″ : 4″-*dimethoxybenzyl*-5-2′ : 3′-*dimethoxyphenoxymethylhydantoin*, m.p. 211°, which is hydrolysed by boiling 20% KOH to *α-amino-β-2 : 3-dimethoxyphenoxy-β′-3″ : 4′-dimethoxyphenyl*iso*butyric acid*, m.p. 184·5° (also +1H_2O). This is converted by HCl and $NaNO_2$ into the corresponding α-OH-acid (+1H_2O, m.p. 107—113°), also obtained by action of fuming HCl–AcOH at room temp. and then at the b.p. on the α-OH-nitrile. H. W.



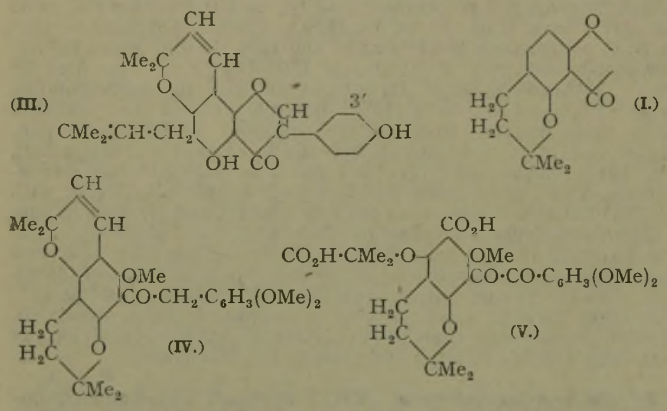
(V.)

Xanthhydrol as a reagent for the characterisation of primary amides. R. F. Phillips and B. M. Pitt (*J. Amer. Chem. Soc.*, 1943, **65**, 1355—1357).—Xanthhydrol + an amide in AcOH–EtOH–H_2O at 85° or AcOH at room temp. of 100° give ~55% (more in AcOH alone) of 9-acylamidoxanthens, useful for identification of the amide (cf. Adriani, A., 1916, i, 155). Di- and tri-chloroacet-, salicyl-, ox-, and picr-amide, guanidine, and cyanoguanidine do not react. CH_2Cl·CO·NH_2 reacts slowly. HCO·NH_2 sometimes, but not always, gives the *compound*, m.p. 184°. NHPhAc does not react, so that probably a CO·NH_2 is essential. 9-Acet-, m.p. 238—240°, -propion-, m.p. 210—211°, -n-, m.p. 185—187°, and -iso-*butyr*-, m.p. 210—211°, -n-, m.p. 166—167°, and -*iso*-valer-, m.p. 182—183°, -n-, m.p. 159—160°, and -iso-*hex*-, m.p. 159—160°, -n-*hept*-, m.p. 154—155° (153—154°), -n-*oct*-, m.p. 147·5—148·5°, -*palmit*-, m.p. 140—142°, -*stear*-, m.p. 139—141°, -phenylacet-, m.p. 194—195°, -*β-phenylpropion*-, m.p. 188—189°, -*α-phenylbutyr*-, m.p. 157—158°, -*chloroacet*-, m.p. 208—209°, -*cyanoacet*-, m.p. 222—223°, -benz-, m.p. 222·5—223·5°, -o-, m.p. 199—200·5°, and -p-*tolu*-, m.p. 224—225°, -p-*nitrobenz*-, m.p. 231—233°, and -2′-*furo*-, m.p. 209—211°, -*amidoxanthen*, 9-*succin*-, m.p. 245—247°, and 9-*phthal*-, m.p. 176—177°, -*imidoxanthen* are prepared. R. S. C.

Crystalline complexes of arsenic, antimony, and bismuth trichlorides with dioxan.—See A., 1943, I, 282.

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

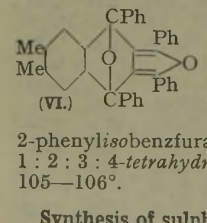
Structures of osajin and pomiferin. M. L. Wolfrom, G. F. Johnson, W. D. Harris, and B. S. Wildi (*J. Amer. Chem. Soc.*, 1943, **65**, 1434—1435).—Fusion of *iso*osajin (**I**) or *iso*pomiferin (**II**) with alkali (no details) gives $COMe_2$ and 2 : 2-dimethylchroman-5 : 7-diol. Osajin (**III**) and (**I**) thus have the annexed structure. Pomiferin and



(**II**) are the corresponding 3′-OH-derivatives. *iso*Pomiferitin Me_3 ether (**IV**) and $KMnO_4$ give an *acid* (**V**), m.p. 204—205° (decomp.) (*Me*$_2$ ester, m.p. 133·5—134°). R. S. C.

Dyes derived from acenaphthenequinone. VIII. (6-Methyl)thionaphthen-acenaphthylene-indigos. S. K. Guha (*J. Ind. Chem. Soc.*, 1943, **20**, 37—39).—1-(6-*Methyl*)*thionaphthenacenaphthyleneindigo*, m.p. 304°, is formed from acenaphthenequinone and 2-hydroxy-6-methylthionaphthen in boiling AcOH–conc. HCl. 1-(6-*Methyl*)-*thionaphthen*-8′-(3′-*chloro*)-, m.p. 274°, -8′-(3′-*bromo*), m.p. 264—265°, and -8′-(1′-*methoxy*)-, m.p. 300°, -*acenaphthyleneindigos* are prepared similarly. All dye cotton red from a hyposulphite vat and wool red from an acid bath. 6 : 6′-*Dimethylthioindigo* has been prepared from 2-hydroxy-6-methylthionaphthen by oxidation with $K_3Fe(CN)_6$. It dyes cotton and wool red from hyposulphite and acid baths respectively. J. H. Ba.

Diene synthesis with an *iso*benzthiophen. C. F. H. Allen and J. W. Gates, jun. (*J. Amer. Chem. Soc.*, 1943, **65**, 1283—1285).—$(CH_2{:}CPh)_2$ and *trans*-$(CHBz{:})_2$, much better in EtOH than in xylene, give 4 : 5-*dibenzoyl*-1 : 2-*diphenyl*-Δ^1-cyclo*hexene* (**I**), m.p. 154—155°, which with S at 200—220° gives 2 : 5 : 4′ : 5′-*tetraphenyl*-3 : 4-*benzthiophen* ["1 : 3 : 5 : 6-*tetraphenyl*iso*benzthiophen*"] (60—70%), m.p. 227—228°. This is yellow, has a strong greenish fluorescence (solid and solution), does not add MeI, and gives no sulphone, but with CrO_3 or HNO_3 in AcOH gives 4 : 5-*dibenzoyl*-1 : 2-*diphenylbenzene* [4 : 5-*dibenzoyl*-o-*terphenyl*] (**II**), m.p. 196—197°, and with $(CH{\cdot}CO)_2O$ (**III**) at the b.p. gives 1 : 4-endo*thio*-1 : 4 : 6 : 7-*tetraphenyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-2 : 3-*dicarboxylic anhydride* (**IV**), m.p. 245° (decomp.). (**IV**) dissociates at the m.p., does not react with *p*-$C_6H_4Me{\cdot}SO_3Me$ at 200°, MeI in $MeNO_2$ or at 150°, or Pb salts, but with boiling HCl–xylene gives H_2S and an ester, hydrolysed by boiling aq. NaOH to 1 : 4 : 5 : 7-*tetraphenylnaphthalene*-2 : 3-*dicarboxylic acid* (**V**), m.p. 310° (decomp.) [*anhydride*, m.p. 310° (decomp.)]. With a little H_3PO_4 in Ac_2O at 110—120°, (**I**) gives 1 : 2 : 4 : 5-*tetraphenyl*-3 : 6-*dihydrobenzfuran*, m.p. 276—277°, converted by Br–NaOAc–AcOH into (**II**), which is also obtained from (**IV**) by Br. Zn dust reduces (**II**) in boiling AcOH or NaOH–EtOH to 1 : 2 : 4 : 5-*tetraphenyl*iso*benzfuran*, m.p. 286—287° (and a white substance, m.p. 248—250°), converted by (**III**) in hot C_6H_6 into 1 : 4-*epoxy*-1 : 4 : 6 : 7-*tetraphenyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-2 : 3-*dicarboxylic anhydride*, m.p. 246—247° (yellow owing to dissociation), which with dry HCl–MeOH and then aq. NaOH gives (**V**). 1 : 2-Diphenyl-4 : 5-dimethyl*iso*benzfuran and *trans*-$(CHBz{:})_2$ in boiling EtOH give 1 : 4-*epoxy*-2 : 3-*dibenzoyl*-1 : 4-*diphenyl*-6 : 7-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 169°, dissociated (mol. wt.) in boiling C_6H_6 and reduced by Zn dust in boiling AcOH to 1′ : 4′-*epoxy*-2 : 5 : 1′ : 4′-*tetraphenyl*-6′ : 7′-*dimethyl*-1′ : 4′-*dihydronaphtha*-2′ : 3′-3 : 4-*furan* (**VI**), m.p. 194—195°. With *p*-$O{:}C_6H_4{:}O$, (**VI**) gives an *adduct*, $C_{44}H_{32}O_4$, m.p. 145—146°, and with (**III**) gives, by hydrolysis etc., an *acid*, $C_{42}H_{32}O_6$, m.p. 271—272°, not reconverted into (**VI**) by $Zn(OAc)_2$ or AcOH. 1-Benzoyl-2-phenyl*iso*benzfuran and (**III**) give 1 : 4-*epoxy*-1-*benzoyl*-4-*phenyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-2 : 3-*dicarboxylic anhydride*, m.p. 105—106°. R. S. C.



Synthesis of sulphanilamide derivatives of thianthren. P. C. Guha and V. M. Dokras (*Current Sci.*, 1943, **12**, 119).—Hydrolysis (HCl) of 2 : 6-diacetamido- yields 2 : 6-diamino-thianthren, m.p. 120° (*p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2$ derivative, decomp. 180°). F. R. G.

Thioketonic esters.—See A., 1943, II, 327.

Piperidinoethyl dodecyl ether.—See B., 1943, II, 273.

Double intramolecular alkylation. V. Prelog. **I. Alkyl derivatives of 1-aza*dicyclo*-[1 : 2 : 2]-heptane.** V. Prelog, S. Heimbach, and A. Rezek. **II. Synthesis of 2-methyl- and 2-ethyl-quinuclidine.** V. Prelog, S. Heimbach, and E. Cerkovnikov. **III. Synthesis of 3-methyl- and 3-ethyl-quinuclidine.** V. Prelog, N. Šoštarič, and E. Gustak. **IV. 1-Aza*dicyclo*-[0 : 5 : 5]-dodecane.** V. Prelog and B. Schönbaum. **V. 2-Substituted quinuclidine derivatives.** V. Prelog and E. Cerkovnikov (*Annalen*, 1940, **545**, 229—242, 243—247, 247—256, 256—259, 259—262).—I. Tetrahydro-4-pyrone, $CHMeBr{\cdot}CO_2Et$, and Zn turnings in boiling C_6H_6 afford *Et* α-4-*hydroxy*-4-*tetrahydropyranylpropionate*, b.p. 100°/0·06 mm., dehydrated by boiling Ac_2O containing a little conc. H_2SO_4 to α-4-*tetrahydropyranylidenepropionate*, b.p. 117—120°/11 mm., which is hydrogenated to *Et* α-4-*tetrahydropyranylpropionate*, b.p. 116—117°/13 mm.; the free *acid* (**I**) has b.p. 129—130°/0·4 mm., m.p. 54—55°. (**I**) is transformed by NaN_3 and H_2SO_4 in presence of $CHCl_3$ into α-*amino*-α-4-*tetrahydropyranylethane* (**II**), b.p. 81°/13 mm., 78°/11 mm. (*picrate*, m.p. 152—153°), also obtained by reduction (Na–EtOH) of *tetrahydropyranyl Me ketoxime*, m.p. 54—55°. The hydrobromide of (**II**) is transformed by 69% HBr at 100° into α-*bromo*-δ-*amino*-γ-β′-*bromoethylpentane hydrobromide*, m.p. 147°, converted by gradual addition of its aq. solution to 0·1N-NaOH at 50° into 7-methyl*dicyclo*-[1 : 2 : 2]-aza-1-heptane (**III**), b.p. 43°/11 mm., also obtained from αδ-dibromo-γ-β′-bromoethylpentane and 20% NH_3–MeOH at 120—130°. (**III**) gives a *hydrochloride*, m.p. 275° (decomp.), *platinichloride*, m.p. 231° (decomp.), *picrate*, m.p. 290—293°, *picrolonate*, m.p. 225—226°, and *methiodide*, m.p. 325°. A similar series of experiments starting from $CHBrEt{\cdot}CO_2Et$ gives *Et* α-4-*hydroxy*-4-*tetrahydropyranyl*-n-*butyrate*, b.p. 113—117°/0·2 mm., *Et* α-4-*tetrahydropyranylidene*-n-*butyrate*, b.p. 124—125°/10 mm., *Et* α-4-*tetrahydropyranyl*-n-*butyrate*, b.p. 119—120°/10 mm., and the corresponding *acid* (**IV**), b.p. 125—130°/0·04 mm. (*anilide*, m.p. 155°). Et_2 4-tetrahydropyranylmalonate, EtI, and NaOEt afford *Et*$_2$ *ethyl*-4-*tetrahydropyranylmalonate*, b.p. 162—164°/13 mm., hydrolysed to the dicarboxylic *acid*, m.p. 174—175°, which is decarboxylated at 200° to (**IV**). Conc. H_2SO_4 and NaN_3 convert (**IV**) at 50° into α-*amino*-α-4-*tetrahydropyranylpropane*, b.p. 100—101°/15 mm. (*picrate*, m.p. 168°; *hydrobromide*, m.p. 167—168°), also obtained by reduction of 4-tetrahydropyranyl Et ketoxime and converted by 68% HBr at 100° into α-*bromo*-δ-*amino*-γ-β′-*bromoethylhexane hydrobromide*, m.p. 156—157°, which with 0·1N-NaOH at 50° affords 7-*ethyl*dicyclo-[1 : 2 : 2]-*aza*-1-*heptane* [*hydrochloride*, m.p. 239—240°; *platinichloride*, m.p. 242° (decomp.); *picrate*, m.p. 198—199°; *picrolonate*, m.p. 233—233·5°; *styphnate*, m.p. 170°; *methiodide*, m.p. 271° (decomp.)]. This base is not identical with that described previously (A., 1939, II, 457); the latter substance does not appear to be homogeneous and probably results from $CHEtBr{\cdot}CH([CH_2]_2{\cdot}Br)_2$ and NH_3 by an abnormal reaction. Similarly $CMe_2Br{\cdot}CO_2Et$ yields *Et* α-4-*hydroxy*-4-*tetrahydropyranyl*-iso*butyrate*, b.p. 100—110°/0·06 mm., *Et* α-4-*tetrahydropyranylidene*-iso*butyrate*, b.p. 124—126°/12 mm., *Et* α-4-*tetrahydropyranyl*iso*butyrate*, b.p. 118—122°/13 mm., and the corresponding *acid*, m.p. 90—91. This is converted into β-*amino*-β-4-*tetrahydropyranylpropane*, b.p. 98—100°/16 mm., the *hydrobromide*, m.p. 203°, of which is transformed by 68% HBr at 100° into α-*bromo*-δ-*amino*-δ-*methyl*-γ-β-*bromoethylpentane hydrobromide*, m.p. 169—170°, from which is derived 7 : 7′-*dimethyl*dicyclo-[1 : 2 : 2]-*aza*-1-*heptane* [*hydrochloride*, m.p. 299—300° (decomp.); *platinichloride*, m.p. 233—234° (decomp.); *picrate*, carbonises at >290°]; the $PhSO_2Cl$ used in purifying the crude base forms 1-*benzenesulphonyl*-2 : 2-*dimethyl*-3-*vinylpyrrolidine* or 1-*benzenesulphonyl*-4-iso*propylidenepiperidine*, m.p. 83°.

II. 4-*Tetrahydropyranylacetyl chloride*, b.p. 110—111°/15 mm., is converted by ZnMeI into 4-tetrahydropyranylacetone, b.p. 102—105°/10 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 135—136°); the corresponding *oxime*, b.p. 150°/14 mm., m.p. 37—38°, is reduced (Na–EtOH) to β-*amino*-α-4-*tetrahydropyranylpropane*, b.p. 93°/12 mm. (*picrate*, m.p. 184°), which is transformed by 70% HBr at 100° into α-bromo-ε-amino-γ-β′-bromoethylhexane hydrobromide (corresponding *picrate*, m.p. 150—150·5°). This with 0·1N-NaOH at 50° yields 2-*methyl*dicyclo-[2 : 2 : 2]-*aza*-1-*octane* (2-*methylquinuclidine*), b.p. 161° (*hydrochloride*, m.p. 327°; *platinichloride*, m.p. 216—217°; *picrate*, m.p. 286°; *styphnate*, m.p. 208·5°; *methiodide*, m.p. 346·5° (decomp.); *picrolonate*, m.p. 226°). Similarly, α-4-*tetrahydropyranylbutan*-β-*one*, b.p. 109°/9 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 117—118°), gives a non-cryst. *oxime*, b.p. 148—154°/8 mm., which is reduced to β-*amino*-α-4-*tetrahydropyranylbutane*, b.p. 104°/12 mm. (*picrate*, m.p. 148°). This affords α-*bromo*-ε-*amino*-γ-β′-*bromoethylheptane hydrobromide*, m.p. 123°, which is converted into 2-*ethylquinuclidine*, b.p. 180—181° (*hydrochloride*, m.p. 239°; *platinichloride*, m.p. 227°; *picrate*, m.p. 170—171°; *picrolonate*, m.p. 219°; *methiodide*, m.p. 290—290·5°).

III. 4-Tetrahydropyranyl Me ketone, $CH_2Br{\cdot}CO_2Et$, and Zn turnings in boiling C_6H_6 afford *Et* β-*hydroxy*-β-4-*tetrahydropyranyl*-n-*butyrate*, dehydrated by $KHSO_4$ at 90° to *Et* β-4-*tetrahydropyranylcrotonate*, b.p. 136°/16 mm., which is hydrogenated (after repeated

distillation over Pt-black in vac.) to *Et β-4-tetrahydropyranylbutyrate*, b.p. 130—131°/12 mm., hydrolysed to the *acid*, b.p. 135—140°/0·4 mm., m.p. 64·5—65°. This is converted by NaN_3 and conc. H_2SO_4 in presence of $CHCl_3$ into *α-amino-β-4-tetrahydropyranylpropane*, b.p. 102°/14 mm., which yields *ε-bromo-α-amino-β-methyl-γ-β′-bromoethylpentane hydrobromide*, m.p. 163—165°, and thence *3-methylquinuclidine* [*3-methyl*dicyclo-[2 : 2 : 2]-*aza*-1-*octane*], b.p. 171° [*hydrochloride*, m.p. 312—324° (sealed capillary) according to the rate of heating; *platinichloride*, m.p. 219°; *picrate*, m.p. 227°; *methiodide*, m.p. 316° (decomp.); *picrolonate*, m.p. 205—206°]. 4-Tetrahydropyranyl Et ketone gives a product which readily loses H_2O to form *Et β-4-tetrahydropyranyl-Δ^α^-pentenoate*, b.p. 92—95°/0·2 mm., reduced (PtO_2 in EtOH) to *Et β-4-tetrahydropyranylvalerate*, b.p. 139—143°/11 mm., which is hydrolysed to the *acid*, b.p. 129—131°/0·02 mm. This is converted successively into *α-amino-β-4-tetrahydropyranylbutane*, b.p. 113°/14 mm., *α-bromo-δ-aminomethyl-γ-β′-bromoethylhexane hydrobromide*, m.p. 177·5—178°, and *3-ethylquinuclidine*, b.p. 78—79°/12 mm. [platinichloride, m.p. 220—223° (decomp.); aurichloride, m.p. 178·5—179°; picrate, m.p. 153°; methiodide, m.p. 55°; *picrolonate*, m.p. 187—188°]. Attempts to resolve the base by *d*-tartaric acid gave the cryst. dl-*3-ethylquinuclidine H d-tartrate*, $[\alpha]_D$ +14·3°±2° in H_2O. Attempted resolution with the aid of *d-α*-bromocamphor-*π*-sulphonic acid leads to an apparently homogeneous salt with m.p. 188—188·5°, $[\alpha]_D$ +76·0°±0·5° in H_2O, whereas the *salt* of the homogeneous (+)-base has m.p. 188—189°, $[\alpha]_D$ +87·1°±2·0° in H_2O; this appears to be a case of partial racemism. $OPh{\cdot}CH_2{\cdot}CHO$ and MgEtBr yield *α-phenoxybutan-β-ol*, b.p. 134°/20 mm., m.p. 28·5°, converted by PBr_3 and C_5H_5N into *β-bromo-α-phenoxybutane*, b.p. 134—137°/23 mm., which with $CHNa(CO_2Et)_2$ affords *Et₂ β-phenoxymethylbutane-αα-dicarboxylate*, b.p. 220°/15 mm., hydrolysed to the *acid*, m.p. 114—115°.

IV. $(CH_2{\cdot}OH)_2$, Na, and EtI give $OEt{\cdot}[CH_2]_5{\cdot}OH$, b.p. 98°/14 mm., converted into $OEt{\cdot}[CH_2]_5{\cdot}Br$, which with $CHNa(CO_2Et)_2$ in abs. EtOH yields *Et₂ ζ-ethoxyhexane-αα-dicarboxylate*, b.p. 165—167°/15 mm. This is converted by $OEt{\cdot}[CH_2]_5{\cdot}Br$ and Na in abs. EtOH into *Et₂ αλ-diethoxyundecane-ζζ-dicarboxylate*, b.p. 180°/3 mm., hydrolysed and decarboxylated to *αλ-diethoxyundecane-ζ-carboxylic acid*, b.p. 180—183°/0·6 mm., which affords *ζ-amino-αλ-diethoxyundecane*, b.p. 178°/13 mm. The corresponding hydrobromide is transformed by 68% HBr at 100° followed by 0·1N-NaOH at 50° into dicyclo-[0 : 5 : 5]-*aza*-1-*dodecane*, b.p. 107—108°/16 mm. (*picrate*, m.p. 136°; *picrolonate*, m.p. 181°; *methiodide*, m.p. 233°).

V. *Et quinuclidine-2-carboxylate* (**V**), b.p. 122—123°/12 mm., converted by boiling 10% HCl into the *hydrochloride*, m.p. >335°, of the acid, is reduced by Na and abs. EtOH to *2-quinuclidylcarbinol*, b.p. 118—120°/14 mm. (*picrate*, m.p. 230—231°; *hydrobromide*, m.p. 308°; *benzoate hydrochloride*, m.p. 245·5—246·5°). OH of this compound is very unreactive and is not replaced by Br by treatment with 69% HBr at 100°. With $SOCl_2$ in boiling $CHCl_3$ *2-chloromethylquinuclidine hydrochloride*, m.p. 234—235° (corresponding *picrate*, m.p. 194—195°), results; this could not be dehalogenated by Zn–HCl or by catalytic reduction. MgPhBr and (**V**) afford *diphenyl-2-quinuclidylcarbinol*, m.p. 265° (closed capillary) (*picrate*, m.p. 253—254°), which reacts very sluggishly. H. W.

Pyrone and related compounds. III. Action of bases on 2 : 6-dihydroxypyrone. R. Kaushal (*J. Indian Chem. Soc.*, 1943, **20**, 127—130).—2 : 6-Dihydroxy-1 : 4-pyrone (**I**) with NH_2Ph (1 mol.) in $CHCl_3$ at room temp. yields *acetone-αγ-dicarboxylic acid monoanilide*, m.p. 120—121°, with excess of NH_2Ph at the b.p. (excess being removed with HCl) yields the *dianilide*, m.p. 157°, and with NH_2Ph and $ZnCl_2$ at the b.p. yields *2 : 6-dihydroxy-1-phenyl-4-pyridone*, m.p. 252° (darkens at 230°) (nitrophenylhydrazone, m.p. 184—185°; *diacetate*, m.p. 190°). NH_4OAc and (**I**) at 0° yield an *oxonium compound*, $C_5H_7O_4N,H_2O$, m.p. 210°, which gives a violet colour with $FeCl_3$, evolves NH_3 on heating, yields with NH_2OH,HCl the *monoxime*, m.p. 180° (decomp.), and with Ac_2O and H_2SO_4 the *diacetate*, m.p. 160°, of (**I**) [also obtained from (**I**) and AcCl (trace of H_2SO_4)]. C_5H_5N and piperidine with (**I**) at 0° yield *oxonium compounds*, m.p. 152° and 139—140° respectively, which give a violet colour with $FeCl_3$ and decompose on warming. A. Li.

Hydroxypyridines.—See B., 1943, II, 212.

Pyridine derivatives.—See B., 1943, II, 245.

Synthesis of a pyridine analogue of hydnocarpic acid and of a lower homologue. F. Brody and M. T. Bogert (*J. Amer. Chem. Soc.*, 1943, **65**, 1075—1080).—$CH_2{:}CH{\cdot}[CH_2]_9{\cdot}OH$ (prep. from $CH_2{:}CH{\cdot}[CH_2]_8{\cdot}CO_2Et$ by Na–Bu^α^OH; 77—82% yield) with best, $SOCl_2$–C_5H_5N at <0° and then 130—140° gives the chloride (83%), b.p. 113—115°/2 mm., which with 2-methylpyridine and commercial $NaNH_2$ at 100° or in boiling C_6H_6 gives *2-Δ^λ^-n-dodecenylpyridine* (**I**) (53%), b.p. 158—159°/4 mm. [*picrate*, m.p. 46—46·5° (46—47°)]. Use of pure $NaNH_2$ and a trace of $Fe(NO_3)_3,6H_2O$ in NH_3, later at 100°, gives *2-Δ^κ^-n-dodecenylpyridine* (**II**) (67%), b.p. 152—153°/4 mm. (*picrate*, m.p. 64·5—65·5°). H_2–Pd-black reduces (**I**) or (**II**) to *2-n-dodecylpyridine* (90%), an oil (*picrate*, m.p. 64·5—65·5°). With AgOBz and then I in C_6H_6, (**I**) and (**II**) give *2-λμ-*, m.p. 71·5—72°, and *2-κλ-dihydroxy-n-dodecylpyridine*, m.p. 87—87·5°, respectively. $KMnO_4$ oxidises (**I**) in $COMe_2$ at <35° to *κ-2-pyridyl-n-undecoic acid* (**III**), m.p. 68·5—69·5° [*picrate*, m.p. 79—79·5°, prepared in Et_2O; *Et* ester *picrate*, m.p. 69—70°, formed in EtOH; hydrochloride; Na salt; *amide* (**IV**), m.p. 96·5—97·5° (*picrate*, m.p. 112·5—113°)]. (**IV**) yields similarly *ι-2-pyridyl-n-decoic acid*, m.p. 55·5—56·5° (*picrate*, m.p. 82·5—83°), the chloride hydrochloride of which yields the oily diazomethyl ketone and thence (**IV**). H_2–Raney Ni reduces (**III**) in *cyclo*hexane at 180°/1700 lb. to *κ-2-piperidyl-n-undecoic acid*, m.p. 158·5—160° (*picrate*, m.p. 92·5—93·5°). R. S. C.

Synthesis of 5-methoxyisatin. E. Ferber and G. Schmolke (*J. pr. Chem.*, 1940, [ii], **155**, 234—240).—$CS(NH{\cdot}C_6H_4{\cdot}OMe\text{-}p)_2$, m.p. 188°, and aq. KCN–$PbCO_3$–EtOH at 50—60° give *C-cyano-NN′-di-p-anisylamidine*, $p\text{-}OMe{\cdot}C_6H_4{\cdot}NH{\cdot}C(CN){:}N{\cdot}C_6H_4{\cdot}OMe\text{-}p$, m.p. 157°, converted (35% NH_3 saturated with H_2S) at 45° into the *C-thiocarbamyl* compound, m.p. 147° (decomp.), which with conc. H_2SO_4 at 65—75°, followed by boiling with dil. mineral acid, yields 5-methoxyisatin, m.p. 201°. A. T. P.

Alkoxyl exchange by γ-alkoxyquinoline derivatives in alcoholic alkali. B. Berinzaghi, V. Deulofeu, R. Labriola, and A. Muruzabal (*J. Amer. Chem. Soc.*, 1943, **65**, 1357—1359).—The 4-OR of skimmianine (**I**), *γ*-fagarine (**II**) (A., 1943, II, 113), and their analogues is labile, being converted into OR′ by KOH–R′OH. Possible reaction mechanisms are discussed. Boiling 10% KOH–EtOH converts (**I**) into the 4-OEt-*analogue* (**III**), $C_{15}H_{15}O_4N$, m.p. 138° (*picrate*, m.p. 194°), which with MeI at 100—110° gives *iso*skimmianine, with $KMnO_4$–$COMe_2$ gives the 4-OEt-*analogues*, m.p. 212° (*phenylhydrazone*, m.p. 178·5°) and 225°, of skimmianal and skimmianic acid, respectively, and with boiling 30% HCl gives 2 : 4-dihydroxy-7 : 8-dimethoxyquinoline. 5% KOH–Pr^α^OH gives similarly the 4-OPr^α^-*analogue* (**IV**), m.p. 95° (*picrate*, m.p. 179—180°), of (**I**). 5% KOH–MeOH at 100° regenerates (**I**) from (**III**) or (**IV**). Similarly, (**II**) yields the 4-OEt-*analogues*, (**V**) m.p. 143° [*picrate*, m.p. 161°; with 10% KOH–MeOH at 90—100° regenerates (**II**)], 192—193° (*phenylhydrazone*, m.p. 185—186°), and 210—211°, of (**II**), *γ*-fagaraldehyde, and *γ*-fagaric acid, respectively. 30% HCl hydrolyses (**V**) to 2 : 4-dihydroxy-7- or -8-methoxyquinoline. R. S. C.

Quinolines.—See B., 1943, III, 160.

Synthesis of 1-substituted aminobenzo(*f*)quinolines. A. C. Mueller and C. S. Hamilton (*J. Amer. Chem. Soc.*, 1943, **65**, 1017—1018).—Adding *Et₂ α-2-naphthyliminosuccinate* (**I**) (prep. from $\beta\text{-}C_{10}H_7{\cdot}NH_2$ and $CO_2Et{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$ by conc. H_2SO_4; 41% yield), m.p. 66—67°, to mineral oil at 230° gives *Et 1-hydroxybenzo*(f)*quinoline-3-carboxylate* [*4-hydroxy-5 : 6-benzquinoline-2-carboxylate*] (65%), m.p. 215—217°, hydrolysed by boiling 5% NaOH to the *acid*, m.p. 302° (loss of CO_2). Decarboxylation at the m.p. gives *4-hydroxy-*, m.p. 286—288°, converted by boiling $POCl_3$ into 4-chloro-5 : 6-benzquinoline, m.p. 62—63° (lit. 67°), which with the appropriate amine at the b.p. gives *4-morpholino-*, m.p. 146—148°, *4-piperidino-*, m.p. 138—140°, *4-γ-morpholino-n-propylamino-*, $+2H_2O$, m.p. 75—76°, and *1-γ-diethylamino-n-propylamino-*, m.p. 59—60°, *-5 : 6-benzquinoline*. H_2–Raney Ni reduces (**I**) in EtOH at 80°/500 lb. to *Et₂ α-2-naphthylaminosuccinate*, m.p. 63—65° (hydrochloride, m.p. 140°; derived acid, m.p. 186°; cf. A., 1892, 860). R. S. C.

[Derivatives of] dihydroresorcinols. A. Sonn and H. Schreiber (*J. pr. Chem.*, 1940, [ii], **155**, 65—76).—*5-iso*Propyldihydroresorcinol (**I**) and CH_2O in warm aq. MeOH give *2 : 2′-methylene-5 : 5′-di*iso*propylbisdihydroresorcinol* (**II**) (90%), m.p. 183—184°, converted by boiling Ac_2O into *1 : 8-diketo-3 : 6-di*iso*propyl-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydroxanthen* (**III**), m.p. 138—140°, which with NH_3–MeOH at room temp. (not 100°) gives *3-amino-3′-hydroxy-5 : 5′-di*iso*propyl-2 : 2′-methylenebis-Δ²-cyclo*hexene* (or the 3-NH: form), m.p. 173—175°. In boiling Ac_2O this gives *4 : 6-diketo-2 : 8-di*iso*propyl-1 : 2 : 3 : 4 : 6 : 7 : 8 : 9-octahydroacridine*, fluorescent, m.p. 287—290°, which could not be hydrogenated. $NEt_2{\cdot}[CH_2]_2{\cdot}NH_2$, (**III**), and NaOAc in boiling MeOH give *4 : 6-diketo-5-β-diethylaminoethyl-2 : 8-di*iso*propyloctahydroacridine*, m.p. ~176°, which in acid slowly regenerates (**II**). *p-* or *m*-$NO_2{\cdot}C_6H_4{\cdot}CHO$ and (**I**) in warm MeOH give *2 : 2′-p-*, m.p. 182—183°, and *-m-nitrobenzylidene-5 : 5′-di*iso*propylbisdihydroresorcinol*, m.p. 153—154°, and thence (boiling Ac_2O) *1 : 8-diketo-9-p-*, m.p. 184—186°, and *-9-m-nitrophenyl-3 : 6-di*iso*propyloctahydroxanthen*, m.p. 148—150°. *2 : 2′-p-Hydroxybenzylidene-5 : 5′-di*iso*propylresorcinol*, m.p. 123—125°, is similarly obtained in aq. EtOH at room temp. and gives *1 : 8-diketo-9-p-acetoxy-*, m.p. 132°, and thence (conc. HCl–EtOH at 100°) *-9-p-*hydroxyphenyl-*3 : 6-di*iso*propyloctahydroxanthen, m.p. 189—190°. Helicin and (**I**) in boiling EtOH give an oil, converted by Ac_2O into *1 : 8-diketo-9-o-β-glucosidoxyphenyl-3 : 6-di*iso*propyloctahydroxanthen tetraacetate*, m.p. 105—106°. $CHPh{:}CH{\cdot}CHO$ and (**I**) in warm MeOH give *2 : 2′-cinnamylidene-5 : 5′-di*iso*propylbisdihydroresorcinol*, m.p. 163—164°. $CN{\cdot}[CH_2]_2{\cdot}CH(OEt)_2$ and (**I**) in boiling EtOH–AcOH give a product, m.p. ~133—137°, converted by boiling Ac_2O into *1 : 8-diketo-9-β-cyanoethyl-3 : 6-di*iso*propyloctahydroxanthen*, m.p. 153—155°. $NEt_2{\cdot}CH_2{\cdot}CH(OEt)_2,HCl$ and (**I**) in warm MeOH give *2 : 2′-vinylidene-5 : 5′-di*iso*propylbisdihydroresorcinol*, m.p. 110°.

OH·CH_2·CHO or CH_2Cl·CHO with (I) in MeOH–H_2O gives 3-*keto*-5 : 5′-*diiso*propyl-2 : 2′-*dihydroresorcinyl*-1 : 2 : 3 : 4 : 5 : 6-*hexahydrobenzfuran* (IV), m.p. 208—210°. *o*-NH_2·C_6H_4·CHO, (I), and KOH in boiling aq. MeOH give 4-keto-2-*iso*propyl-1 : 2 : 3 : 4-tetrahydroacridine, m.p. indefinite (*picrate*, m.p. 193—194°). (II) and its analogues and (IV) are monoenolic forms, since they are sol. in NaOH. R. S. C.

Polarographically controlled syntheses, with reference to organic chemistry. J. J. Lingane, C. G. Swain, and M. Fields (*J. Amer. Chem. Soc.*, 1943, **65**, 1348—1353).—The use of the polarograph as a control in electrolytic syntheses is suggested, and applied to the reduction of 9-*o*-iodophenylacridine to 9-*o*-iodophenyl- and 9-phenyldihydroacridine. Almost quant. yields of high purity were obtained. W. R. A.

Preparation and therapeutic properties of certain acridine derivatives. IV. 5-Methylacridines, further 5-styrylacridines, and their quaternary salts. W. Sharp, M. M. J. Sutherland, F. J. Wilson, and (in part) C. H. Browning and K. M. Calver (*J.C.S.*, 1943, 344—347; cf. A., 1943, II, 105).—3-Nitro- is reduced ($SnCl_2$ + HCl) to 3-amino-5-methylacridine, m.p. ~200° (decomp.), the *Ac* derivative, decomp. ~260° (does not melt at 360°), of which with *p*-$C_6H_4Me·SO_3Me$ at 145° yields its *metho*-p-*toluenesulphonate*, m.p. 226°, converted by pptn. with aq. NH_3, boiling the base with conc. HCl, and the resulting iodide with AgCl into 3-*amino*-5-*methylacridine methochloride*, m.p. >200° (decomp.). 5 : 2 : 1-NO_2·C_6H_3Cl·COMe, *p*-NH_2·C_6H_4·NHAc, and anhyd. K_2CO_3 at 125° yield 4-*nitro*-4′-*acetamido*-2-*acetyldiphenylamine*, m.p. 207° (reddens at ~120°), cyclised by AcOH–conc. H_2SO_4 at 125° to 3-*nitro*-7-*amino*-, decomp. ~270° (does not melt at 380°) [*Ac* derivative, darkens ~280° (does not melt at 360°)], reduced (anhyd. $SnCl_2$) to 3 : 7-diamino-5-methylacridine (I), sinters at ~200° (decomp.), the Ac_2 derivative, m.p. ∢360°, of which is converted via the metho-*p*-toluenesulphonate into 3 : 7-*diamino*-5-*methylacridine methochloride*, decomp. ~200°. Similarly 4-*nitro*-2-*acetyl*-4′-*methyldiphenylamine*, m.p. 132°, yields 3-*nitro*-, decomp. ~235° (does not melt at 360°), and 3-amino-5 : 7-dimethylacridine, decomp. ~170° [*Ac* derivative, decomp. ~250° (does not melt at 360°); *methochloride*, decomp. >200°]. 4-*Nitro*-3-*acetamido*-2-*acetyldiphenylamine* (prep. as above from *m*-NH_2·C_6H_4·NHAc) has m.p. 229°. 3-Nitro-5-methylacridine with *o*- and *m*-NO_2·C_6H_4·CHO alone at 100° yields respectively α-(o-, decomp. 170° (does not melt at 360°), and α-(m-*nitrophenyl*)-β-5-(3-*nitroacridyl*)*ethanol*, decomp. 175°, but with *p*-NO_2·C_6H_4·CHO and Ac_2O at 130° gives 3-*nitro*-5-p-*nitro*-, darkens >250° (does not melt at 360°), converted as above into 3-amino-5-*p*-amino-styrylacridine, decomp. >200° (Ac_2 derivative, m.p. ∢360°; *methochloride*, decomp. ~250°). Similarly 3-nitro-5 : 7-dimethyl- yields 3-*nitro*-5-p-*nitro*-, m.p. ∢360°, and 3-amino-5-*p*-amino-styryl-7-methyl-, decomp. ~200° (Ac_2 derivative, m.p. ∢360°; *methochloride*, decomp. >250°), and 3-nitro-7-acetamido-5-methyl- yields 3-*nitro*-7-*acetamido*-5-p-*nitro*-, m.p. ∢360° (darkens >250°), and 3 : 7-diamino-5-*p*-amino-styryl-acridine, decomp. ~180° (Ac_3 derivative, m.p. ∢360°; *methochloride*, decomp. ~200°). Therapeutic properties of these and other acridine derivatives are recorded. (I) and 3 : 6(or 3 : 8)-diamino-5-methylacridine show antiseptic properties, but 5-aminostyrylacridines do not. The methochlorides have enhanced antiseptic action (especially those of amino-5-amino-styrylacridines), and in some cases trypanocidal action. A. Li.

Chemotherapy of malaria. S. J. Das-Gupta (*J. Indian Chem. Soc.*, 1943, **20**, 137—138).—2-*Chloro*-7-*methoxy*-, m.p. 225°, and 7-*methoxy*-5-(β-*diethylaminoethyl*)-, m.p. 209—210° (from the thiolacridine and $Br·[CH_2]_2·NEt_2$ in PhOH containing NaOH at 100—110°), and 2-*chloro*-7-*methoxy*-, m.p. 195—197°, and 7-*methoxy*-5-(γ-*diethylaminopropyl*)-*thiolacridine*, m.p. 180—181° (similar prep.), are strongly antiseptic against paramecia. A. Li.

Pyrroles and pyrromethenes.—See B., 1943, II, 313.

Direct replacement of oxygen in hydantoins and barbiturates by sulphur. H. R. Henze and P. E. Smith (*J. Amer. Chem. Soc.*, 1943, **65**, 1090—1092).—The appropriate hydantoins and P_2S_3 in boiling tetrahydronaphthalene give 5 : 5-*dimethyl*- (I) (30%), m.p. 147·5—148°, 5 : 5-*diphenyl*- (18%), m.p. 260—261° (decomp.), and, better in decahydronaphthalene, 5-*phenyl*-5-*methyl*- (61%), m.p. 176·5—177°, and 5-*phenyl*-5-*ethyl*-*thiohydantoin* (55%), m.p. 174·5—175°. Barbital and phenobarbital give similarly 5 : 5-*diethyl*- (II) (56%), m.p. 196·5—197°, and 5-*phenyl*-5-*ethyl*-2 : 4 : 6-*trithiobarbituric acid* (22%), m.p. 175—177°, respectively. Boiling 5% NaOH hydrolyses (II) to $CEt_2(CO·NH_2)_2$ (proof of structure). M.p. are corr. None of the products has analgæsic or anticonvulsant activity, and only (I) and (II) are hypnotic. R. S. C.

Stimulation of formation of additive compounds between bases and phenols.—See A., 1943, I, 259.

Action of phenylcarbimide on 4-hydroxymethylantipyrine. P. Duquénois and H. Amal (*Rev. Fac. Sci. Istanbul*, 1942, **7**, 1—5).—PhNCO and 4-hydroxymethylantipyrine (I) give 1-*phenyl*-2 : 3-*dimethyl*-4-*anilinoformylmethylpyrazolone*-5-*anil* (II), m.p. 271·5° (yellow at ~265°), and CO_2. (II) is hydrolysed by boiling dil. H_2SO_4 to CO_2 and NH_2Ph. An analogous compound is not produced from (I) and PhNCS. H. W.

Action of phosphorus pentachloride and thionyl chloride on antipyrine-4-carboxylic acid. P. Duquénois and H. Amal (*Rev. Fac. Sci. Istanbul*, 1942, **7**, 6—12).—Antipyrine-4-carboxylic acid (I) and $SOCl_2$ in dry C_6H_6 at 80—90° give 5-chloro-1-phenyl-3-methylpyrazole-4-carboxylic acid (II), m.p. 227°, partly sublimes at 170—180°. With PCl_5, directly or in presence of light petroleum, (I) gives (II) and the corresponding *chloride* (III), m.p. 74°, also obtained from the Ca salt and PCl_5 in presence of $CHCl_3$. With a large excess of the requisite alcohol (III) gives *Me*, m.p. 74° and *Et*, m.p. 68°, 5-*chloro*-1-*phenyl*-3-*methylpyrazole*-4-*carboxylate*. H. W.

Barbituric acids.—See B., 1943, II, 246.

Pyrimidines. CLXXVIII. Chlorination of 2 : 4-diketotetrahydropyrimidines by action of a mixture of hydrogen peroxide and hydrochloric acid. CLXXIX. Reaction of hydrochloric acid with 5 : 5-dichloro-6-methylhydrouracil. T. B. Johnson (*J. Amer. Chem. Soc.*, 1943, **65**, 1218—1219, 1220—1222).—CLXXVIII. 30% H_2O_2 + conc. HCl at room temp. effects nearly quant. chlorination of 2 : 6-diketotetrahydropyrimidines. 5 : 5-Dichloro-4-hydroxyhydrouracil is obtained from uracil, 6-hydroxy-2-ethylthiolpyrimidine, cytosine, 5-iodouracil, or, with CO_2, uracil-5-carboxylic acid. Thymine gives 5-*chloro*-4-*hydroxy*-5-*methylhydrouracil*, m.p. 202—203°. 4-Methyluracil gives 5 : 5-dichloro-4-hydroxy-4-methylhydrouracil. 5-Bromo- and 5-nitro-uracil give 5-chloro-5-nitro- and 5-chloro-5-nitro-4-hydroxy-hydrouracil, respectively. *iso*Cytosine gives 5 : 5-*dichloro*-2-*amino*-4-*hydroxy*-6-*ketohexahydropyrimidine hydrochloride*. Orotic acid gives 5-*chlorouracil*-4-*carboxylic acid*, m.p. >300°. Hydrouracil does not react.

CLXXIX. 5 : 5-Dibromo-4-hydroxy-4-methylhydrouracil in boiling conc. HCl or Ac_2O gives 5-bromo-6-methyluracil, but 5 : 5-dichloro-4-hydroxy-4-methylhydrouracil gives the *ether*, $(NH<^{CO·CCl}_{CO·N}>CMe)_2O$, m.p. 270—275° (decomp.) (mol. wt. in boiling C_6H_6). (I) is converted by $SnCl_2$–dil. HCl at 100° or conc. aq. NH_3 at room temp. (1 week) into 5-chloro-6-methyluracil and by boiling HI (*d* 1·5) into 6-methyluracil. R. S. C.

Pyrimidines.—See B., 1943, III, 193.

Reactions of amidines with derivatives of malonic acid. G. W. Kenner, B. Lythgoe, A. R. Todd, and A. Topham (*J.C.S.*, 1943, 388—390).—In presence of NaOEt in EtOH, $CH_2(CO_2Et)_2$ with NH:CH·NH_2,HCl (room temp.) yields 4 : 6-*dihydroxy*-, decomp. >230°, and with α-furylamidine hydrochloride (I) (at the b.p.) yields 4 : 6-*dihydroxy*-2-α-*furyl*-*pyrimidine*, decomp. >290°. With $CH_2(CN)_2$, NH:CMe·NH_2,HCl and NH:CPh·NH_2,HCl (room temp.) yield 4-amino-5-cyano-2 : 6-dimethyl-, m.p. 218°, and -2 : 6-*diphenylpyrimidine*, m.p. 211°, respectively, whilst (I) at the b.p. yields β-(2′-*furyl*)-β-*aminomethylenemalononitrile*, m.p. 182°, which further reacts with (I) to give 4-*amino*-5-*cyano*-3 : 6-*di*-2′-*furylpyrimidine*, m.p. 245—246°. NH:CH·NH_2,HCl with NH_2·CH:C(CN)$_2$ at room temp. yields 4-amino-5-cyanopyrimidine (II), and with CN·CH_2·CO_2Et gives, according to conditions, NH_2·CH:C(CN)·CO_2Et (converted by MeCS·NH_2 and NaOEt in EtOH into 4-amino-2-methylpyrimidine-5-carboxylate), Et methylenebiscyanoacetate (III), or a *compound*, $C_9H_9O_3N_3$ (? 4-amino-6-hydroxy-3-carbethoxy-5-cyanopyridine), m.p. 280—281° (decomp.). With CN·CH_2·CO_2Et, NH:CPh·NH_2,HCl yields β-amino-α-cyano-β-phenylacrylate (IV) and 4-amino-6-hydroxy-2-phenylpyrimidine, whilst NH:CPh·OEt gives only (IV) (small yield). NH:CH·NH_2,HCl and $CH_2Ac·CO_2Et$ yield a *compound*, $C_{11}H_{15}O_5N$ (? $CO_2Et·CAc:CH·NH·CO·CH_2Ac$), m.p. 78—79° [which could not be prepared from $CH_2Ac·CO_2Et$ and NH_2·CH:C(CN)·CO_2Et]. NH:CH·OEt,HCl yields with $CH_2(CN)_2$, (II), with CN·CH_2·CO_2Et (without NaOEt), NH_2·CH:C(CN)·CO_2Et, or (with NaOEt) a small amount of the latter with (III), and with $CH_2Ac·CO_2Et$, (III) and a small amount of solid, m.p. 201°. A. Li.

Preparation and reactions of benziminazole-2-carboxylic acid and 2-benziminazolylacetic acid. R. A. B. Copeland and A. R. Day (*J. Amer. Chem. Soc.*, 1943, **65**, 1072—1075).—2-Hydroxymethylbenziminazole [prep. from *o*-$C_6H_4(NH_2)_2$ and OH·CH_2·CO_2H], m.p. 171—172°, and $KMnO_4$ give benziminazole-2-carboxylic acid (I) (71%), +$2H_2O$, m.p. 169—171° (loss of CO_2), which in boiling $SOCl_2$ gives 3 : 6-*diketodi*(*benziminazole*-1′ : 2′-)1′ : 2-4 : 5-*tetrahydropyrazine* (II), m.p. >300°. In boiling conc. HCl or N-NaOH, (II) gives (I), in hot 10% HCl–EtOH gives the *Et* ester (III), m.p. 212·7—213·7° or 228—230° (block), of (I), and in NaOEt–EtOH gives the *Na* derivative of (III), which in 1 : 1 AcOH–H_2O gives (III) but in warm H_2O gives (I). In NaOMe–MeOH, (II) gives the *Me* ester, m.p. 187·3°, of (I). With NH_3 or the appropriate amine in hot H_2O, (II) gives *benziminazole*-2-*carboxyl*-*amide*, m.p. >300°, -*methyl*-, m.p. 246·5°, -*ethyl*-, m.p. 210—211°, -β-*hydroxyethyl*-, m.p. 219—220°, -β-*methoxyethyl*-, m.p. 138°, -n-*butyl*-, m.p. 180·5—181·5°, -*benzyl*-, m.p. 172·4°, -cyclo*hexyl*-, m.p. 269·5°, -*dimethyl*-, m.p. 223—224°, -*diethyl*-, m.p. 124·5°, add -*di*-n-*butyl*-*amide*, m.p. 101·2°, and -*morpholide*, m.p. 181·2°. *o*-$C_6H_4(NH_2)_2$ and CN·CH_2·CO_2Et at 165—200° (63%) or

180° (70%) give *2-cyanomethylbenziminazole*, m.p. 209·7—210·7°, hydrolysed by boiling 50% H_2SO_4 or NaOH–aq. EtOH to *2-benziminazolylacetic acid*, m.p. 116° [loses CO_2, resolidifies, remelts at 176° (2-methylbenziminazole)], or by 9% HCl–EtOH to the *Et* ester, m.p. 128·5—129·5°, thereof and thence (aq. NH_2R) giving the *amide*, m.p. 244—247° (decomp.), -methyl-, m.p. 214—216·5° (decomp.), -*n*-butyl-, m.p. 209·5—212·5° (decomp.), and -β-methoxyethyl-amide, m.p. 183·5—185° (decomp.). M.p. are corr. R. S. C.

Quinoxaline formation and the ortho-effect. R. C. Fuson, C. H. McKeever, N. Rabjohn, and H. W. Gray (*J. Amer. Chem. Soc.*, 1943, **65**, 1028—1029).—6 : 2 : 4 : 1-OMe·$C_6H_2Me_2$·COMe (prep. from 1 : 3 : 5-$C_6H_3Me_2$·OMe by Ac_2O–$AlCl_3$ in boiling CS_2) with SeO_2 and a little H_2O in boiling dioxan gives 6-methoxy-2 : 4-dimethylphenylglyoxal, b.p. 90—120°/4 mm., which, in contrast to 2 : 4 : 6 : 1-$C_6H_2Me_3$·CO·CHO (I) (A., 1939, II, 162), with *o*-$C_6H_4(NH_2)_2$ in boiling AcOH gives *2-6′-methoxy-2′ : 4′-dimethylphenylglyoxaline*, m.p. 83·5—84°. 2 : 6 : 1-$(OMe)_2C_6H_3$·CO·CHO, b.p. 115—117°/5 mm., gives *2-2′ : 6′-dimethylphenylglyoxaline*, m.p. 95·5—96·5°, and, when shaken with 30% NaOH, gives *2 : 6-dimethoxymandelic acid*, m.p. 146—147°. 3 : 5 : 2 : 4 : 6 : 1-$(NO_2)_2C_6Me_3$·CO·CHO (prep. from the COMe derivative by SeO_2 in boiling aq. dioxan), softens at 116°, m.p. 122—125°, gives *2-3′ : 5′-dinitromesitylglyoxaline*, m.p. 197·5—198°, the hindrance of (I) being overcome by chelation of the NO_2 and Me. R. S. C.

Niementowski reaction. Use of methyl anthranilate or isatoic anhydride with substituted amides or amidines in the formation of 3-substituted 4-keto-3 : 4-dihydroquinazolines. Course of the reaction. J. F. Meyer and E. C. Wagner (*J. Org. Chem.*, 1943, **8**, 239—252).—In the prep. of 4-keto-3 : 4-dihydroquinazolines the yields may be decreased by the formation of stable quinazolone anthranilates in the reaction mixture, thus making part of the anthranilic acid (I) unavailable for the synthesis. This behaviour, observed in the prep. of 3-phenyl-3 : 4-dihydroquinazol-4-one (II), seems not to be general and its interference can be minimised by the use of >1 equiv. of (I). The *anthranilate*, m.p. 132·2° (corr.), *benzoate*, m.p. 131—132°, *salicylate*, m.p. 168—169°, *phenylacetate*, m.p. 113—114°, and *formate*, m.p. 119—120°, of (II), the *anthranilate*, m.p. 111—113°, of 3-m-*tolyl-3 : 4-dihydroquinazol-4-one*, and the *anthranilate*, m.p. 119—121°, of 3-*p*-tolyl-3 : 4-dihydroquinazol-4-one are reported. *o*-NH_2·C_6H_4·CO_2Me (III) can replace (I) in the Niementowski reaction, its use permitting (and requiring) higher reaction temp. than can be maintained with (I). With respect to yield and applicability this modification of the Niementowski reaction is without advantage. Diaryl-formamidines (IV) or -acetamidines can be used instead of amides in the Niementowski reaction with either (I) or (III). Yields are good when (III) and (IV) react. This reaction shows a functional analogy between amides and amidines considered respectively as aquo-ammono-acids and ammono-acids. A new quinazolone synthesis from isatoic anhydride and diarylamidines is described, high yields resulting from the use of diarylformamidines. The synthesis follows two divergent courses, each leading to the same product. By use of acetamidines only one reaction course leading to the quinazolone is open (the other terminating with the formation of the anthranilanilide), with the result that yields are relatively lower. (III) and NH_2Ac afford *o*-NHAc·C_6H_4·CO_2Me, 2-methyl-3 : 4-dihydroquinazol-4-one, and traces of NH_3. This result indicates the sequence of reactions by which (III) and amides yield quinazolones and provides collateral experimental support for the two assumed steps in the reaction course proposed by Bogert *et al.* for the Niementowski synthesis. H. W.

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

Synthesis of purine nucleosides. I. Model experiments on synthesis of 9-alkylpurines. J. Baddiley, B. Lythgoe, D. McNeil, and A. R. Todd. **II. Synthesis of adenine.** J. Baddiley, B. Lythgoe, and A. R. Todd (*J.C.S.*, 1943, 383—386, 386—387).—I. With aq. HCS_2Na, 4 : 5-diamino-6-hydroxy-2-methyl-, 4 : 5 : *6-triamino-2-methylthiol-*, m.p. 182° {prep. by reduction [$(NH_4)_2S$] of the product from 4 : 6-diamino-2-methylthiolpyrimidine and HNO_2}, 4 : *6-diamino-2-methyl-* (I), m.p. 294—295° (sealed tube) (*picrate*, decomp. >250°), 5-amino-4-methylamino-2-hydroxy-6-methyl-, and the product of nitrosation and reduction (as above) of *6-amino-4-methylamino-2-methylthiol-pyrimidine*, m.p. 143—144° (from the 4-Cl-compound and aq. NH_2Me at 100° in a sealed tube), yield *5-thioformyl* derivatives, m.p. >260° (decomp. without melting), 235° (decomp., rapid heating), (no definite m.p.), <300°, and 185—186° (evolution of H_2S) respectively, which when boiled in H_2O or (better) quinoline or other anhyd. org. solvent yield respectively *6-hydroxy-2-methylpurine*, decomp. >360°, *2-methylthioladenine* (II), m.p. 290° (decomp.), *2-methyladenine*, m.p. <300° (*picrate*, decomp. >250°), *2-hydroxy-6 : 9-dimethylpurine*, m.p. <300°, and *2-methylthiol-9-methyladenine*, m.p. 261—262° [also obtained from (II), MeI, and EtOH–NaOH at room temp.], deaminated by dil. AcOH followed by $Ba(NO_2)_2$ at 60—65° to *6-hydroxy-2-methylthiol-9-methylpurine*, m.p. 332° (decomp.). (I) is obtained from 4 : 6-dihydroxy-2-methylpyrimidine by treating with $POCl_3$, heating the resulting *Cl_2-compound*, m.p. 48—49°, with MeOH–NH_3 at 130°, and the *4-chloro-6-amino*-compound, m.p. 190—191°, so formed with MeOH–NH_3 at 200°.

II. $CH_2(CN)_2$ with NH:CH·NH_2,HCl and NaOEt in EtOH at room temp. yields *4-amino-5-cyanopyrimidine*, m.p. 250° (*picrate*, m.p. 189°) [also obtained from NH_2·CH_2·CH(CN)$_2$, HCS·NH_2, and NaOEt in boiling EtOH], which with boiling Ac_2O gives *acetylformamidomethylenemalononitrile*, m.p. 124—125°. PhN_2·CH(CN)$_2$, NH:CH·NH_2,HCl, and NaOEt in EtOH at room temp., then at the b.p., yield 4 : *6-diamino-5-benzeneazopyrimidine*, m.p. 282—286° (decomp.), hydrogenated (Raney Ni) to 4 : 5 : *6-triaminopyrimidine*, m.p. 257°, the *thioformyl* derivative, decomp. >200° (evolution of H_2S), of which in boiling H_2O, C_5H_5N, or quinoline yields adenine. A. Li.

Wing pigments of butterflies. IX. "Anhydroleucopterin" and "purpuroflavin." H. Wieland, A. Tartter, and R. Purrmann (*Annalen*, 1940, **545**, 209—219).—Renewed investigation has shown that "anhydroleucopterin" (A., 1933, 1310) is a deoxyleucopterin (I), $C_6H_5O_2N_5$, and thus an isomeride of xanthopterin (II). Its re-oxidation to leucopterin (III) has not been achieved. Reduction of leucopterin chloride is effected with difficulty by HI–AcOH and leads to *6-deoxyleucopterin* (IV), which does not give the murexide reaction and in N-Na_2CO_3 shows a more marked fluorescence than (I) in ultra-violet light. (IV) is obtained synthetically by heating 2 : 4 : 5-triaminopyrimidine hydrochloride with $Na_2C_2O_4$ and $H_2C_2O_4$ at 260°. It is probable that one of the O of the oxalyl CO groups has been replaced by H in the formation of (I). Fuming HI reacts immediately with (I) with separation of I, but the hydro-product is very readily dehydrogenated, even by diluting the solution. Reduction by HI is an excellent method of separating (I) from (III). Similarly (II) is immediately reduced by HI but the colourless compound is not immediately dehydrogenated when the solution is diluted. The previous distinction (*loc. cit.*) between (III) and *iso*leucopterin (V) was based on a supposed difference in behaviour towards 0·1N-NaOH. The method is now found untrustworthy and examination of the Ba salts shows (V) to be non-existent. ψ-Leucopterin (*loc. cit.*) is impure (III). 4 : 5-Diamino-2 : 6-dihydroxypyrimidine condenses with alloxan in H_2O at room temp. to *4-aminopurpuric acid*, CO·NH·CO / NH·C(NH₂) >C·N:C< CO·NH / CO·NH >CO, m.p. >270°, which under the influence of acid, alkali, or increased temp. or when kept in solution passes into *dialloxazine*, NH·CO·C·N:C–CO·NH / CO·NH·C·N:C·NH·CO, m.p. >270°. H. W.

Wing pigments of butterflies. VIII. Pterobilin, the blue pigment from *Pieridæ* wings. H. Wieland and A. Tartter (*Annalen*, 1940, **545**, 197—208; cf. A., 1937, II, 392).—After treatment with Et_2O the wings are extracted with H_2O and the blue chromoprotein is pptd. from the aq. extract by $(NH_4)_2SO_4$. It is decomposed by dil. HCl or more simply by MeOH into the protein and *pterobilin*, m.p. >315°, softens and blackens at 200°, which is thus obtained from the wings of *P. brassicæ*, *P. rapæ*, *P. napi*, *Gonepterix rhamni*, *C. rurina*, and *C. statira*, but not from *P. cratægi*. It is converted by CH_2N_2 in Et_2O–EtOAc into the *Me_2* ester, melting at 232—234° to a blue melt which becomes red-violet at ~275° and yellow-brown at 300°. This gives the Gmelin reaction and, in contrast to the esters of biliverdin and uteroverdin, is remarkably stable to conc. H_2SO_4 at 100°. It contains 3 active H. The *Zn* salt, $C_{35}H_{36}O_6N_4Zn$, m.p. >300°, appears from its behaviour towards I to contain 2 vinyl groups. With $FeCl_3$ in glacial acetic acid the ester affords *ferrobilin*, m.p. >300°. The chemical and physical properties of pterobilin indicate that it is a derivative of the bilitriene group with 4 Me, 2 C_2H_4·CO_2H, and 2 CH:CH_2 groups in the β-positions. The arrangement of these substituents must differ from that in bilirubin or biliverdin. H. W.

Constitution of the prosthetic group of cytochrome-*c*. K. Zeile and H. Meyer (*Z. physiol. Chem.*, 1939, **262**, 178—198).—The crude adduct of protoporphyrin (prep. from hæmin by HBr–AcOH at 40°) or hæmatoporphyrin, when melted with *l*-cysteine hydrochloride, exchanges the two Br or OH, respectively, for ·S·CH_2·CH(NH_2)·CO_2H, giving dicysteine-protoporphyrin (I), which with CH_2N_2–MeOH–Et_2O–conc. HCl (a little) gives the *Me_4* ester (II) (~80%; ~50% obtained by HCl–MeOH), $C_{44}H_{56}O_8N_6S_2$, amorphous, $[\alpha]^{17}_{white}$ +27° in 0·1% HCl. (II) is removed from Et_2O by 0·006% HCl and by a citrate buffer having pH 2·97 but not 4·92 (hence purification). (I) is only slightly sol. at the isoelectric point, pH 4, but readily at other pH. Acyl derivatives and urethanes could not be obtained, possibly because (II) is unstable, *e.g.*, to chromatography and keeping in Et_2O–N_2 in the dark. Acidic hydrolysis of cytochrome-*c* usually gives mixtures because of re-synthesis, but use of ~10^{-4}M. solutions in 20% H_2SO_4, neutralisation, adsorption on kaolin, elution by dil. aq. NH_3, and esterification (HCl–MeOH) gives ~67% of an *isomeride* (III), +H_2O, $[\alpha]^{17}_{white}$ +172° in 0·1% HCl, of (II). (II) and (III) are indistinguishable in solubility, partition coeff., and absorption spectra (detailed). When Fe is introduced into (II), the hæmochromogen spectrum (max. at 550 mμ.) appears at once. Thus, the NH_2 of the side-chain is co-ordinated with the Fe. R. S. C.

Colouring matters of bile. W. Siedel (*Angew. Chem.*, 1940, **53**, 397—403).—A review.

Porphyrin-like products of the reaction of pyrrole with benzaldehyde. S. Aronoff and M. Calvin (*J. Org. Chem.*, 1943, **8**, 205—223).—The reaction of pyrrole with PhCHO yields six porphyrin-like compounds which may be separated chromatographically. At present they may be distinguished, when separated, by absorption spectra and crystal forms. At least two of these, and possibly all six, are isomeric. The two known isomerides are not interconvertible by means of their Cu complexes or hydrochlorides. Their acid vals. are 13·5 and 19·5 respectively. Various distinguishing properties, including polybasicity, are discussed. A method for the spectroscopic determination of polybasic ionisation const. in a system with >2 mol. species is presented. The absorption spectra of the Cu salts of the isomerides are given. The nature of the porphyrin nucleus is discussed. The possible structure of these isomerides is presented and a new class of compound, carboporphines, is proposed. H. W.

***X*-Ray crystallography of ætioporphyrin-1.**—See A., 1943, I, 251.

Di-triazine compounds.—See B., 1943, II, 213.

2-Thiol-5 : 5-dimethyloxazoline.—See B., 1943, II, 231.

Stereoisomeric forms of additive compounds of alcohols and substituted 7-nitrostilbenes.—See A., 1943, II, 325.

Reactions of 4-β-chloroethylmorpholine and rates of reaction of 4-β-chloroethylmorpholine and other halides with sodium propoxide. S. Malkiel [with J. P. Mason] (*J. Org. Chem.*, 1943, **8**, 199—204).—4-β-Chloroethylmorpholine (**I**) is transformed by boiling aq. Na_2SO_3 into *Na β-4-morpholinoethylsulphonate*, converted by picric acid in EtOH into *β-4-morpholinoethylsulphonic acid picrate*, m.p. 178·8—182·0°. Gradual addition of (**I**) to MgPhBr at 100° leads to 4-β-phenylethylmorpholine, b.p. 132—135°/5 mm. (picrate, m.p. 170°). *Et₂ β-4-morpholinoethylmalonate*, b.p. 168—176°/4 mm., from (**I**) and $CHNa(CO_2Et)_2$ in EtOH, gives a *methiodide*, m.p. 92·2° (corr.), but does not afford a cryst. picrate, 3 : 5-dinitrobenzoate, *p*-toluenesulphonate, or quaternary metho-*p*-toluenesulphonate. Towards NaOPr^a (**I**) is less reactive than CH_2PhCl but more reactive than $Ph\cdot[CH_2]_2\cdot Cl$ and very much more reactive than Bu^aCl, $OPh\cdot[CH_2]_2\cdot Cl$, or $OEt\cdot[CH_2]_2\cdot Cl$. H. W.

Action of sulphonazides on heterocyclic compounds. (Miss) B. S. Alamela and K. Ganapathi (*Current Sci.*, 1943, **12**, 119).—The action of $p\text{-}NHAc\cdot C_6H_4\cdot SO_2N_3$ on thiazole, 2 : 4-dimethyl- and 2-hydroxy-4-methyl-thiazole, C_5H_5N, and glyoxaline does not yield any new compounds. F. R. G.

Thiazan-3 : 5-dicarboxylic acid derivatives.—See B., 1943, II, 212.

Thiazolines.—See B., 1943, II, 312.

Thiazoles. XXVII. Thiazole analogue of hydnocarpic acid. F. Brody and M. T. Bogert (*J. Amer. Chem. Soc.*, 1943, **65**, 1080—1082; cf. A., 1943, II, 110).—*Undecenoyl iodide* (prep. from the chloride by NaI in boiling, dry $COMe_2$; 91% yield), b.p. 104°/2 mm., $CN\cdot CH_2\cdot CO_2Et$, and K_2CO_3 at 130—150°/18—20 mm. give *Et α-cyano-Δ$^\lambda$-tridecenoate* (83%), b.p. 142—144°/1 mm., slowly reduced by H_2S and a little $N([CH_2]_2\cdot OH)_3$ in EtOH, cold and then at 50°, to *Et α-carbethoxy-Δ$^\lambda$-tridecenothioamide* (66%), m.p. 63·5—64°. With $CH_2Cl\cdot CHO,H_2O$ (prep. from the acetal by boiling with anhyd. $H_2C_2O_4$) in C_6H_6 at ~70°, this gives by condensation, hydrolysis, and decarboxylation, 2-Δ$^\lambda$-*dodecenylthiazole* (63%), b.p. 127°/1 mm. (*picrate*, m.p. 91—92°), oxidised by $KMnO_4$ in $COMe_2$ at <40° to *λ-2-thiazolyl-n-undecoic acid* (70%), m.p. 40—41·5° [*picrate*, m.p. 100—106° (decomp.)]. 2 : 4-Dimethylthiazole and $n\text{-}C_6H_{13}\cdot CHO$ in Ac_2O at 240—265° give α-4-methyl-2-thiazolyl-Δ$^\alpha$-*n*-octene (*picrate*, m.p. 73°). R. S. C.

Reaction of carbon disulphide with amine sulphides. E. S. Blake (*J. Amer. Chem. Soc.*, 1943, **65**, 1267—1269).—The products obtained from $(NR_2)_2S$ or $(NR_2\cdot CS)_2$ by CS_2 depend on the nature of R. Adding *bisdimethylamine sulphide*, $(NMe_2)_2S$ (prep. from $NHMe_2$ by SCl_2 in Et_2O at <5°; 54·1% yield) (1 mol.), f.p. 20°, b.p. 33·5—36°/14 mm., with cooling and stirring to CS_2 (excess; 2 mols. required) gives 99·1% of pure $(NR_2\cdot CS_2)_2$ and S (1 atom). Similarly, $(NEt_2)_2S$ (prep. as above; 52·2% yield), b.p. 79—80°/14 mm., gives $(NEt_2\cdot CS_2)_2$, an unidentified gas, and S. *Dimorpholine disulphide* [prep. from morpholine (**I**) and S_2Cl_2 in light petroleum (b.p. 87—98°) at <5°; 85·4% yield], m.p. 124—125°, and a trace of (**I**) in boiling CS_2 give *di-N-γ-oxapentamethylenethiuram trisulphide*, $(O<^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}>N\cdot CS)_2S_3$ (**II**) (96·2%), m.p. 152—153°, and S; *dimorpholine sulphide* (prep. as above but by SCl_2; 42·2% yield), m.p. 125—126°, gives similarly, but more slowly, (**II**) (94·3%) and only a trace of S. Piperidine sulphide (4 mols.) and CS_2 (8 mols. required) in C_6H_6 at room temp. give di-*N*-pentamethylenethiuram hexa- (**III**) (1 mol.), m.p. 137—138° (lit. 129°), and di-sulphide (**IV**) (3 mols.), m.p. 137°. Piperidine disulphide (2 mols.) and CS_2 (4 mols. required) give similarly (**III**) (1) and (**IV**) (1 mol.). Benzthiazole-2-sulphen*cyclo*hexylamide (1) and CS_2 (1 mol. required) in Et_2O give 2-thiolbenzthiazole (**V**) (93·9%), *cyclo*hexylthiocarbimide (**VI**) (86%), b.p. 97—98°/11—12 mm., 222°/749 mm., and S (1 atom). Benzthiazole-2-sulphenpiperidide and CS_2 in $COMe_2$ or, much more slowly, Et_2O, both at room temp., give di-2-benzthiazolyl disulphide (1) and (**V**) (1 mol.). Amine sulphoxides do not react with CS_2. R. S. C.

Phenthiazines.—See B., 1943, II, 310.

Methylene-blue and other indicators in general acids.—See A., 1943, I, 257.

Dimeric and other forms of methylene-blue. Absorption and fluorescence of the monomer.—See A., 1943, I, 248.

Aldehyde derivatives of heterocyclic compounds.—See B., 1943, II, 278.

Sulphanilamide derivatives possessing heterocyclic rings : sulphanilamidothiodiazoles. P. C. Guha and D. B. Das Gupta (*Current Sci.*, 1943, **12**, 120).—2 : 5-Diamino-, 2-amino-, 2-amino-5-methyl-, and 2-amino-5-methylthiol-1 : 3 : 4-thiodiazole with $p\text{-}NHAc\cdot C_6H_4\cdot SO_2Cl$ yield the sulphanilacetamido-derivatives, m.p. 250—254°, >300°, 200° (decomp.), and 216—218° respectively, deacetylated to the corresponding sulphanilamides, m.p. 223°, 213—214°, 186—187°, and 198°. F. R. G.

Synthesis of sulphanilamide derivatives of mixed sulphides possessing heterocyclic rings. P. C. Guha and V. M. Dokras (*Current Sci.*, 1943, **12**, 120).—Phenyldithiodiazolonyl disulphide with NH_2Ph gives the aminophenyl sulphide ($p\text{-}NHAc\cdot C_6H_4\cdot SO_2$ derivative, m.p. 222°, the deacetylated compound of which has m.p. 173°) and with $p\text{-}NH_2\cdot C_6H_4\cdot SO_2\cdot NH_2$ yields 2-*p*-sulphonamidoanilinothiol-4-phenylthiazolthione. F. R. G.

Pyrazoles.—See B., 1943, II, 302.

Cyanine dyes.—See B., 1943, II, 246, 247, 268.

Fluorescence of monomethine-cyanine dyes.—See A., 1943, I, 248.

VII.—ALKALOIDS.

Alkaloids of the *Lycopodium* species. III. *Lycopodium annotinum*, L. R. H. F. Manske and L. Marion (*Canad. J. Res.*, 1943, **21, B**, 92—96).—*L. annotinum*, L., contains the lactone base *annotinine* (0·84), $C_{16}H_{21}O_3N$, m.p. 232° (*perchlorate*, m.p. 267°), obscurine (0·09), lycopodine (0·07), and (<0·01% each) *alkaloids* L8, $C_{16}H_{25}O_2N$, m.p. 180° [*perchlorate*, m.p. 318° (decomp.) (bath preheated to 300°)], *L*9, m.p. 122°, probably a mixture of $C_{16}H_{23}ON$ [*perchlorate*, m.p. 276° (previous darkening)] and $C_{20}H_{31}O_4N$, m.p. 98° (*perchlorate*, m.p. 273·5°), *L*10, $C_{16}H_{27}ON$ (*perchlorate*, m.p. 223°), *L*11, $C_{16}H_{21}O_3N$, m.p. 176° (*perchlorate*, m.p. 239°), and *L*12, $C_{18}H_{25}O_3N$, m.p. 119° (*perchlorate*, m.p. 244°). All m.p. are corr. A. Li.

Cinchona alkaloids in pneumonia. XI. Ethers of *apo*cupreine. R. S. Tipson, (Miss) M. A. Clapp, and L. H. Cretcher (*J. Amer. Chem. Soc.*, 1943, **65**, 1092—1094; cf. A., 1942, II, 336).—*β-α'-*, m.p. 34—35°, and *β-β'-phenylethoxyethyl* p-*toluenesulphonate*, m.p. 39—40°, are prepared. *βγ-*iso*Propylideneglyceryl* α-p-*toluenesulphonate*, m.p. 49—50°, α 0, in boiling 0·5N-HCl gives *glyceryl* α-p-*toluenesulphonate*, m.p. 54°. The method of Butler *et al.* (A., 1938, II, 341) gives apo*cupreine β-methoxy-*, m.p. 156°, [α] −184° in EtOH (*dihydrochloride*, [α] −223° in H_2O), *β-ethoxy-*, m.p. 111—112°, [α] −179° in EtOH [*dihydrochloride*, +3H_2O, [α] (anhyd.) −220° in H_2O], *β-n-propoxy-*, m.p. 100—102°, [α] −173° in EtOH (*dihydrochloride*, [α] −213° in H_2O), *β-n*-butoxy-, m.p. 98—99°, [α] −165° in EtOH, and *β-α'-phenylethoxyethyl ether* (**I**), m.p. 170—171°, [α] −132° in EtOH (dihydrochloride, [α] −160° in H_2O), *βγ-*iso*propylidene-α-glyceryl*, m.p. 186—188°, [α] −169° in EtOH, *α-glyceryl*, amorphous, [α] −167° in EtOH, −266° in 0·1N-HCl [*dihydrochloride*, +2H_2O, [α] (anhyd.) −218° in H_2O], and n-*dodecyl ether*, m.p. 127°, [α] −145° in EtOH (*dihydrochloride*, [α] −156° in EtOH, −129° in 0·1N-HCl). The $OH\cdot[CH_2]_2$ ether is best prepared by hydrolysis of (**I**) (cf. *loc. cit.*). R. S. C.

Alkaloid of *Rauwolfia canescens*, Linn. III. Degradation products of rauwolscine. A. Mookerjee (*J. Indian Chem. Soc.*, 1943, **20**, 11—19).—Rauwolscine (**I**), which contains 2 active H, gives an *Ac* derivative, m.p. 216—218° (decomp.), with Ac_2O and NaOAc. Rauwolscinic acid at 300°/5 mm. yields harman and 3-ethylindole and when fused with KOH gives indole-2-carboxylic acid, *iso*phthalic acid, harman, and an indole. A partial formula for (**I**) is suggested. J. H. Ba.

Aconite alkaloids. XV. Kobusine, a new aconite alkaloid. H. Suginome and F. Shimanouti (*Annalen*, 1940, **545**, 220—228).—*Kobusine* (**I**), $C_{20}H_{27}O_2N$, m.p. 268°, $[\alpha]_D^{22}$ +83·61° in $CHCl_3$, is isolated from the residues remaining after removal of jesaconitine from the extracts of *Aconitum sachalinense*, Fr. Schmidt. It gives a *hydrobromide* (+1H_2O), m.p. 285° (decomp.), $[\alpha]_D^{18}$ +40·68° in H_2O, *hydrochloride* (**II**) (+1·5H_2O), decomp. 300°, $[\alpha]_D^{21}$ +41·4° in H_2O, anhyd. *perchlorate*, m.p. 220° (decomp.), *platinichloride*, red-brown needles or nearly colourless prisms, which blacken at 262°, and *picrate*, m.p. 277°. (**I**) cannot be hydrolysed and is stable

towards KOH–EtOH. It does not contain OMe or NHMe but is a *tert.* base since it affords a *methiodide*, m.p. 287° (decomp.). It does not react with CH_2N_2 or with CO reagents. With AcCl it affords a *diacetate*, m.p. 139—140°. (**I**) contains 2 double linkings one of which is attached to N since hydrogenation (PtO_2 in AcOH) followed by acetylation (AcCl) affords *triacetyltetrahydrokobusine*, m.p. 183—184° (decomp.). (**II**) is transformed by $NaNO_2$ into the corresponding *nitrite*, decomp. 242°, softens at 230°. Review of the empirical formulæ of the aconite alkaloids indicates the correctness of those adopted by Majima *et al.* derived from the parent bases $C_{19}H_{29}N$ and $C_{20}H_{31}N$ but suggests that atisine is $C_{22}H_{31}O_2N$ [instead of $C_{22}H_{33}O_2N$ advanced by Lawson *et al.* (A., 1937, II, 527)] and that neoline is $C_{24}H_{39}O_6N$ or $C_{23}H_{37}O_5N$ and neopelline is $C_{33}H_{45}O_8N$ or $C_{32}H_{43}O_8N$ (cf. Freudenberg *et al.*, A., 1938, II, 47). H. W.

VIII.—ORGANO-METALLIC COMPOUNDS.

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

Mercuri-compounds.—See B., 1943, II, 247; III, 161, 193.

Silicon methyl halides.—See B., 1943, II, 248.

Tin triphenyl oxide [bis-tin triphenyl ether]. O. Schmitz-Dumont (*Z. anorg. Chem.*, 1941, **248**, 289—296).—Dehydration of $SnPh_3$·OH with MeCN yields $(SnPh_3)_2O$, m.p. 122—123·5°, which gives $SnPh_2O + SnPh_4$ above its m.p., and is easily hydrolysed to $SnPh_3$·OH. C. R. H.

Condensations by sodium. XXVI. Metallation of benzene, toluene, and xylene. Orienting influence of sodium and the influence of alkyl groups on metallation. A. A. Morton, E. L. Little, jun., and W. O. Strong, jun. **XXVII. Disodium furylene. Aromatic properties of furan.** A. A. Morton and G. H. Patterson (*J. Amer. Chem. Soc.*, 1943, **65**, 1339—1346, 1346—1348; cf. A., 1943, II, 114).—XXVI. Dialkylation of C_6H_6 or PhMe by NaC_5H_{11} in n-C_5H_{18} is the main reaction if a small amount of aromatic hydrocarbon is used with vigorous stirring. Thus, after carboxylation, C_6H_6 gives 51% of m-$C_6H_4(CO_2H)_2$ (with 4·5% of BzOH), and PhMe gives 40% of m-CO_2H·C_6H_4·CH_2·CO_2H. Alkylation of xylenes is wholly or mainly nuclear; monometallation and alkylation gives p- (36%), m- (37%) [*diamide*, m.p. 213—214° (corr.)], and o-$C_6H_4(CH_2$·$CO_2H)_2$ (19% with a small amount of CO_2H·C_6H_3·CH_2·CO_2H). The m-orientation for C_6H_6 and PhMe is explained by the Na derivatives acting as salts, in which the Na is never far distant from the anion; the Na^+ thus exerts a predominating influence on further substitution. Other reactions of organo-metallic compounds are similarly accounted for. The lower reactivity of xylenes, particularly o-xylene, is due to the retarding effect of alkyl with, perhaps, accessory steric reasons.

XXVII. Furan (method as above) yields furan-2-carboxylic (27%) and -2 : 5-dicarboxylic acid (6·5%). The m-orienting influence of Na is overcome by ether grouping. R. S. C.

IX.—PROTEINS.

Experiments with melanin. E. Kovács and M. Engel (*Magyar Orv. Arch.*, 1941, **42**, 225—232).—Melanin reduces ammoniacal solutions of Ag salts to Ag and, owing to its large surface area, fixes the Ag formed. It also retards the reduction of such solutions by aldehydes and the action of blood-catalase on H_2O_2. This effect is due to the surface action of the melanin (protective colloid). M. A. B.

Coloured copper complexes formed by the biuret reaction with proteins and protein fission products. A. Küntzel and T. Dröscher (*Biochem. Z.*, 1940, **306**, 177—204).—NHMeAc and OH·CH_2·CO·NH·CH_2·CO_2Me give no biuret reaction. Deaminated (HNO_2) glycylglycylglycine ester gives a red colour, whilst NHMe·CO·CH_2·CO·NHMe gives only a pale blue colour. Structural formulæ advanced by the authors and others for these Cu–peptide complexes are discussed. Whilst peptide complexes are formed only in strongly alkaline solution, NH_2-acid–Cu complexes are formed in neutral or dil. acid or alkaline solutions. Glycine (**I**) (2 mols.) forms a complex with Cu (1 mol.) that is stable only in neutral solution; with 4 mols. of (**I**), 1 mol. of Cu gives in alkaline solution a ppt. of $[Cu(NH_2R$·$CO_2Na)_4](OH)_2$. Optical extinction curves indicate that intact and hydrolysed gelatin form a complex of Cu–(**I**) type. In dil. acid, neutral, or dil. alkaline solution, proteins give a green or green-blue colour, due to (**I**)-type reaction with the NH_2 or CO_2H groups; in conc. alkaline solutions, the red colour due to the stable peptide complex is also present. The formation of basic complexes is also postulated. Colour and extinction data for gelatin (**II**) at various stages of hydrolysis (NH_2-N up to 62·8%) and with different ratios of Cu : N indicate that the more complex is the protein product, the greater is the proportion of red component, and that the Cu : N ratio greatly affects the colour. During hydrolysis, not only are NH_2 and CO_2H groups liberated but also peptide groupings are released from the lattice structure of the intact protein and thus enabled to form their characteristic Cu complexes. With alkaline Cu–protein solutions, the saturation val. of Cu : N ratio, found by Jesserer and Lieben (A., 1937, II, 478) to be 1 : 6, is shown to be 1 : 2·38 for (**II**); such systems are probably supersaturated with $Cu(OH)_2$. Supersaturation with $Cu(OH)_2$ does not occur with hydrolysed (**II**). The normal saturation ratio for caseinogen is 1 : 6·9 and for ovalbumin, 1 : 4·1; the latter gives unstable, supersaturated systems with a ratio as low as 1 : 1·25. (**II**) alone of the three proteins gives a yellow solution on heating the Cu complex at pH 8·5—9. F. O. H.

Salmon protein as source of histidine, arginine, lysine, cystine, tyrosine, and tryptophan. L. Arrigoni and L. Fischer (*J. Amer. Pharm. Assoc.*, 1943, **32**, 155—160).—Dried, defatted muscle protein of canned pink salmon (*Oncorhynchus gorbuscha*) contains 1·55, 4·62, 6·22, 1·05, 0·86, and 0·97%, respectively, of the above NH_2-acids (isolated as such or as derivatives, *e.g.*, picrolonates). F. O. H.

Dicarboxylic and basic amino-acids of edestin, ovalbumin, and β-lactoglobulin. A. C. Chibnall, M. W. Rees, and E. F. Williams (*Biochem. J.*, 1943, **37**, 372—388).—Following hydrolysis for 23 hr. with 20% HCl, all excess of HCl is removed by repeated evaporation in a vac. after addition of H_2O. The subsequent fractionation of the hydrolysate requires the adoption of certain definite conditions, in order to minimise the overall loss of N. Cystine and the major part of the aspartic acid must be removed before the introduction of either $Ba^{\cdot\cdot}$ or SO_4''; the excess of either can then be removed as $BaSO_4$ without appreciable loss of N; Cl′ can then also be removed as AgCl without loss of N. Where phosphotungstic acid is used to ppt. bases, it can be removed without loss of N by means of C_5H_{11}·OH–Et_2O, provided that the aq. phase is first saturated with Et_2O and Et_2O–H_2O is used for all aq. washings. Cystine (and residual humin) is removed from hydrolysates, by addition of Cu_2O, as cysteine Cu^I mercaptide. Subsequent operations are standard but with observance of the precautions detailed. $CuCO_3$ must be free from SO_4'', Cl′, and other metals. 12-Phosphotungstic acid must be N- and Na-free. Ag_2O and Cu_2O must be free from salts and alkali, and $Ca(OH)_2$ free from SO_4'' and Fe. The overall losses of N in the analysis of edestin, ovalbumin, and β-lactoglobulin are 2·95, 2·86, and 1·25% respectively, of the total protein-N. Vals. for the arginine content of horse carboxyhæmoglobin and cattle hæmoglobin throw doubt on the accuracy of Vickery's flavianic acid method in some cases. P. G. M.

Nitrogen distribution and basic amino-acids in horseradish peroxidase and horse-liver catalase, determined by new micro-method.—See A., 1943, III, 840.

Crystalline horse-liver catalase.—See A., 1943, III, 841.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Volatile hydrogenation derivatives of lignin. A. Bailey (*J. Amer. Chem. Soc.*, 1943, **65**, 1165—1168).—Hydrogenation (Raney Ni; 260°/6500 lb.) of Western hemlock lignin in $Bu^{\alpha}OH$ and efficient fractionation of the volatile products gives H_2O 17·9, Pr^{β}_2 0·6, MeOH 0·2, tetrahydrofurfuryl alcohol 1·2, EtOH 0·3 (probably derived from CHEt:CMe·CHO), CMe_2Et·OH 1·0, $Bu^{\beta}OH$ 1·2, and $CHMePr^{\beta}$·OH 0·3%. Use of Cu chromite gives different products. In H_2O the products are different from those formed in BuOH or dioxan. The nature of the lignin affects that of the products. R. S. C.

Properties of lignin esters. J. J. McNair and E. C. Jahn (*Paper Trade J.*, 1943, **117**, *TAPPI Sect.*, 85—89).—Nine esters of lignin (prep. from *Abies grandis*, Lindl., by 70% H_2SO_4) and org. acids have solubilities very similar to that of lignin, are completely destroyed by treatment with, alternately, Cl_2 and Na_2SO_3, and slowly condense with PhOH, NH_2Ph, and MeCHO. Some fractionation occurs during esterification with resulting decrease or increase in OMe content, but no loss of OMe. The lignin nitrate is more sol. R. S. C.

Lignin and related compounds. LXV. Re-ethanolysis of isolated lignins. W. B. Hewson and H. Hibbert. **LXVI. Ethanolysis of maple wood.** E. West, W. S. MacGregor, T. H. Evans, I. Levi, and H. Hibbert. **LXVII. Isolation and identification of α-4-hydroxy-3 : 5-dimethoxyphenylpropan-β-one and α-4-hydroxy-3-methoxyphenylpropan-β-one from maple wood ethanolysis products. Metabolic changes in lower and higher plants.** M. Kulka and H. Hibbert. **LXIX. Isolation of α-4-hydroxy-3-methoxyphenylpropan-β-one and α-ethoxy-α-4-hydroxy-3-methoxyphenylpropan-β-one from the ethanolysis products of spruce wood.** E. West, A. S. MacInnes, and H. Hibbert. **LXX. Hydrogenolysis and hydrogenation of maple wood. LXXI. Course of formation of native lignin in spruce buds.** J. R. Bower, jun., L. M. Cooke, and H. Hibbert (*J. Amer. Chem. Soc.*, 1943, **65**, 1173—1176, 1176—1180, 1180—1185, 1187—1192, 1192—1195, 1195—1198; cf. A., 1943, II, 301).—LXV. Lignin, obtained from maple wood by repeated treatment for short periods with HCl–EtOH, is treated exhaustively with HCl–EtOH and separated into fractions sol. and insol. in Et_2O, light petroleum, NaOH, $NaHSO_3$, and acid. The monomeric products resemble those obtained by exhaustive ethylation of the wood, proving that

they are derived from the lignin and supporting the view that the process involves polymerisation and depolymerisation.

LXVI. The H_2O-sol. oils obtained by ethanolysis of maple wood are freed from resin (which causes decomp. of the monomeric fractions) by pouring the solution in $COMe_2$ into light petroleum and then exhaustively extracted from H_2O by C_6H_6 and fractionated as above.

LXVII. The H_2O-sol. oils (from maple wood) sol. in $NaHSO_3$ (see above) are converted into oximes, vanillin and syringaldehyde being thus eliminated as non-reactive. Pptn. of the Ni salts then removes diketones. Hydrolysis of the residual oximes by 7N-H_2SO_4 and fractionation yields 4-*hydroxy*-3-*methoxy*- (**I**), b.p. 115°/0·15 mm. (*semicarbazone*, m.p. 157—158°; *thiosemicarbazone*, m.p. 187—188°), and 4-*hydroxy*-3 : 5-*dimethoxy-benzyl Me ketone* (**II**), m.p. 68—69° (*semicarbazone*, m.p. 155—156°). Syringaldehyde, $EtNO_2$, NH_2Me,HCl, and Na_2CO_3 in EtOH at room temp. give *β-nitro-α-4-hydroxy*-3 : 5-*dimethoxy*-Δ^{α}-*propene*, m.p. 103—104°, converted by Fe–$FeCl_3$–HCl–H_2O–EtOH into (**II**). Vanillin gives similarly *β-nitro-α-4-hydroxy-3-methoxyphenyl*-Δ^{α}-*propene*, m.p. 101—102°, and thence (**I**). Hydrogenation in presence of Pd–C in C_5H_5N at 65° may replace reduction by Fe–HCl. The products from wood resemble the phenolic acids formed by moulds.

LXIX. Spruce wood yields (**I**) as above and 3 : 4 : 1-$OMe{\cdot}C_6H_3(OH){\cdot}CH(OEt){\cdot}COMe$ (cf. *loc. cit.*) [as NH_4 salt or semicarbazone; absorption max. at 1060 A. ($E_{max.}$ 1·66), min. at 1145 A.; with CrO_3 gives 2 AcOH; yields the known veratrole derivative].

LXX. Hydrogenation of 3 : 4 : 1-$OH{\cdot}C_6H_3(OMe){\cdot}CO{\cdot}[CH_2]_2{\cdot}OH$ (**III**) in presence of Cu chromite in dioxan at 280°/3000 lb. (cold) gives *γ-cyclo*hexylpropan-α-ol (**IV**) (76%) and 4-*n*-propyl*cyclo*hexanol (**V**) (24%). The supposedly pure (**V**) obtained by similar hydrogenation of maple wood or maple ethanol-lignin is shown by improved fractionation to contain much (**IV**). The results support the view that the terminal chains of lignin are $CH_2{\cdot}OH$ or $CH_2{\cdot}O{\cdot}C$.

LXXI. Hydrogenation (Cu chromite) of mature spruce wood (35—40 years old) gives 1·9% of (**V**), 1·4% of (**IV**), and 0·9% of γ-4-hydroxy*cyclo*hexylpropan-α-ol. None of these products is obtained from spruce tips 2·5—3 weeks old. Tips which are 3·5—4 months old give 0·8% of (**V**), *i.e.*, 20% of the lignin products. (**III**) added prior to hydrogenation increases the yields by the expected amount, thus proving absence of decomp. R. S. C.

Oxidation of solutions of humic acids and related substances. H. Niklas and C. Genninger (*Kolloid-Z.*, 1940, **93**, 225—233).—Present knowledge of the effect of oxidising agents on humic acids is discussed with special reference to H_2O_2 and the catalytic influence of $Fe(OH)_3$. C. R. H.

Fumigacin.—See A., 1943, III, 770.

XI.—ANALYSIS.

Modern methods of preparative organic chemistry. IV. Chromatographic adsorption. H. Brockmann (*Angew. Chem.*, 1940, **53**, 384—390).—A review.

Infra-red spectroscopy as an organic analytical tool. R. C. Gore (*J. Chem. Educ.*, 1943, **20**, 223—229).—A review. L. S. T.

Simple semi-micro-arrangement for the kinetics of hydrogenation.—See A., 1943, I, 287.

Qualitative test for methoxy- and other alkoxy-groups. W. C. Tobie (*Ind. Eng. Chem.* [*Anal.*], 1943, **15**, 433—434).—The substance in AcOH is treated with HI in a test-tube which holds a plug of cotton gauze impregnated with $Pb(OAc)_2$–NaOH–$Na_2S_2O_3$, which absorbs interfering substances. Above the plug a test-paper impregnated with $Hg(NO_3)_2$–HNO_3 indicates a positive test by formation of HgI_2 (orange or vermilion). The sensitivity limits are ~5 mg. for vanillin and ~10 mg. for codeine. J. D. R.

Determination of butadiene in presence of other unsaturated and saturated gaseous hydrocarbons. J. F. Cuneo and R. L. Switzer (*Ind. Eng. Chem.* [*Anal.*], 1943, **15**, 508—509).—The gases are passed through an aq. $Hg(NO_3)_2$–$NaNO_3$–HNO_3, which absorb alkylenes and alkadienes. A sample is also hydrogenated and the mol.-% of alkadiene calc. as the mol.-% unsaturation by hydrogenation minus the mol.-% unsaturation by $Hg(NO_3)_2$ absorption. J. D. R.

Macro-molecular compounds. CCXL. Fractionation of multimolecular substances by partition between two liquid phases. G. V. Schultz and E. Nordt (*J. pr. Chem.*, 1943, [ii], **155**, 115—128).—Fractionation of a heterogeneous polymer by partition between two immiscible solvents is considered theoretically. Partition of polyethylene oxide between H_2O and C_6H_6–$CHCl_3$ (increasing amounts of $CHCl_3$) is achieved, the average mol. wt. of material in the org. layer changing progressively from 6500 to 3550. R. S. C.

Sensitivity of chemical reactions. IV. Reactions of organic compounds. Z. Karaoglanov (*Z. anal. Chem.*, 1941, **121**, 92—127; cf. A., 1941, I, 427).—Sensitivities, expressed as μg. per 10 c.c., are tabulated and discussed for certain reactions, carried out under different conditions, of EtOH; CH_2O; MeCHO; $CCl_3{\cdot}CHO,H_2O$; furfuraldehyde; $COMe_2$; HCO_2H; lactic acid; tartaric acid, $CO(NH_2)_2$; fructose; glucose; lactose; sucrose; and starch. L. S. T.

Bromatometric determination of *l*-ascorbic acid (vitamin-*C*). E. Schulek, J. Kovács, and P. Rózsa (*Z. anal. Chem.*, 1941, **121**, 17—20).—The sample containing 1—200 mg. of *l*-ascorbic acid (**I**) is dissolved in 10 ml. of H_2O, 0·5 g. of KBr and 5—10 c.c. of 10% HCl are added, and the solution is titrated with 0·01 or 0·1N-$KBrO_3$ (*p*-ethoxychrysoidine hydrochloride). An indicator correction must be applied when 0·01N-$KBrO_3$ solutions are used. 1 c.c. of 0·1N-$KBrO_3$ ≡ 8·805 mg. of (**I**). Typical data are recorded, and the mechanism of the reaction is discussed. L. S. T.

Determination of formaldehyde. R. Wolf (*Rev. Brasil. Quím.*, 1943, **15**, 159—162).—Iodometric determination of CH_2O is preferred. F. R. G.

Identification of organic bases by means of the optical properties of diliturates (nitrobarbiturates). Aliphatic amines. E. M. Plein and B. T. Dewey (*Ind. Eng. Chem.* [*Anal.*], 1943, **15**, 534—537).—The optical crystallographic data for 22 primary aliphatic amine 5-nitrobarbiturates and for 5-nitrobarbituric acid are described. The optical properties provide a means of identifying pure amines and some mixtures of amines. J. D. R.

Xanthhydrol as reagent for primary amides.—See A., 1943, II, 334.

Sensitivity of chemical reactions. V. Reactions of organic compounds. Z. Karaoglanov (*Z. anal. Chem.*, 1941, **121**, 190—209).—Data for well-known reactions of PhOH, NH_2Ph, resorcinol, pyrogallol, and salicylic acid carried out under varying conditions are tabulated. Certain general conclusions arising from these and data obtained previously (see above) are discussed. Reactions of org. compounds in the reduction of $AgNO_3$ and Fehling's solution, in the reaction with Br–H_2O, and the CHI_3 reaction are compared. L. S. T.

Analytical chemistry of the *p*-hydroxybenzoic esters. F. Reimers (*Z. anal. Chem.*, 1941, **122**, 404—418).—Saponification (in aq. solution) and titration to pH 6·8 (using bromothymol-blue and a comparison buffer solution) is possible, but not suitable. Bromination after saponification, using $KBrO_3$, excess of KBr and KCl, and keeping for 15 min. in the dark, uses 6 equivs. to give $C_6H_2Br_3{\cdot}OH$; the pure esters afford the following vals.: Me 99·7%, Et 99·6%, Pr^{α} 99·6%, CH_2Ph 98·3%. Bromination of the esters uses 4 equivs. to give $OH{\cdot}C_6H_2Br_2{\cdot}CO_2R$ (R = Pr^{α}, m.p. 106—109°, R = CH_2Ph, m.p. 109—110°); the esters in EtOH solution give: Me 99·2%, Et 97·6%, Pr^{α} 99·3%, CH_2Ph 96·5%, and in NaOH solution give: Et 100·9%, CH_2Ph 97·5%. Combining the two methods gives the degree of hydrolysis of Na salts, which was found to vary in various commercial samples (from 2·6% to 52·0%), and to rise considerably on keeping solutions over periods of 1, 5, 21, and 90 days. Mixtures of esters can be analysed by a micro-refraction method (cf. Kofler, A., 1937, I, 427), by finding the temp. at which *n* is identical with that of a glass powder. The Et ester has *n* 1·5101 at 117·5—118·5°, the Pr^{α} ester at 98—99°; the composition of mixtures can be read from a calibration graph (almost linear) to 5%. S. A. M.

Determination of *p*-benzoquinone and assay of quinhydrone. E. Schulek and P. Rózsa (*Z. anal. Chem.*, 1941, **121**, 258—264).—The reduction of benzoquinone (**I**) to quinol by EtOH in presence of conc. HCl forms the basis of the method. The sample (0·5—50 mg.) is dissolved in 1—4 c.c. of 96% EtOH and then mixed with 5—10 c.c. of 38% HCl. The solution is diluted with H_2O to make the [HCl] 5 wt.-%, and titrated with 0·005 or 0·05N-$Ce(SO_4)_2$ (0·2% *p*-ethoxychrysoidine) until the red colour changes to yellow. The indicator correction must be determined. 1 c.c. of 0·05N-$Ce(SO_4)_2$ ≡ 2·7008 mg. of (**I**). In assaying quinhydrone, the quinol content is determined directly by titration with $Ce(SO_4)_2$. Typical data obtained by the new method are recorded. L. S. T.

Determination of sodium dehydro*iso*androsterone sulphate in water or urine.—See A., 1943, III, 780.

Bromatometric determination and quantitative purity testing of cinchona alkaloids containing the vinyl group. E. Schulek and J. Kovács (*Z. anal. Chem.*, 1941, **121**, 21—23).—The sample (0·1—0·2 g. of quinine) is dissolved in 10 c.c. of H_2O, 20 c.c. of 20% HCl and 1 g. of KBr are added, and the solution is titrated with 0·1N-$KBrO_3$ (*p*-ethoxychrysoidine hydrochloride), or the solution is overtitrated with 0·1N-$KBrO_3$, the excess of which is determined iodometrically. Typical data are given. Tabulated analyses of numerous commercial samples of cinchona alkaloids and their salts show that quinine and its salts, quinidine, cinchonine, and cinchonidine contain considerable quantities of a constituent that cannot be brominated. L. S. T.

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ERRATA.

Abstracts A., II, 1943.

Page	Line	
207	14	For "*α-ureido-*" read "*α-carbamido-*."
207	17	For "*α-carbamido-*" read "*α-carboxylamino-*."

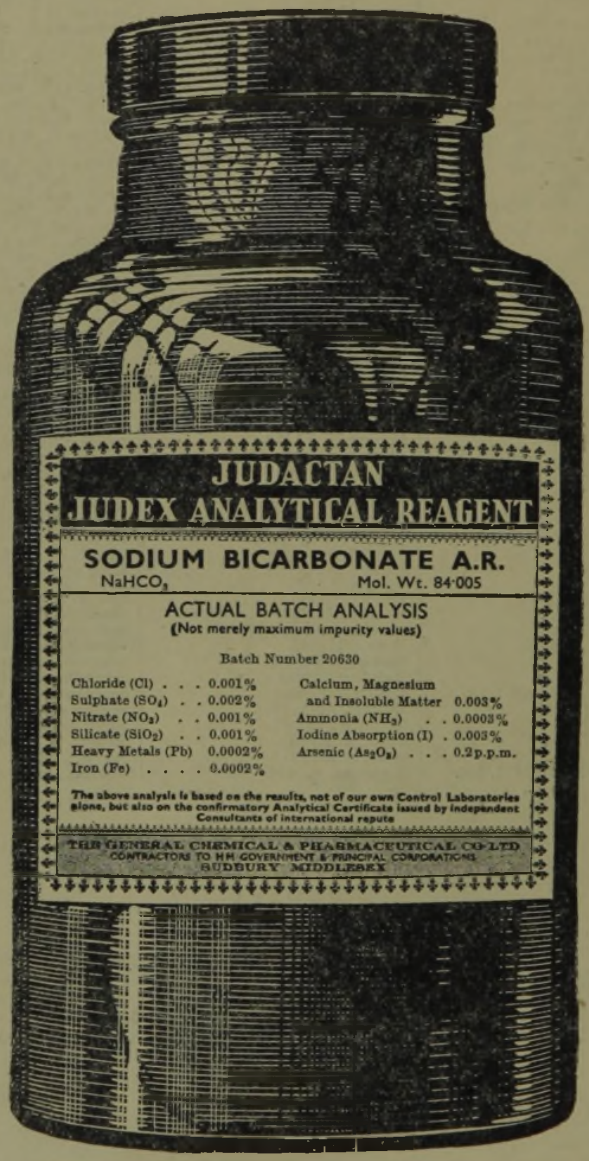
JUDACTAN

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

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