BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

OCTOBER, 1944

A II—ORGANIC CHEMISTRY

CONTENTS

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Hydrolysis of trimethylethylene dibromide [βγ-dibromo*iso*pentane]. Mechanism of ketone formation. C. M. Suter and H. D. Zook (*J. Amer. Chem. Soc.*, 1944, **66**, 738—742).—Conversion of βγ-dibromo*iso*pentane (prep. from $CMe_2{:}CHMe$ by Br–CCl_4 at 10—20° or, much less well, from $CMe_2Et{\cdot}OH$ by Br), m.p. 12—13°, b.p. 59·5—61°/19 mm., into $COMePr^{\beta}$ is shown to proceed by way of $CHMeBr{\cdot}CMe_2{\cdot}OH$ and possibly $OH{\cdot}CHMe{\cdot}CMe_2{\cdot}OH$ by measuring the rates of hydrolysis in H_2O and aq. dioxan. The same may also hold for $CH_2Br{\cdot}CMe_2Br$. R. S. C.

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Configuration of the βγ-butylene glycols. S. A. Morell and A. H. Auernheimer (*J. Amer. Chem. Soc.*, 1944, **66**, 792—796).—Reactions described below prove the configurations assigned. Heating *L*(+)-$(CHMe{\cdot}OH)_2$, b.p. 180—182°/745 mm., α {$[\alpha]_D^{23}$ (homogeneous) here and below} +1·06°; with Ac_2O, C_6H_6, and a little H_2SO_4 gives *L*(−)-$(CHMe{\cdot}OAc)_2$, b.p. 190—192°/745 mm., α −0·60° (cf. Winstein *et al.*, A., 1939, II, 401), which, when passed over stainless steel at 595°, yields $(CH_2{:}CH)_2$, AcOH, and *L*(−)-$CH_2{:}CH{\cdot}CHMe{\cdot}OAc$, b.p. 111·5—113·5°/745 mm., α −1·71°. Hydrolysis by aq. NaOH at 100° then gives *L*(+)-$CH_2{:}CH{\cdot}CHMe{\cdot}OH$, b.p. 96·2—96·5°/745 mm., α +0·68°, hydrogenated (PtO_2) at 45 lb. to *L*(+)-$CHMeEt{\cdot}OH$, b.p. 99—100°/745 mm., α +0·24° (cf. Kenyon *et al.*, A., 1925, i, 771). *DL*-$CH_2{:}CH{\cdot}CHMe{\cdot}OH$, b.p. 96·0—96·5°/745 mm., gives similarly *DL*-$CHMeEt{\cdot}OH$, b.p. 99—100°/745 mm. *D*(−)-$(CHMe{\cdot}OH)_2$ (**I**), α −12·85°. gives, as above, *D*(+)-$(CHMe{\cdot}OAc)_2$ (**II**), α +1·35°, and thence *D*(−)-$CH_2{:}CH{\cdot}CHMe{\cdot}OH$, α −1·28°. Whereas in H_2SO_4–Ac_2O–C_6H_6, (**I**), α −12·99°, is partly racemised to yield (**II**), α +4·98°, in Ac_2O alone at 100° it gives (**II**), α +13·73°, whence NaOH–MeOH–H_2O regenerates (**I**), α −12·95°, thus rendering Walden inversion during acetylation very improbable. *d* and *n* are given for these substances. R. S. C.

Optical isomerides of butane-βγ-diol produced by fermentation.—See A., 1944, III, 696.

Organ extracts. VI. Isolation of chimyl alcohol (*d*-α-hexadecylglycerol) from testes extract and its identity with "testriol." V. Prelog, L. Ruzicka, and F. Steinmann (*Helv. Chim. Acta*, 1944, **27**, 674—677).—The isolation of chimyl alcohol, m.p. 64°, $[\alpha]_D$ +2·5° in $CHCl_3$ (diphenylurethane, m.p. 97·5—98·5°; di-*p*-nitrobenzoate, m.p. 59—60°, $[\alpha]_D^{16}$ −29·8° in $CHCl_3$), is described (cf. Baer and Fischer, A., 1941, II, 311). Oxidation by $Pb(OAc)_4$ gives CH_2O and hexadecoxyacetaldehyde (*oxime*, m.p. 79—80°). The alcohol is identical with the " testriol " of Hirano (*J. Pharm. Soc. Japan*, 1936, **56**, 122), which therefore has not the structure $OH{\cdot}CMe_2{\cdot}[CH_2]_{14}{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$ assigned by him. All optically active α-glyceryl ethers have the same configuration whatever their source. H. W.

βδ : γε-Dimethylene-*DL*-xylitol and βδ-methylenexylitol. R. M. Hann, A. T. Ness, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1944, **66**, 670—673).—*DL*-Xylitol with 37% aq. CH_2O–conc. HCl at 50° gives βδ : γε-*dimethylene*-DL-*xylitol* (**I**), m.p. 201—202° (crystallo-optical data of this and the *L*-isomeride given) [α-*acetate*, m.p. 156—157° (crystallographic data); α-*benzoate*, m.p. 164—165°; α-*carbanilate*, m.p. 196—197°], the α-p-*toluenesulphonate*, m.p. 145—146°, of which with NaI in, best, CH_2Ac_2 at 120° or boiling Ac_2O gives the α-*iodide*, m.p. 144—145°. H_2–Raney Ni reduces this in KOH–MeOH at 22° to βδ : γε-*dimethylene*-α-*deoxy*-DL-*xylitol*, m.p. 155—156°, also obtained from βγ : δε-di*iso*propylidene-α-deoxy-*DL*-xylitol by conc. HCl–CH_2O–H_2O at 50°. With H_2SO_4 in AcOH–Ac_2O at 5°, (**I**) gives γ-*acetoxymethyl*-βδ-*methylene*-DL-*xylitol* αε-*diacetate*, m.p. 138—139°, which consumes 3 mols. of aq. NaOH and in NaOMe–MeOH–$CHCl_3$ gives βδ-*methylene*-DL-*xylitol*, m.p. 108—109° (*triacetate*, m.p. 87—88°; *tribenzoate*, m.p. 117—118°; *tri*-p-*toluenesulphonate*, m.p. 198—199°) (cf. following abstract), converted by BzCl–C_5H_5N at 25° into the αε-*dibenzoate*, m.p. 139—140°, but unaffected by aq. $NaIO_4$ (proof of structure). R. S. C.

Acetolysis of trimethylene-*D*-sorbitol. βδ-Methylene- and αγ : βδ-dimethylene-*D*-sorbitol. A. T. Ness, R. M. Hann, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1944, **66**, 665—670).—Structures assigned below are proved by the reactions recorded. They prove that acetolysis of $CH_2{:}$ derivatives of sugar-alcohols occurs where the $CH_2{\cdot}O$ is linked to a primary C (cf. A., 1944, II, 118). *D*-Sorbitol, 37% aq. CH_2O, and conc. HCl at 50° give (? αγ : βδ : εζ-)trimethylene- (**I**) (68%), m.p. 212—216°, $[\alpha]_D^{20}$ −30·8° in $CHCl_3$, and αγ : βδ-*dimethylene*-D-*sorbitol* (**II**) (8%), m.p. 174—175°, $[\alpha]_D^{20}$ −29·6° in H_2O (cf. Schulz *et al.*, A., 1894, i, 438). With a little conc. H_2SO_4 in AcOH–Ac_2O, (**I**) gives γε-*di*(*acetoxymethyl*)-βδ-*methylenesorbitol* αζ-*diacetate*, m.p. 111—112°, $[\alpha]_D^{20}$ +29·8° in $CHCl_3$, which consumes 4 mols. of NaOH and with 0·2N-NaOMe–MeOH in $CHCl_3$ at 5° gives βδ-*methylene*-*D*-*sorbitol* (**III**), m.p. 163—164°, $[\alpha]_D^{20}$ −9·8° in H_2O (*tetra-acetate*, m.p. 150—151°, $[\alpha]_D^{20}$ −1·5° in $CHCl_3$). (**III**) consumes 1 mol. of $Pb(OAc)_4$–AcOH, aq. $NaIO_4$, or HIO_4. With HIO_4 it gives 0·85 mol. of CH_2O and a reducing sugar, which with H_2–Raney Ni at 100°/133 atm. yields βδ-*methylene*-D-*xylitol*, m.p. 108—109°. In Ac_2O–C_5H_5N at 25° (**II**) gives the εζ-*diacetate*, m.p. 135—136°, $[\alpha]_D^{20}$ −12·8° in $CHCl_3$, in BzCl–C_5H_5N gives the εζ-*dibenzoate*, m.p. 134—135°, $[\alpha]_D^{20}$ −54·8° in $CHCl_3$, and in aq. $NaIO_4$ (1 mol. consumed) at 25° gives 0·98 mol. of CH_2O and aldehydo-αγ : βδ-*dimethylene*-L-*xylose*, $+H_2O$ (lost at 140—145°/vac.) (**IV**), sinters 150°, m.p. 175—180°, and anhyd., m.p. 189—192°, $[\alpha]_D^{20}$ −38·7° in H_2O (*oxime*, m.p. 227—228°, $[\alpha]_D^{20}$ −272° in C_5H_5N, −215·0° in H_2O). H_2–Raney Ni reduces (**IV**) in H_2O at 25° to βδ : γε-*dimethylene*-L-*xylitol* (**V**), m.p. 217—219°, $[\alpha]_D^{20}$ −25·3° in H_2O [α-*acetate*, m.p. 153—154°, $[\alpha]_D^{20}$ +2·8° in $CHCl_3$ (crystallo-optical data given)], which in H_2SO_4–Ac_2O–AcOH at 0° gives γ-*acetoxymethyl*-βδ-*methylenexylitol* αε-*diacetate*, m.p. 139—140°, α 0; the derived αεζ-*triacetate*, m.p. 94—95°, $[\alpha]_D^{20}$ +11·0° in $CHCl_3$, with NaOMe–MeOH–$CHCl_3$ gives (**III**). CH_2O–HCl converts (**V**) into (**I**) (m.p. 210—214°). R. S. C.

αγ : βδ-Dibenzylidene-*D*-sorbitol. S. J. Angval and J. V. Lawler (*J. Amer. Chem. Soc.*, 1944, **66**, 837—838).—βδ-Benzylidene-*D*-sorbitol (A., 1935, 1104) has m.p. 176—177°, $[\alpha]_D^{17}$ −1·1° in H_2O, and is obtained (17% yield) from αγ : βδ-dibenzylidene-*D*-sorbitol (**I**) (A., 1942, II, 390) by hot AcOH–EtOH–H_2O, thus proving the structure of (**I**). The structure of αγ : βδ : εζ-tribenzylidene-*D*-sorbitol, dimorphic, m.p. 203° and ~195—199° (190°) (cf. A., 1937, II, 83), is proved by similar hydrolysis to (**I**) [εζ-diacetate, m.p. 208—209° or between 202° and 206° (lit. 201—204°)]. Meunier's $(CHPh{:})_2$ compound, m.p. 162° (A., 1889, 479), was a mixture. M.p. are corr. R. S. C.

Volemitol hepta-acetate. W. D. Maclay, R. M. Hann, and C. S. Hudson (*J. Org. Chem.*, 1944, **9**, 293—297).—Treatment of natural or synthetic volemitol [*D*-manno-*D*-*talo*heptitol] with Ac_2O and NaOAc gives almost quantitatively volemitol hepta-acetate (**I**), m.p. 63°, $[\alpha]_D^{20}$ +36·1° in $CHCl_3$, +30·8° in glacial AcOH, identical with the product of Bougault *et al.* (A., 1903, i, 62), de-acetylated to pure volemitol (**II**). The compound described by Bourquelot (A., 1896, i, 273) and by Ettel (A., 1933, 47) is mannitol hexa-acetate (**III**). Photomicrographs of (**I**) and (**III**) are given. Directions are given for the isolation of (**II**) from the mixture of it with *D*-perseitol which results from the reduction of *D*-mannoheptulose. H. W.

Polymerisation of simple vinyl ethers. Vinyl *iso*butyl ether. M. F. Schostakovski and F. P. Sidelkovskaja (*J. Gen. Chem. Russ.*, 1943, **13**, 428—435).—Polymerisation of $Bu^{\beta}O{\cdot}CH{:}CH_2$ can be effected by BF_3,Et_2O, $FeCl_3$, $AlCl_3$, $ZnCl_2$, $SnCl_4$, I, or anhyd. $SnCl_2$; $SnCl_2$ (2 wt.-% on the ether) gives a polymer of mol. wt. (by η in C_6H_6) 1795—2000, separated into fractions of differing mol. wt. by pptn. from C_6H_6 with MeOH. The total polymer gives with aq. 20% HNO_3 at 100°/12 hr. $H_2C_2O_4$ and a liquid product, b.p. 97—105°, whilst with Na in $Bu^{\gamma}OH$, followed by treatment with H_2O, it gives polyvinyl alcohol (?), $\eta_{sp.}$ 0·2325, mol. wt. (η) 5280. F. H.

Acetylenic ethers. IV. Hydration. T. L. Jacobs and S. Searles, jun. (*J. Amer. Chem. Soc.*, 1944, **66**, 686—689; cf. A., 1943, II, 89).—Rates of hydration of CH:C·OR (*A*) (R = Et, Bu, and Ph) are measured dilatometrically in H_2O or 12·5—42·7% EtOH at 25° and pH 2·255—6·47. The reaction is of first order with respect to [*A*] and [H_3O^+]. The mechanism is: (*A*) + $H_3O^+ \rightarrow (CH_2{:}C{\cdot}OR)^+$ (*B*) + H_2O; (*B*) + $H_2O \rightarrow [CH_2{:}C(OR){\cdot}OH_2]^+ \rightarrow (+H_2O)$ $CH_2{:}C(OR){\cdot}OH$ (*C*) + H_3O^+; (*C*) → ROAc. R. S. C.

Unsaturated synthetic glycerides. VI. Polymorphism of *s*-mono-oleyl-disaturated triglycerides. B. F. Daubert and T. H. Clarke (*J. Amer. Chem. Soc.*, 1944, **66**, 690—691; cf. A., 1944, II, 211).—Heating and cooling curves yield the following transition points: α-monostearin, forms I 81·8°, II 78·0°, III 25·4°, IV 48·5° (Malkin's β, β′, α, and γ forms, respectively); α-monomyristin, forms I 71·0°, II 67·5°, III 55·3°, IV 21·3°; glyceryl β-oleate αγ-diacylate in which the acyl is stearyl, forms I 41·6°, II 37·0—37·6°, III 29·8°, IV 22·3°, palmityl, forms I 35·2°, II 30·4°, III 20·8°, IV 12·0°, myristyl, forms I 26·3°, II 21·5°, III 12·3°, IV 2·1°, dodecoyl, forms I 16·5°, II 11·0°, III 1·4°, IV −7·1° to −7·5°, and *n*-decoyl, forms I 6·2°, II 0·6, III −10·2°, IV −16·4°. R. S. C.

Ester interchange. H. J. Wright, J. B. Segur, H. V. Clark, S. K. Coburn, E. E. Langdon, and R. N. DuPuis (*Oil and Soap*, 1944, **21**, 145—148).—The application of ester-interchange reactions to triglycerides, *e.g.*, the formation of fatty acid esters of MeOH, EtOH, PrOH, OH·$[CH_2]_2$·O·CH_2Ph, polyhydric alcohols, furfuryl alcohol, etc., and liberation of glycerol by interaction of glyceride and the alcohol (or Me esters and polyhydric alcohols) in presence of Pb or alkaline salts as catalyst, is briefly reviewed. A continuous method of production, viz., mixing glyceride, MeOH, and NaOH catalyst at 65° for 5 min. and then centrifuging, yielded 85% of the theoretical glycerol. The utilisation of, *e.g.*, the Me and Et esters (which are obtained very pale) in soap-making, and of other esters as possible plasticisers for lacquers and synthetic rubbers, or the furfuryl esters for resin formation, is considered. E. L.

Preparation of ethyl ε-bromo-*n*-hexoate. G. B. Brown and C. W. H. Partridge (*J. Amer. Chem. Soc.*, 1944, **66**, 839).—*cyclo*-Hexanone and $K_2S_2O_8$ (cf. Robinson *et al.*, A., 1937, II, 196) give *n*-hexo-ε-lactones, converted by 48% HBr–conc. H_2SO_4 at room temp. and then 100° and finally by boiling H_2SO_4–EtOH into Br·$[CH_2]_5$·CO_2Et (45—55% over-all), b.p. 120—125°/14 mm. R. S. C.

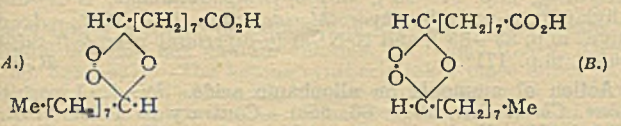
Polymerisation of undecenoic acid in presence of boron fluoride. J. R. Cann and E. D. Amstutz (*J. Amer. Chem. Soc.*, 1944, **66**, 839—840).—Undecenoic acid and gaseous BF_3 at room temp. give an oily polymer having reduced I val. and acid val., much of the CO_2H being "esterified" with the C:C. After hydrolysis the polymer gives a CHI_3 test, proving this interpretation. CHMe:CH·CO_2H and fatty acids from drying oils behave similarly. R. S. C.

Reformatsky condensations involving vinylogues of halogenoacetic esters. II. Methyl γ-bromosenecioate. R. C. Fuson and P. L. Southwick (*J. Amer. Chem. Soc.*, 1944, **66**, 679—681; cf. A., 1938, II, 442).—A method of lengthening a C chain by an isoprene unit is described. $CH_2{:}CMe{\cdot}CH_2Cl$ and CuCN (cf. Tamele *et al.*, A., 1941, II, 82) give *β-methylallyl cyanide* (76%), b.p. 134·5—136·5°, which with Br–$CHCl_3$ (cooling) yields *βγ-dibromoisovaleronitrile*, b.p. 89°/2—3 mm., converted by K_2CO_3 in boiling COMeEt into *γ-bromosenecionitrile* (~50%), b.p. 84°/8 mm., or by boiling H_2SO_4–MeOH [5 : 8 (vol.)] into *Me βγ-dibromoisovalerate*, b.p. 84—85°/3 mm. With K_2CO_3 in boiling COMeEt this gives impure $CH_2Br{\cdot}CMe{:}CH{\cdot}CO_2Me$ (**I**), b.p. 63—66°/3 mm., better obtained by the method of Ziegler *et al.* (A., 1943, II, 2, 32). PhCHO, (**I**), Zn, and a trace of I in boiling C_6H_6–Et_2O give esters, b.p. 146—148°/2—3 mm. and 152—176°/2—3 mm., hydrolysed (KOH–EtOH) to *δ-phenyl-β-methyl-Δ$^{\alpha\gamma}$-pentadienoic acid, forms* A, m.p. 158·5—159·5°, and B, m.p. 156·5—157·5°, respectively (cf. *loc. cit.*). Form *B* is accompanied by some *δ-phenyl-β-methyl-Δ$^{\alpha}$-buteno-δ-lactone*, m.p. 61—62°. Form *A* is also obtained by condensing CHPh:CH·COMe and $CH_2Br{\cdot}CO_2Et$ by Zn and subsequently hydrolysing by KOH–EtOH. R. S. C.

Ozonides and their fission. A. Rieche, R. Meister, and H. Sauthoff [with, in part, H. Pfeiffer] (*Annalen*, 1942, **553**, 187—249).—Review of the properties of the ozonides and comparison with the alkyl peroxides confirms Staudinger's formulation, CHR<O·O / O>CHR. Pure ozonides are best obtained by use of O_3 passed through 0·01N-NaOH and dried with P_2O_5. MeCl and EtCl are the most suitable solvents; CCl_4 and EtOAc are also useful but AcOH is unsuitable since it is very hygroscopic, difficult to remove, and causes hydrolysis. The ozonisation of $(CHMe)_2$ and C_2H_4 is described. In no case has there been any indication of a labile intermediate such as the "molozonide" of Staudinger. The physical properties of the ozonides are intermediate between those of the corresponding dialkyl and hydroxydialkyl peroxides. Refractometric measurements show that only one peroxide group is present in the ozonides, in which it exists in the same form as in the peroxides. Absorption curves permit only qual. conclusions but show close similarity in constitution between peroxides and ozonides. The parachor vals. indicate the presence of a 4- or 5-membered ring. Determination of active O in peroxides and ozonides is seldom quant. but for ozonides a val. in excess of that required for one active O has never been observed. The use of the acetal formula does not involve any essential alteration in the Harries scheme for the decomp. of ozonides. Examination of the more tractable ozonide (**I**) of oleic acid confirms Harries' observation of its decomp. by Fe into the peroxides of nonaldehyde and azelaicsemialdehyde. In AcOH these substances are unimol. but in freezing dioxan or boiling Et_2O or $COMe_2$ a double mol. wt. is observed. Fresh analyses, determination of active O, and observed decomp. essentially into 2 mols. of aldehyde and 1 mol. of H_2O_2 show that the compounds are respectively dihydroxynonyl peroxide {Me·$[CH_2]_7$·CH(OH)·O}$_2$ and the dicarboxylic acid {CO_2H·$[CH_2]_7$·CH(OH)·O}$_2$; the former has been obtained synthetically from nonaldehyde and H_2O_2. Similarly, Harries' "formaldehyde peroxide" is $(OH{\cdot}CH_2{\cdot}O)_2$. The first step in the fission of ozonides of *n*-olefines in the presence of H_2O is therefore the hydrolysis of the ether bridge. The invariable production of symmetrical dialdehyde peroxides and not mixed dihydroxyalkyl peroxides by the fission of ozonides is due to an exchange reaction since a hydroxyalkyl peroxide is shown to react with an aldehyde different from that contained in the peroxide with production of a symmetrical dihydroxyalkyl peroxide, 2OH·CHR′·O_2H + 2R″CHO → (OH·CHR′·O)$_2$ + (OH·CHR″·O)$_2$. Hydrolysis of ozonides is initiated by rupture of the ether ring. Dihydroxyalkyl peroxides are thus produced and form an equilibrium with hydroxyalkyl H peroxides, aldehyde, and H_2O_2. Hydroxyalkyl H peroxides yield carboxylic acids and H_2O. The ozonides of $(CAlk_2{:})_2$ and $(CAr_2{:})_2$ have a peculiar position. Direct conversion of olefines into carboxylic acids is possible when ozonisation occurs in a warm hydrolysing solvent, *e.g.*, aq. AcOH. Thus oleic acid is smoothly transformed into pelargonic and azelaic acid and undecenoic into sebacic and formic acid. Thermal fission of ozonides, usually in presence of a catalyst, occurs: CHR<O·O / O>CHR′ → R′CHO + CHR′O_2 (→ RCO_2H) and CR_2<O·O / O>CHR′ → $CR_2O_2{\cdot}$ + R′CHO. Catalytic fission in presence of Fe^{II} salts, Ag, Pd, or Pt probably proceeds: CHR<O·O / O>CHR → R·C(:O)·O·CHR·OH → RCO_2H + RCHO; intramol. disproportionation accompanies hydrolysis and becomes the main reaction in anhyd. media. It appears probable that the weakening of the C–C union in the formation of ozonides depends on diradical formation and hence can be explained in the manner advanced by Criegee for the dehydrogenation of αβ-glycols. During the ozonisation of (**I**) in EtOAc or CCl_4, CH_4, CO, and CO_2 are evolved in amount corresponding to the shortening by 1 unit of 14% of the chain of (**I**); no theoretical explanation is advanced. $(OH{\cdot}CHMe{\cdot}O)_2$ is converted by P_2O_5 in dry Et_2O or MeCl into a peroxide, b.p. 27°/55 mm., identical with that derived by the ozonisation of $(CHMe)_2$, thus directly establishing the structure of the ozonide; more complex compounds are obtained simultaneously.

Ozonisation of the simpler olefines gives viscous products which remain after removal of the monomerides and may form the main product if ozonisation is prolonged. The relatively small mol. wt. observed for these compounds in freezing AcOH is due to hydrolysis by the solvent, which increases with time; in C_6H_6, dioxan, and cineole much higher vals. are obtained so that the supposed "dimerides" are really polymerides which may contain a small proportion of dimerides. The latter are shown to exist by the isolation of dimeric butene ozonide $O(CHMe{\cdot}O{\cdot}O{\cdot}CHMe)_2O$ in addition to the monomeride from $(OH{\cdot}CHMe{\cdot}O)_2$ and P_2O_5, and of the cryst. highly explosive tetramethylene diperoxide from P_2O_5 and $(OH{\cdot}CH_2{\cdot}O)_2$. Most ozonisation products hitherto described in the literature as dimeric ozonides are multimol. and true dimeric products have thus far been isolated only by synthesis from dihydroxyalkyl peroxides. Determinations of mol. wt., parachor, mol. refraction, and ultra-violet absorption spectrum indicate that the viscous liquids, regarded previously as dimerides, are mixtures of multimol. ozonides containing as a mean 4—6 mols. Polymeric butene ozonide is therefore CHMe<O_2–CHMe–O / [O·CHMe·O_2]$_x$>CHMe. In the rings peroxide groups and ether bridges alternate, ·O_2·CR_2·O·CR_2·O_2·CR_2·O·CR′$_2$, but the ring structure is not definitely established. Fission of the complex ozonides is essentially the same as that of the mono- and di-merides; thus butene ozonide and alkali give equimol. amounts of AcOH and MeCHO and alkali and mol. Ag cause decomp. with elimination of H. Complex butene ozonide like the dimeride becomes more viscous and gradually highly explosive and sensitive to trituration when kept in absence of moisture. At 80—90°/vac. this dangerous "cracking" is complete in 2 hr., leading to a compound $(C_2H_4O_2)_x$ in which all the O is peroxidic; MeCHO is evolved and the product appears to be polymeric ethylidene peroxide. Experiments with pure oleic and elaidic acid show that the ozonides (*A* and *B*) are closely similar but nevertheless distinct from one another and that apparently

only one compound is formed in each case. The constitutions (*A*) and (*B*) are assigned. It is therefore impossible that even a



momentary rupture of the acid mols. into diradicals and direct intrusion of the O_3 mol. can occur. Addition of O_3 leads to a very short existence of a primary ozonide and hence to a single C–C linking; during rupture of this linking and establishment of the ether bridge free rotation is possible for an instant but the fixation of substituents occurs at definite places of the C atoms.

The tendency towards the formation of multimol. ozonides is more pronounced with simple than with complex olefines and is very dependent on the solvent, occurring much more readily in CCl_4 than in EtOAc. Polymerisation must occur at the instant when the C–C linking is ruptured; subsequent polymerisation of a monomeride has never been observed but a multimol. compound can become further polymerised. This is indicative of a chain reaction along the lines : $\dot{C}{:}\dot{C} + O_2 \rightarrow {:}O{\cdot}O{\cdot}\dot{C}{\cdot}\dot{C}{\cdot\cdot} + \dot{C}{:}\dot{C} \rightarrow {\cdot\cdot}O{\cdot}O{\cdot}\dot{C}{\cdot}\dot{C}{\cdot}\dot{C}{\cdot\cdot}$ or

$\dot{C}{:}\dot{C} + O_2 \rightarrow {\cdot\cdot}O{\cdot}O{\cdot}\dot{C}{\cdot}\dot{C}{\cdot\cdot} + O_2 + \dot{C}{:}\dot{C} \rightarrow {\cdot\cdot}O{\cdot}O{\cdot}\dot{C}{\cdot}\dot{C}{\cdot}O{\cdot}O{\cdot}\dot{C}{\cdot}\dot{C}{\cdot\cdot\cdot}$ etc. or

$\dot{C}{:}\dot{C} + O_3 \rightarrow {\cdot\cdot}O{\cdot}O{\cdot}\dot{C}{\cdot}O{\cdot}\dot{C}{\cdot\cdot} + O_3 + \dot{C}{:}\dot{C} \rightarrow {\cdot}O{\cdot}O{\cdot}\dot{C}{\cdot}O{\cdot}\dot{C}{\cdot}O{\cdot}O{\cdot}\dot{C}{\cdot}O{\cdot}\dot{C}{\cdot\cdot\cdot}$.

The third type of change could occur through primary ozonides and the rupture of the C·C linking occurs through their transformation. Rupture of the chain can be caused by ring formation; this is probably the case with the multimol. ozonides of the simpler olefines or when a mixture or fission product of the ozonide adds to the reactive terminal positions, thus causing inactivation. Intrusion of ethylenic residues is to be expected, thus involving a polymerisation of the olefine. This does not occur if the concn. of O_3 or O_2 is so high that every radical is immediately trapped. The co-operation of mol. O_2 is to be expected particularly when the concn. of O_3 in the solution is low.

Ozonisation of $(:CHMe)_2$ under the conditions laid down by Harries for the production of the oxozonide and removal of all volatile matter from the product gives a residue similar to Harries' material; a similar product is also obtained by the after-treatment of multimol. butene ozonide with O_3. Physical properties and chemical behaviour towards alkali and $FeSO_4$ show that the product is multimol. ethylidene peroxide, $(C_2H_4O_2)_3$. H. W.

Production of organic peracids and salts thereof.—See B., 1944, II, 219.

Production of lævulic acid [from wood].—See B., 1944, II, 220.

Dehydration of β-hydroxy-βγγ-trimethyl-*n*-valeric acid. M. S. Newman and R. Rosher (*J. Org. Chem.*, 1944, **9**, 221—225).—Dehydration of $OH{\cdot}CMeBu^{\gamma}{\cdot}CH_2{\cdot}CO_2H$ (I) and its ester proceeds without mol. rearrangement. $OH{\cdot}CMeBu^{\gamma}{\cdot}CH_2{\cdot}CO_2Me$ (II), b.p. 88—90°/14 mm., is obtained in 66% yield by gradually adding a solution of $CH_2Br{\cdot}CO_2Me$ and pinacolone in dry C_6H_6 to Zn foil in presence of a little I. The yield of this or the Et ester (III), b.p. 104—107°/18 mm., sinks to ~53% if all the reactants are placed together at once. Treatment of (II) with $COCl_2$ and C_5H_5N in Et_2O followed by hydrolysis, heating (III) with I followed by hydrolysis, or heating (I) with Ac_2O leads to a mixture of a solid acid (IV), m.p. 84·5—85·0° (corr.), and a liquid acid (V), each of which yields the same *amide*, m.p. 141—142° (corr.); they are regarded as geometrically isomeric forms of *βγγ-trimethyl-Δ$^{\alpha}$-pentenoic acid*. Catalytic reduction (PtO_2) of (IV) or (V) gives βγγ-trimethyl-*n*-valeric acid [identified as the amide, m.p. 166—167° (corr.)] in 83% yield. (IV) or (V) is transformed by NaOH at 225° into pinacolone, identified as the 2 : 4-dinitrophenylhydrazone, m.p. 124—125°. Reaction between (II) or (III) and I is erratic, sometimes giving a lachrymatory liquid, probably iodopinacolone. Al_2O_3 at 300—325° causes cleavage of (II). $POCl_3$ in boiling C_6H_6 transforms (III) into *β-tert.*-butyl-γ-butyrolactone (VI), b.p. 117°/20 mm., m.p. 99—100°, more easily obtained by heating (I), (II), (III), (IV), or (V) with 50% H_2SO_4 under reflux. (VI) is very resistant towards hydrogenation either by HI or in presence of Raney Ni. It is completely degraded by $KMnO_4$ or 50% HNO_3 but untouched by CrO_3. It is readily hydrolysed by alkali, but the liberated acid immediately reverts to (VI). With MgPhBr (VI) affords (?) 2 : 2-*diphenyl*-4-tert.-*butyltetrahydrofuran*, m.p. 79·5—80·0°. H. W.

Autoxidation of ascorbic acid in presence of copper.—See A., 1944, I, 228.

***l*-Amino-acid oxidase of *Proteus vulgaris*.** P. K. Stumpf and D. E. Green (*J. Biol. Chem.*, 1944, **153**, 387—399; cf. A., 1944, III, 688).—2 : 4-*Dinitrophenylhydrazones* of the following are described : 2-indolylpyruvic acid, m.p. 169°, α-ketohexoic acid, m.p. 134°, α-ketoisohexoic acid, m.p. 155°, α-ketovaleric acid, m.p. 160°, 2-iminazolyl pyruvic acid, m.p. 239° (decomp.) [*hydrochloride* (+2H_2O), m.p. 192° (decomp.)], δ-guanido-α-ketovaleric acid, m.p. 267° (decomp.) [*hydrochloride*, (+1H_2O), m.p. 216° (decomp.)]. J. N. A.

Reaction of diazomethane with ammonium salts of organic acids. M. Frankel and E. Katchalski (*J. Amer. Chem. Soc.*, 1944, **66**, 763—765).—NH_4, NH_2Me, NH_2Et, $NHMe_2$, or NEt_3 salts of malonic, succinic, or phthalic acid with CH_2N_2 in Et_2O give 72—92% of the Me_2 ester and the appropriate amine (which is not methylated; cf. A., 1944, II, 15). NH_4Cl and CH_2N_2–Et_2O give NH_3 (69%) and MeCl (53%). R. S. C.

***p*-Carboxyphenylhydrazones of palmit-, m.p. 101—102° (decomp.), and stearaldehyde, m.p. 105° (decomp.), and corresponding carboxymethoximes, m.p. 68—89° and 81—82°, thiosemicarbazones, m.p. 109° and 112°, and glyceryl acetals, m.p. 48—49° and 57° respectively.**—See C., 1944, 117.

Synthesis of hydroxycitronellal.—See B., 1944, II, 220.

Tests of mechanism for the photochemical decomposition of acetone.—See A., 1944, I, 229.

Silver (Ag^{III}) ethylenedibiguanide hydroxide and its salts.—See A., 1944, I, 230.

Peptidases of intestinal mucosa. E. L. Smith and M. Bergmann (*J. Biol. Chem.*, 1944, **153**, 627—651).—The following are preps. of di- and tri-peptides as substrates for the study of peptidase action (cf. A., 1944, III, 689). *l*-Hydroxyproline (I), with carbobenzyloxyglycyl chloride (II) and 2N-NaOH at room temp. yields *carbobenzyloxyglycyl-l-hydroxyproline*, m.p. 124—124·5°, hydrogenated (Pd-black) in aq. MeOH–AcOH to glycyl-*l*-hydroxyproline, $[\alpha]_D^{26}$ −128·4° in H_2O (cf. Abderhalden and Köppel, A., 1928, 1041). (I) is esterified by HCl–$CH_2Ph{\cdot}OH$ to *l-hydroxyproline CH_2Ph ester hydrochloride*, m.p. 147—150°, which with carbobenzyloxyglycylglycine azide gives *carbobenzyloxydiglycyl-l-hydroxyproline CH_2Ph ester*, m.p. 123—127°, converted as above into *diglycyl-l-hydroxyproline*, $[\alpha]_D^{26}$ −97·7° in H_2O. Similarly prepared are *carbobenzyloxydiglycyl-l-proline CH_2Ph ester*, m.p. 87°, and *diglycyl-l-proline*, $[\alpha]_D^{26}$ −101·5° in H_2O. The *Me* ester *hydrochloride* (III), m.p. 162—164° (decomp.), of (I), coupled with (II) and treated with MeOH–NH_3, affords *carbobenzyloxyglycyl-l-hydroxyprolineamide*, m.p. 208°, which on hydrogenation etc. gives *glycyl-l-hydroxyproline diketopiperazine*, $[\alpha]_D^{26}$ −190·4° in H_2O. Similarly prepared are *carbobenzyloxyglycyl-l-prolineamide*, m.p. 150—151°, and glycyl-*l*-proline diketopiperazine, m.p. 213°, $[\alpha]_D^{26}$ −197·3° in H_2O (cf. Fischer and Reif, A., 1908, i, 1007). (III) with H_2O–$CHCl_3$–MgO, $CH_2Ph{\cdot}O{\cdot}COCl$, and finally C_5H_5N followed by HCl yields *carbobenzyloxy-l-hydroxyproline hydrazide*, m.p. 149—149·5°, from which are prepared in the usual way *carbobenzyloxy-l-hydroxyprolylglycine CH_2Ph ester*, m.p. 153°, and *l-hydroxyprolylglycine*, $[\alpha]_D^{26}$ −22·42° in H_2O. Also prepared are *l-prolineamide hydrochloride*, m.p. 173—175°, and *l-hydroxyprolineamide*, m.p. 139°. F. O. H.

Effect of dielectric constant and temperature on the catalysed decomposition of azodicarbonate ion.—See A., 1944, I, 227.

Interaction of diazomethane with α-cyanocrotonic acid. W. G. Young, L. J. Andrews, S. L. Lindenbaum, and S. J. Cristol (*J. Amer. Chem. Soc.*, 1944, **66**, 810—811).—$CHMe{:}C(CN){\cdot}CO_2H$ (I) (modified prep.), m.p. 96—99° (lit. 80°, 92°), with CH_2N_2–Et_2O gives $CMe_2{:}C(CN){\cdot}CO_2Me$ (II), m.p. 19·5—21°, b.p. 90—91°/5 mm. [absorption max. at 230 mμ. (ε 11,100) in 95% EtOH], also obtained (m.p. 21·5—22°) by Cope's method (A., 1938, II, 5), but the Ag salt with MeI gives *Me α-cyanocrotonate* (III), m.p. 20—22°, b.p. 75·5—76·8°/4—5 mm. [absorption max. at 220 mμ. (ε 8400) in 95% EtOH]. In 3N-NaOH, (II) or (III) gives $COMe_2$ or MeCHO, respectively, but with O_3 in CH_2Cl_2, (III) gives a little MeCHO whereas (II) is unaffected. CH_2N_2 converts (III) into (II). Formation of (II) from (I) probably occurs by way of (III) and the pyrazoline, which is too unstable to exist as such. The mechanism of its formation and decomp. is discussed. R. S. C.

α-Toluenesulphonamido-δ-hydroxyvaleramide, m.p. 182—183° (decomp.).—See A., 1944, III, 605.

Resolution of α-xanthogenopropionic acid into optically active isomerides. A. Fredga and M. Tenow (*Arkiv Kemi, Min., Geol.*, 1943, **17, B**, No. 3, 5 pp.).—(−)-, m.p. 70—71°, $[\alpha]_D^{26}$ −91·1° in EtOAc, −81·8° in EtOH (resolved through the cinchonidine salt, EtOH), and (+)-*xanthogenopropionic acid* (I), m.p. 70—70·5°, $[\alpha]_D^{25}$ +92° in EtOAc (*strychnine* salt, +1H_2O), are prepared. (I) and conc. NH_3 (1 day), followed by H_2O_2, yield $NH_2{\cdot}CS{\cdot}OEt$ and disulphidodi-α-propionic acid, m.p. 113—115°, $[\alpha]_D^{25}$ −410° in H_2O. A. T. P.

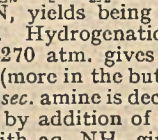
Basically substituted aliphatic nitriles. Their catalytic reduction to [di]amines. F. C. Whitmore, H. S. Mosher, R. R. Adams, R. B. Taylor, E. C. Chapin, C. Weisel, and W. Yanko (*J. Amer. Chem. Soc.*, 1944, **66**, 725—731).—$CH_2{:}CH{\cdot}CN$ (I) and NHR_2 yield, by 1 : 4-addition, $NR_2{\cdot}[CH_2]_2{\cdot}CN$ (*A*), the rate of reaction being piperidine > morpholine > $NHEt_2$ and for other $NHAlk_2$ slower as the mol. wt. of R increases; in some cases a catalyst (noted with temp. of prep. below) is needed. The rate is not $\propto k$ of NHR_2. The reaction is reversible, since (i) higher (*A*) dissociate slowly at the

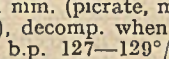
b.p. to give NHR_2; notably (*A*) (R = $[CH_2]_2$·OH) dissociates completely when distilled, (ii) yields are increased by using an excess of either reactant, (iii) hydrogenation (Raney Ni) of (*A*) (NR_2 = morpholino) at 190° gives 35% of morpholine, and (iv) (*A*) (R = H) dissociates when kept into NH_3 and a tarry polymeride of (I). NH_2·$[CH_2]_n$·OH and (I) in presence of NaOMe give good yields of NR_2·$[CH_2]_n$·O·$[CH_2]_2$·CN. Hal·$[CH_2]_3$·CN and NHR_2 give NR_2·$[CH_2]_3$·CN, yields being much improved by use of a solvent (C_6H_6–$CHCl_3$). Hydrogenation (Raney Ni) of (*A*) at, usually, 90—130°/67—270 atm. gives the diamine with minor amounts of the *sec.* amine (more in the butyro- than in the propio-nitrile series); the amount of *sec.* amine is decreased by presence of an excess of NH_3 and increased by addition of primary amine before hydrogenation. Shaking (I) with aq. NH_3 gives mainly $NH([CH_2]_2$·$CN)_2$ (II), b.p. 165°/4 mm. (picrate, an oil), and $N([CH_2]_2$·$CN)_3$, but with liquid NH_3 (7 mols.) at ~40° gives NH_2·$[CH_2]_2$·CN (22%), b.p. 66—69°/1 mm. (picrate, m.p. 178°), and (II) (64%). The following are described: NR_2·$[CH_2]_2$·CN in which R = Et (best prepared at room temp. and then the b.p.), b.p. 196°/735 mm., 104—106°/35 mm. (picrate, m.p. 85°), Pr^a, b.p. 116°/20 mm. (picrate, m.p. 111°), Bu^a, b.p. 141°/20 mm. (picrate, m.p. 75°), *n*-amyl, b.p. 159—161°/19 mm. (picrate, an oil), and *n*-hexyl, b.p. 145—146°/2 mm. (picrate, an oil); *β-ethylaminopropionitrile* (best at <30° and then 100°), b.p. 92—95°/30 mm. (*picrate*, m.p. 163°); *di-(β-cyanoethyl)ethylamine*, b.p. 200—202°/30 mm. (*picrate*, m.p. 170°); *β-piperidino-*, b.p. 129—130°/30 mm. (*picrate*, m.p. 160°), and *β*-morpholino-propionitrile, b.p. 149°/20 mm. (picrate, m.p. 139·5°); NR_2·$[CH_2]_3$·CN, in which R = Et, b.p. 101—103°/21 mm. (picrate, m.p. 69—70°), and OH·$[CH_2]_2$ (prep. at room temp.), decomp. when distilled (*picrate*, m.p. 108—109°); *γ*-piperidino-, b.p. 127—129°/25 mm. (picrate, m.p. 117°), and *γ-morpholino-n-butyronitrile*, b.p. 148—150°/25 mm. (*picrate*, m.p. 152—153°); *β-hydroxy-β′β″-dicyanotriethylamine*, decomp. when distilled (*picrate*, m.p. 137—138°); $(CN·[CH_2]_2)_2O$; *NN-diethyl-N′N′-di-β′-cyanoethylpropylene-αγ-diamine*, m.p. 233—235°/25 mm. (*picrate*, m.p. 166—167°); *β-di-(γ′-diethylamino-n-propyl)aminopropionitrile* (at 100°; catalyst: trace of Cu-bronze), b.p. 153°/3 mm. (*picrate*, m.p. 157—158°); *β-β′-morpholinoethyl-*, b.p. 183°/20 mm. (*picrate*, m.p. 176·5°), and *β-γ′-morpholino-n-propyl-*, b.p. 178—180°/9 mm. (*picrate*, m.p. 148—149°), *-aminopropionitrile*; *β-β′-diethylaminoethoxypropionitrile* (prep. at 25°), b.p. 145°/25 mm. (*picrate*, m.p. 75°); *β-γ′-diethylamino-n-propoxypropionitrile*, b.p. 148—150°/25 mm. (picrate, an oil); *β-δ′-diethylamino-α′-methyl-n-butoxypropionitrile*, b.p. 125—130°/3 mm. (picrate, an oil); *β*-N-*methylanilinopropionitrile* (at 180°; catalyst: $CuSO_4$,$5H_2O$; $CH_2Ph·NMe_3·OH$ is ineffective), b.p. 175—177°/29 mm. (*picrate*, m.p. 118°); *9-β-cyanoethylcarbazole* (catalyst: $CH_2Ph·NMe_3·OH$), m.p. 155·5°; *1-β-cyanoethyl-1 : 2 : 3 : 4-tetrahydroquinoline* (in AcOH at 125°; other catalysts ineffective), b.p. 192°/10 mm. (*picrate*, m.p. 172°); NH_2·$[CH_2]_2$·NR_2 in which R = H, b.p. 138°/735 mm. (picrate, m.p. 178°), Et, b.p. 168°/735 mm. (picrate, m.p. 194°), Pr^a, b.p. 94°/20 mm. (picrate, m.p. 181°), and Bu^a, b.p. 121°/20 mm. (picrate, m.p. 188°); *di-(γ-diethylamino-n-propyl)amine*, b.p. 107°/3 mm. (*picrate*, m.p. 153—154°); *N-ethylpropylene-αγ-diamine*, b.p. 156°/735 mm. (*picrate*, m.p. 193°); *γ*-piperidino-, b.p. 205°/730 mm. (picrate, m.p. 209—210°), and *γ*-morpholino-*n*-propylamine, b.p. 219°/733 mm. (picrate, m.p. 166°); *di-(γ-piperidino-*, b.p. 153°/2 mm. (*picrate*, m.p. 193°), and *di-(γ-morpholino-n-propyl)amine*, b.p. 185°/5 mm. (*picrate*, m.p. 213—215°); NR_2·$[CH_2]_4$·NH_2 in which NR_2 = NEt_2, b.p. 85—88°/18 mm. (picrate, m.p. 185—186°), piperidino-, b.p. 118—120°/25 mm. (picrate, m.p. 160·5°), and *morpholino-*, b.p. 122°/20 mm. (*picrate*, m.p. 148°); *di-(δ-piperidino-*, b.p. 220—225°/25 mm. (*picrate*, m.p. 202—203°), and *di-(δ-morpholino-n-butyl)amine*, b.p. 200—202°/3 mm. (*picrate*, m.p. 136°); *γ-di-(β′-hydroxyethyl)amino-n-propylamine*, b.p. 158°/2 mm. (*picrate*, m.p. 157—158°); *di-γ-amino-n-propyl ether*, b.p. 113°/32 mm. (picrate, an oil); *γ-γ′-diethylamino-n-propylamino-n-propylamine*, b.p. 142—144°/25 mm.; *di-(γ-γ′-diethylamino-n-propylamino-n-propyl)amine*, b.p. 253—260°/25 mm. (*picrate*, m.p. 197°); *γ-di-(γ′-diethylamino-n-propyl)amino-n-propylamine*, b.p. 155—165°/3 mm. (*picrate*, m.p. 162·5°); *γ-β′-morpholinoethyl-*, b.p. 120—123°/2 mm. (*picrate*, m.p. 208°), and *γ-γ′-morpholino-n-propyl-*, b.p. 137—140°/1·5 mm. (*picrate*, m.p. 205°), *-amino-n-propylamine*; *γ-β′*-diethylaminoethoxy-, b.p. 118—122°/25 mm. (picrate, an oil), *γ-γ′-diethylamino-n-propoxy-*, b.p. 130—132°/25 mm. (picrate, an oil), *γ-δ′-diethylamino-α-methyl-n-butoxy-*, b.p. 80—83°/2 mm. (*picrate*, m.p. 88—89°), and *γ*-N-*methylanilino-*, b.p. 171—172°/40 mm. (*picrate*, m.p. 189°); *hydrobromide*, m.p. 120°), *-n-propylamine*; *di-(γ-β′-diethylaminoethoxy-*, b.p. 175°/3 mm. (picrate, an oil), *di-(γ-γ′-diethylamino-n-propoxy-*, b.p. 182°/3 mm. (picrate, an oil), and *di-(γ-δ′-diethylamino-α-methyl-n-butoxy-*, b.p. 210—215°/3 mm. (picrate, an oil), *-n-propyl)amine*; *9-γ-amino-n-propylcarbazole*, cryst., b.p. 228°/3 mm. (*picrate*, m.p. 206—207°; *hydrochloride*, m.p. 273°); *1-γ-amino-n-propyl-1 : 2 : 3 : 4-tetrahydroquinoline*, b.p. 132—135°/3 mm. *β-γ′-Diethylamino-n-propylamino-n-propionitrile*, b.p. 163—165°/2 mm. (picrate, m.p. 123°), is prepared from NEt_2·$[CH_2]_2$·NH_2 by (I) or Br·$[CH_2]_2$·CN, thereby proving the structure of the products. The appropriate diamine with *p*-NHAc·C_6H_4·SO_2Cl–K_2CO_3–$COMe_2$–H_2O and then 20% HCl yields N^1-*γ-diethylamino-*, m.p. 109—110°, *-di-n-propylamino-*, m.p. 98—98·5°, -di-*n*-butylamino-(*hydrochloride*, m.p. 110—115°), *-piperidino-*, m.p. 105·5—106° (*Ac* derivative, m.p. 109—111°), and *-morpholino-*, m.p. 94·5—95° (*Ac* derivative, m.p. 97—98°), -n-*propylsulphanilamide*, N^1N^1-di-(*γ*-diethylamino-*n*-propyl)- (*hydrochloride*, m.p. 195—197°; *Ac* derivative, m.p. 83—85°), and N^1N^1-*di-(γ-piperidino*-n-*propyl)-sulphanilamide*, m.p. 171°. R. S. C.

Action of ammonia on allophanic azide. W. L. Lipschitz (*J. Amer. Chem. Soc.*, 1944, **66**, 658).—Contrary to Thiele *et al.* (A., 1899, i, 118), allophanic azide with conc. aq., dil. aq., or liquid NH_3 gives only biuret. R. S. C.

II.—SUGARS AND GLUCOSIDES.

Action of copper sulphate on phenylosazones of sugars. Phenyl-D-glucosotriazole. R. M. Hann and C. S. Hudson (*J. Amer. Chem. Soc.*, 1944, **66**, 735—738).—Phenyl-*D*-glucosazone (I) (5 g.) and $CuSO_4$ (2 mols.) in boiling H_2O give *2-phenyl-D-glucosotriazole* (II) (2—3 g.), m.p. 195—196°, $[\alpha]_D^{20}$ −81·6° in C_5H_5N (*tetra-acetate*, m.p. 81—82°, $[\alpha]_D^{20}$ −25·6° in $CHCl_3$; *tetrabenzoate*, m.p. 112—113°, $[\alpha]_D^{20}$ +3·0° in $CHCl_3$), and NH_2Ph (20% isolated as NHPhAc) (cf. A., 1934, 633). Triazoles are similarly obtained (no details given) from the phenylosazones of *L*-sorbose (50%; m.p. 158—159°), *D*-galactose (III) (47%; m.p. 110—111°), *D*-altrose (62%; m.p. 134—135°), *D*-xylose (40%; m.p. 88—90°), cellobiose (62%; m.p. 164—165°), lactose (IV) [62%; (V), m.p. 180—181°], and turanose (VI) (70%; m.p. 193—194°). The reaction occurs in two stages, evident with the sol. phenylosazones of (IV) and (VI); a red Cu–osazone complex first forms and then decomposes to the colourless triazole, leaving the solution green owing to the Cu–NH_2Ph colour. (V) is hydrolysed by acids as readily as is (IV) and yields (II) and (III). (I) is readily identified by this reaction in acidified aq. Pr$^\beta$OH (cf. C., 1944, Part 4). R. S. C.


(III.)

Acyclic sugar orthoacetate. M. L. Wolfrom and D. I. Weisblat (*J. Amer. Chem. Soc.*, 1944, **66**, 805—806).—Crude 1-chloro-1-ethylthiol-*aldehydo-D*-galactose penta-acetate, m.p. 95—98° (A., 1941, II, 211), with $CaSO_4$ and Ag_2CO_3 in EtOH at room temp. gives *D*-galactose Et_2 monothioacetal penta-acetate (A., 1940, II, 205) and a small amount of *1-ethylthiol*aldehydo-D-*galactose Et* 1 : 2-*orthoacetate tetra-acetate*,  {R = $[CH(OAc)]_3$·CH_2·OAc}, m.p. 125—126°, $[\alpha]_D^{24}$ +54° in $CHCl_3$, from which 5 Ac are removed by acid but only the 4 normal Ac by alkali. R. S. C.

Methyl-3-methyl-4 : 6-ethylidene-β-glucosides. R. E. Reeves (*J. Amer. Chem. Soc.*, 1944, **66**, 845).—Mixed methyl-3-methyl-α- and -β-glucosides (from the syrupy triacetate) with paraldehyde and a little conc. H_2SO_4 at room temp. give *methyl-3-methyl-4 : 6-ethylidene-α-*, m.p. 106—107° (corr.), $[\alpha]_D^{25}$ +114°, $[\alpha]_{Hg\ blue}^{25}$ +246° in H_2O, and *-β-glucoside*, m.p. 133—134° (corr.), $[\alpha]_D^{25}$ −66°, $[\alpha]_{Hg\ blue}^{25}$ −126° in H_2O (with MeI–Ag_2O gives the known 2 : 3-Me_2 compound, m.p. 103—105°). R. S. C.

Action of ultra-violet light on cellulose. I. Irradiation effects. II. Post-irradiation effects. R. A. Stillings and R. J. van Nostrand (*J. Amer. Chem. Soc.*, 1944, **66**, 753—760).—The photolysis of cellulose (I) in O_2 and in N_2 has been studied (for apparatus see C., 1944, Part 4). Glucose and cellobiose (II) have been irradiated in N_2. (I) in N_2 is considerably degraded (lowering of degree of polymerisation and α-cellulose content, increase in Cu no., and liberation of CO and CO_2), the degradation increasing with time of exposure. These changes are not related to the presence of O_2 in the N_2 or in the (I). Rate of degradation increases with increasing O_2 in the gas phase, but rate of change of chain length and Cu no. do not correspond with a first-order reaction. *β-d*-Glucose and (II) liberate CO and CO_2, but more slowly than (I). If (I) which has been irradiated in the absence of O_2 is left in air the changes brought about by irradiation continue to occur but cease when air is absent. Post-irradiation effects are enhanced by increased temp. to 70° and also by O_2 instead of air, but diminished by replacement of O_2 by N_2. Reintroduction of O_2 causes production of post-irradiation effects. For (I) irradiated in O_2 the post-irradiation effects are less marked and of shorter duration. W. R. A.

III.—HOMOCYCLIC.

Thermal decomposition of substituted *cyclo*hexenes. F. O. Rice and M. T. Murphy (*J. Amer. Chem. Soc.*, 1944, **66**, 765—767).—On pyrolysis at ~700° 1-methyl-, 3-vinyl-, and 1-phenyl-*cyclo*hexene yield the expected substituted butadiene and C_2H_4. Ethyl*cyclo*hexene does not yield the expected ethylbutadiene. Dipentene gives a high yield of isoprene, but 3-*p*-menthene does not give *iso*propylbutadiene although it gives a high yield of CH_2:CHMe. W. R. A.

Debromination of pentaerythrityl bromide by zinc. Isolation of *spiro*pentane. M. J. Murray and E. H. Stevenson (*J. Amer. Chem. Soc.*, 1944, **66**, 812—816).—A detailed account of work already

reported (A., 1944, II, 215). Raman spectra are recorded for *spiro*pentane, methylene- and methyl-*cyclo*butane, and *cyclo*butanone. R. S. C.

Friedel–Crafts synthesis of ketones and hydrocarbons by means of aluminium chloride and gallium chloride. H. Ulich (*Oel u. Kohle*, 1943, **39**, 523—527).—The ketone synthesis takes place either as a homogeneous reaction after $AlCl_3$ has gone into solution in the form of an additive complex or as a surface reaction if excess of solid $AlCl_3$ is present. The hydrocarbon synthesis is autocatalytic and proceeds rapidly after a heavy oily phase has been formed by addition of $AlCl_3$ to the reaction products. Addition of C_2H_4 to C_6H_6 proceeds by formation of EtCl if HCl is present, but direct addition by a surface reaction on $AlCl_3$ is possible. Since $GaCl_3$ is readily sol. in C_6H_6 the hydrocarbon synthesis with $GaCl_3$ is a purely homogeneous reaction. Addition of C_2H_4 to C_6H_6 is direct and not accelerated by HCl. PhEt is the main reaction product. R. B. C.

Esters of *p*-toluenesulphonic acid. R. S. Tipson (*J. Org. Chem.*, 1944, **9**, 235—241).—Esters of *p*-$C_6H_4Me{\cdot}SO_3H$ are obtained usually in >75% yield by the action of *p*-$C_6H_4Me{\cdot}SO_2Cl$ on the requisite alcohol or phenol in dry C_5H_5N which must be shielded from atm. moisture. Generally, but not always, the temp. of the reacting mixture should be ≯0°. Nothing is gained in small experiments by addition of the reactants in portions. Technical *p*-$C_6H_4Me{\cdot}SO_2Cl$ suffices, an excess of ~10% being used. Under these conditions chlorination is never observed even with $OPh{\cdot}[CH_2]_2{\cdot}OH$ or 2 : 4 : 1-$(NO_2)_2C_6H_3{\cdot}OH$, which readily yield Cl-compounds with *p*-$C_6H_4Me{\cdot}SO_2Cl$ in warm (or hot) C_5H_5N or $NPhEt_2$. The tendency towards the production of pyridinium salts, usually pronounced with EtOH, $CH_2Ph{\cdot}OH$, and 2 : 4 : 1-$(NO_2)_2C_6H_3{\cdot}OH$, is overcome by neutralising the excess of C_5H_5N as soon as esterification is considered to be complete. *β-Methoxyethyl*, b.p. 141°/0·2 mm., m.p. 10°, *-ethoxyethyl*, b.p. 122°/0·1 mm., m.p. 18·5°, *-n-propoxyethyl*, b.p. 140°/0·1 mm., m.p. 8°, *-n-butoxyethyl*, b.p. 142°/0·1 mm., *-phenoxyethyl*, m.p. 80—81°, and *diethylcarbinyl*, m.p. 43—44°, *p-toluenesulphonate* are new. *apo*Cupreine gives a *mono-p-toluenesulphonate*, amorphous, $[\alpha]_D^{24}$ +14·8° in abs. EtOH. H. W.

Interaction of benzene with butadiene in presence of sulphuric acid and hydrogen fluoride catalysts. V. N. Ipatiev, H. Pines, and R. E. Schaad (*J. Amer. Chem. Soc.*, 1944, **66**, 816—817).—The low-boiling fraction obtained from $(CH_2{:}CH)_2$ and an excess of C_6H_6 in H_2SO_4 at 0—5° (14% yield) or HF at 5—20° (59% yield) is $CHPhEt{\cdot}CH_2Ph$, b.p. 148°/12 mm. (NHAc-derivative, m.p. 219°), also obtained [b.p. 141°/12 mm. (*NHAc*-derivative, m.p. 227°), from $CH_2Ph{\cdot}COPh$ by interaction with MgEtBr, followed by dehydration over activated Al_2O_3 at 350°, and hydrogenation (Raney Ni; C_6H_{12}; 50°/100 atm.). $COPh_2$ and $MgPr^{\alpha}Br$ etc. lead to $CHPh_2Pr^{\alpha}$, b.p. 145°/16 mm. (*NHAc*-derivative, m.p. 201—203°). COPhMe and $MgBr{\cdot}[CH_2]_2{\cdot}Ph$ etc. lead to $CHPhMe{\cdot}[CH_2]_2{\cdot}Ph$, b.p. 291° (*NHAc*-derivative, m.p. 194°). R. S. C.

Pyrolysis of [asymmetric] diphenylethane compounds.—See B., 1944, II, 221.

Mechanism of peroxide-initiated styrene polymerisation.—See A., 1944, I, 227.

Morphine-like properties of [αβ-]diphenylethylamine and related compounds. E. C. Dodds, W. Lawson, and P. C. Williams (*Proc. Roy. Soc.*, 1944, **B**, **132**, 119—132; see also A., 1944, III, 683).—The following are obtained by reduction (Na–Hg, EtOH–AcOH) of the appropriate ketoxime: *αβ-di-p-anisylethylamine*, m.p. 103—104° (hydrochloride, m.p. 210—212°); *β*-phenyl-*α*-*p*-anisyl-, an oil (*hydrochloride*, m.p. 215—217°), demethylated by HI (*d* 1·7) to β-phenyl-*α*-*p*-hydroxyphenyl-ethylamine (*hydrochloride*, m.p. 194—195°); *β-cyclohexyl-α-phenylethylamine*, b.p. 162—164°/12 mm. (*Bz* derivative, m.p. 168°; picrate, m.p. 183—184°; hydrochloride, m.p. 280—282°); *β-cyclohexyl-α-p-anisylethylamine*, b.p. 130—135°/0·2 mm. (hydrochloride, m.p. 246—248°). $COPh{\cdot}CHPh{\cdot}NH_2$,HCl and MgEtI (6 mols.) give *β*-hydroxy-*αβ*-diphenyl-*n*-butylamine, an oil (*hydrochloride*, m.p. 215—217°); *β*-hydroxy-*αβ*-diphenyl-*n*-propyl- (*hydrochloride*, m.p. 248—250°) and -n-butyl-dimethylamine (*hydrochloride*, m.p. 251—252°) are similarly obtained from $COPh{\cdot}CHPh{\cdot}NMe_2$,HCl and MgAlkI. *Ph hexahydrobenzyl ketone*, b.p. 169—170°/12 mm. (2 : 4-dinitrophenylhydrazone, m.p. 157—158°; oxime, m.p. 100—101°), is prepared from *cyclo*hexylacetyl chloride, C_6H_6, and $AlCl_3$. H. B.

***p*-Dimethylamino-derivatives of nitrostyrene.** D. E. Worrall and L. Cohen (*J. Amer. Chem. Soc.*, 1944, **66**, 842).—*p*-$NMe_2{\cdot}C_6H_4{\cdot}CHO$ with $MeNO_2$ or $EtNO_2$ and a little $n\text{-}C_5H_{11}{\cdot}NH_2$ at 100° gives *β-nitro-p-dimethylaminostyrene* (I), m.p. 179—180·5°, and *β-nitro-α-p-dimethylamino-*Δ^{α}*-propene*, m.p. 118—120°, respectively. With $NHPh{\cdot}NH_2$ (excess), (I) gives *p*-$NMe_2{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}NHPh$ and with Br–$CHCl_3$ first at the b.p. and then in sunlight gives *α-bromo-β-nitro-p-dimethylaminostyrene*, m.p. 121°. R. S. C.

***o*-Diphenylyl- and 2-di*cyclo*hexylyl-carbimide, *s*-di-*o*-diphenylyl- and *s*-di-2-di*cyclo*hexylyl-carbamide.** H. Fraenkel-Conrat and H. S. Olcott (*J. Amer. Chem. Soc.*, 1944, **66**, 845).—The appropriate amine and $COCl_2$ in boiling PhMe give *o-diphenylyl-*, b.p. 100°/0·5—1 mm., and 2-*dicyclohexylyl-carbimide*, b.p. 89—90°/0·5—1 mm., converted by aq. C_5H_5N at room temp. and 100°, respectively, into *s-bis-o-diphenylyl-*, m.p. 182°, and *s-bis-2-dicyclohexylyl-carbamide*, m.p. 225—228°. R. S. C.

Derivatives of sulphanilamide.—See B., 1944, III, 186.

***p*-Aminobenzenesulphonacylamides.**—See B., 1944, III, 167.

Orientation in the diphenyl series. (A) Preparation of 2- and 4-aminodiphenyl-4′-sulphonamides. A. H. Popkin and G. B. McVea. **(B) Derivatives of 2-aminodiphenyl.** A. H. Popkin, G. M. Perretta, and R. Selig (*J. Amer. Chem. Soc.*, 1944, **66**, 796—798, 833—834).—(A) NHAc, NH_2,HCl, or NH_2 attached to Ph_2 acts in acid as a *m*-orienting group, directing substituents to $C_{(4')}$. *o*- or *p*-$C_6H_4Ph{\cdot}NH_2$,HCl in $ClSO_3H$ at 10° and later 60° give, after treatment with NH_3, 2- and 4-$NH_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$-4′, respectively. The same products are obtained from the free amines, which, however, are less reactive than their salts, requiring temp. up to 90° for sulphonation.

(B) *o*-$C_6H_4Ph{\cdot}NH_2$ with Me_2SO_4–30% NaOH at <30° gives 92% of a 66 : 34 mixture of *o*-$C_6H_4Ph{\cdot}NMe_2$ (I), b.p. 115—116°/2—3 mm., and *o*-$C_6H_4Ph{\cdot}NHMe$ (II) [isolated as *Ac* derivative (III), m.p. 98—99°] (cf. Evans *et al.*, A., 1939, II, 414), and with MeOH–H_2SO_4 gives an 87 : 13 mixture of (I) and (II). The structure of (III) is proved by synthesis from *o*-$C_6H_4Ph{\cdot}NHAc$ (IV) by Na, followed by MeI, in hot xylene. (III) is less readily hydrolysed by MeOH–conc. aq. HCl than is (IV). $CuSO_4$, PhOH, and aq. NaCl convert (I) into an analogue of methyl-violet. R. S. C.

Synthesis of 1 : 2-diamino*cyclo*butane. Z. I. Schuikina (*J. Gen. Chem. Russ.*, 1943, **13**, 373—381).—For the purpose of studying its behaviour towards oxidising agents, 1 : 2-diamino*cyclo*butane was prepared. $(CH_2{\cdot}CHBr{\cdot}CO_2Et)_2$ (Stephen *et al.*, *J.C.S.*, 1913, **103**, 271) with NaCN (Fuson *et al.*, A., 1929, 794) gives Et_2 1-cyano*cyclo*butane-1 : 2-dicarboxylate, hydrolysed [$Ba(OH)_2$] to *cyclo*butane-1 : 1 : 2-tricarboxylic acid, which is decarboxylated at 150° to mixed *cis*- and *trans-cyclo*butane-1 : 2-dicarboxylic acids, and the mixture is then treated with conc. aq. HCl at 190°/4 hr. to give wholly the *trans*-form. The derived Me_2 ester (MeOH–HCl or $-H_2SO_4$) with NH_3 gives the diamide, which with KOBr affords 1 : 2-*diamino*cyclo*butane* (I) [*hydrochloride* (II), decomp. 240° without melting; *platinichloride*; *picrate* $+1H_2O$, resinifies at >200°]. Treatment of (II) with solid KOH and then with fused BaO gives a mixture of (I) and pyrrole (?). F. Hi.

Diazoamino-compounds.—See B., 1944, III, 186.

Action of aluminium chloride on phenyl ethers. G. Baddeley (*J.C.S.*, 1944, 330—332).—Alkylation of the PhOH nucleus is solely *para*- in presence of $AlCl_3$, whereas that of homologues is directed by alkyl in the nucleus. Ethylation occurs more readily than methylation and the products readily isomerise. PhOMe and $AlCl_3$ (1 mol.) give a complex, $PhO(Me){\cdot}AlCl_3$, which decomposes at >40° to $PhO{\cdot}AlCl_2$ and MeCl, and at 100° for 2 hr. affords PhOH (I) in quant. yield. With 2 mols of $AlCl_3$, the products formed from PhOMe at 100°/1 hr. are (I) (68%), *p*-cresol (II) (16%), *o*-4-xylenol (III) (8%), and hemimellithenol (IV) (5%). The methylating agent is probably MeCl,$AlCl_3$, and no *o*-cresol is formed. Similarly, (I), Et_2O, and $AlCl_3$ (2·8 mols.) at 100° for 3 hr. give 15% of *p*-$C_6H_4Et{\cdot}OH$ but no *o*-isomeride. *p*-$C_6H_4Me{\cdot}OMe$ (V) and 0·5, 1·25, or 2 mols. of $AlCl_3$ at 100° for 2·75, 3, or 1 hr. give 50% of (V) + 50% of (II), 40% of (II) + 40% of (III) + 10% of (IV), or 30% of (II) + 40% of (III) + 20% of (IV) + a substance (VI), m.p. 125° (probably $C_6Me_5{\cdot}OH$), respectively. With $AlCl_3$ (1·1 mols.) at 100°, PhOMe affords (I) (95%), *m*-$C_6H_4Me{\cdot}OMe$ gives *m*-cresol (80%) and (III) (15%), whilst 1 : 3 : 5-$C_6H_3Me_2{\cdot}OMe$ gives *m*-5-xylenol (70%), (IV) (20%), and higher homologues containing (VI). *o*-$C_6H_4Me{\cdot}OMe$ and $AlCl_3$ similarly yield *o*-cresol, *p*- (38%) and *o*-3-xylenol, and *iso-ψ*-cumenol (24%), m.p. 95°. *p*-$C_6H_4Me{\cdot}OEt$ and $AlCl_3$ (2 mols.) at 100° for 10 min. give (II), 1 : 2 : 4-$C_6H_3MeEt{\cdot}OH$ (VII) (27%), and 2 : 6-*diethyl*-p-*cresol* (VIII) (18%), m.p. 59° (also obtained by Clemmensen reduction of 4 : 2 : 6 : 1-$OH{\cdot}C_6H_2Et_2{\cdot}CHO$). (II), EtBr, and $AlCl_3$ at 20° for 3 days afford 26% of (VII) and 31% of (VIII). *p*-$C_6H_4Et{\cdot}OH$ and MeBr similarly give some 1 : 6 : 3-$C_6H_3MeEt{\cdot}OH$. A mixture of equal amounts of *m*- and *p*-$C_6H_4Me{\cdot}OMe$ at 125—130° yields (III) and *m*- (54%) + *p*-cresol (46%); interconversion of these cresols is not appreciable and thus methylation of *p*-$C_6H_4Me{\cdot}O{\cdot}AlCl_2$ is at least as ready as that of the *m*-isomeride. (II) and $AlCl_3$ (5 mols.) in Et_2O at 75—80° for 4 hr. or 100° for 1 hr. give (VII) (9 or 18%), whereas at 80° for 48 hr. or 100° for 3·5 hr., 1 : 5 : 3-$C_6H_3MeEt{\cdot}OH$ (IX) (45 or 40%) is formed, probably by isomerisation of (VII). Similarly, ethylation of *m*-cresol at 100° for 30 hr. gives 38% of (IX), probably formed from the 6-isomeride. Ethylated cresols are accompanied by an alkali-insol. substance, b.p. 138°/20 mm. Alkylation occurs in the *o*-position to $\cdot O{\cdot}AlCl_2$ only when the *p*- and both *m*-positions are occupied by alk. Products are identified by mixed m.p., directly or of their *p*-nitrobenzoates. p-*Nitrobenzoates* (m.p. in parentheses) of the following phenols are prepared: PhOH (129°); *o*- (94°), *m*- (87°), and *p*-cresol (100°); *o*-3- (104·5°), *o*-4- (128°), *m*-2- (99°), *m*-4- (113°), *m*-5- (109°), and *p*-xylenol (88°); *o*- (57°), *m*- (68°), and

p-C_6H_4Et·OH (80°); 4- (88°), 5- (84°), and 6-ethyl-*m*-cresol (116°); 2- (116°) and 3-ethyl-*p*-cresol (98°); hemimellithenol (147°).
A. T. P.

***β-p-* and *β-o*-Anisylpropylmethylamines.**—See B., 1944, II, 248.

Dimerisation of 6-methoxy-3 : 4-dihydronaphthalene. R. B. Woodward and R. H. Eastman (*J. Amer. Chem. Soc.*, 1944, **66**, 674—679).—6-Methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene (**I**) and Pb_3O_4 in Ac_2O–AcOH yield 1-*acetoxy*-6-*methoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (**II**), b.p. 144—149°/3 mm. Hydrogenation of 1-keto-6-methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene (**III**) [absorption max. at 276 mμ. (log ε 4·22)] is erratic, yielding (**I**) or 1-hydroxy-6-methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene (**IV**), b.p. 175°/16 mm. Contrary to Long *et al.* (A., 1942, II, 96), 46% HBr converts (**II**) or (**IV**) into 6 : 6′-*dimethoxy*-1 : 2 : 3 : 4 : 3′ : 4′-*hexahydro*-1 : 2′-*dinaphthyl* (**V**), m.p. 76—77° [absorption max. at 274 mμ. (log ε 4·25)], purified by chromatography (Al_2O_3), the dimeric nature of which is proved by its mol. wt. (Rast) and consumption of 1 BzO_2H to give the 1′ : 2′-*oxide*, m.p. 127—128·5° [absorption max. at 283 mμ. (log ε 3·54)]. Hydrogenation of (**V**) gives an oily H_8-derivative, which in boiling 57% aq. HI–AcOH gives 6 : 6′-*dimethoxy*-1 : 2 : 3 : 4 : 1′ : 2′ : 3′ : 4′-*octahydro*-1 : 2′-*dinaphthyl*, mixed stereoisomerides, m.p. up to 187—190°; demethylation of (**V**) is anomalous. $KMnO_4$–$NaHCO_3$ oxidises (**V**) at 0° to give small yields of *β*-2-*carboxy*-5-*methoxyphenylpropionic acid*, m.p. 201·5—203°, and 6 : 6′-*dimethoxy*-1 : 2 : 3 : 4-*tetrahydro*-1 : 2′-*dinaphthyl* (**VI**), m.p. 107·5—108·5°, but CrO_3–AcOH gives only a little (**VI**). With 10% Pd–C in CO_2 at 300° (or, less well, S at 200—300°), (**V**) gives 6 : 6′-*dimethoxy*-1 : 2′-*dinaphthyl* (**VII**), m.p. 91—92°, converted by 57% HI–AcOH into 6 : 6′-*dihydroxy*-1 : 2′-*dinaphthyl*, m.p. 187—188·5°. Freshly distilled 2 : 6-$C_{10}H_6$Br·OMe (prep. from the naphthol by MeOH–H_2SO_4), m.p. 105—106°, b.p. 160—164°/3 mm., with Mg and a little I in Et_2O and then boiling C_6H_6 gives the Grignard reagent, which with (**III**) gives 6 : 6′-*dimethoxy*-3 : 4-*dihydro*-1 : 2′-*dinaphthyl*, m.p. 126°, and thence by Pd–C at 300° yields (**VII**) or by H_2–PtO_2 in AcOH gives (**VI**). Distillation of crude (**IV**) sometimes gives 7-*methoxy*-1 : 2-*dihydronaphthalene*, b.p. 107—111°/2·5 mm. [absorption max. at ~270 mμ. (log ε ~4·0)], converted by 46% HBr into (**V**). R. S. C.

α-Chloro-αββ-tri-*p*-anisylethylene.—See B., 1944, II, 248.

Constitution of compounds of the type R_2SX_2, R_2SeX_2, and R_2TeX_2.—See A., 1944, I, 192.

Substituted sulphanilamidophenols.—See B., 1944, III, 168.

Water-soluble derivatives of 4 : 4′-diaminodiphenyl sulphone.—See B., 1944, III, 185.

Specificity of the action of *i*-inositol, growth factor of micro-organisms.—See A., 1944, III, 615.

αγ : βδ-Dibenzylidene-*D*-sorbitol.—See A., 1944, II, 286.

Preparation of β-amino-α-3 : 4-dihydroxyphenylbutan-α-ol. C. M. Suter and A. W. Ruddy (*J. Amer. Chem. Soc.*, 1944, **66**, 747—748).—*o*-$C_6H_4(OH)_2$ and Pr^aCOCl in PhCl at 50°, followed by $AlCl_3$ first in the cold and then at 110°, give 3 : 4 : 1-$(OH)_2C_6H_3$·$COPr^a$ (**I**) (68%), m.p. 146—146·5°, the $(CH_2Ph)_2$ ether (**II**), m.p. 86—87°, of which yields with Br–$CaCO_3$ in CH_2Cl_2 *α-bromo*-3 : 4-*dibenzyloxybutyrophenone*, m.p. 100—101°. This does not react smoothly with NH_3 or $(CH_2)_6N_4$ but with $CHPh_2$·NH_2 in boiling EtOH etc. gives *α-benzhydrylamino*-3 : 4-*dibenzyloxy*-n-*butyrophenone hydrochloride* (75%), m.p. 175—176° (decomp.), converted by H_2–Pd–sponge in EtOH at 55—70°/50 lb. into *β-amino-α*-3 : 4-*dihydroxyphenyl*-n-*butan-α-ol hydrochloride*, m.p. 199—200° (decomp.). R. S. C.

Preparation of iodine-containing *X*-ray contrast substances. IV. Ethyl iodophenylundecoate (" pantopaque "). W. Baker, E. E. Cook, and (in part) W. G. Leeds (*J.S.C.I.*, 1944, **63**, 223—224; cf. A., 1944, II, 24).—A detailed process is described for the prep. of Et iodophenylundecoate, an *X*-ray contrast substance for the visualisation of the spinal canal and other body cavities. Undecenoic acid and C_6H_6 are condensed to give phenylundecoic acid, which is directly iodinated in AcOH solution in presence of HIO_3, and the product esterified. The overall yield of purified material is 70%.

Effect of substituents on dissociation constants of carboxylic acids.—See A., 1944, I, 224.

Rearrangement of 5-bromosalicylic acid and its ethers by hydrolysis of the bromomagnesium salts. M. Paty and R. Quelet (*Compt. rend.*, 1943, **217**, 229—231).—2 : 5 : 1-OMe·C_6H_3Br·CO_2MgBr (**I**) (from the acid and MgEtBr) is converted by dil. HCl into 4 : 3 : 1-OMe·C_6H_3Br·CO_2H. 4 : 3 : 1-OH·C_6H_3Br·CO_2H is similarly produced starting from 2 : 5 : 1-OH·C_6H_3Br·CO_2H. No rearrangement occurs when, *e.g.*, (**I**) is decomposed by Et_2O–HCl. It is not certain that H_2O is solely responsible for the rearrangement. It is possible that similar rearrangement occurs during decomp. of the carbonation products of the Mg derivatives of 2 : 4-dihalogenoanisoles (*ibid.*, 1942, **214**, 910). F. R. S.

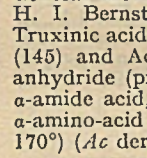
Amines related to epinephrine. I. Amines of the " eprocaine " type. R. Hill and G. Powell (*J. Amer. Chem. Soc.*, 1944, **66**, 742—743).—3 : 4 : 1-$(OH)_2C_6H_3$·CO·CH_2Cl and *p*-NH_2·C_6H_4·CO_2R in boiling H_2O give *Et* (**I**), m.p. 220—221° (darkens) (lit. 201°) [*triacetate* (**II**), m.p. 143—144°], *Pr*^{a}, m.p. 210—211° (*triacetate*, m.p. 129—131°, *Bu*^{a}, m.p. 196—196·5° (*triacetate*, m.p. 120°), *β*-diethylaminoethyl (**III**) [hydrochloride, m.p. ~205° (darkens)], *β*-di-*n*- (**IV**) (*hydrochloride*, m.p. 223—224°), and -*iso*-propylaminoethyl [*hydrochloride*, m.p. ~225° (darkens)], and *β*-di-*n*-butylaminoethyl (*hydrochloride*, m.p. 227—230°) *p*-3′ : 4′-dihydroxyphenacylaminobenzoate. Ac_2O–20% NaOH converts (**I**) into a *diacetate*, m.p. 179—181°; (**II**) etc. are prepared by warm Ac_2O–H_2SO_4. 0·1N-NaOH hydrolyses (**IV**) to p-3′ : 4′-*dihydroxyphenacylaminobenzoic acid*, decomp. 241° (bath preheated at 230°). (**III**) [= Eprocaine] has pressor as well as anæsthetic activity (cf. Osborne, *Science*, 1935, **85**, 105), though it causes tissue damage, but the simple alkyl esters have no anæsthetic action. R. S. C.

***N*-Hydroxy-α-amino-acids as possible intermediates in the oxidative degradation of α-amino-acids.** R. E. Steiger (*J. Biol. Chem.*, 1944, **153**, 691—692).—*N*-Hydroxy-*dl*-*β*-phenylalanine, m.p. 164—165° (corr.; decomp.), rapidly *N*-acetylated and converted into the azlactone, which is dissolved in boiling 67% AcOH to open the ring, yields α-acetamidocinnamic acid, converted into phenylpyruvic acid by boiling with N-HCl. This demonstrates the possibility of converting an *N*-hydroxy-α-amino-acid into an α-keto-acid through the α-imino-acid. J. F. M.

Alkaline fading of tetraiodophenolsulphonephthalein.—See A., 1944, I, 211.

Semi-nitrile of α-hydroxy-β-phenyl-α-benzylsuccinic acid. P. Cordier and J. Moreau (*Compt. rend.*, 1943, **217**, 199—201).—Condensation of CH_2Ph·CN with CH_2Ph·CO·CO_2H in 3% KOH gives 22% of a mixture of the stereoisomerides, m.p. 200° (**I**) (18%) and 158° (**II**) (4%), of CN·CHPh·C(OH)(CH_2Ph)·CO_2H (cf. A., 1935, 975). HCl–AcOH with (**II**) affords the corresponding *imide*, m.p. 161°, with a trace of α-phenyl-*β*-benzylmalcic anhydride (cf. *loc. cit.*). Conc. H_2SO_4 with (**II**) yields a mixture of the corresponding *amide*, m.p. 210°, and CH_2Ph·CO·CHPh·CO·NH_2, m.p. 165°.
F. R. S.

Truxillic acids. I. Rearrangement of ζ-truxinamic acids. General theory of molecular rearrangements. I. S. Goldstein and H. I. Bernstein (*J. Amer. Chem. Soc.*, 1944, **66**, 760—763).—*β*-Truxinic acid and fused KOH give δ- and thence (169 g.), by NaOAc (145) and Ac_2O (365 g.) at 200—210°, ζ-truxinic acid (**I**). The anhydride (prep. by Ac_2O) of (**I**) with NH_3–C_6H_6 gives ζ-truxinic-α-amide acid, which with 0·5N-NaOCl at 38—40° gives ζ-truxinic-α-amino-acid (**II**), m.p. 178—180° (decomp.; bath preheated at 170°) (*Ac* derivative, m.p. 224—225°). With NH_3–EtOH, (**I**) gives the NH_4 salt, which at 200—210° yields the imide, converted by 10% KOH–EtOH into the *b*-amide-acid, m.p. 229—230° (decomp.; bath preheated at 220°), and thence, as above, the *b*-amino-acid (**III**), m.p. 171—173° (*Ac* derivative, m.p. 124—125°). With NOBr–Et_2O at −5° or aq. HNO_2 at 40°, (**II**) gives the lactone (**IV**), m.p. 133° (cf. Schenck, A., 1932, 1029). NOBr converts (**III**) into a Br-acid, m.p. 137—139°, and HNO_2 gives an oil with traces of a substance, m.p. 188—189°. These results do not accord with theory (A., 1942, II, 312). R. S. C.


(IV.)

Synthesis of β-bromoethylphthalimide. T. O. Soine (*J. Amer. Pharm. Assoc.*, 1944, **33**, 141—142).—*o*-$C_6H_4(CO)_2N$·$[CH_2]_2$·OH (from NH_2·$[CH_2]_2$·OH and phthalimide at 100°) with PBr_3 at 100° for 2 hr. affords *o*-$C_6H_4(CO)_2N$·$[CH_2]_2$·Br (81%). F. O. H.

Association of ketyls.—See A., 1944, I, 214.

Nuclear acylations according to Friedel–Crafts. II. W. Borsche and J. Barthenheier [with, in part, P. Grötsch] (*Annalen*, 1942, **553**, 250—259).—The possibility is examined that the presence of OAlk may facilitate the acylation of simple C_6H_6 derivatives in which the Friedel–Crafts reaction is inhibited by certain substituents. The following changes are effected usually in gently boiling CS_2: *o*-OMe·C_6H_4·COMe [2 : 4-dinitrophenylhydrazone, m.p. 196—198° (lit. 160°)] to 2 : 4 : 1-$C_6H_3Ac_2$·OH, m.p. 95° (*bis*-2 : 4-*dinitrophenylhydrazone*, decomp. ~320°); *p*-OMe·C_6H_4·COMe (2 : 4-*dinitrophenylhydrazone*, m.p. 233—234°) is unchanged; *o*-OMe·C_6H_4·CO_2Me to unchanged material and *Me* 2-*hydroxy*-5-*acetylbenzoate*, m.p. 62° (2 : 4-*dinitrophenylhydrazone*, m.p. 237—238°); *o*-OMe·C_6H_4·CN to 2-*methoxy*-5-*acetylbenzonitrile*, m.p. 155° (2 : 4-*dinitrophenylhydrazone*, m.p. 283°), with a large amount of initial material containing a small porportion of an unidentified ketone (2 : 4-*dinitrophenylhydrazone*, m.p. 228°); *o*-NO_2·C_6H_4·OMe (in $PhNO_2$ instead of CS_2) to 3 : 4 : 1-NO_2·C_6H_3(OMe)·COMe (**I**) (2 : 4-*dinitrophenylhydrazone*, m.p. 262°) and 1 : 3 : 4-CH_2Ph·CO·$C_6H_3(NO_2)$·OMe (**II**) (2 : 4-*dinitrophenylhydrazone*, m.p. 224—225°); *o*-NO_2·C_6H_4·OMe with $[CH_2]_4(COCl)_2$ to *αζ-diketo-αζ-di*-3-*nitro*-4-*methoxyphenylhexane*, m.p. 245—246° (*bis*-2 : 4-*dinitrophenylhydrazone*, decomp. 300°); *m*-NO_2·C_6H_4·OMe to *m*-NO_2·C_6H_4·OAc, m.p. 50—51° (lit. 55—56°); *p*-NO_2·C_6H_4·OMe to *p*-NO_2·C_6H_4·OAc, m.p. 79—80°. (**I**) is converted by saturated NH_3–EtOH at 100° into 3-*nitro*-4-*aminoacetophenone*, m.p. 153—154°, reduced (best very rapidly) by H_2 in

presence of Pd–C in MeOH to 3 : 4-*diaminoacetophenone*, m.p. 132—133°, which in warm MeOH is very smoothly transformed by Ac_2 into 6-*acetyl*-2 : 3-*dimethylquinoxaline*, m.p. 117—119°, by Bz_2 into 6-*acetyl*-2 : 3-*diphenylquinoxaline*, m.p. 171—172°, and by phenanthraquinone into 6-*acetyl*-1 : 2-3 : 4-*dibenzophenazine*, m.p. 278°; with boiling AcOH–4N-HCl it gives 5-*acetyl*-2-*methylbenziminazole*, m.p. 190—191° (2 : 4-*dinitrophenylhydrazone*, decomp. 336°), and with 2N-HCl and $NaNO_2$ at 0° it affords 5-*acetylaziminobenzene*, m.p. 164—165° (2 : 4-*dinitrophenylhydrazone*, decomp. 305°). 3-*Nitro*-4-*methylaminoacetophenone*, m.p. 170°, is catalytically reduced to 3-*amino*-4-*methylaminoacetophenone*, m.p. 123—124°, which gives 5-*acetyl*-1-*methylaziminobenzene*, m.p. 144—145°. (I) is converted by N_2H_4,H_2O in EtOH at 100° into 3-*nitro*-4-*methoxyacetophenonehydrazone*, m.p. 101°, and 6-*acetylbenzazimidol*, $COMe\cdot C_6H_3<^{N(OH)}_{\quad\quad N}>N$, m.p. 195° (2 : 4-*dinitrophenylhydrazone*, sudden decomp., 242°). SeO_2 and (II) in Ac_2O at 160° give 3-*nitro*-4-*methoxybenzil*, m.p. 116—118°, less advantageously obtained by hydrolysis of the resin which results from *p*-$NO\cdot C_6H_4\cdot NMe_2$ and (II); 2-*phenyl*-3-3′-*nitro*-4′-*methoxyphenylquinoxaline* has m.p. 155—157°. H. W.

Nuclear acylations according to Friedel-Crafts. III. W. Borsche and F. Sinn (*Annalen*, 1942, **553**, 260—277).—Generally the interposition of two CH_2 groups between the C_6H_6 nucleus and negative substituents such as NO_2, CO, or CN is necessary to overcome the resistance to acylation according to Friedel–Crafts caused by these substituents. The reagents in order of decreasing activity are halogenoacetyl halides, and the halides of aliphatic, aromatic-aliphatic, and aromatic acids. The experiments are performed in CS_2 and with 2 mols. of $AlCl_3$ to 1 mol. of acid chloride or anhydride; the proportion of the latter to the second reactant varies. The mixtures are kept for 14—16 hr. at room temp., gently boiled for a few hr., and worked up as usual. $CH_2Ph\cdot NO_2$ is partly unchanged and partly resinified by acid chlorides. *α-Nitro-β-phenylethane*, b.p. 128—135°/14 mm., from $Ph\cdot[CH_2]_2\cdot I$ and $AgNO_2$ in Et_2O at room temp., and AcCl give a 75% yield of isomeric α-nitro-β-acetylphenylethanes from which the p-*isomeride*, m.p. 29° (2 : 4-*dinitrophenylhydrazone*, m.p. 209—210°), is isolated and identified by oxidation to *p*-$C_6H_4(CO_2H)_2$; with BzCl a small amount of (?) nitrobenzoylphenylethane (2 : 4-*dinitrophenylhydrazone*, m.p. 133—137°) results. $Ph\cdot[CH_2]_3\cdot NO_2$ (I) and AcCl yield *α-nitro-γ*-p-*acetylphenylpropane*, m.p. 31—33° (2 : 4-*dinitrophenylhydrazone*, m.p. 196°), oxidised exclusively to *p*-$C_6H_4(CO_2H)_2$ and converted by reduction of its Na salt by $SnCl_2$ and conc. HCl followed by treatment with NH_2OH into the *dioxime*, m.p. 138—139°, of *β-p*-acetylphenylpropaldehyde; the intermediate monoxime could not be hydrolysed satisfactorily to the aldehyde. (I) and BzCl readily yield *α-nitro-γ*-p(?)-*benzoylphenylpropane*, b.p. 222—226°/0·6 mm., m.p. 33—35° (2 : 4-*dinitrophenylhydrazone*, m.p. 117°), but reaction occurs less readily with $(CH_2\cdot CO)_2O$, giving *β*-p(?)-*γ′-nitropropylbenzoylpropionic acid*, m.p. 115·5°, converted by N_2H_4,H_2O in MeOH into 3-*keto*-6-p-*γ-nitropropylphenyl*-2 : 3 : 4 : 5-*tetrahydropyridazine*, m.p. 139—140°. Attempted acylation of $Ph\cdot[CH_2]_2\cdot CHO$ leads only to a black resin but its oxime and BzCl give a small yield of *β-p*-benzoylphenylpropionitrile, m.p. 83—84° (2 : 4-*dinitrophenylhydrazone*, m.p. 185°, softens greatly at 164°). CH_2PhBz and AcCl readily give mainly *α-keto-α-phenyl-β*-p-*acetylphenylethane*, m.p. 159—160° [*dioxime*, m.p. 180—182°; *bis*-2 : 4-*dinitrophenylhydrazone*, m.p. 230° after softening; oxidised to a mixture of BzOH and *p*-$C_6H_4(CO_2H)_2$], with a small proportion of m-*acetyldeoxybenzoin*, m.p. 73—74° [*dioxime*, m.p. 135°; oxidised to *m*-$C_6H_4(CO_2H)_2$]. CH_2PhBz and $CH_2Ph\cdot COCl$ yield *phenylacetyldeoxybenzoin*, m.p. 175°, softens at 170°, but CH_2PhBz and BzCl do not react.

[With F. W. Roell.] $Ph\cdot[CH_2]_2\cdot Bz$ and Ac_2O give *α-keto-α-phenyl-γ*-p(?)-*acetylphenylpropane*, m.p. 72—73° (*bis*-2 : 4-*dinitrophenylhydrazone*, m.p. 195°), which with PhCHO and alkali yields *α-keto-α-phenyl-γ*-p(?)-*cinnamoylphenylpropane*, m.p. 98°. *α-Keto-α-phenyl-γ-benzoylphenylpropane*, m.p. 92—93°, is obtained similarly from BzCl. α-Keto-αδ-diphenylbutane, m.p. 57° (from $Ph\cdot[CH_2]_3\cdot CN$ and MgPhBr) (2 : 4-*dinitrophenylhydrazone*, m.p. 145°), and BzCl give *α-keto-α-phenyl-δ-benzoylphenylbutane*, m.p. 79°. $Ph\cdot[CH_2]_4\cdot Bz$ and AcCl give *α-keto-α-phenyl-ε-acetylphenylpentane*, m.p. 65° (*cinnamylidene* derivative, m.p. 90°), whilst BzCl gives *α-keto-α-phenyl-ε-benzoylphenylpentane*, m.p. 58°.

$CH_2Ph\cdot CO_2Et$ is transformed by AcCl followed by esterification into Et *p*-acetylphenylacetate, b.p. 183°/16 mm., m.p. 62—63° (lit. 68—69°). $Ph\cdot[CH_2]_2\cdot CO_2Et$ and AcCl give a mixture of *Et* p(?)-*acetylphenylpropionate*, b.p. 194—197°/16 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 146—147°), and the corresponding *acid*, m.p. 119° [*oxime*, m.p. 151—152°; non-cryst. Me ester (2 : 4-*dinitrophenylhydrazone*, m.p. 163—164°)]; with $CH_2Ph\cdot COCl$ it gives (after esterification) a mixture of isomeric Et phenylacetylphenylpropionates (2 : 4-dinitrophenylhydrazone, m.p. 94—104°) [from which after hydrolysis *β*-p(?)-*phenylacetylphenylpropionic acid*, m.p. 135—136°, is isolated] and (?) *Et phenylacetylphenylacetylpropionate*, $C_{27}H_{26}O_4$, m.p. 143—145°.

[With F. W. Roell.] $Ph\cdot[CH_2]_2\cdot CO_2Me$ and BzCl afford *Me benzoylphenylpropionate*, m.p. 74° (2 : 4-*dinitrophenylhydrazone*, m.p. 136°), hydrolysed to the *acid*, m.p. 97°. $(CH_2\cdot CO)_2O$ converts $CH_2Ph\cdot CO_2Et$ into *β-carbethoxyethylbenzoylpropionic acid*, m.p. 113—114° (corresponding *dicarboxylic acid*, m.p. 193—195°).

$Ph\cdot[CH_2]_2\cdot CN$ with AcCl gives *β*-p-*acetylphenylpropionitrile*, m.p. 44—46° (2 : 4-*dinitrophenylhydrazone*, m.p. 215°), oxidised exclusively to *p*-$C_6H_4(CO_2H)_2$; with $CH_2Ph\cdot COCl$ it yields *β*-p(?)-*phenylacetylphenylpropionitrile*, m.p. 113—115°, accompanied by (?) phenylacetylphenylacetylphenylpropionitrile, b.p. 320—340°/0·6 mm.; with BzCl it affords *β-benzoylphenylpropionitrile*, b.p. ~200°/1 mm., m.p. 83—84°, and with $(CH_2\cdot CO)_2O$ it yields *β*-p-*β′-cyanoethylbenzoylpropionic acid*, m.p. 151—152°, converted by N_2H_4,H_2O in boiling EtOH into 3-*keto*-6-p-*γ-cyanopropylphenyl*-2 : 3 : 4 : 5-*tetrahydropyridazine*, m.p. 173°. H. W.

1 : 2-Addition of magnesium methyl iodide to mesityl ketones. R. C. Fuson, M. D. Armstrong, W. E. Wallace, and J. W. Kneisley (*J. Amer. Chem. Soc.*, 1944, **66**, 681—684).—2 : 4 : 6 : 1-$C_6H_2Me_3\cdot COBu^t$ does not react with MgMeI. 2 : 4 : 6 : 1-$C_6H_2Me_3\cdot COPh$ and MgMeI in boiling Et_2O and then C_6H_6 give, by 1 : 2-addition and spontaneous dehydration, *α-mesitylstyrene* (I) (64%), b.p. 120°/3 mm., also obtained in poor yield from COPhMe by 2 : 4 : 6 : 1-$C_6H_2Me_3\cdot MgBr$. H_2–PtO_2 reduces (I) in 95% EtOH to *α-phenyl-α-mesitylethane*, b.p. 154—155°/4 mm. With fuming HNO_3 in Ac_2O–AcOH at 0°, (I) gives *β-nitro-α*-3-*nitromesitylstyrene* (II), m.p. 144—145°, reduced by H_2–PtO_2 in EtOAc to *β-phenyl-β*-3-*nitromesitylvinylamine* (III), m.p. 100—101° (*Ac*, m.p. 199—200°, and *Bz* derivative, m.p. 143—144°). $SnCl_2$–conc. HCl–EtOH at the b.p. reduces (II) or (III) to *di-(β-phenyl-β*-3-*aminomesitylvinyl)amine* (IV), m.p. 184—186°. (III) is neutral and resists hydrolysis but in HCl–EtOH–H_2O gives *di-(β-phenyl-β*-3-*nitromesitylvinyl)amine*, m.p. 235—236°, also reduced to (IV) by $SnCl_2$. *Benzoylisodurene* (prep.: Friedel–Crafts; 78% yield), m.p. 60—61°, b.p. 159—164°/4 mm., with MgMeI as above gives *α*-iso*durylstyrene* (V) (42%), b.p. 152—154°/3 mm., and a *substance*, $C_{34}H_{38}O_2$, m.p. 191—192·5°. (V) is also obtained (10% yield) from COPhMe by 2 : 3 : 4 : 6 : 1-$C_6HMe_4\cdot MgBr$, with H_2–Raney Ni at 50°/2000 lb. gives *α-phenyl-α*-iso*durylethane*, m.p. 54·5—55°, b.p. 160°/5 mm., and with fuming HNO_3 in Ac_2O–AcOH yields, in 2 days, *ββ-dinitro-α*-5-*nitro*iso*durylstyrene*, m.p. 193—194°. 2 : 4 : 6 : 1-$C_6H_2Me_3\cdot CO\cdot C_6H_4Me$-*p* and MgMeI give impure 2 : 4 : 6 : 1-$C_6H_2Me_3\cdot C(C_6H_4Me\text{-}p):CH_2$ and thence *β-nitro-α*-p-*tolyl-α*-3-*nitromesitylethylene*, m.p. 174—175°. The styrene derivatives are oxidised by $KMnO_4$ or CrO_3 and absorb Br in CCl_4 with slow evolution of HBr. R. S. C.

Normal and *ψ*-esters of *o*-benzoylbenzoic acid types. II. M. S. Newman and B. T. Lord (*J. Amer. Chem. Soc.*, 1944, **66**, 731—732; cf. A., 1942, II, 100).—Normal *forms* of *Me* 2-*benzoyl*- (I), m.p. 50·4—51·6°, 2-3′ : 4′-*dimethylbenzoyl*- * (II), m.p. 62·6—63·6°, and 2-*mesitoyl*- * (III), m.p. 110·8—111·8°, -3 : 6-*dimethylbenzoate* and of -o-2′ : 4′-*dimethylbenzoylbenzoate* * (IV), m.p. 64·6—65·6°, are obtained from the appropriate acids by CH_2N_2–Et_2O. The *ψ-forms* of (I)* m.p. 113·6—114·4°, (II) m.p. 86·8—87·2°, and (IV), m.p. 62·2—63·2°, are prepared from the acid chlorides by MeOH–C_5H_5N, but (III) is formed also by this method. Forms marked * are obtained from the acid by HCl–MeOH. R. S. C.

Behaviour of γ-keto- and aldehydo-acid derivatives at the dropping mercury electrode. I. Esters and anhydrides. S. Wawzonek, H. A. Laitinen, and S. J. Kwiatkowski (*J. Amer. Chem. Soc.*, 1944, **66**, 827—830).—All esters of *o*-$C_6H_4Bz\cdot CO_2H$ (I) are reduced polarographically in 0·1M-NBu^n_4I–50% dioxan to α-phenylphthalide, but *n*- and cyclic esters behave differently. Cyclic esters are not hydrolysed in an alkaline buffer ($NMe_4\cdot OH$–NMe_4I–H_3PO_4–50% dioxan) and the half-wave potentials are independent of pH; the ease of reduction increases with increasing ionisation const. of the alcoholic or phenolic component. Me and Et *n*-esters resemble $COPh_2$. Aryl *n*-esters are reduced at ~1·28 v. Anhydrides of (I) are also reduced but their behaviour does not permit conclusions as to structure. R. S. C.

Behaviour of 3 : 6-dimethylphthalic anhydride in Friedel–Crafts and Grignard condensations. M. S. Newman and B. T. Lord (*J. Amer. Chem. Soc.*, A., 1944, **66**, 733—735).—2 : 5-Dimethylfuran and $(CH\cdot CO)_2O$ in Et_2O give an adduct, m.p. 59—63°, which with 90% H_2SO_4 at −6° to 0° (later 10°) gives 3 : 6 : 1 : 2-$C_6H_2Me_2(CO)_2O$ (I) and some 2 : 5 : 1-$C_6H_3Me_2\cdot CO_2H$. With MgPhBr, 2 : 4 : 1-$C_6H_3Me_2\cdot MgBr$, or 2 : 4 : 6 : 1-$C_6H_2Me_3\cdot MgBr$ in boiling C_6H_6 (1 hr.), (I) gives 2-*benzoyl*- (II) (81%), m.p. 182·6—183·2°, 2-2′ : 4′-*dimethylbenzoyl*- (III) (56%), m.p. 165·2—165·8°, and 2-*mesitoyl*- (IV) (44%; 27% in boiling Et_2O in 2 hr.), m.p. 174·8—175·6°, -3 : 6-*dimethylbenzoic acid*, respectively. With $AlCl_3$–C_6H_6, -*m*-xylene, or -mesitylene under optimum conditions (detailed), (I) gives (II) (57%), (III) 96%), or (IV) (34%), respectively. The structure of (IV) is proved by heating with a little of its Cu salt at 192—195°, yielding 2 : 4 : 6 : 2′ : 5′-*pentamethylbenzophenone*, m.p. 77—78°, which is also obtained from 2 : 5 : 1-$C_6H_3Me_2\cdot COCl$, *s*-$C_6H_3Me_3$, and $AlCl_3$ in CS_2 at room temp. M.p. are corr. R. S. C.

Condensation of chrysene with succinic anhydride. J. W. Cook and W. Graham (*J.C.S.*, 1944, 329—330).—Chrysene, $(CH_2\cdot CO_2)O$, and $AlCl_3$ in $PhNO_2$ at 20° for 6 hr. give *β*-(4- or 5-chrysenoyl)-

propionic acid (I), m.p. 218—221° [and not the 1-derivative as suggested by Beyer (A., 1938, II, 236)], and some β-2-isomeride, m.p. 192—194°. γ-(4- or 5-Chrysenyl)butyric acid, m.p. 210·5—212·5° (cf. *loc. cit.*), is converted by PCl_5–C_6H_6, then $SnCl_4$, at room temp. for 20 hr. into 5′- or 8′-*keto*-5′ : 6′ : 7′ : 8′-*tetrahydro*-1 : 2-(2′ : 3′-*naphtha*)*phenanthrene*, decomp. >275°. This with N_2H_4,H_2O in NaOEt–EtOH at 200° in a sealed tube gives 5′ : 6′ : 7′ : 8′-*tetrahydro*-1 : 2-(2′ : 3′-*naphtha*)*phenanthrene*, m.p. 217—218°, dehydrogenated by Pd–C at 300° (sealed tube; vac.) to 1 : 2-(2′ : 3′-naphtha)phenanthrene, m.p. 292—294° (2 : 7-dinitroanthraquinone *complex*, m.p. 278—279°). A. T. P.

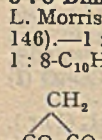
Equilibrium mixture of *cis*- and *trans*-2 : 6-dimethyl*cyclo*hexanone. R. Cornubert and P. Anziani (*Compt. rend.*, 1943, **217**, 197—199).—The methods (lit.) of prep. of 2 : 6-dimethyl*cyclo*hexanone (I) give an equilibrium mixture of *cis*- and *trans*-isomerides. Ring-contraction probably occurs in the supposed prep. of (I) by the method of Ruzicka *et al.* (A., 1931, 1302) from 1 : 3-dimethyl-Δ³-*cyclo*hexene. F. R. S.

Orientation phenomena during reduction of a cyclanone or its oxime. P. Anziani and R. Cornubert (*Compt. rend.*, 1943, **217**, 233—235).—Reduction of 2 : 6-dimethyl*cyclo*hexanone (I), using Pt in acid, alkaline, or neutral solution, gives the same alcohol (phenylurethane, m.p. 158°), whilst Na in moist Et_2O, EtOH, or BuOH leads to a phenylurethane, m.p. 132° (cf. Skita, A., 1924, i, 25). Reduction of the oxime, m.p. 79°, of (I) with H_2–Pt-black in AcOH–HCl or in a neutral medium gives an amine differing from that formed with Na–EtOH. It is concluded that the isomeride obtained does not depend on the acid medium but rather on the use of Pt. F. R. S.

[Ionones.] (A) L. Palfray, (B) Y. R. Naves and P. Bachmann (*Helv. Chim. Acta*, 1944, **27**, 626).—(A) A reply to the criticisms by Naves and Bachmann (A., 1944, II, 103) of the paper by Kandel (A., 1939, II, 169).
(B) A reply. J. W. S.

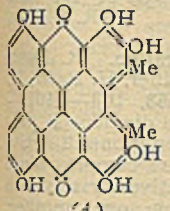
Reaction between cyclic β-diketones and Grignard reagents. III. 2-Benzoyl-2-methyl-1-hydrindone. T. A. Geissman and V. Tulagin (*J. Amer. Chem. Soc.*, 1944, **66**, 719—722).—Keeping $CH_2Ph{\cdot}CH(CO_2Et)_2$, MeI, and NaOEt in C_6H_6 and then hydrolysing by hot NaOH–EtOH–H_2O gives $CH_2Ph{\cdot}CMe(CO_2H)_2$ (80%), m.p. 139·5—140° (lit. 135°), which with, successively, $SOCl_2$–C_5H_5N (little)–C_6H_6, PCl_5–C_6H_6, and $AlCl_3$–C_6H_6 yields 2-*benzoyl*-2-*methyl*-1-*hydrindone* (I) (good yield), m.p. 62·5—63·5°. The structure of (I) is proved by cleavage by boiling 30% NaOH to BzOH and 2-methyl-1-hydrindone (II). Interaction of (I) with MgPhBr in boiling C_6H_6–Et_2O gives 1-*hydroxy*-1-*phenyl*-2-α-*hydroxybenzhydryl*-2-*methylhydrindane* (III) (4 pts.), m.p. 214—215°, and $CPh_3{\cdot}OH$ + (II) (1 pt. each). Thus, formation of a chelated intermediate does not alone suffice to produce cleavage of β-diketones by MgRHal. The structure of (III) is proved by oxidation by boiling aq. HNO_3 to $COPh_2$ and *o*-$C_6H_3Bz{\cdot}CO_2H$ as sole products. $CHPh_2{\cdot}CNa(CO_2Et)_2$ and MeI in Et_2O give an ester, hydrolysed to *benzhydrylmethylmalonic acid*, m.p. 143—145° (gas), which with PCl_5–C_6H_6 and then $AlCl_3$ or $SnCl_4$ in C_6H_6 gives 1 : 3-*diphenyl*-2-*methylhydrindene*, m.p. 91—92°, but in CS_2 gives a tar. $(CH_2Ph)_2CH{\cdot}CO_2H$ with $SOCl_2$–C_6H_6–C_5H_5N and then CH_2N_2 gives a *diazo-ketone*, m.p. 72—74°, and thence γγ′-*diphenylisovaleric acid*, m.p. 85—86° (obtained also less well by a Reformatsky reaction), which by ring-closure ($SOCl_2$; $SnCl_4$–C_6H_6) yields 1-*keto*-3-*benzyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 54—56°. This gives the *Me* 2-*glyoxylate*, m.p. 85—87°, converted by heating with soft glass at 175° into *Me* 1-*keto*-3-*benzyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-2-*carboxylate*, m.p. 77—78°. MeI–NaOMe–C_6H_6 then gives *Me* 1-*keto*-3-*benzyl*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-2-*carboxylate*, m.p. 114—115°, hydrolysis of which is difficult. R. S. C.

Reaction between cyclic β-diketones and Grignard reagents. II. 8 : 8-Dimethylperinaphthindane-7 : 9-dione. T. A. Geissman and L. Morris (*J. Amer. Chem. Soc.*, 1944, **66**, 716—719; cf. A., 1942, II, 146).—1 : 8-$C_{10}H_6(CO)_2O$ with KOH–Me_2SO_4–MeOH gives 89% of 1 : 8-$C_{10}H_6(CO_2Me)_2$ (I) and with $CH_2(CO_2Et)_2$–$ZnCl_2$ at 170—175° gives perinaphthindane-7 : 9-dione (*A*), new m.p. 247° (decomp.), which with MeI–NaOEt–EtOH at 100° gives 8-*methyl*- (60%), m.p. 183—185° [obtained in very poor yield from (I) by $EtCO_2Et$–Na], and thence by MeI–NaOMe–$COMe_2$–MeOH (little) at the b.p. gives 8 : 8-dimethyl-perinaphthindane-7 : 9-dione (II) (30—40%), m.p. 99—101° (2 : 4-*dinitrophenylhydrazone*, m.p. 208—210°). Adding MgPhBr (1 mol.) to (II) in Et_2O–C_6H_6 at 0° gives slowly 7-*hydroxy*-7-*phenyl*-8 : 8-*dimethylperinaphthindan*-9-*one* (III), m.p. 190°, but 3 mols. of MgPhBr at room temp. give 7 : 9-*dihydroxy*-7 : 9-*diphenyl*-8 : 8-*dimethylperinaphthindane* (IV), m.p. 168°, or at 80° give 7-*hydroxy*-1 : 7-*diphenyl*-8 : 8-*dimethylperinaphthindan*-9-*one* (V), m.p. 238—239°. With a drop of conc. HCl in boiling MeOH, (III) or (V) gives its *Me ether*, m.p. 214—216° or 224°, respectively, and with HCl–$CaCl_2$–C_6H_6 gives the 7-*Cl*-derivative, m.p. 156° (decomp.) or 158—162° (decomp.), respectively. A trace of HCl in MeOH at the b.p. converts (IV) into the 7 : 9-*epoxy*-compound, m.p. 134°. Structures are confirmed by behaviour in the Grignard machine. R. S. C.


(A.)

Hypericin, the photodynamic pigment of St. John's wort (*Hypericum perforatum*). H. Brockmann, F. Pohl, K. Maier, and M. N. Haschad (*Annalen*, 1942, **553**, 1—52; cf., A., 1939, 483).—*Hypericin* (I) appears to be a hexahydroxy-2 : 2′-dimethylnaphthadianthrone. Extraction of the dried blossoms of *H. perforatum* with Et_2O removes chlorophyll and carotenoids, after which (I) is removed from the residue by MeOH. From this solution it is obtained cryst. by addition of HCl–MeOH and is subsequently cryst. by adding HCl–MeOH to the solution in C_5H_5N. The blue-black pigment has no definite m.p. but decomposes at >330° and cannot be sublimed in a high vac. The marked red fluorescence of its solutions in C_5H_5N disappears on addition of acid. (I) gives green solutions in alkali, sensitive to air. Adsorption on CaC_2O_4 shows that (I) is homogeneous. (I) does not contain OMe. Oxidation (Kuhn–Roth) affords AcOH. Analyses and determinations of the mol. wt. of the *hexabenzoate* (II), m.p. ~228°, and *hexa*-p-*bromobenzoate*, m.p. ~270° [from (I) and the requisite chloride in C_5H_5N], establish the formula $C_{30}H_{16}O_8$ or, possibly, $C_{30}H_{18}O_8$. (I) is scarcely attacked by CH_2N_2 and is so sensitive to alkali that it cannot be methylated by Me_2SO_4 or MeI. With Ac_2O in C_5H_5N (I) affords a difficultly cryst., unstable acetate. (II) is insol. in cold Claisen solution. The remaining two O atoms are present in the quinone group since reductive benzoylation leads to an amorphous *octabenzoate*. Oxidation of (I) readily leads to small fragments. Distillation of (I) with Zn dust gives very small amounts of a red sublimate (III), also formed in very small yield when (I) is heated with conc. HI at 200° and the product dehydrogenated by Cu powder at 400° or Pd–asbestos at 350°, or when (I) is heated with Zn dust in molten $ZnCl_2$–NaCl. The amount of (III) obtained is too small for analysis but it is identified by absorption spectrum, fluorescence, chromatography and mixed chromatography (over Al_2O_3 II), and behaviour towards Br as *meso*anthrodianthrene. This cannot, however, be the parent hydrocarbon of (I) since it is not in accord with the % of H or the presence of 2 Me. During the formation of (III) a new ring must be formed by participation of the 2 Me so that the parent material is either 2 : 2′-dimethyl*meso*benzdianthrene or 2 : 2′-dimethylnaphthadianthrene and (I) is consequently a $(OH)_6$-derivative of 2 : 2′-dimethylhelianthrone (IV) or of 2 : 2′-dimethyl*meso*-naphthadianthrone (V). Model experiments show that (III) is produced in somewhat better yield than from (I) when (IV) or (V) is reduced with HI and then dehydrogenated. Distillation of (IV) or (V) with Zn dust also gives (III) whereas treatment of (IV) with Zn dust in molten NaCl–$ZnCl_2$ or distillation of (IV) with Zn dust in a high vac. gives 2 : 2′-*dimethylbenzdianthrene* (VI) in addition to (III); under the same conditions (IV) gives (III) with a small proportion of blue 2 : 2′-*dimethyl*meso*naphthadianthrene* (VII). Under all experimental conditions naphthadianthrone yields exclusively the blue naphthadianthrene whereas, in addition, meso*benzdianthrene* is obtained when helianthrone is distilled with Zn dust in a high vac. or treated with Zn dust in molten $ZnCl_2$–NaCl. It does not appear possible under any conditions to obtain (VI) or (VII) from (I); this observation supports the naphthadianthrone structure for (I). Attempts to discriminate between the helianthrone and naphthadianthrone structures for (I) based on oxidation, behaviour towards conc. H_2SO_4, and photochemical behaviour of (I) and its derivatives and helianthrone and its compounds do not give well defined results. The acetates of reduced helianthrone and its 2 : 2′-Me_2 derivative and of (V) have nearly the same absorption bands and therefore nearly the same colour as the corresponding parent hydrocarbons, one of which is red and the other blue. Reductive acetylation therefore affords a ready means of discriminating between a helianthrone and naphthadianthrone. Acetylating reduction of (II) gives a blue Ac derivative with bands very similar to those of (VII) or its 10 : 10′-$(OAc)_2$-derivative. If, therefore, the OBz groups do not influence appreciably the position of the absorption bands it follows with certainty that (I) is a hexahydroxy-2 : 2′-dimethylnaphthadianthrone. The behaviour of the dibenzoate of 4 : 4′-dihydroxyhelianthrone when reductively acetylated appears to show that this is the case but the dibenzoate of 4 : 4′-dihydroxynaphthadianthrone could not be investigated on account of the sparing solubility. Further experiments are required to enable a definite decision to be made. Distillation of (I) with Zn dust can proceed beyond the formation of (III), giving yellow or colourless H_4- or H_6-derivatives which are invariably obtained as final products of reductive acetylation in C_5H_5N; in Ac_2O these are obtained only from hydroxylated quinones and only when C_5H_5N is present, whereas OH-free quinones are not reduced beyond the coloured stage. (I) is not sensibly reduced by Zn dust in AcOH at room temp. and resembles in this respect many polynuclear quinones which do not give vats; in C_5H_5N containing a little AcOH in absence of air (I) gives a brown-red solution with ill-defined absorption bands. Addition of B_2O_3–Ac_2O to the red solution of (I) in Ac_2O causes immediate formation of a green solution with red fluorescence and new, well-marked absorption bands, thus indicating the presence of at least two α-OH groups. Warming the green solution causes slight displacement of the bands

towards shorter λ but the green colour persists. One or more β-OH are therefore considered to have been acetylated but the acetylation remains incomplete since identical products are not obtained thus and by the action of B_2O_3–Ac_2O on the acetate or benzoate of (I). The colours of the solutions suggest that the green solution contains one or two α-OH groups in addition to those esterified by B_2O_3–Ac_2O. (The possibility of the replacement of Ac or Bz groups during the action of B_2O_3–Ac_2O is established by experiments with quinizarin, chrysazin, and anthrarufin.) The annexed structure (*A*) is therefore tentatively suggested for (I). Other examples of the presence of polynuclear compounds in plants are cited and suggestions for their genesis under biological conditions are discussed. (See also A., 1944, III, 708.) H. W.



(*A*.)

IV.—STEROLS AND STEROID SAPOGENINS.

Preparation of steroidal carbinols.—See B., 1944, III, 169.

Neutral, non-saponifiable fraction of ox-bile. W. H. Pearlman (*J. Amer. Chem. Soc.*, 1944, **66**, 806—809).—Inspissated ox-bile (15 kg.; 70% solids) yields a non-saponifiable fraction, whence are obtained cholesterol (>50 g.) and *alcohols A*, $C_{27}H_{40}O_3$ (40 mg.), m.p. 300° {*acetate*, m.p. 216—217°; benzoate, m.p. 155—157° [absorption max. at 2310 (ε 13,470) and 2720 A. (ε 973)]}, *B* [? a 3(β)-hydroxy*allo*pregnane derivative], $C_{21}H_{36}O_2$ (15 mg.), m.p. 192—193° {digitonide; *dibenzoate*, m.p. 234—235° [absorption max. at 2310 (ε 27,700) and 2720 A. (ε 1985)]}, *C*, $C_{25-26}H_{40-42}O_4$ (46 mg.), m.p. 255—257° [*acetate*, m.p. 187°, with KOH in 90% MeOH regenerates *C* (m.p. 260°)], *D*, $C_{24}H_{40}O_3$ (28 mg.), m.p. 232—233° (*acetate*, m.p. 111°, $[\alpha]_D^{18}$ +72° in EtOH), and *E*, $C_{24}H_{42}O_4$ (20 mg.), m.p. 202° (an impure fraction, m.p. 204—206°, had $[\alpha]_D^{25}$ +37° in EtOH) (*diacetate*, m.p. 142·5°). Pregnane-3(β) : 20(α)-diol has m.p. 182° (cf. Marker *et al.*, A., 1938, II, 12) and gives a *dibenzoate*, m.p. 167—168°. M.p. are corr. R. S. C.

Sterols of *Calycanthus floridus*. J. W. Cook and M. F. C. Paige (*J.C.S.*, 1944, 336—337).—Unsaponifiable components comprise ~1·6% of the oil extracted by C_6H_6 from the seeds of *C. floridus*. Hydrolysis is carried out by boiling KOH–MeOH for 8 hr. The phytosterol mixture, mainly m.p. 135—137°, consists of <70% of β-sitosterol, m.p. 137·5—138·5°, $[\alpha]_D^{18}$ −34° in $CHCl_3$ (isolated through the benzoate), a little α-sitosterol, and probably sitostanol, but no stigmasterol. Incomplete reduction (Meerwein–Ponndorff) of 7-keto-cholesteryl acetate and benzoylation gives 7-hydroxycholesterol dibenzoate (I) and some 7-*ketocholesteryl benzoate*, m.p. 159·5—161°, the opaque liquid then becoming green at 182·5° and colourless and clear at 183·5°, also obtained from 7-ketocholesterol and BzCl–C_5H_5N at room temp. (I) and boiling NPhMe$_2$ (8 hr.) yield 7-dehydrocholesteryl benzoate, which is converted into α- and thence into β-cholestenyl benzoate (cf. Schenck *et al.*, A., 1937, II, 59), which is hydrogenated (PtO_2–AcOH–Et_2O) to *cholestanyl hexahydrobenzoate*, m.p. 158·5—159°, hydrolysed to hexahydrobenzoic acid, m.p. 29—30°, and cholestanol, m.p. 141·5—142·5°. The *trans*-configuration assigned to the C–D ring fusion of the sterols is probably correct. A. T. P.

Sterol, m.p. 155—157°, $[\alpha]_D^{25}$ −55·8° in $CHCl_3$ (acetate, m.p. 134—135° : 3 : 5-dinitrobenzoate, m.p. 222—223°, $[\alpha]_D^{25}$ −17·3° in $CHCl_3$), from the common bean, *Phaseolus vulgaris*.—See A., 1944, III, 624.

Lactones of the *cyclo*pentanopolyhydrophenanthrene series.—See B., 1944, III, 168.

Preparation of 24-keto- and 24-hydroxy-cholesterol and [their] derivatives. B. Riegel and I. A. Kaye (*J. Amer. Chem. Soc.*, 1944, **66**, 723—724).—3-Acetoxy-Δ^5-cholenyl chloride with CdPr$^\beta_2$–Et_2O and then KOH–MeOH gives 24-*ketocholesterol* (I) (53%), m.p. 137—138·5°, $[\alpha]_D^{26}$ −37° in $CHCl_3$ {*acetate* (II), m.p. 127·5—128° (not fluid), turbid 129—130°, meniscus formed at 131°, $[\alpha]_D^{26}$ −41° in $CHCl_3$ (*oxime*, softens 155°, m.p. 156—158·5°); *semicarbazone*, m.p. 166—168°}, which is a good starting point for sterol syntheses. With 85% N_2H_4,H_2O and NaOEt in EtOH at 200°, (I) gives cholesterol. Al(OPr$^\beta$)$_3$–Pr$^\beta$OH at the b.p. reduces (II), with hydrolysis, to 24-*hydroxycholesterol* (94%), m.p. 166—169°, which yields only the *diacetate*, softens 93°, m.p. 95—96°. The 3-*p-toluenesulphonate*, softens 115°, m.p. 119—120° (decomp.), $[\alpha]_D^{26}$ −35° in $CHCl_3$, of (I) with dry KOAc in boiling MeOH gives 24-*keto-i-cholesteryl Me ether* (53%), m.p. 90·5—91·5°, $[\alpha]_D^{26}$ +52° in $CHCl_3$, reduced by Al(OPr$^\beta$)$_3$–Pr$^\beta$OH to 24-*hydroxy-i-cholesteryl Me ether*, an oil, $[\alpha]_D^{27\cdot5}$ +31° in $CHCl_3$. M.p. are corr. R. S. C.

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Rearrangements in the terpene series. I. Isomerisation and esterification of α-pinene. M. S. Kharasch and W. B. Reynolds (*J. Org. Chem.*, 1944, **9**, 148—154).—α-Pinene (I) is heated at 135—140° with *p*-OMe·C_6H_4·CO_2H, CHPh:CH·CO_2H, BzOH, *o*-OMe·C_6H_4·CO_2H, 1-$C_{10}H_7$·CO_2H, OEt·CH_2·CO_2H, *o*- and *m*-NO_2·C_6H_4·CO_2H, *o*-C_6H_4Bz·CO_2H, *o*-OH·C_6H_4·CO_2H, *o*-C_6H_4Cl·CO_2H, *o*-C_6H_4Br·CO_2H, 3 : 5 : 1-$(NO_2)_2C_6H_3$·CO_2H, CH_2Cl·CO_2H, 2 : 5 : 1-OH·C_6H_3Br·CO_2H, 2 : 4 : 1-$(NO_2)_2C_6H_3$·CO_2H, or CCl_3·CO_2H. The terpene, largely *d*-limonene, is removed with steam, the residual ester is hydrolysed, and the liberated borneol with a small proportion of *iso*borneol is determined. High yields under these conditions are obtained over a very narrow range of ionisation const., $K = 3{\cdot}7 \times 10^4$ to 8×10^4. At higher temp. acids with lower K are fairly effective. The yields of bornyl esters formed by acids of < optimum K (*e.g.*, BzOH) are greatly improved by addition of *o*-$C_6H_4(OH)_2$, *o*- and *m*-cresol, PhOH, β-$C_{10}H_7$·OH, resorcinol, and *p*-NO_2·C_6H_4·OH, but not of PhOMe, $PhNO_2$, quinoline, or PhCN at 140°. This improvement is due to increased availability of H$^+$, not to increase in the dielectric const. of the reaction medium or to isomerisation of (I) to camphene. *d*-α-Pinene when heated with a mixture of an org. acid and amide is converted into *d*-limonene in good yield; the amide appears to inhibit esterification. The principal products formed in the reaction of (I) with org. acids can be explained by assuming the preliminary capture of a proton by (I); the unstable ion thus formed rearranges and stabilises itself in various ways. H. W.

Synthetic production of camphor from pinene. B. G. S. Acharya (*J. Univ. Bombay*, 1944, **12**, A, Part 5, 29—30; cf. A., 1943, II, 239).—Pinene hydrochloride (1 mol.), dry Na stearate (2 mols.), Na_2CO_3 (1 mol.), and NaOH (1 mol.), refluxed for 24 hr. and distilled, give camphene (I) in 90% yield, convertible into camphor without further purification. A slight increase in yield is obtained by working in N_2 and distilling under reduced pressure. Residues from distillation can be used again for 8—9 times. Yields of (I) using mowda, coconut, ground-nut, castor, linseed, and cottonseed oil, and mutton tallow in place of stearic acid are 90, 84, 69, 73, 71, 68, and 87%, respectively. A. T. P.

VI.—HETEROCYCLIC.

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

Terpene ethers etc.—See B., 1944, II, 198.

Acetylene derivatives. XXII. Condensation of dimethylvinylethinylcarbinol and vinyl*iso*propenylacetylene with *o*- and *p*-cresol. I. N. Nazarov and F. I. Gotman. **XXIII. Dimerisation of dimethylvinylethinylcarbinol to 1 : 1 : 3 : 3-tetramethyl-4-vinyl*iso*coumarone with elimination of water.** I. N. Nazarov and G. P. Vercholetova (*Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1941, 545—555, 556—572).—XXII. *o*-Cresol condenses with dimethylvinylethinylcarbinol (I) or vinyl*iso*propenylacetylene (II) (H_3PO_4 catalyst) in the same way as phenol (*ibid.*, 1940, 314) giving the readily polymerised p-[αα-*dimethyl*-α-(*vinylethinyl*)]-*o*-*cresol*, b.p. 129—130°/2 mm. The *Me ether*, b.p. 115—116°/2 mm., m.p. 30—30·5°, is oxidised by $KMnO_4$ in $COMe_2$ to $H_2C_2O_4$ and α-(4-*methoxy*-3-*methylphenyl*)iso*butyric acid*, m.p. 108°, further oxidised by HNO_3 to 4-methoxy-3-methylbenzoic acid.

m-Cresol condenses with (I) or (II) giving about equal amounts of neutral and acidic products. The latter contain p-[αα-*dimethyl*-α-(*vinylethinyl*)]-m-*cresol* (III) (*phenylurethane*, m.p. 112—112·5°), which is readily polymerised and is hydrogenated to 3-*methyl*-4-αα-*dimethylamylphenol*, b.p. 138—140°/3 mm. The *Me ether* of (III), also obtainable from *m*-C_6H_4Me·OMe and (I) or (II), b.p. 125—126°/3 mm., is oxidised to $H_2C_2O_4$ and (impure) α-(4-*methoxy*-2-*methylphenyl*)iso*butyric acid*, further oxidised to 4-methoxy-2-methylbenzoic acid. The neutral product of the reaction is 3 : 3 : 6-*trimethyl*-2-*allylidenecoumarone* (IV), b.p. 122·5—123°/7 mm. (IV) is hydrogenated to 3 : 3 : 6-*trimethyl*-2-*propylcoumarone*, b.p. 114—114·5°/6·5 mm., and ozonised to 2-*keto*-2 : 3 : 6-*trimethylcoumarone* (V), b.p. 114°/8 mm., sometimes accompanied by an *aldehyde*, $C_{13}H_{14}O_2$. (V) is hydrolysed by alkali to α-(2-*hydroxy*-4-*methylphenyl*)iso*butyric acid*, m.p. ~145° with reconversion into (V), and by NH_3 to the *amide*, m.p. ~150°. Opening of the lactone ring of (V) followed by methylation affords α-(2-*methoxy*-4-*methylphenyl*)-iso*butyric acid*, m.p. 136—136·5°, oxidised by HNO_3 to a *nitromethoxytoluic acid*, m.p. 220—220·5°.

XXIII. The compound previously obtained in small amount from (I) with H_2SO_4 or Ac_2O can be obtained in 70—80% yield by the action of HCO_2H, H_3PO_4, or $FeCl_3$ in C_6H_6; it is 1 : 1 : 3 : 3-*tetramethyl*-4-*vinyl*iso*coumarone* (VI), b.p. 81°/3·5 mm., polymerised to a glass. It forms a *hydrochloride*, m.p. 88·25°, and a *dibromide*, m.p. 109·5°, and is oxidised by $KMnO_4$ to 1 : 1 : 3 : 3-*tetramethyl*iso-*coumarone*-4-*carboxylic acid*, m.p. 190—191°, whilst ozonisation also affords the corresponding *aldehyde*, b.p. 105—106°/6·5 mm., m.p. 52—53°, and HCO_2H. (VI) is hydrogenated to 1 : 1 : 3 : 3-*tetramethyl*-4-*ethyl*iso*coumarone* (VII), b.p. 78—79°/3·5 mm., which on further reduction (Ni catalyst, 6 hr. at 130—140° and 2 hr. at 160°) gives a *product*, $C_{14}H_{22}O$, probably (ethyl*iso*propylphenyl)dimethyl carbinol, m.p. 25—25·5°. At higher temp. hydrogenation of the nucleus also takes place and one of the products, b.p. 182—186°, appears to be ethyl*iso*propyl*cyclo*hexane. G. A. R. K.

Formation of a chromone by the von Pechmann condensation of ethyl acetoacetate with 2-chloro-*m*-5-xylenol. R. Adams and J. W. Mecorney (*J. Amer. Chem. Soc.*, 1944, **66**, 802—805).—1 : 3 : 2 : 5-

$C_6H_2Me_2Cl{\cdot}OH$ (I) and $CH_2Ac{\cdot}CO_2Et$ in conc. H_2SO_4 at 100° (30 min.) and then room temp. (1 week) give 6-*chloro*-2 : 5 : 7-*trimethylchromone* (II) (35%), m.p. 145—146° (and an oil), the structure of which is proved as follows. (II) gives a 2-*styryl*-compound, m.p. 186—186·5°, with hot KOH–EtOH gives 2-*chloro*-4-*acetoacetyl*-m-5-*xylenol* (III) (45%), m.p. 148—150° [transient red $FeCl_3$ colour in AcOH (not H_2O, EtOH, or $COMe_2$); in warm AcOH + a drop of conc. HCl regenerates (II)], and with boiling aq. NaOH gives 5 : 1 : 3 : 2 : 4-$OH{\cdot}C_6HMe_2Cl{\cdot}COMe$ (IV), dimorphic, m.p. 106—110° and 89·5—90° (clear at 110°) (cf. lit.) (known Me ether, m.p. 76—77°). Ac_2O–H_2SO_4 at 100° converts (I) into its acetate, m.p. 48°, whence $AlCl_3$ at 50° yields (IV), which with Na and EtOAc gives (III). 4 : 5 : 7-Trimethylcoumarin, m.p. 181° (lit. 175—176°), and H_2SO_4–HNO_3 at −5° to −10° give the 6-NO_2- (80%), m.p. 209—211° (lit. 208°), and thence (Sn–$SnCl_2$–conc. HCl–EtOH at room temp. or, less well, Fe powder in 75% EtOH) the 6-NH_2- (64%), m.p. 199—200°, and (diazo-reaction) 6-*Cl*-derivative (83%), m.p. 194—195·5°, whence O_3 in EtOAc–MeOH and then NaOH–aq. MeOH yields (IV). M.p. are corr. R. S. C.

Brominated 4-hydroxycoumarins. C. F. Huebner and K. P. Link (*J. Amer. Chem. Soc.*, 1944, **66**, 656).—Heating $CH_2Ph{\cdot}COCl$ and 2 : 5 : 1-$OH{\cdot}C_6H_3Br{\cdot}CO_2Me$ at the b.p. and then further with C_5H_5N gives *Me* 5-*bromo*-2-*phenylacetoxybenzoate*, m.p. 68—70°, which with Na at 200° yields 6-*bromo*-4-*hydroxy*-3-*phenylcoumarin*, m.p. 252—254°, which crystallises from H_2O at pH 5—6. *Me* 5-*bromo*-2-*acetoxybenzoate*, m.p. 33—35°, with Na in kerosene at 200° gives 6-bromo-4-hydroxycoumarin, which with an excess of CH_2O in boiling EtOH yields 3 : 3′-*methylenebis*-6-*bromo*-4-*hydroxycoumarin*, m.p. 326—327° (*Me*$_2$ *ether*, m.p. 218—220°). R. S. C.

Chemistry and biochemistry of plant materials. IX. Formation of dihydroflavonol and flavonol and synthesis of chalkone–flavanone–flavonol glucosides. L. Reichel and J. Stevdel (*Annalen*, 1942, **553**, 83—97).—The inter-relationships of *o*-hydroxychalkone (I), flavanone (II), flavonol (III), and dihydroflavonol (IV) have been examined. Under the experimental conditions (I) is quantitatively converted by ⅛ mol. of NaOH into (II) whereas with 1 mol. of NaOH (I) is unchanged, and (II) is converted completely into (I). Direct oxidation of (II) to (III) by H_2O_2 does not therefore occur; H_2O_2 reacts exclusively with (I). (IV) is formed from (I) suspended in MeOH by the action of alkaline H_2O_2 at room temp. With $\frac{1}{16}$ mol. of NaOH and 5 mols. of H_2O_2 the yield of (IV) is small; it is good (~50%) with ¼ mol. of NaOH; with 1 mol. of NaOH the yield is 8%, with 11% of (III). (IV) is dehydrogenated by alkaline H_2O_2 or by mol. O_2 to (III). A new autoxidisable system is represented by (IV); H_2O_2 produced by dehydrogenation autoxidation is identified by catalase. (IV) is an intermediate in the synthesis of (III). (II) and ¼ mol. of NaOH give traces of (III) with 93% of unchanged (II). With 2 mols. of NaOH the products are 75% of (II) and 19% of (III); (IV) could never be identified and appears to be dehydrogenated to (III) under the experimental conditions. Under corresponding conditions (II) and 2 mols. of NaOH afford 46·2% of (I), which is an intermediate in the synthesis of (III). In 0·01M. solution in MeOH, (I), ⅛ mol. of NaOH, and 1 mol. of H_2O_2 give 67·9% of (II) in 18 days at room temp. Production of (IV) is first observed with 10 mols. of H_2O_2, the yield being 13·4% with 69·6% of (II). With increasing [OH′] isomerisation of (I) to (II) proceeds more slowly until finally (I) remains unchanged. With ½ mol. of NaOH and 1 mol. of H_2O_2 (III) is formed in 29% yield. With 1 mol. of NaOH the yield is only slightly increased. (IV) cannot be detected since it is dehydrogenated to (III). (II) is unchanged by ⅛ mol. of NaOH and 10 mols. of H_2O_2; under these conditions it is not transformed into (I). 20% of (III) is formed by use of 1 mol. of NaOH and 2 mols. of H_2O_2. An electronic explanation of the changes is advanced. H. W.

Dibenzfuran. XX. 2 : 3 : 6 : 7-Derivatives. H. Gilman, J. Swiss, H. B. Willis, and F. A. Yeoman (*J. Amer. Chem. Soc.*, 1944, **66**, 798—801; cf. A., 1939, II, 342).—3 : 6-Dibromodibenzfuran, NaOH, Cu-bronze, Cu, and $CuSO_4{,}5H_2O$ at 235—240° give impure 3 : 5-dihydroxy- and thence (Me_2SO_4–NaOH) 3 : 6-*dimethoxy*-*dibenzfuran* (45·5% over-all), m.p. 88—89°. With Br–AcOH at room temp. this gives 4 : 5- (? 4 : 7-) (2 pts.), m.p. 196—197°, and 2 : 7-*dibromo*-3 : 6-*dimethoxydibenzfuran* (I) (1 pt.), m.p. 260—261°. With $LiBu^a$ and then Me_2SO_4 in Et_2O–C_6H_6, (I) gives 3 : 6-dimethoxy-, m.p. 144—145°, and thence by HBr–AcOH–H_2O 3 : 6-dihydroxy-2 : 7-dimethyldibenzfuran (II), sinters 228°, m.p. 231—232°. 1 : 4 : 2 : 5-$C_6H_2MeI(OMe)_2$ (III) and Cu give [2 : 5 : 4 : 1-$(OMe)_2C_6H_2Me{\cdot}]_2$ (50—84%), m.p. 134° (cf. Erdtmann, A., 1936, 184), whence HBr–AcOH gives a very small yield of (II). CuCN and (III) at 240° give 2 : 5-*dimethoxy*-p-*tolunitrile* (73%), m.p. 130—131°, hydrolysed by NaOH–EtOH–H_2O to the *acid* (41%), m.p. 125—126°, which is also obtained (35% yield) from (III) by $LiBu^a$ (not by the Grignard reagent) and then CO_2 and is oxidised by aq. $KMnO_4$ to 2 : 5 : 1 : 4-$(OMe)_2C_6H_2(CO_2H)_2$, thus proving the orientation of (1)—(III). 1 : 2 : 5-$C_6H_3Me(OMe)_2$ gives 4 : 1 : 2 : 5-$NO_2{\cdot}C_6H_2Me(OMe)_2$ (IV), hydrogenated (Raney Ni; EtOH; 100°/30—45 lb.) to the unstable amine, m.p. 108·5—109·5° (*Ac* derivative, m.p. 160—162°), whence (III) is obtained by a diazo-reaction, thus proving the orientation of (IV). Br and a trace of Fe in CCl_4 convert (IV) into 1 : 4 : 2 : 5-$C_6H_2MeBr(OMe)_2$, m.p. 168°, whence HBr–AcOH and then Ac_2O give 1 : 4 : 2 : 5-$C_6H_2MeBr(OAc)_2$, m.p. 253—254°. Conc. HNO_3 in AcOH at 45° converts 2 : 5 : 1 : 4-$(OMe)_2C_6H_2Me{\cdot}CO_2H$ or (III) into (V). R. S. C.

Dinaphthylene dioxide. III. Acylation and nitration. R. Pummerer, E. Buchta, W. Gündel, W. Kiessling, K. Pfeiffer, H. Rath, K. Schuler, and H. Stinlendörfer (*Annalen*, 1942, **553**, 103—146).—Benzoylation and phthaloylation of dinaphthylene dioxide (I) proceed relatively simply since only one mono- and only one di-derivative is produced in each case. Nitration is more complex since invariably two mono- and thence three di-derivatives arise which can only be separated chromatographically from one another. The reaction of 1 mol. of (I) with 2 mols. of BzCl and somewhat > 2 mols. of $AlCl_3$ in CS_2 or, more rapidly, in PhCl at 132° gives essentially 5 : 5′-dibenzoylnaphthylene dioxide (II), m.p. 324° (lit. 318°), with a small porportion of 5-*benzoylnaphthylene dioxide* (III), m.p. 252°. (III) is the main product when 1 mol. of BzCl is added gradually to a well-stirred mixture of somewhat > 1 mol. proportion of (I) and $AlCl_3$ in PhCl at 10—50°. The entry of >2 Bz is never observed even when a large excess of BzCl is used. (II) and Br vapour give essentially a Br_4-derivative, softens at 400°. (II) is much more resistant than (I) to oxidation and cannot be converted into a quinone by use of CrO_3 or Bz_2O_2. This does not immediately justify the assumption that Bz is attached to $C_{(4')}$ (Stinzendörfer, *Diss., Erlangen*, 1936). (I) is transformed by *o*-$C_6H_4Br{\cdot}COCl$ into *mono*-, m.p. 308°, and *di*-, m.p. 346°, -*o*-*bromobenzoylnaphthylene oxide*, which when boiled with quinoline and alkali pass respectively into 4 : 5-*benzoylenedinaphthylene dioxide*, m.p. 323°, and 5 : 4 : 5′ : 4′-*dibenzoylenedinaphthylene dioxide* (IV), from which a vat could not be obtained even in presence of C_5H_5N. The constitution of (IV) is established by its formation from *Bz*-2′-hydroxybenzanthrone, whereby also the attachment of Bz to $C_{(5)}$ in (II) and (III) is proved. *o*-$C_6H_4(CO)_2O$, (I), and $AlCl_3$ in boiling PhCl afford 5 : 5′-*di*-o-*carboxybenzoyldinaphthylene dioxide* (V), decomp. >330° (also $+2C_5H_5N$), converted by boiling Ac_2O into the corresponding *anhydride*, m.p. >330°, and by boiling HNO_3 (*d* 1·32) into a $(NO_2)_3$-derivative. Ring-closure of (V) or of the corresponding mono-derivative is greatly impeded by the pronounced tendency towards anhydride formation. H_2SO_4 causes sulphonation and oxidation in addition to the desired reaction, but (V) is transferred into 5 : 6 : 5′ : 6′-*diphthaloyldinaphthylene dioxide* (VI), decomp. 320—330° after darkening and softening, by boiling with P_2O_5 in BzCl–$C_6H_3Cl_3$. $POCl_3$ cannot replace P_2O_5 and the change does not occur with P_2O_5 in boiling $C_6H_3Cl_3$ in absence of BzCl. (VI) is a reddish-brown vat dye. Nitration of (I) is almost as easy as that of a phenol and mono-nitration is best effected by the action of 13% aq. HNO_3 on (I) in PhCl or $PhNO_2$. The product after removal of unchanged (I) cannot be separated into its components by crystallisation but is separated by chromatography over Al_2O_3 into violet 4- (VII), m.p. 324—325°, and red 6- (VIII), m.p. 313—315°, -*nitrodinaphthylene dioxide*. (VII) is reduced by granulated Sn and HCl to 4-*aminodinaphthylene dioxide* (IX) (*CHPh*: derivative, m.p. 236—238°), the *Ac*, m.p. 330° (decomp.) after darkening, and *Ac*$_2$ derivative, m.p. >250°, becomes brown at 260° and black at 350—360°, of which are obtained by addition of Zn dust to a suspension of (VII) in boiling Ac_2O–AcOH–C_5H_5N. (VIII) is similarly reduced to x-*aminodinaphthylene oxide*, which affords an *Ac*$_2$ compound, m.p. 258—259°, but could not be converted into a CHPh: derivative. It could not be deaminated by 18% HCl under O_2 at 185°; this treatment transforms (VII) into 4 : 4′-dinaphthone dioxide, thus proving that NH_2 is attached to $C_{(4)}$ of (IX). Treatment of a suspension of finely-divided (I) in AcOH with 10% HNO_3 at 100° and chromatography of the product over Al_2O_3 leads to the isolation of raspberry-red (X), m.p. 310°, softens at 285°, brick-red (XI), m.p. >300° after darkening, and (in very small amount) violet (XII), m.p. >320° after darkening, *dinitrodinaphthylene dioxide*. (X) is reduced by granulated Sn and HCl to a *diamine* [red (*CHPh*:)$_2$ derivative, m.p. 291—292° (corr.); *diformyl* derivative, m.p. 345—346° (corr.)]. (XI) yields a brick-red *amine* [(*CHPh*:)$_2$ derivative, m.p. 314°; *triformyl* compound, decomp. >360°]. (X) and (XI) are also obtained from both (VII) and (VIII) whereas (XII) arises only from (VII) in 1—2% yield. (X) and (XI) can contain only 1 NO_2 at $C_{(4)}$ or $C_{(4')}$ whilst the other must be in that position which is already occupied in (VIII). (X) and (XI) do not contain the NO_2 groups in symmetrical positions. (XII) may be symmetrical and is then the 4 : 4′-compound; the minute amount available has prevented its attempted conversion into the 4 : 4′-quinone. (X) and (XI) are differentiated by the presence of the two NO_2 in the same nucleus in one case and in different nuclei in the other. Since there is no evidence of ring formation from the corresponding amines and PhCHO and HCO_2H it follows that $C_{(3)}$ and $C_{(5)}$ are not favoured for entry of the second NO_2. Only $C_{(6)}$ and $C_{(7)}$ remain and of these $C_{(6)}$ is preferred. 34% HNO_3 converts finely-divided (I) into *trinitrodinaphthylene dioxide*; the $(NO_2)_4$-compound, which decomposes at a very high temp., is obtained from (I) with cold, fuming HNO_3 or boiling 50% HNO_3 and the $(NO_2)_6$-derivative by very prolonged heating of (1) with HNO_3 (*d* 1·38).

[With A. Rieche and P. von Miller.] Dinaphthone dioxide (**XIII**) is transformed by boiling 50% HNO_3 into *dinitrodinaphthone dioxide* (**XIV**), decomp. at >360° without melting, which is reduced by $Na_2S_2O_4$ and NaOH in boiling H_2O to *diaminodinaphthone dioxide*; this does nor appear to give a simple Bz derivative with boiling BzCl. Cold nitrating acid converts (**I**) into *trinitrodinaphthone dioxide*, which gives a green product with NH_2Ph, red substances with $NPhMe_2$ and quinoline, and olive-green products with toluidine and xylidine. These reactions are not shown by (**XIV**). H. W.

Synthetic thiophan derivatives. E. R. Buchman and H. Cohen (*J. Amer. Chem. Soc.*, 1944, **66**, 847—848).—$CO_2Et{\cdot}CH_2{\cdot}S{\cdot}[CH_2]_2{\cdot}CO_2Et$ with Na in C_6H_6 gives Et 3-ketotetrahydrothiophen-4-carboxylate, b.p. 96°/4 mm. [phenylhydrazone, m.p. 100—101° (cf. Karrer *et al.*, A., 1944, II, 167); *semicarbazone*, m.p. 176°], converted by acid into *3-ketotetrahydrothiophen*, b.p. 83—85°/29 mm., unstable [*semicarbazone*, m.p. 196° (decomp.); 2 : 4-*dinitrophenylhydrazone*, m.p. 179° (decomp.)]. $CO_2Et{\cdot}CHMe{\cdot}S{\cdot}[CH_2]_2{\cdot}CO_2Et$ gives similarly *Et 3-keto-2-methyltetrahydrothiophen-4-carboxylate*, b.p. 93—95°/4·5 mm., and thence *3-keto-2-methyltetrahydrothiophen*, b.p. 82°/28 mm. (*semicarbazone*, m.p. 185—186°; *dinitrophenylhydrazone*, m.p. 161—162°). R. S. C.

Thiophan derivatives. R. B. Woodward and R. H. Eastman (*J. Amer. Chem. Soc.*, 1944, **66**, 849—850).—$SH{\cdot}CH_2{\cdot}CO_2Me$, $CH_2{:}CH{\cdot}CO_2Me$, and piperidine give $CO_2Me{\cdot}CH_2{\cdot}S{\cdot}[CH_2]_2{\cdot}CO_2Me$, converted by NaOMe in PhMe at 110° into, mainly, *Me 3-ketotetrahydrothiophen-4-carboxylate*, m.p. 37—38°, b.p. 128·5—129·5°/20 mm. [reddish-violet $FeCl_3$ colour; *semicarbazone*, m.p. 189·5—190°; *CHPh:*, m.p. 158—159°, and *furfurylidene* derivative (**I**), m.p. 157—158°], but in Et_2O at room temp. gives the *2-carboxylate* (**II**), b.p. 116—116·5°/9 mm. (*semicarbazone*, m.p. 187—187·5°; *CHPh:*, m.p. 129—130°, and *furfurylidene* derivative, m.p. 139·5—140°). Hydrolysis of either product gives *3-ketotetrahydrothiophen*, b.p. 58·2—58·4°/7 mm. [(*CHPh:*)$_2$, m.p. 187·5°, and *difurfurylidene* derivative, m.p. 191—192°]. With I or $FeCl_3$ etc., (**II**) gives a *compound*, $C_{12}H_{14}O_6S_2$, m.p. 188·5—189·5° [(*CHPh:*)$_2$ derivative, m.p. 236°], converted by desulphurisation into (?) δε-*dicarbomethoxy*-n-*octane*-γζ-*dione*, m.p. 125—126°, which with dil. acid yields (?) 2 : 5-*diethylfuran*-3 : 4-*dicarboxylic acid*, m.p. 152—153°. (**I**) contains the S–C skeleton of biotin. (Cf. preceding abstract.) R. S. C.

Thiophan compounds. V. P. Karrer, R. Keller, and E. Usteri (*Helv. Chim. Acta*, 1944, **27**, 237—246; cf. A., 1944, II, 167).—Thiophan derivatives are described containing $\cdot[CH_2]_4{\cdot}CN$ and $\cdot[CH_2]_4{\cdot}CO_2H$ attached to $C_{(2)}$. $Br{\cdot}[CH_2]_4{\cdot}CN$ and $CHNa(CO_2Et)_2$ in abs. EtOH at 50° give *Et$_2$ δ-cyano*-n-*butylmalonate*, b.p. 127—129°/0·01 mm. The corresponding *acid*, m.p. 116°, is transformed by Br in CCl_4–Et_2O at 20° into the non-cryst. *α-bromo-ε-cyanopentane-αα-dicarboxylic acid*, which passes at 100°/15 mm. into α-bromo-ε-cyanohexoic acid, which with CH_2N_2 in Et_2O affords the *Me* ester, b.p. 114—116°/0·02 mm. This is transformed by $SH{\cdot}[CH_2]_2{\cdot}CO_2Et$ and NaOEt in EtOH into *β-carbethoxyethyl ε-cyano-α-carbomethoxy*-n-*amyl sulphide*, b.p. 162—165°/0·01—0·02 mm., which with NaOEt in PhMe at 35° affords *Et 3-keto-2-δ-cyano*-n-*butylthiophan-4-carboxylate* (**I**), b.p. 153—155° (bath)/0·01—0·02 mm. (**I**) is converted by Br in CCl_4 at 0° into an unstable Br_1-derivative, which is gradually hydrolysed by boiling, dil. mineral acid and simultaneously oxidised by air to 3 : 4-*dihydroxy-2-δ-carboxy*-n-*butylthiophen*, m.p. 183°, which gives a dark blue colour with $FeCl_3$. (**I**) is hydrolysed and decarboxylated by a boiling mixture of dil. H_2SO_4 and AcOH to *3-keto-2-δ-carboxyl*-n-*butylthiophan* (**II**), m.p. 68°, which is more conveniently obtained by condensing $Br{\cdot}[CH_2]_4{\cdot}CO_2Et$ with $CHNa(CO_2Et)_2$ to *Et$_3$* n-*pentane-ααε-tricarboxylate*, b.p. 184°/15 mm.; this is hydrolysed to the *acid*, m.p. 88—89°, which yields successively the *α-Br*-derivative, decomp. 136—137°, non-cryst. α-bromopimelic acid, and *Et$_2$ α-bromopimelate*, b.p. 101—103°/0·005 mm. $SNa{\cdot}[CH_2]_2{\cdot}CO_2Et$ converts this compound into *β-carbethoxyethyl αε-dicarbethoxy*-n-*amyl sulphide*, b.p. 165—170°/0·02 mm., transformed by NaOEt in xylene into *Et 3-keto-2-δ-carbethoxy*-n-*butylthiophan-4-carboxylate*, b.p. 148—155° (bath)/0·02 mm., converted by acid ketonic fission into (**II**). Passage of Br through a solution of (**II**) in MeOH kept acid to Congo-red by gradual addition of $CaCO_3$ gives *3-keto-4-hydroxy-2-δ-carboxy*-n-*butylthiophan*, m.p. 117—118° (*dioxime*, decomp. ~215° according to the rate of heating and size of crystal). (**I**) couples with $p{\cdot}NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ to *Et 4-p-nitrobenzeneazo-3-keto-2-δ-cyano*-n-*butylthiophan-4-carboxylate*, which, like the compound with $p{\cdot}SO_3H{\cdot}C_6H_4{\cdot}N_2Cl$, could not be reduced to the 4-NH_2-compound. H. W.

Synthesis of 2 : 4-diarylthiophens. E. Campaigne (*J. Amer. Chem. Soc.*, 1944, **66**, 684—686).—"Anhydroacetophenone disulphide," $CPhMe\langle^{S\text{—}CPh}_{S{\cdot}CPhMe}\rangle CH$ (**I**) (modified prep.; cf. Baumann *et al.*, A., 1895, i, 362), m.p. 107—108°, at 180° gives a tar containing very small amounts of 2 : 4-diphenylthiophen (**II**), in boiling xylene gives an unsaturated, highly coloured mixture, but with Cu chromite in boiling xylene gives 83% of (**II**), m.p. 120·6—121·5° [picrate, m.p. 133·1—133·6° (lit. 133—134°); 5-HgCl derivative, m.p. 222—223°]. *p*-$OMe{\cdot}C_6H_4{\cdot}COEt$, H_2S, and HCl in EtOH at 0° give "*anhydro*-p-*methoxypropiophenone disulphide*" [2 : 4 : 6-*tri*-p-*anisyl*-4-*methyl*-2-*ethyl*-1 : 3-*dithia*cyclo*hexane*] (53·5%), m.p. 158·1—158·6°, which in xylene gives a tar but no thiophen derivative, is unchanged in boiling EtOH alone or with Cu chromite, and with Cu chromite in boiling xylene gives 2 : 4-*di*-p-*anisyl*-3 : 5-*dimethylthiophen* (**III**) (66%), m.p. 112·3—112·8° (no derivatives formed). The reaction mechanism is thus: (**I**) → CSPhMe + $SH{\cdot}CPh{:}CH{\cdot}CPh{:}CH_2$ (**IV**); (**IV**) → (**II**) + H_2, Cu chromite or, less well, CSPhMe acting as H-acceptor. KOH in $(CH_2{\cdot}OH)_2$ at 225°/0·5 mm. hydrolyses (**III**) to 2 : 4-*di*-p-*hydroxyphenyl*-3 : 5-*dimethylthiophen* (61%), darkens 185°, m.p. 194—196° (*diacetate*, m.p. 125·9—126·9°). Absorption max. of (**II**) and (**III**) in MeOH are very similar (250, 265, and 280 mμ.), but ε differ notably. M.p. are corr. R. S. C.

Action of Grignard reagents on oximes. IV. Aliphatic Grignard reagents and mixed ketoximes. K. N. Campbell, B. K. Campbell, L. G. Hess, and I. J. Schaffner (*J. Org. Chem.*, 1944, **9**, 184—186).—Ethyleneimines are obtained from aliphatic Grignard reagents and aryl alkyl ketoximes best in PhMe at 95—100°; higher temp. cause excessive formation of tar. MgEtBr and $CPhMe{:}N{\cdot}OH$ give 2-*phenyl*-2-*ethylethyleneimine* (**I**), b.p. 85—86°/7 mm. (somewhat hygroscopic *hydrochloride*, m.p. 191—191·5°; *phenylthiocarbamide*, m.p. 99—100°; *α-naphthylcarbamide*, m.p. 129—130°), which does not reduce $KMnO_4$ in $COMe_2$ at room temp. It is hydrolysed by short boiling with 4N-HCl or 2N-H_2SO_4 to α-amino-β-phenylbutan-β-ol (**II**) and by longer boiling with 6N-HCl to CHPhEt·CHO. (**I**) is obtained synthetically by successive action of $SOCl_2$ and KOH in EtOH on (**II**). Similarly $CPhMe{:}N{\cdot}OH$ and $MgPr^aBr$ afford 2-*phenyl*-2-n-*propylethyleneimine*, b.p. 90—91°/3 mm. (*hydrochloride*, m.p. 68—69°; *phenylthiocarbamide*, m.p. 100°), hydrolysed to *α-phenyl-α-aminomethyl*-n-*butyl alcohol*, b.p. 125—126°/7 mm. (*Bz* derivative, m.p. 112—113°), obtained also from $CH_2Bz{\cdot}NH_2$,HCl and $MgPr^aBr$. $CPhEt{:}N{\cdot}OH$ and MgEtBr afford *2-phenyl-3-methyl-2-ethylethyleneimine*, b.p. 77—79°/3 mm. (*hydrochloride*, m.p. 158—159°; *phenylthiocarbamide*, m.p. 130—131°), hydrolysed by 2N-H_2SO_4 to $NH_2{\cdot}CHMe{\cdot}CPhEt{\cdot}OH$, b.p. 106—108°/5 mm. (*hydrochloride*, m.p. 230°; *Bz* derivative, m.p. 160°), obtained synthetically from $COPh{\cdot}CHMe{\cdot}NH_2$,HCl and MgEtBr. H. W.

Antispasmodics and anticonvulsants. III. Miscellaneous amides and esters. J. H. Billman and J. L. Rendall (*J. Amer. Chem. Soc.*, 1944, **66**, 745—746; cf. A., 1943, II, 262).—The following activities (*W* = weak; *I* = ineffective) as anticonvulsants and antispasmodics respectively are reported. $(CH_2Ph)_2CH{\cdot}CO{\cdot}O{\cdot}CH_2Ph$ (*W*, *I*), m.p. 81·5°; $CH_2Ph{\cdot}CHPh{\cdot}CO{\cdot}O{\cdot}CH_2Ph$ (*I*, *I*), b.p. 197—201°/1 mm.; CH_2Ph lævulate (—, *W*), b.p. 148—150°/3 mm.; *CH_2Ph 2-pyrrolidone-5-carboxylate* (*I*, *W*), b.p. 202—204°/2 mm.; *$NEt_2{\cdot}[CH_2]_2$ γ-diethylamino-α-phenyl*-n-*butyrate* (*I*, *I*), b.p. 170—173°/1 mm., *2-pyrrolidone-5-carboxylate* (*I*, *I*), b.p. 183—184°/3 mm., nicotinate (*I*, *I*), b.p. 130—132°/2 mm., and acetoacetate, b.p. 113°/2 mm.; benzyl- (—, *W*), m.p. 147·5°, and N-*benzyl*-N′-*triphenylmethyl-carbamide* (*W*, *I*), m.p. 228°; p-*dibenzylacetamido-benzophenone* (*I*, *I*), m.p. 60°, and *-acetophenone* (*W*, *I*), m.p. 135—136°. Preps. are by standard methods. R. S. C.

Magnesium *p*-2′ : 5′-dimethyl-1′-pyrrylphenyl bromide and [the corresponding] lithium [compound]. H. Gilman and G. J. O'Donnell (*J. Amer. Chem. Soc.*, 1944, **66**, 840).—Adding 1—2 drops of conc. HCl to *p*-$C_6H_4Br{\cdot}NH_2$ in hot $(CH_2Ac)_2$ gives *p*-bromo-2′ : 5′-dimethyl-1′-pyrrylbenzene (96%), m.p. 74°, which with Mg or, more readily, Li and then CO_2 gives *p*-2′ : 5′-dimethyl-1′-pyrrylbenzoic acid (72 and 80% yield, respectively), m.p. 196—197°. R. S. C.

Nitrogen compounds in petroleum distillates. XXV. Isolation and identification of 3- and 4-*cyclo*pentylpyridines from Californian petroleum. H. L. Lochte, E. D. Thomas, and P. Truitt (*J. Amer. Chem. Soc.*, 1944, **66**, 550—552; cf. A., 1943, II, 172).—When the aq. solution of the hydrochlorides of petroleum bases, b.p. 210—213°, is extracted with $CHCl_3$ (*loc. cit.*), the bases recovered from the aq. layer yield, by fractional distillation and fractional extraction, 3- (**I**), b.p. 215·5°/747 mm. (*picrate*, m.p. 117·5°), and 4-cyclopentylpyridine (**II**), b.p. 218°/744 mm. (*picrate*, m.p. 145—146°; *platinichloride*, decomp. 225—227°). Structures are proved by synthesis (cf. Emmert *et al.*, A., 1943, II, 384; Crouch *et al.*, A., 1943, II, 206). Adding $HgCl_2$–*cyclo*pentanone to $AlCl_3$ and a trace of I in C_5H_5N at the b.p. gives 1-2′-*pyridyl*cyclo*pentanol*, m.p. 83°, dehydrated by conc. H_2SO_4 at 100° to 1-2′-pyridyl-Δ^1-*cyclo*pentene, b.p. 238—239°/748 mm., whence H_2–PtO_2 in AcOH yields 2-*cyclo*pentylpyridine, b.p. 217—218°/750 mm. (*picrate*, m.p. 106·5°). Et_2 *cyclo*pentylmalonate (**III**), $CH_2{:}CH{\cdot}CN$, and NaOEt in dioxan at 35—40° and then 50° give *Et$_2$* cyclo*pentyl-β-cyanoethylmalonate* [*Et γ-cyano-α-carbethoxy*-α-cyclo*pentyl*-n-*butyrate*], b.p. 162°/10 mm., converted by boiling conc. HCl into α-cyclo*pentylglutaric acid* (**IV**), *form*, m.p. 69°, b.p. 176—177°/1·5 mm. The Na derivative of (**III**) with $Br{\cdot}[CH_2]_2{\cdot}CO_2Et$ in boiling xylene gives *Et$_2$ α-carbethoxy-α*-cyclo*pentylglutarate* (72%), b.p. 168—170°/2·4 mm., converted by boiling 10% aq. KOH into a *form*, m.p. 152·5°, of (**IV**). The *dichloride* (prep. by $SOCl_2$), b.p. 140—145°/4·5 mm., of (**IV**) (m.p. 69°) yields the *diamide*, m.p. 174° (evolution of NH_3), converted at 200°/5 mm. into the *imide* (**V**), m.p. 131°, also obtained from (**IV**) (m.p. 152·5°) by AcCl, followed by NH_3 and then heating. PCl_5

converts (V) at 43° (exothermally) and then 100° into 2 : 5 : 6-*trichloro*-3-cyclo*pentylpyridine*, m.p. 141°, which with H_2–Pd–C in MeOH at 20 lb. gives (I) (picrate, m.p. 118·7°). *cyclo*Pentanealdehyde, b.p. 136°, $CN{\cdot}CH_2{\cdot}CO{\cdot}NH_2$, and KOH in H_2O–EtOH give *αα'-dicyano-β-cyclopentylglutardiamide*, m.p. 213° (decomp.), hydrolysed by hot conc. HCl to *β-cyclopentylglutaric acid*, m.p. 111·5°; this is successively boiled with AcCl to give the anhydride, treated with NH_3 at 130°, heated at 210—230°, and treated with PCl_5 and finally H_2–Pd–C in MeOH, giving (II) (picrate, m.p. 146°).

R. S. C.

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

Behaviour of γ-keto- and aldehydo-acid derivatives at the dropping mercury electrode. II. Amides of *o*-benzoylbenzoic acid. S. Wawzonek, H. A. Laitinen, and S. J. Kwiatkowski (*J. Amer. Chem. Soc.*, 1944, **66**, 830—833).—Amides of *o*-$C_6H_4Bz{\cdot}CO_2H$ (I) are reduced polarographically in 0·1M-NBu_4I–50% dioxan, usually to the corresponding 1-keto-3-phenyl*iso*indole. The no. and position of the waves usually permit deductions as to the approx. amounts of cyclic and open-chain forms. *o*-$C_6H_4Bz{\cdot}CO{\cdot}NHPh$ (II), m.p. 195°, with $SOCl_2$ and then MeOH or with conc. HCl–MeOH at room temp. and then the b.p. gives 1-*keto*-3-*methoxy*-2 : 3-*diphenyl*-1 : 3-*dihydro*isoindole, m.p. 128—129° [regenerates (II) in conc. HCl–AcOH at room temp.], but the anil, m.p. 221°, gives the Me *n*-ester of (I). The ethylamide (III) of (I) similarly gives 1-*keto*-3-*methoxy*-3-*phenyl*-2-*ethyl*-1 : 3-*dihydro*isoindole, m.p. 73—75° (75—78°), which regenerates (III) in conc. HCl–AcOH. With $SOCl_2$–C_6H_6 and then NHPhMe–C_6H_6 at room temp. (I) gives the open-chain *methylanilide*, m.p. 144—146°.

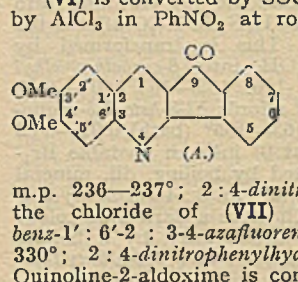
R. S. C.

Syntheses of quinolines from *o'*-aminobenzylidene-*p*-toluidines. W. Borsche and W. Ried [with, in part, J. Barthenheier] (*Annalen*, 1943, **554**, 269—290).—The synthesis of 6 : 7-dihydroxyquinoline is described and the limits of the synthesis of substituted quinolines from Schiff's bases and CO compounds are experimentally explored. *o*-$NH_2{\cdot}C_6H_4{\cdot}CHO$ is heated with $AcCO_2H$ in alkaline solution, which is then acidified and evaporated, thus giving quinoline-2-carboxylic acid in good yield. Similar treatment of a mixture of 6-aminoveratrylidene-*p*-toluidine (I) and $AcCO_2H$ leads to 6 : 7-*dimethoxyquinoline-2-carboxylic acid*, m.p. 215°, in 75% yield which diminishes to 60—65% when NaOH is absent or replaced by piperidine. The *picrate* has m.p. 215°. The acid is decarboxylated by Cu-bronze at 225°/high vac. to 6 : 7-*dimethoxyquinoline* (II), b.p. 135°/0·5 mm. [freely sol. *hydrochloride* and *sulphate*; *picrate*, m.p. 252°; *methiodide* (III), m.p. 258°], also obtained from (I), $CHMe{:}N{\cdot}OH$, and KOH in boiling EtOH. Determination of OMe in (II) according to Vieböck gives about half the expected val. probably because some of the MeI which is formed is involved in the production of methiodide and thus escapes volatilisation; in accordance with this hypothesis (III) evolves the amount of MeI required for 2 OMe. 6-Aminopiperonylidenetoluidine (IV) analogously affords 6 : 7-*methylenedioxyquinoline-2-carboxylic acid*, m.p. 231° (decomp.) (*picrate*, m.p. 182—183°), decarboxylated in a high vac. to 6 : 7-*methylenedioxyquinoline*, m.p. 116—117° (*picrate*, m.p. 245°). $CH_2Ph{\cdot}CO{\cdot}CO_2H$ behaves similarly to $AcCO_2H$. With (I) it gives 6 : 7-*dimethoxy*-3-*phenylquinoline-2-carboxylic acid*, m.p. 151—152°, decarboxylated to 6 : 7-*dimethoxy*-3-*phenylquinoline*, m.p. 90—91°, and with (IV) it yields 6 : 7-*methylenedioxy*-3-*phenylquinoline-2-carboxylic acid*, m.p. 172° (decomp.), and thence 6 : 7-*methylenedioxy*-3-*phenylquinoline*, m.p. 132°. *o'*-Aminobenzylidene-*p*-toluidine (V) with $CH_2Ac{\cdot}CO{\cdot}CO_2Et$ yields *Et* 3-*acetylquinoline-2-carboxylate*, m.p. 93—94°, which does not give a picrate or a 2 : 4-dinitrophenylhydrazone but is transformed by $N_2H_4.H_2O$ in boiling EtOH into 4 : 5-2′ : 3′-*quinolinopyridazinone*, decomp. >320°. Similarly (I) gives *Et* 6 : 7-*dimethoxy*-3-*acetylquinoline-2-carboxylate*, m.p. 187—188°, converted into 6-*keto*-3-*methyl*-4 : 5-2′ : 3′-(6′ : 7′-*dimethoxyquinolino*)-1 : 6-*dihydropyridazine*, m.p. ~315°, darkens at 295°. 6 : 7-*Dimethoxy*-3-*acetylquinoline-2-carboxylic acid*, m.p. 194° (decomp.), is decarboxylated to 6 : 7-*dimethoxy*-3-*acetylquinoline*, m.p. 161—162° (2 : 4-*dinitrophenylhydrazone*, m.p. 301°). Analogously, (IV) gives *Et* 6 : 7-*methylenedioxy*-3-*acetylquinoline-2-carboxylate*, m.p. 160—161° (corresponding *pyridazinone*, m.p. 355—357°).

$CH_2Bz{\cdot}CO{\cdot}CO_2Et$ behaves similarly, giving with (V) *Et* 3-*benzoylquinoline-2-carboxylate*, m.p. 89° (6-*keto*-3-*phenyl*-4 : 5-2 : 3-*quinolino*-1 : 6-*dihydropyridazine*, m.p. 308—310°), with (I) *Et* 6 : 7-*dimethoxy*-3-*benzoylquinoline-2-carboxylate*, m.p. 196—197° (6-*keto*-3-*phenyl*-4 : 5-2′ : 3′-6′ : 7′-*dimethoxyquinolino*-1 : 6-*dihydropyridazine*, m.p. 316—318°), hydrolysed to 6 : 7-*dimethoxy*-3-*benzoylquinoline-2-carboxylic acid*, m.p. 206—207°, decarboxylated to 6 : 7-*dimethoxy*-3-*benzoylquinoline*, m.p. 156—157°, and with (IV) *Et* 6 : 7-*methylenedioxy*-3-*benzoylquinoline-2-carboxylate*, m.p. 247—248°. (V) does not yield the desired 2-acylquinolines or other well-defined products with αβ-diketones $COR{\cdot}COMe$ or with $COMe{\cdot}CPh{:}N{\cdot}OH$. With $COMe{\cdot}CH{:}N{\cdot}OH$ (V) affords mainly quinoline-2-aldoxime, m.p. 188—189° (*picrate*, m.p. 226—227°), and an unidentified substance, m.p. 226—227°, insol. in alkali. Similarly, (I) gives 6 : 7-*dimethoxyquinoline-2-aldoxime*, m.p. 243° (*picrate*, m.p. 253—254°; a methiodide could not be prepared), and an alkali-insol. *by-product*, $C_{33}H_{24}O_5N_4$, m.p. 267—269° (*Ac* derivative, m.p. 176—177°; 2 : 4-*dinitrophenylhydrazone*, m.p. 275—276°), which could not be identified. (V) likewise affords 6 : 7-*methylenedioxyquinoline-2-aldoxime*, m.p. 252—253° (*picrate*, vigorous decomp. >340°), and an alkali-insol. *substance*, $C_{14}H_{10}O_3N_2$, m.p. >365°. $COMe{\cdot}CH{:}N{\cdot}NHPh$ and (V) in presence of piperidine at 160—170° appear to give the *anil*, *o*-$C_6H_4Me{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}N{:}CMe{\cdot}CH{:}N{\cdot}NHPh$, m.p. 221° (quinoline-2-aldehydephenylhydrazone has m.p. 203°), which could not be distilled without complete decomp. and is indifferent towards boiling Ac_2O and KOH–EtOH. Analogously constituted *compounds*, m.p. 151—152° and 173—174° respectively, are derived from (I) and (IV). αγ-Diketones and β-CO-esters with the group Ac react readily in all cases. Thus (V) and CH_2Ac_2 give 3-acetyl-2-methylquinoline, m.p. 57—58° (*picrate*, m.p. 233—234° after darkening; 2 : 4-*dinitrophenylhydrazone*, m.p. 216—217°). 6 : 7-*Dimethoxy*-3-*acetyl*-2-*methylquinoline*, m.p. 142—143° (*picrate*, m.p. 265—266°), and 6 : 7-*methylenedioxy*-3-*acetyl*-2-*methylquinoline*, m.p. 171—172° (*picrate*, m.p. 234—236°), are derived similarly from (I) and (IV) respectively. A 2 : 4-dinitrophenylhydrazone could not be obtained from 6 : 7-*dimethoxy*-3-*benzoyl*-2-*methylquinoline*, m.p. 158°, very smoothly prepared from CH_2AcBz and (I) in presence of piperidine at 100°. CH_2Ac_2 is transformed by a boiling solution of 2 : 4-$(NO_2)_2C_6H_3{\cdot}NH{\cdot}NH_2$ into 1-2′ : 4′-*dinitrophenyl*-3 : 5-*dimethylpyrazole*, m.p. 119—120°; CH_2AcBz similarly yields 5-*phenyl*-1-2′ : 4′-*dinitrophenyl*-5-*methylpyrazole*, m.p. 128—129°. $CH_2Bz{\cdot}CO_2Et$ and (V) afford the non-cryst. *Et* 2-*phenylquinoline*-3-*carboxylate* (*picrate*, m.p. 159—160°), hydrolysed to the acid, m.p. 229°. Similarly (I) gives *Et* 6 : 7-*dimethoxy*-2-*phenylquinoline*-3-*carboxylate*, m.p. 155° [*acid* (VI), m.p. 238—239° (decomp.)], and (IV) yields *Et* 6 : 7-*methylenedioxy*-2-*phenylquinoline*-3-*carboxylate*, m.p. 149°, hydrolysed to the *acid* (VII), m.p. 283—284° (with formation of 6 : 7-methylenedioxy-2-phenylquinoline, m.p. 110°). (V) and Ac_2O alone or in presence of Et_2O at room temp. yield *o'-acetamidobenzylidene*-p-*toluidine*, m.p. 148—149°, which is deacetylated but does not give carbostyril under the influence of alkali. Under the same conditions (I) is transformed directly into 2-*hydroxy*-6 : 7-*dimethoxyquinoline*, m.p. 179° (with some *p*-$C_6H_4Me{\cdot}NHAc$, m.p. 150—152°), and (IV) into 2-*hydroxy*-6 : 7-*methylenedioxyquinoline*, m.p. 158—159°.

Treatment of (II) with boiling AcOH–HI (*d* 1·7) leads to 6 : 7-*dihydroxyquinoline hydriodide*, converted by aq. H_2SO_4 into the corresponding *sulphate*, m.p. ~270°, darkens at 240°; this is transformed by $NaHCO_3$ into the *Na*$_1$ compound, m.p. >360°, slowly darkens >225°, of 6 : 7-dihydroxyquinoline (VIII), which gives (Schotten–Baumann) 6 : 7-*dibenzoyloxyquinoline*, m.p. 135—136°; (VIII) affords a *picrate*, m.p. 270°. (II) is demethylated by pyridinium chloride at 180—190° to (VIII), m.p. 248—250°, softens at 230° (also +2H_2O), isolated by pptn. of the Pb salt, which is treated with H_2S. 6 : 7-*Dimethoxy*-2-*methylquinoline* (+2H_2O), m.p. 285°, becomes discoloured at 240°, and softens at ~265°, is obtained similarly.

(VI) is converted by $SOCl_2$ into the *chloride*, m.p. 225°, cyclised by $AlCl_3$ in $PhNO_2$ at room temp. into 3′ : 4′-*dimethoxybenz*-1′ : 6′-2 : 3-4-*azafluorenone* (*A*), m.p. 290—295° (2 : 4-*dinitrophenylhydrazone*, m.p. 315—316°). Analogously, 6 : 7-methylenedioxy-3-phenylquinoline-2-carboxyl chloride gives 3′ : 4′-*methylenedioxybenz*-1′ : 6′-2 : 3-1-*azafluorenone*, m.p. 276—277° (*oxime*, m.p. 236—237°; 2 : 4-*dinitrophenylhydrazone*, decomp. 332°), and the chloride of (VII) is cyclised to 3′ : 4′-*methylenedioxybenz*-1′ : 6′-2 : 3-4-*azafluorenone*, m.p. 245—246° (*oxime*, m.p. 330°; 2 : 4-*dinitrophenylhydrazone*, blackens >320°, m.p. >360°).



Quinoline-2-aldoxime is converted by boiling Ac_2O into 2-cyanoquinoline, m.p. 93°, from which a picrate or methiodide could not be obtained. The oxime is transformed by $NHPh{\cdot}NH_2$ and conc. HCl in boiling EtOH into quinoline-2-aldehydephenylhydrazone, m.p. 203—204° (*hydrochloride*, m.p. 277—278°). Attempts to obtain quinoline-2-aldehyde by treatment of the oxime with CH_2O, *o*-$C_6H_4(CO)_2O$, or dil. H_2SO_4 were unsuccessful. The *oxime sulphate* has m.p. 203—204°. Analogous methods lead to 6 : 7-*dimethoxyquinoline-2-nitrile*, m.p. 232—233°, and -2-*aldehydephenylhydrazone*, m.p. 170° (*hydrochloride*, m.p. 257—258°), and to 6 : 7-*methylenedioxyquinoline-2-nitrile*, m.p. 253—254°, and -2-*aldehydephenylhydrazone*, m.p. 245—246° (*hydrochloride*, m.p. 299—300°).

H. W.

Quinolines patterned as " open models " of atabrine. H. Gilman and S. M. Spatz (*J. Amer. Chem. Soc.*, 1944, **66**, 621—625).—*m*-$C_6H_4Cl{\cdot}Li$ (I) {prep. from *m*-C_6H_4ClBr and $LiBu^a$ in Et_2O–N_2 at −35° [for, best (69·7%), 9 min.]} with 6-methoxyquinoline in Et_2O–N_2 at, best, 0° gives, after hydrolysis, 6-*methoxy*-2-m-*chlorophenylquinoline* (49·3—53%), m.p. 110—111° (*picrate*, m.p. 196—197°), converted by BzO_2H in $CHCl_3$ at 0° into the N-*oxide* (73%), m.p. 153—154° (*picrate*, m.p. 158·5—159°), which with $POCl_3$ at 100° and then the b.p. gives 4-*chloro*-6-*methoxy*-2-m-*chlorophenylquinoline* (II) (63·2—63·8%), m.p. 153—154°. (II) is also obtained from 4-chloro-6-methoxyquinoline and (I) in 34·7% yield and with $NEt_2{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}NH_2$ at 200—205° gives 4-δ-*diethylamino*-α-*methyl*-n-*butylamino*-6-*methoxy*-2-m-*chlorophenylquinoline* (III) (60·7%), amorphous. 6-*Methoxy*-, m.p. 194—195° (*picrate*, m.p. 205°; N-*oxide*, m.p. 166—168°), 4-*chloro*-6-*methoxy*-, m.p. 163·5—164°, and 4-δ-*diethylamino*-α-*methyl*-n-*butylamino*-6-*methoxy*- (IV), amorphous,

-2-p-*chlorophenylquinoline* are similarly prepared. *o*-OMe·C_6H_4Li and quinoline lead similarly to 2-o-*anisyl*-, b.p. 201—204° (203·5°)/2 mm. [*hydrochloride*, m.p. 184·5—185° (decomp.); *picrate*, m.p. 177—178°; N-*oxide*, m.p. 178—178·5° (*picrate*, m.p. 133·5—134°)], 4-*chloro*-2-o-*anisyl*-, m.p. 96—98° (*picrate*, m.p. 200—201°), 4-δ-*diethylamino*-α-*methyl*-n-*butylamino*-2-o-*anisyl*-*quinoline* (V), b.p. 248—255°/0·025 mm. Similar reactions lead to 6-methoxy- (N-*oxide*, m.p. 170—171°), 4-chloro-6-methoxy-, m.p. 110—111°, and 4-δ-*diethylamino*-α-*methyl*-n-*butylamino*-6-*methoxy*-2-*phenylquinoline* (VI), amorphous. (III), (IV), and (VI), but not (V), show antimalarial activity. R. S. C.

Arylation of *iso*quinoline derivatives. II. Synthesis of 1-*m*-nitrophenyl-3 : 4-dihydro*iso*quinoline, 1-*o*-nitrophenyl-3 : 4-dihydro*iso*quinoline, and their derivatives. V. M. Rodionov and E. V. Javorskaja (*J. Gen. Chem. Russ.*, 1943, **13**, 491—496).—The object of the work was the prep. of *iso*quinoline antimalarials. Ph·$[CH_2]_2$·NH_2 with *m*-NO_2·C_6H_4·COCl gave m-*nitrobenz*-β-*phenylethylamide*, m.p. 119—120° (62% yield), which with P_2O_5 in boiling xylene gave 1-m-*nitrophenyl*-3 : 4-*dihydroisoquinoline* (64%), m.p. 51—52° (*hydrochloride*, m.p. 213—214°), reduced by Fe–AcOH to the m-NH_2-compound (I) (71%), m.p. 119—120° [*hydrochloride*, m.p. 280—281° (decomp.); *Ac* derivative (69%), m.p. 114—117°], is reduced by Sn–HCl to 1-m-*aminophenyl*-1 : 2 : 3 : 4-*tetrahydroisoquinoline* (78%), m.p. 126—127°. NEt_2·$[CH_2]_3$·Cl and (I) gave 3-γ-*diethylaminopropylamino*-1-*phenyl*-3 : 4-*dihydroisoquinoline* (II) (48%), m.p. 226—229° (*hydrochloride*, hygroscopic, m.p. indef.). Ph·$[CH_2]_2$·NH_2 with *o*-NO_2·C_6H_4·COCl gave o-*nitrobenz*-β-*phenylethylamide* (65%), m.p. 115—116°, which with P_2O_5 in boiling xylene gave 1-o-*nitrophenyl*-3 : 4-*dihydroisoquinoline* (73%), m.p. 84—85° (*hydrochloride*, m.p. 211—213°), reduced (Fe–AcOH) to the o-NH_2-compound (52%), m.p. 95—96° (*Ac* derivative), which was reduced (Sn, aq.-alcoholic HCl) to 1-o-*aminophenyl*-1 : 2 : 3 : 4-*tetrahydroisoquinoline* (82%), m.p. 108—109°, and with NEt_2·$[CH_2]_3$·Cl gave 1-*o*-γ-diethylaminopropylaminophenyl-3 : 4-dihydro*iso*quinoline (III) (47%), m.p. 215—219°. (II), (III), and 1-p-γ-*diethylaminopropylaminophenyl*-3 : 4-*dihydroisoquinoline* (*ibid.*, 1941, **11**, 446) were inactive as avian antimalarials. F. Hi.

Hydantoins of sulphur-containing amino-acids. J. V. Karabinos and J. L. Szabo (*J. Amer. Chem. Soc.*, 1944, **66**, 649—650).—Syntheses are effected following the discovery that the hydantoin ring is unaffected by Na in liquid NH_3. Thus Na converts *l*-cystine hydantoin (I) in NH_3 into l-*cysteine hydantoin* (II), m.p. 144—145° (cf. Boyd, A., 1934, 195). *S*-Benzylhomocysteine in hot aq. KCNO and then hot HCl gives the *hydantoin*, m.p. 103—104°, whence Na–NH_3 yields dl-*homocysteine hydantoin* (III), m.p. 121—122°. Homocystine with KCNO and then HCl similarly yields *homocystine hydantoin* (IV), m.p. 204—205°, and thence (III). I oxidises (II) to (I) or (IV) to (III). M.p. are taken on a microscope stage. R. S. C.

Dehydration of hydantoin-5-propionic acid. J. L. Szabo and J. V. Karabinos (*J. Amer. Chem. Soc.*, 1944, **66**, 650—651).—Hydantoin-5-propionic acid, m.p. 170°, with P_2O_5 in boiling xylene gives the *hydantoin-5-propio*-1-*lactam*, NH<CO·N—CO>CH_2 (I) (78%), m.p. CO·CH·CH_2 201°, and with boiling Ac_2O gives the *Ac* derivative (88%), m.p. 147—148°, of (I), also obtained from (I) by Ac_2O. The structure of (I) follows by analogy from conversion of 2-thiohydantoin-5-propio-1-lactam (prep. from 2-pyrrolidone-5-carboxylic acid and NH_4CNS in AcOH–Ac_2O at 100°) by hydrolysis by boiling N-HCl into 2-thiohydantoin-5-propionic acid and recovery therefrom by P_2O_5 in boiling PhMe. R. S. C.

Double invert soaps : symmetrical dipiperidinium salts. J. B. Niederl and A. E. Lanzilotti (*J. Amer. Chem. Soc.*, 1944, **66**, 844—845).—By AlkBr in hot 95% EtOH are prepared *methylenebis*-1-*piperidinium di*-n-*heptyl*, m.p. 178°, -n-*octyl*, m.p. 162°, -n-*tetradecyl*, m.p. 183°, and -n-*hexadecyl dibromide*, m.p. 176°, and *benzylidenebis*-1-*piperidinium di*-n-*heptyl*, m.p. 177°, -n-*octyl*, m.p. 165°, -n-*tetradecyl*, m.p. 181°, and -n-*octadecyl dibromide*, m.p. 179°. R. S. C.

Sulphanilamidopolyalkylpyrimidines.—See B., 1944, III, 142.

Amides of nicotinic and related acids. II. J. H. Billman and J. L. Rendall (*J. Amer. Chem. Soc.*, 1944, **66**, 540—541; cf. A., 1943, II, 262).—The following are prepared, usually by heating the appropriate acid and (high-boiling) amine in xylene with continuous removal of H_2O or from the ester and amine: *nicotin-benzyl*- (I), m.p. 72—73°, -n-*amyl*-, b.p. 170—171°/1 mm., -*allyl*-, b.p. 158—161°/1 mm., and -*dibutylaminopropyl-amide*, b.p. 226—230°/2 mm.; *pyridine*-4-*carboxyl*-*benzyl*-, m.p. 84·5—85°, -n-*amyl*-, b.p. 158—159°/2 mm., -*allyl*-, b.p. 158—159°/2 mm., and -*dibutylaminopropyl-amide*, b.p. 236—240°/2 mm.; *pyridine*-2-*carboxyl*-*benzyl*-, m.p. 87—87·5°, -n-*amyl*-, b.p. 135—138°/2 mm., -*allyl*-, b.p. 166—170°/2 mm., and -*dibutylaminopropyl-amide*, b.p. 209—212°/1 mm.; *pyrazinecarboxyl*-, m.p. 116°, and *quinoline*-3-*carboxyl*-*benzylamide*, m.p. 139—139·5°; *pyrazine*-2 : 3-*di*(*carboxyl*-*benzyl*-, m.p. 171—171·5°, and -n-*amyl*-*amide*), m.p. 145·5—146°. Quinoxaline is prepared from *o*-$C_6H_4(NH_2)_2$ (27·0) and (OH·CH·$SO_3H)_2$ (68·8 g.) in H_2O (<700 ml.). (I) has antispasmodic activity. R. S. C.

Quinoxaline formation and the ortho-effect. Influence of bromine atoms and nitro-groups. R. C. Fuson and Q. F. Soper (*J. Org. Chem.*, 1944, **9**, 193—200).—Quinoxaline formation is made possible by the introduction of Br or NO_2 into the mesityl ring of mesitylglyoxal or Ph mesityl diketone. In the latter compound the effect persists even when the substituent is on the Ph ring. Arylglyoxals which are not sufficiently reactive to yield quinoxalines always form Schiff's bases. Benzils, on the other hand, always form quinoxalines if they react at all. Substitution of Br or NO_2 on either aromatic nucleus of a benzil enhances its tendency to undergo reaction with *o*-$C_6H_4(NH_2)_2$. The H-bonding theory alone does not provide an adequate explanation of these observations. Most of the following $(CO)_2$-compounds are obtained by oxidising the ketone with a small excess of SeO_2 in boiling, wet dioxan: 3-*nitromesityl*- (I), m.p. 217—218·5° (corr.), 2 : 4 : 6-*triisopropylphenyl*- (II), b.p. 129—135°/4·5 mm. [*phenylhydrazone*, m.p. 158·5—159·5° (corr.); *semicarbazone*, m.p. 179—180° (corr.); *hydrazone*, m.p. 153—154° (decomp.)], 3-bromomesityl- (III), (2 : 4-*dinitrophenylhydrazone*, m.p. 203—205°), and 3-bromo-5-nitromesityl-glyoxal (IV) (2 : 4-*dinitrophenylhydrazone*, m.p. 260—261°), *mesityl Me*, b.p. 138—139°/17 mm., p-*nitrophenyl mesityl*, m.p. 115—116° (corr.), m-*nitrophenyl mesityl*, m.p. 108—108·5° (corr.), and p-*bromophenyl mesityl diketone*, m.p. 102—103° p-, m.p. 211—211·5° (corr.), and m-*nitrophenylmesityl*-, m.p. 144—146°, *phenyl*-3′-*nitromesityl*-, m.p. 151—152° (corr.), 4′-*nitrophenyl*-3′′-*nitromesityl*-, m.p. 198—199° (corr.), 3′-*nitrophenyl*-3′′ : 5′′-*dinitromesityl*-, m.p. 188—189° (corr.), *phenyl*-3′ : 5′-*dibromomesityl*-, m.p. 187—188°, 4′-*bromophenylmesityl*-, m.p. 190—191°, *di*-o-*tolyl*-, m.p. 132—133°, and *nitrodi*-o-*tolyl*-*quinoxaline*, m.p. 197·5—198·5°, are described. Acetomesitylene is converted by HNO_3 (*d* 1·51), AcOH, and Ac_2O into 3-*nitroacetomesitylene*, b.p. 157—159°/8 mm., m.p. 23°, which does not give an oxime. 2 : 4 : 6-Triisopropylphenylglyoxal is converted by fuming HNO_3 and glacial AcOH into 3 : 5-*dinitro*-2 : 4 : 6-*triisopropylphenylglyoxylic acid*, m.p. 90—92°, which does not react with 2 : 4-$(NO_2)_2C_6H_3$·NH·NH_2. 3 : 5-*Dinitro*-2 : 4 : 6-*triisopropylacetophenone*, m.p. 144—145°, and 3-*nitrophenyl* 3′ : 5′-*dinitromesityl diketone*, m.p. 184—185° (corr.), are obtained from the parent ketone and fuming HNO_3. *Ph* 3-*nitromesityl diketone*, m.p. 89·5—90·5°, from COPh·CO·$C_6H_2Me_3$, fuming HNO_3, AcOH, and Ac_2O at room temp., is oxidised by H_2O_2 in boiling dioxan to BzOH and 3-nitromesitoic acid. *p*-NO_2·C_6H_4·CH_2·COCl, *s*-$C_6H_3Me_3$, and $AlCl_3$ in CS_2 afford p-*nitrobenzyl mesityl ketone*, m.p. 96—97° (corr.). m-*Nitrobenzyl mesityl ketone*, m.p. 133·5—134·5° (corr.), is obtained analogously. Nitration of the diketone leads to 4-*nitrophenyl* 3′-*nitromesityl diketone*, m.p. 99·5—101° (corr.). 3 : 5-Dibromo-2 : 4 : 6-trimethylbenzoin is oxidised by $CuSO_4$ in aq. C_5H_5N to Ph 3 : 5-dibromomesityl diketone, m.p. 101—104°. *s*-$C_6H_3Me_3$, *p*-C_6H_4Br·CH_2·COCl, and $AlCl_3$ in CS_2 give p-*bromobenzyl mesityl ketone*, m.p. 82—83°. Mesitil and fuming HNO_3 produce 3 : 3′ : 5 : 5′-*tetranitromesitil*, m.p. 317—319° (decomp.), which does not react with *o*-$C_6H_4(NH_2)_2$. A similar behaviour is shown by 3-*nitrophenyl* 3′ : 5′-*dinitro*-2′ : 4′ : 6′-*triisopropylphenyl diketone*, m.p. 166—167°, and 4 : 4′-dimethoxy-2 : 6-xylil. (I), (II), and (III) with *o*-$C_6H_4(NH_2)_2$ give Schiff's *bases*, $C_{28}H_{26}O_6N_4$, $C_{40}H_{52}O_2N_2$, and $C_{28}H_{26}O_2N_2Br_2$, m.p. 258—258·5° (corr.), 173—174°, and 165—167° or 202° (softens at 177° when slowly heated), whereas (IV) appears to yield a *quinoxaline*, $C_{17}H_{14}O_2N_3Br$, m.p. 156—157° (decomp.). H. W.

Structure of indanthrone, indigo, and some of their derivatives. R. Gill and H. I. Stonehill (*J. Soc. Dyers and Col.*, 1944, **60**, 183—186).—The relation in the properties of indigo and indanthrone is explained by assigning H-bonded formulæ, which are resonance hybrids of the keto- and enol forms; this is supported by the different properties of *N*-methylindanthrone, which cannot form a H-bonded structure. H. A. P.

Gliotoxin, the antibiotic principle of *Gliocladium fimbriatum*. II. General chemical behaviour and crystalline derivatives. W. F. Bruce, J. D. Dutcher, J. R. Johnson, and L. M. Miller. **Structure of gliotoxin : (III) degradation by hydriodic acid; (IV) action of selenium.** J. D. Dutcher, J. R. Johnson, and W. F. Bruce (*J. Amer. Chem. Soc.*, 1944, **66**, 614—616, 617—619, 619—621; cf. A., 1944, II, 116).—II. In boiling 10% NaOH, gliotoxin (I) gives NH_2Me, H_2S (40—60%), S (a little), and a red, amorphous, alkali-sol. substance containing N and S. In boiling 15% $Ba(OH)_2$ it gives a cryst. product, whence sublimation yields a little indole-2-carboxylic acid (II). (I) is inert towards PhNCO, and with CH_2N_2, MeI, or Me_2SO_4 gives gums. It gives no reactions for OMe or OEt, CO, CH_2O_2, or CH_2S_2. It reacts with $AgNO_3$–NH_3, Folin's reagent, or nitroprusside, probably owing to liberation of S″ by the alkali. $KMnO_4$, aq. Br, or NaOCl yields SO_4''. Na_2SO_3, $SnCl_2$, HI, Al–Hg, Zn– or Sn–acid gives H_2S. $Hg(OAc)_2$ or $AgNO_3$ liberates only 1 atom of S. $CuSO_4$, $Pb(OAc)_2$, or $BaCl_2$ has no effect. In C_5H_5N, (I) shows 2—3 active H (MgEtBr); with boiling Ac_2O or BzCl it gives gums, but at room temp. yields a *di*-p-*bromo*-, m.p. 193° (decomp.), $[\alpha]_D$ +20° in $CHCl_3$, and *di*-p-*nitro-benzoate*, m.p. 189° (decomp.), $[\alpha]_D^{22}$ +13° in $CHCl_3$, but no reaction occurs with *p*-C_6H_4Me·SO_2Cl or *o*-$C_6H_4(CO)_2O$–C_5H_5N. (I) thus contains an indole nucleus.

III. With red P and HI in boiling AcOH, (I) gives 1 : 4-*diketo-*

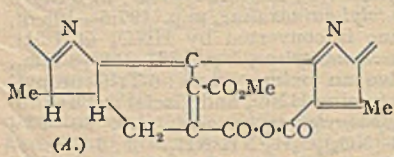
2 : 3-*dimethyltetrahydropyrazino*[1, 2a]*indole* [3 : 6-*diketo*-1 : 2-*dimethylindolo*-1′ : 2′-4 : 5-*tetrahydropyrazine*] (**III**), m.p. 122°, 2 H_2S, and 2 H_2O. The structure of (**III**) is proved by synthesis and by hydrolysis by 0·5N-KOH–MeOH at room temp. to N-*indole*-2-*carboxyl*-N-*methylalanine* (**IV**), m.p. 187° [Et ester (**V**), m.p. 127°], whence boiling 20% aq. KOH–N_2 yields (**II**). The chloride (prep. by $SOCl_2$–Et_2O) of (**II**) and *dl*-NHMe·CHMe·CO_2Et in Et_2O gives (**V**) (m.p. 126°), whence hydrolysis yields (**IV**) and cyclisation by 1% HCl–EtOH at room temp. yields (**III**). (**III**) is also obtained if synthetic (**V**) (probably containing a trace of HCl) is kept in EtOH.

IV. Se and (**I**) at 230—250° give 1 : 3 : 4-*triketo*-2-*methyltetrahydropyrazino*[1, 2a]*indole* [2 : 3 : 6-*triketo*-1-*methylindolo*-1′ : 2′-4 : 5-*tetrahydropyrazine*] (**VI**), m.p. 253—255°, 2H_2S, H_2O, and a derivative from 1 C. In N-KOH–MeOH at room temp., (**VI**) consumed 2 KOH, giving *indole*-2-*carboxylmethylamide* (**VII**), m.p. 220° [*picrate*, m.p. 168—170° (decomp.); *I*-derivative, m.p. 186°, prepared by aq. I–KI–NaOH] (and ? $H_2C_2O_4$), whence boiling 25% aq. KOH–N_2 yields (**II**) and NH_2Me. The chloride of (**II**) and NH_2Me in C_6H_6 give (**VII**), which with COCl·CO_2Et in C_5H_5N–Et_2O at room temp. gives (**VI**), m.p. 255°. R. S. C.

Nuclear acylations according to Friedel–Crafts.—See A., 1944, II, 297.

1 : 3 : 5-Triazines.—See B., 1944, II, 198.

Chlorophyll. CXV. Chloroviolins. M. Strell and E. Iscimenler (*Annalen*, 1942, **553**, 53—66).—The conversion of "unstable chlorins" into chloroviolins (cf. *A*) is described. "Unstable chlorin 7" Me_1 ester (**I**) is converted by BzCl in C_5H_5N into *chloroviolin* Me_1 *ester* (**II**), m.p. >330° (*Cu* compound, m.p. >320°), which is not (*A*), sol. in alkali. Fractionation of (**II**) with 18% HCl and esterification of the alkali-sol. portion leads to *chloroviolin* Me_3 *ester* (**III**), gradual decomp. >270°. Cold, dil. KOH–MeOH also causes fission of (**II**), but prolonged action causes profound decomp. The removal of H_2O by BzCl appears mainly catalytic and is sp.; AcCl, $PhSO_2Cl$, BzCN, and NH_2Bz have no effect and BzBr is somewhat less efficient. The spectra of the chloroviolins are closely similar to those of the neopurpurins. (**III**) may also be regarded as neopurpurin 6 Me_3 ester. In addition to (**II**), an amorphous compound with chlorin spectrum is also obtained from (**I**) particularly when impure C_5H_5N is used. Phæoporphyrin a_7 lactone appears to be benzoylated by BzCl in C_5H_5N; the chloroviolin reaction appears confined to the chlorin system. "Unstable chlorin 7" Me_2 ester does not show the change, which is undergone by "unstable chlorin 7" if reaction is rapid. The reaction is also negative with pyrrochlorin-7-glycollic acid and "unstable chlorin 5." "Unstable mesochlorin 7 Me_1 ester" gives *mesochloroviolin* Me_1 *ester* (**IV**), m.p. 292°, $[\alpha]_{20}$ −343°, and Me_3 ester (**V**), m.p. 198°, $[\alpha]^{20}$ −495° (with filter), −990° (violet colour, without filter), which yield *salts*, $C_{35}H_{32}O_5N_4Cu$, m.p. >310°, $[\alpha]^{20}$ +396° (with filter), +992° (without filter, green colour), and $C_{37}H_{38}O_6N_4Zn$, m.p. 218°, respectively. Important support for the assumption of a neopurpurin-like structure is found in the conversion of (**IV**) or (**V**) by HI into *chloroviolinporphyrin* Me_3 ester, m.p. 278° (*Cu* salt, $C_{27}H_{36}O_6N_4Cu$, m.p. 301°). H. W.


(*A*.)

Chlorophyll. CXVI. Purpurin 3, its meso-compound and derivatives. Synthesis of inactive mesopurpurin 3. H. Fischer and F. Gerner (*Annalen*, 1942, **553**, 67—82).—Attempts to oxidise mesophyllochlorin esters give negative results but free mesophyllochlorin is oxidised by finely-divided $KMnO_4$ in C_5H_5N to mesopurpurin 3, converted by CH_2N_2 into the Me_3 ester (**I**), m.p. 166°, which gives the typical reactions with NH_2OH and CN·CH_2·CO_2Et + NH_2Et and is identical with the substance obtained from *iso*chlorin e_4; 7 : 8-dihydroxymesophyllochlorin Me ester, m.p. 131°, is isolated as by-product. Synthetic mesophyllochlorin (from phyllohæmin) is similarly oxidised to optically inactive mesopurpurin 3, transformed into the Me_3 ester, m.p. 178°. (**I**) gives *salts*, $C_{33}H_{36}O_3N_4FeCl$, m.p. 182°, $[\alpha]^{20}_{white}$ +4000° in $COMe_2$, and $C_{33}H_{36}O_3N_4Cu_3$, m.p. 173°, $[\alpha]^{20}_{white}$ ~+140° in $COMe_2$, which are remarkably stable, and $C_{33}H_{36}O_3N_4Zn$, m.p. 193, dextrorotatory in $COMe_2$, which is decomposed by 16% HCl. Purpurin 3 Me ester, (**II**), $MeNO_2$, and NH_2Et in C_5H_5N at 100° afford *γ-nitrovinylpyrrochlorin Me ester*, m.p. 197°, in ~80% yield. With CN·CH_2·CO_2Et and NH_2Et in C_5H_5N mesopurpurin 3 Me ester gives *Et mesopyrrochlorin-γ-α′-cyanoacrylate Me ester*, m.p. 226°. Moist Ag_2O oxidises (**II**) in MeOH–dioxan containing C_5H_5N to 7 : 8-*dihydroxypurpurin* 3 *Me ester*, m.p. 196°, $[\alpha]^{20}_{white}$ +1500° in $COMe_2$, which gives a positive reaction with NH_2OH but appears indifferent to BzCl. With $KMnO_4$ in C_5H_5N (**II**) gives 2-*carboxy*-2-*devinylpurpurin* 3 Me_2 *ester*, m.p. 181°, $[\alpha]^{20}_{white}$ +1250° in $COMe_2$. Unesterified purpurin 3 is transformed by MgEtBr followed by CH_2N_2 into *γ-γ′-hydroxypropylpyrrochlorin Me ester*, m.p. 211° $[\alpha]^{20}_{green}$ +1240° in $COMe_2$, which gives a positive reaction with BzCl and passes when heated into pyrrochlorin (**III**) and a *substance*, (?) $C_{38}H_{50}O_2N_4$, m.p. 189°, $[\alpha]^{20}_{white}$ +1060° in $COMe_2$, which also reacts with BzCl, gives (**III**) when heated, and does not contain OMe. Attempts to prepare *γ-β′*-hydroxyethylpyrrochlorin Me ester are described. H. W.

Chlorophyll. CXVII. Partial synthesis of 6-formylmeso*iso*chlorin e_4. H. Fischer and F. Gerner (*Annalen*, 1942, **553**, 146—165).—The action of ClCO·NH_2 and $SnBr_4$ on the Cu derivative (**I**) of meso*iso*chlorin e_4 Me_2 ester in dry $CHCl_3$ gives *bromomeso*-iso*chlorin* e_4 *Me*$_2$ *ester*, decomp. ~130°, $[\alpha]^{20}_{red}$ −210°, $[\alpha]^{20}_{white}$ +420° in $COMe_2$, which spectroscopically closely resembles mesomethylphæophorbide *a*. The Cu compound of mesophyllochlorin similarly yields *bromomesophyllochlorin Me ester*, decomp. ~120°, $[\alpha]^{20}_{red}$ ±0°, $[\alpha]^{20}_{white}$ +396°, $[\alpha]^{20}_{green}$ +993° in $COMe_2$, which passes when heated into mesophyllochlorin and phylloporphyrin. Under similar conditions the Cu compound (**II**) of mesopurpurin 3 is dehydrated to γ-formylpyrroporphyrin; if the CHO group is protected by oximation the product is *bromo-γ-formylpyrroporphyrin Me ester*, m.p. 224°, unchanged spectroscopically when heated with AcOH or KOH–MeOH. Gradual addition of $SnBr_4$ to (**I**) in CH_2Cl·OMe at 0° gives deoxophyllerythrin (**IV**), m.p. 268°, and a Cu complex (**III**), which, when shaken with HBr–AcOH, esterified with CH_2N_2, and extracted successively with 2% and 7% HCl affords *meso*iso*chlorin* e_4 6-*Me ester Me*$_2$ *ether*, m.p. 159°, $[\alpha]^{20}_{white}$ −668° in $COMe_2$ (*Cu* derivative, m.p. 170°, $[\alpha]^{20}_{white}$ −1260° in $COMe_2$), the spectrum of which is displaced towards the red in comparison with that of meso*iso*chlorin e_4 and is unchanged by AcOH or KOH–MeOH. The compound is stable towards cold conc. H_2SO_4 or $KMnO_4$–C_5H_5N but is converted by HI–AcOH at 70° into *iso*chloroporphyrin e_4. *Mesophyllochlorin* 6 *Me ether Me ester*, m.p. 168° (*Cu* derivative, m.p. 137°, $[\alpha]^{20}_{white}$ −475° in $COMe_2$), is obtained analogously. Similarly (**II**) is transformed into a Cu derivative, converted by HBr–AcOH into *γ-formylpyrroporphyrin* 6 *Me ether Me ester*, m.p. 279°, and γ-formylpyrroporphyrin-6-carbinol which reacts with BzCl. Similarly successive treatments of (**III**) with HBr in AcOH and CH_2N_2 lead to *meso*iso*chlorin* e_4 6-*carbinol Me*$_2$ *ester*, m.p. 151°, $[\alpha]^{20}_{white}$ −505° in $COMe_2$, which is not changed spectroscopically by BzCl, and is converted by HI in AcOH at 70° into meso*iso*chlorin e_4 and *iso*chloroporphyrin e_4. It gives (**IV**) when heated with $(CH_2$·$CO)_2O$ at 220° or $AcCO_2H$ at 155°. In molten resorcinol it passes into deoxophæoporphyrin a_5, identified spectroscopically. It is oxidised by CrO_3 in AcOH to rhodoporphyrin-γ-carboxylic acid. It is oxidised by CrO_3 in C_5H_5N at 45° or, preferably, by $KMnO_4$ in AcOH to 6-*formylmeso*iso*chlorin* e_4 *Me*$_2$ *ester*, m.p. 159°, $[\alpha]^{20}_{white}$ +1635° in $COMe_2$; NH_2OH or KOH in MeOH or PrOH induces the chlorin spectrum. 15% HCl causes rapid resinification. It is resistant to $KMnO_4$ or CrO_3 in C_5H_5N at 50° but is decomposed at higher temp. H. W.

Partial syntheses of devinyl- and 2-acetyl-2-devinylphyllochlorin. H. Fischer and F. Balat (*Annalen*, 1942, **553**, 166—186).—Optically inactive mesophyllochlorin Me ester is converted by $Fe(OAc)_2$ and NaCl in AcOH into the *salt*, $C_{33}H_{38}O_2N_4ClFe$, m.p. 237°, whereas the corresponding active salt has m.p. 246°; the *salt*, $C_{33}H_{38}O_2N_4Cu$, m.p. 150°, is obtained in the usual manner. The prep. of the active mesophyllochlorin Me ester (**I**) from chlorin e_6 is greatly improved by the substitution of boiling $C_{10}H_8$ for quinoline; vinylphylloporphyrin is obtained simultaneously in minor amount. The Fe^{II} complex salt of (**I**) is transformed by molten resorcinol at 175°, followed by successive treatments with $Fe(OAc)_2$ in AcOH and conc. HCl and then by extraction with 3% and then 8—10% HCl, esterification, and chromatography over Al_2O_3, into 2-*devinylphyllochlorin Me ester*, m.p. 156°, $[\alpha]^{20}_{690-720}$ −775° in $COMe_2$ (*salt*, $C_{31}H_{34}O_2N_4ClFe$, m.p. 209°, $[\alpha]^{20}_{690-720}$ −1000° in $COMe_2$). 2-Vinylphylloporphyrin Me ester is converted by $Fe(OAc)_2$ in AcOH containing NaCl into the *complex*, $C_{33}H_{34}O_2N_4ClFe$, m.p. 288°, which passes in resorcinol at 200° into a substance which after removal of Fe and esterification yields 2-*de-ethylphylloporphyrin Me ester*, m.p. 214° (*Fe* salt). The latter salt is treated successively with Na and boiling C_5H_{11}·OH under H_2, 15% HCl, $FeCl_3$ at 40°, and CH_2N_2, thus giving 2-*devinylphyllochlorin Me* ester (**III**), m.p. 147°, spectroscopically identical with the optically active material. (**III**) is converted by HBr–AcOH into 2-α-bromomesophyllochlorin, hydrolysed by 15% HCl and then esterified to 2-α-*hydroxymesophyllochlorin Me ester* (**IV**), m.p. 131°, $[\alpha]^{20}_{690-720}$ −657° in $COMe_2$. Analogously (**III**) is converted by HBr followed by boiling MeOH into 2-α-*methoxymesophyllochlorin Me ester*, amorphous, m.p. 130—140°, spectroscopically almost identical with (**IV**). Oxidation of (**IV**) by finely-powdered $KMnO_4$ in C_5H_5N leads to 2-*acetyl*-2-*devinylphyllochlorin Me ester* (**V**), m.p. 206° [*Zn* salt, m.p. 151°, hydrogenated (PtO_2 in MeOH) and then transformed by conc. HCl into (**IV**)]. BzCl and C_5H_5N convert (**IV**) into the *benzoate*. At 135°/0·1 mm., (**IV**) passes into phyllochlorin, m.p. 190°, $[\alpha]^{20}_{690-720}$ −832° in $COMe_2$, which gives a positive reaction with CHN_2·CO_2Et. In boiling C_5H_5N containing NH_2OH,HCl and anhyd. Na_2CO_3 (**V**) yields an *oxime*. The hæmin of (**III**) with $SnBr_4$ in Ac_2O with subsequent removal of Fe affords 2 : 6-*diacetyl*-2-*devinylphyllochlorin Me ester*, m.p. 199°, $[\alpha]^{20}_{690-720}$ −752° in $COMe_2$ (*dioxime*). (**III**) is converted by Br in $CHCl_3$–AcOH followed by CH_2N_2 into the *compound*, $C_{31}H_{33}O_2N_4Br_3$, m.p. 182°, the spectrum of which is greatly displaced towards the red in comparison with that of (**III**), and in which one Br appears to be labile. H. W.

Double invert soaps : symmetrical dimorpholinium salts. J. B. Niederl and E. J. Kenney (*J. Amer. Chem. Soc.*, 1944, **66**, 840—841).—By AlkBr in boiling 95% EtOH are prepared *methylenebis*-1-*morpholinium di*-n-*butyl*, m.p. 144° (decomp.), -n-*heptyl*, m.p. 141° (decomp.), -n-*octyl*, m.p. 143° (decomp.), -n-*tetradecyl*, m.p. 165° (decomp.), and -n-*hexadecyl dibromide*, m.p. 180° (decomp.), and *benzylidenebis*-1-*morpholinium di*-n-*butyl*, m.p. 174°, -n-*heptyl*, m.p. 153°, -n-*octyl*, m.p. 156°, -n-*tetradecyl*, m.p. 175°, and -n-*hexadecyl dibromide*, m.p. 178°. R. S. C.

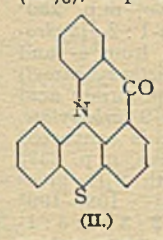
Two acid redox indicators of the oxazine series. Semiquinone theory. H. Eggers and H. Dieckmann (*Biochem. Z.*, 1942, **310**, 233—254).—Na_2 3-*dimethylaminophenonaphthoxazine*-9 : 12-*disulphonate*, prepared by condensation of *R*-acid with *p*-NO·C_6H_4·NMe_2, or with *p*-NH_2·C_6H_4·NMe_2 followed by oxidation, and K_2 3-*dimethylaminophenonaphthoxazine*-7 : 9-*disulphonate* prepared by condensation of *G*-acid with *p*-NO·C_6H_4·NMe_2, are H_2O-sol. indicators, stable over a wide range of pH, and suitable for oxidation–reduction determinations. In aq. solution, a small amount of the dyes is present in the form of semiquinone radicals. The normal potentials for the dyes from *R*-acid and *G*-acid are +0·105 and +0·115 v., respectively. Light absorption by aq. solutions of the dyes does not obey Beer's law. Max. absorption with the *R*-acid and *G*-acid dyes are at 550 and 540 mμ., respectively. The dye derived from *R*-acid catalyses the oxidation of hæmoglobin to methæmoglobin by O_2.
J. N. A.

2-Amino-4-ω-carboxyalkylthiazoles. Their reaction with acetylsulphanilyl chloride. W. M. Ziegler (*J. Amer. Chem. Soc.*, 1944, **66**, 744—745).—Substitution by CO_2H·$[CH_2]_n$ hinders interaction of 2-aminothiazole with *p*-NHAc·C_6H_4·SO_2Cl (I), the effect being a max. at n = ~4 (cf. A., 1942, II, 153). CO_2Et·$[CH_2]_n$·CHAc·CO_2Et (n = 1, 2, 3, or 10) with Br–CS_2 at 0° (later room temp.) and then $CS(NH_2)_2$–H_2O at room temp. gives 2-*amino*-4-*αβ-dicarbethoxyethyl*-, m.p. 118—119°, -*αγ-dicarbethoxy*-n-*propyl*-, m.p. 87—88°, -*αδ-dicarbethoxy*-n-*butyl*-, m.p. 83—84°, and -*αλ-dicarbethoxy*-n-*undecyl-thiazole*, m.p. 79—80°, converted by boiling conc. aq. HCl–EtOH into *γ*-2-*amino*-4-*thiazylpropionic*, m.p. 213—214° (*hydrochloride*, m.p. 243—245°), *δ*-2-*amino*-4-*thiazyl*-n-*butyric*, m.p. (+H_2O) 99—101° or (anhyd.) 125—127° (*hydrochloride*, m.p. 207—209°), *ε*-2-*amino*-4-*thiazyl*-n-*valeric*, m.p. 202—203·5° (*hydrochloride*, m.p. 235—237°), and *μ*-2-*amino*-4-*thiazyl*-n-*dodecoic acid*, m.p. 105—107° (*hydrochloride*, m.p. 178—179·5°), respectively. With (I) in C_5H_5N at 100° and then boiling 2N-HCl, these give *γ*-2-*sulphanilamido*-4-*thiazylpropionic* (33%), m.p. 143—145° [*hydrochloride*, m.p. 277—279° (partial decomp.)], and *δ*-2-sulphanilamido-4-thiazyl-*n*-butyric acid (11%) [*hydrochloride*, m.p. 204—206° (partial decomp.)]; *μ*-2-N⁴′-*acetylsulphanilamido*-4-*thiazyl*-n-*dodecoic acid* (40% yield), m.p. 98—100°, resists 2N-HCl and is destroyed by hot 2N-NaOH. The final products are ineffective against streptococci and pneumococci. M.p. are corr. R. S. C.

Preparation of *o*-aminobenzyl- and *β*-aminoethyl-thiazolium salts. H. T. Clarke (*J. Amer. Chem. Soc.*, 1944, **66**, 652).—*o*-NO_2·C_6H_4·CH_2Cl and 4-methylthiazole (I) in a little C_6H_6 at 95—100° give 3-*o*-*nitro*- (75%), decomp. 186·5—187°, reduced by Sn–SnCl₂–2N-HCl to 3-*o*-amino-benzyl-4-methylthiazolium chloride (*hydrochloride*, decomp. 204—212°). *o*-$C_6H_4(CO)_2N$·$[CH_2]_2$·Br and (I) at 95—100° give 4-*methyl*-3-*β-phthalimidoethyl*-, m.p. 238° (slight decomp.), and thence (boiling 48% HBr) 4-methyl-3-*β*-aminoethyl-thiazolium bromide [*hydrobromide*, m.p. 222·5—223·5° (decomp.)]. R. S. C.

Sulphonamides in the benziminazole, benzthiazole, and benztriazole series. C. F. H. Allen, A. Bell, and C. V. Wilson (*J. Amer. Chem. Soc.*, 1944, **66**, 835—837).—Methods of preparing SO_2R derivatives of these heterocyclic systems are developed.
o-NO_2·C_6H_4·NH·CO·CO_2Et and $ClSO_3H$ at 100° give 3 : 4 : 1-NO_2·$C_6H_3(NH_2)$·SO_2Cl, m.p. 152—153° [obtained in only 3—4% yield from *o*-NO_2·C_6H_4·NH_2 by $ClSO_3H$; derived amide (I), m.p. 206—207°], which with NH_2R and KOAc or NaOAc in AcOH gives 3-*nitro*-4-*aminobenzenesulphon*-p-*acetamidoanilide*, m.p. 265—266°, and -o-*hydroxyanilide* (II), m.p. 205—206°. 3 : 4 : 1-NO_2·C_6H_3Cl·SO_2Cl (III) gives similarly 4-*chloro*-3-*nitrobenzenesulphon*-p-*chloro*- (IV), m.p. 120—121° -p-*acetamido*-, m.p. 188—190°, -o-*hydroxy*-, m.p. 143—145°, and -2′-*hydroxy*-4′-*methyl*-, m.p. 155—156°, -*anilide*. H_2–Raney Ni or $Na_2S_2O_4$ reduces (I) to 3 : 4-*diaminobenzenesulphonamide*, m.p. 174—175°, which with HNO_2 gives *benztriazole*-5-*sulphonamide*, m.p. 236—237°, or with HCO_2H or AcOH gives *benziminazole*-, m.p. 213—214°, and 2-*methylbenziminazole*-5-*sulphonamide*, m.p. 221°, respectively. With OH·$[CH_2]_2$·NH_2 (V) in boiling C_5H_5, (III) gives 4-*chloro*-3-*nitro*-, m.p. 125°, but with an excess of (V) gives 3-*nitro*-4-*β-hydroxyethylamino-benzenesulphon-β-hydroxyethylamide*, m.p. 158°. 3 : 4 : 1-NO_2·C_6H_3Cl·SO_2·NHR with 1 : 1 85% $N_2H_4.H_2O$–EtOH at the b.p. gives 1-*hydroxybenztriazole*-5-*sulphon*-*amide*, m.p. 222° (decomp.), -o-*hydroxyanilide*, m.p. 228° (decomp.), and -*β-hydroxyethylamide*, m.p. 168° (decomp.). H_2–Raney Ni in EtOH at 90°/40 lb. reduces (II) to the diamine, which with CS_2 and 40% NaOH at the b.p. yields 2-*thiolbenziminazole*-5-*sulphon*-o-*hydroxyanilide*, m.p. 265° (decomp.). 2-*Thiolbenziminazole*-5-*sulphon*-p-*acetamidoanilide* (similarly prepared) in conc. HCl–EtOH at the b.p. gives the p-*aminoanilide*, m.p. 240—242° (decomp.). Hot aq. Na_2S–S converts (IV) into 2-*thiolbenzthiazole*-5-*sulphon*-p-*chloroanilide*, m.p. 208—210° (decomp.). 2-*Thiolbenzthiazole*-5-*sulphon*-p-*acetamido*-, m.p. 284—285° (decomp.), -o-*hydroxy*-, m.p. 246—248° (decomp.), and -2′-*hydroxy*-4′-*methyl*-*anilide*, m.p. 218—220° (decomp.), are similarly prepared. R. S. C.

Metalation of phenthiazine. H. Gilman, D. A. Shirley, and P. R. Van Ess (*J. Amer. Chem. Soc.*, 1944, **66**, 625—627).—Adding LiPh–Et_2O–N_2 to phenthiazine (I), keeping for 35 hr., then pouring the mixture onto Et_2O–solid CO_2, and finally hydrolysing with H_2O gives *phenthiazine*-1-*carboxylic acid* (52%), m.p. 264—264·5°, the Me ester, m.p. 113—113·5°, of which with PhI, K_2CO_3, and Cu-bronze at the b.p. yields *Me* 10-*phenylphenthiazine*-1-*carboxylate* (60%), m.p. 123·5—124·5°. Structures are proved by cyclisation of the derived acid by PCl_5–xylene at room temp. and then $SnCl_4$–xylene at 0° to 9-*quino*[3, 2, 1-kl]-*phenthiazone* (II), (85%), m.p. 218—219°. *o*-C_6H_4I·CO_2Me, (I), K_2CO_3, and Cu-bronze in xylene–$PhNO_2$ give 10-o-*carbomethoxyphenylphenthiazine* (42%), m.p. 143—144°; ring-closure of the derived (15% aq. KOH) *acid*, m.p. 214—215°, as above yields 60% of (II), proving the structure of the latter. Conversion of 2-*carbethoxydiphenylamine*, b.p. 184—187°/6 mm., by S etc. into phenthiazine and coupling of (*o*-NH_2·C_6H_4·S)₂ with 3 : 2 : 1-NO_2·C_6H_3Br·CO_2H–NaOAc–EtOAc at the b.p. or with *o*-C_6H_4Cl·CO_2K–NaOAc–Cu-bronze–C_5H_{11}·OH at the b.p. could not be achieved. R. S. C.



(II.)

Hemicyanine dyes.—See B., 1944, II, 244.

VII.—ALKALOIDS.

Total synthesis of quinine. R. B. Woodward and W. E. Doering (*J. Amer. Chem. Soc.*, 1944, **66**, 849).—The following synthesis is briefly recorded. 7-Hydroxy*iso*quinoline → 7-*hydroxy*-8-*piperidinomethyl*-, m.p. 81·5—82·5°, → 7-*hydroxy*-8-*methyl*-, m.p. 232—233·5°, → (H_2–PtO_2) 7-*hydroxy*-8-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-, m.p. 246—250°, → 7-*hydroxy*-1-*acetyl*-8-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-, m.p. 191—198° → (H_2–Raney Ni) mixed 7-*hydroxy*-1-*acetyl*-8-*methyldecahydro*- (cis-*compound*, m.p. 126—128°; *cis* refers to ring-junctions) → mixed → cis-7-*keto*-1-*acetyl*-8-*methyldecahydro*-iso*quinoline*, +H_2O, m.p. 80·5—82·5° → (OEt·NO–NaOEt) 10-*oximino*-1-*acetylhomomeroquinene Et* ester, dimorphic, m.p. 96—98° (labile) and 108·5—109·5°, → the 10-NH_2-compound (*H₂*-derivative, +$2H_2O$, m.p. 186·5—188°) → (MeI–K_2CO_3) quaternary *iodide* → (alkali) dl-*homomeroquinene*, m.p. 219—220° (decomp.) [isolated by way of the *carbamide* derivative, m.p. 165·2—165·8° (decomp.)] → *N*-benzoylhomomeroquinene Et ester. By condensation with Et quininate etc. by Rabe's and Prelog's methods this yields *dl*-quinotoxine, whence *d*-quinotoxine, an oil, $[\alpha]_D$ +43°, is obtained by means of its dibenzoyl-*D*-tartrate, m.p. 185·5—186°. With earlier work this constitutes a total synthesis of quinine. R. S. C.

Colchicine and related compounds. III. J. W. Cook, W. Graham, and (in part) A. Cohen, R. W. Lapsley, and C. A. Lawrence. **IV. Synthesis of 2 : 3 : 4 : 5-, 2 : 3 : 4 : 6-, and 2 : 3 : 4 : 7-tetramethoxy-9-methylphenanthrenes.** G. L. Buchanan, J. W. Cook, and J. D. London (*J.C.S.*, 1944, 322—325, 325—329).—III. 3 : 4 : 5-*Trimethoxy-benzanilide*, m.p. 136—137°, prepared from the corresponding benzoyl chloride and NH_2Ph, with PCl_5 gives the chloro-imine, reduced ($SnCl_2$–HCl) to the -benzaldehyde, the *diacetate*, m.p. 112—113°, of which yields no cryst. nitration product. *α*-Cyano-*α*-*p*-anisyl-*β*-(3 : 4 : 5-trimethoxyphenyl)ethylene is brominated to the 2-*Br*-compound (I), m.p. 141—142·5°, hydrolysed (6N-NaOH) to a mixture of *α*-p-*anisyl*-*β*-(2-*bromo*-3 : 4 : 5-*trimethoxyphenyl*)*acrylamide*, m.p. 179—181°, and a gum oxidised ($KMnO_4$) to 3 : 4 : 5 : 2 : 1-$(OMe)_3C_6HBr$·CO_2H; (I) could not be cyclised. 2 : 3 : 4 : 5 : 1-NO_2·$C_6H(OMe)_3$·CHO and *p*-OMe·C_6H_4·CH_2·CN afford *α-cyano*-*α*-p-*anisyl*-*β*-(2-*nitrotrimethoxyphenyl*)*ethylene*, m.p. 164·5—165·5°. 3 : 4 : 5 : 1-$(OMe)_3C_6H_2$·CHO and *p*-OH·C_6H_4·CH_2·CN give *α-cyano*-*α*-p-*hydroxyphenyl*-*β*-(3 : 4 : 5-*trimethoxyphenyl*)*ethylene*, m.p. 169·5—170·5°, which is reduced (Na–EtOH) to *α*-p-*hydroxyphenyl*-*β*-(3 : 4 : 5-*trimethoxyphenyl*)*acrylamide*, m.p. 211°. 3 : 4 : 5 : 1-$(OMe)_3C_6H_2$·CH_2·OH (3 : 5-*dinitrobenzoate*, m.p. 147—148°), obtained by reduction of the aldehyde, with $SOCl_2$ and $NPhMe_2$ gives the *chloride* (II), m.p. 60—61°. 3 : 4 : 5 : 1-$(OMe)_3C_6H_2$·CH_2·OH may also be prepared by methylation (MeI–NaOEt) of the syringic alcohol, m.p. 131—132°, obtained from 1 : 3-dimethylpyrogallol and aq. CH_2O–NaOH; if the methylation is carried out with C_6H_4Me·SO_3Me, the product is 1 : 2 : 3 : 5 : 6 : 7-*hexamethoxy*-9 : 10-*dihydroanthracene*, m.p. 201°. 4-Methoxy*cyclo*hexanone is brominated to the 2-Br-compound (III), the identity of which is shown by its conversion by $CS(NH_2)_2$ into 2-*amino*-6-*methoxy*-4 : 5 : 6 : 7-*tetrahydrobenzthiazole*, m.p. 141·5—144°. $CH_2(CO_2Et)_2$ and Na with (II) give *Et* 3 : 4 : 5-*trimethoxybenzylmalonate*, m.p. 67—71° (hydrolysed and decarboxylated to *β*-3 : 4 : 5-*trimethoxyphenylpropionic acid*, m.p. 100—102°), the Na compound of which with (III) forms, after hydrolysis, not the required product but a mixture containing 3 : 4 : 5-*trimethoxybenzylmalonic acid*, m.p. 115—116°. 2 : 4 : 1-$(NO_2)_2C_6H_3$·CH_2·CO_2Me with N_2H_4 affords

2 : 4-*dinitrophenylacethydrazide*, m.p. 135·5—137°. A series of experiments with 3 : 4 : 5 : 1-$(OMe)_3C_6H_2$·CH_2·CO·NH_2 has failed to give the required methoxylated phenanthrenes. P_2O_5 with *N*-acetylcolchinol Me ether gives the same product (**IV**) as that obtained by Hofmann degradation of colchinol Me ether (cf. Windaus, A., 1924, i, 1089). Colchicine and CN·CH_2·CO·NH_2 yield a *product*, decomp. 205°, which is probably a quinoline or *iso*quinoline derivative.

IV. 3 : 4 : 5 : 1-$(OMe)_3C_6H_2$·COCl with anhyd. HCN in quinoline gives 1-(3′ : 4′ : 5′-*trimethoxybenzoyl*)-1 : 2-*dihydroquinaldinonitrile*, m.p. 176—177°, hydrolysed (H_2SO_4) to 3 : 4 : 5 : 1-$(OMe)_3C_6H_2$·CHO, also obtained through 3 : 4 : 5-*trimethoxybenzhydrazide* (+MeOH), m.p. 128—129°, and the *benzenesulphonyl* derivative, m.p. 250° (decomp.). 1-(*o*-, m.p. 173°, and 1-(*m*-*nitrobenzoyl*)-1 : 2-*dihydroquinaldinonitrile*, m.p. 171°, are similarly prepared from *o*- and *m*-NO_2·C_6H_4·CHO, and the 1-(2′-*nitro*-3′ : 4′ : 5′-*trimethoxybenzoyl*) compound, m.p. 168°, is also prepared from the appropriate acid chloride. *Me* 2 : 3 : 4 : 6-*tetramethoxyphenanthrene*-9-*carboxylate*, m.p. 96—97°, prepared from the acid with CH_2N_2, is converted through the hydrazide and *benzenesulphonyl* derivative, m.p. 237° (decomp.), into the -9-*aldehyde*, m.p. 119°, which with N_2H_4 gives 2 : 3 : 4 : 6-*tetramethoxy*-9-*methylphenanthrene*, m.p. 108—109° (*picrate*, m.p. 115°). *m*-OMe·C_6H_4·CH_2·CO_2Na and 2 : 3 : 4 : 5 : 1-NO_2·$C_6H(OMe)_3$·CHO with Ac_2O, followed by acidification, yield a mixture of cis-, m.p. 139—140° (main product), and trans-2-*nitro*-3 : 4 : 5-*trimethoxy*-α-m-*methoxyphenylcinnamic acids*, m.p. 181°, reduced (aq. NH_3–$FeSO_4$) respectively to the 2-NH_2-*acid*, m.p. 162°, and 6 : 7 : 8-*trimethoxy*-3-(*m*-*methoxyphenyl*)*carbostyril*, m.p. 185—186°. The diazotised NH_2-acid is decomposed in Na_2CO_3 solution to a mixture of 2 : 3 : 4 : 7-, m.p. 236°, and 2 : 3 : 4 : 5-*tetramethoxyphenanthrene*-9-*carboxylic acids*, m.p. 162—163° and subsequently 185°. A series of experiments leads to 2 : 3 : 4 : 7-*tetramethoxy*-9-*methylphenanthrene*, m.p. 116—117° (*picrate*, m.p. 150°), through the *Me* ester, m.p. 103°, *hydrazide*, m.p. 199°, *benzenesulphonhydrazide*, m.p. 250°, and the *aldehyde*, m.p. 134—135°. 2 : 3 : 4 : 5-*Tetramethoxy*-9-*methylphenanthrene*, m.p. 102° (*picrate*, m.p. 135°), is similarly obtained through the *hydrazide*, m.p. 182°, *benzenesulphonhydrazide*, m.p. 232°, and the *aldehyde*, m.p. 92°. None of the three -9-methylphenanthrenes is identical with (**IV**), to which the structure 2 : 3 : 4 : 6(or 7)-tetramethoxy-9-methylphenanthrene had been assigned. F. R. S.

Ultra-violet absorption spectra od solutions of yohimbine, corynanthine, corynantheine, and some of their derivatives.—See A., 1944, I, 191.

VIII.—ORGANO-METALLIC COMPOUNDS.

Action of cæsium on ethylene. L. Hackspill and R. Rohmer (*Compt. rend.*, 1943, **217**, 152—153).—Cs and C_2H_4 slowly form a solid *substance*, $C_2H_4Cs_2$, hydrolysed quantitatively to CsOH and C_2H_6. F. R. S.

Long-chained organo-metallic compounds. R. N. Meals (*J. Org. Chem.*, 1944, **9**, 211—218; cf. A., 1944, II, 66).—A series of long-chained organo-metallic compounds of Li, Na, K, Ca, Hg, As, Sn, and Pb has been prepared. The NaR, KR, and CaRI types examined are insol. in hydrocarbons including the kerosene fractions. Incidental to the prep. of these MR compounds there are formed R(−H), R·H, and R·R hydrocarbons as a consequence of disproportionation and coupling reactions. The prep. of $NaC_{12}H_{25}$-*n* in poor yield in Et_2O is of interest because of the ready cleavage of Et_2O by the simpler NaAlk compounds. Compounds LiR can be prepared in several solvents, the most suitable appearing to be light petroleum, b.p. 60—70°. Substances RCl are most suitable for the prep. of LiR types. 1 : 2 : 3-$C_6H_3(OMe)_3$ is metallated by $LiC_{12}H_{25}$-*n* in an *ortho*-position to give 2 : 3 : 4 : 1-$(OMe)_3C_6H_2$·CO_2H on subsequent carbonation. The long-chained organo-mercury halides are not particularly suitable as derivatives for rigid differentiation of contiguous, even-membered types. Thus $HgC_{16}H_{33}Cl$, $HgC_{18}H_{37}Cl$, and an equinol. mixture of them have m.p. 114—115°, 115—116°, and 113° respectively. Compounds $SnAlk_3Cl$ and $PbAlk_3Cl$ show greater differences in m.p. between homologues than do the Hg alkyl chlorides, but they are only of limited applicability as derivatives for differentiation of contiguous, even-membered homologues because of the small m.p. depressions of mixtures. $Sn(C_{16}H_{33})_4$ and $Pb(C_{16}H_{33})_4$ have m.p. 41·5—42·5° and 42°, respectively, and a mixture of equal parts of them melts at 42°. The following are reported in addition to those listed previously (*loc. cit.*): *Hg dodecyl acetate*, m.p. 64—65°; (*Hg docedyl*)$_2$ *sulphate*, m.p. 160—161°; (*Hg dodecyl*)$_3$ *phosphate*, m.p. 84—86°; *Hg octadecyl cyanide*, m.p. 98·5—99°; *Pb tri*-n-*dodecyl nitrate*, m.p. 44—45°, and *acetate*, m.p. 59°. The m.p. for the compounds $Hg(C_{12}H_{25})_2$, $Hg(C_{14}H_{29})_2$, $Hg(C_{16}H_{33})_2$, and $Hg(C_{18}H_{37})_2$ show a regular variation with chain length expressible by the relationship $M = 32 \pm 13\sqrt{(n-11)}$, where M is the m.p. and n the no. of C of the alkyl group. H. W.

Phenolic mercurials. J. B. Niederl and A. J. Shukis (*J. Amer. Chem. Soc.*, 1944, **66**, 844).—The appropriate phenol with the requisite amount of $Hg(OAc)_2$ in 1 : 10 : 10 AcOH–EtOH–H_2O at the b.p. give 2-*acetoxymercuri*-, m.p. 158° (corresponding *HgCl* compound, m.p. 161°), 2 : 6-*diacetoxymercuri*-, m.p. 181° [corresponding $(HgCl)_2$ compound, m.p. 238° (decomp.)], 3-*hydroxy*-2 : 6-*diacetoxymercuri*-, m.p. 183° (decomp.), 2-*acetoxymercuri*-6-*methyl*-, m.p. 149°, -4-*aαγγ-tetramethyl*-n-*butylphenol*, 1 : 1-*di*-4′-*hydroxy*-2′-*acetoxymercuri*-6′-*methyl*-, m.p. 200° (decomp.) [corresponding $(HgCl)_2$ compound, m.p. 225° (decomp.)], and 1 : 1-*di*-4′-*hydroxy*-2′ : 6′-*diacetoxymercuri*-, m.p. 210° (decomp.) [corresponding $(HgCl)_4$ compound, m.p. 222° (decomp.)], -*phenylcyclohexane*, and *ββεε-tetra*-4′-*hydroxy*-2′ : 6′-*diacetoxymercuriphenyl*-n-*hexane*, m.p. 308° (decomp.) [corresponding $(HgCl)_8$ compound, m.p. 247° (decomp.)]. R. S. C.

Preparation of aromatic mercury salts of organic acids.—See B., 1944, III, 169.

Organomagnesium compounds. II. Reaction of Grignard reagents with carbonyl compounds. A. N. Nesmejanov and V. A. Sazonova (*Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1941, 499—517).—Using filtered and titrated Grignard reagents in an atm. of N_2, it is shown that the same compound CRR′R″·O·MgX,Et_2O is produced in all three reactions: (i) COR′R″ + MgRX,Et_2O, (ii) CORR′ + MgR″X,Et_2O, and (iii) CRR′R″·OH + MgEtX,Et_2O. The reaction product is thus a true alcoholate, as originally formulated by Grignard (A., 1902, i, 142) and contrary to the later views of Hess *et al.* (A., 1921, i, 777; 1924, i, 859), Meisenheimer *et al.* (A., 1921, i, 654; 1925, i, 527; 1926, 68), and Pfeiffer and Blank (A., 1939, II, 360), who postulate the formation of complexes which may or may not undergo internal rearrangement. The work of these authors is criticised in detail.

CHPhEt·OH (**I**) and MgEtBr in Et_2O afford CHPhEt·O·MgBr,Et_2O (**II**), biaxial prisms with negative optical sign and $r > v$[1], stable in dry air and converted by EtOAc into the acetate of (**I**) and by *p*-NO_2·C_6H_4·COCl into the *p*-nitrobenzoate of (**I**). The Et_2O in (**II**) can be removed by heating and partly replaced by PhCHO, the exchange being reversible. (**II**) with dil. H_2SO_4 affords C_2H_6. (**II**) is also formed from PhCHO and MgEtBr, the identity of the product being confirmed by the cryst. form, solubility in Et_2O, action of EtOAc and *p*-NO_2·C_6H_4·COCl, and formation of C_2H_6 from (**I**) by decomp. with aq. NH_4Cl; no C_2H_4 is produced by heating (**II**) in C_6H_6. EtCHO and MgPhBr in Et_2O also give (**II**), identified as before. CPhMeEt·OH and MgEtBr in Et_2O afford CPhMeEt·O·MgBr,Et_2O (**III**), biaxial prisms with negative optical sign and $v > r$. It is converted by EtOAc into an ester, decomp. on distillation, and does not react with *p*-NO_2·C_6H_4·COCl. The Et_2O can be removed on heating with partial decomp. (**III**) is also formed from MgEtBr and COPhMe in Et_2O, identified as above by optical properties and solubility in Et_2O. MgEtBr and $COPh_2$ in cold Et_2O afford CPh_2Et·O·MgBr,Et_2O (**IV**), giving CPh_2Et·OH with aq. NH_4Cl and no $COPh_2$. If the reaction mixture was boiled for 5 hr. some $CPh_2{:}CH_2$ was also isolated. MgBu$^\beta$Br and $COPh_2$ in Et_2O afford $CHPh_2$·O·MgBr,Et_2O (**V**), biaxial pyramids with positive optical sign and $r > v$, giving $CHPh_2$·OAc with EtOAc; (**V**) is also formed from $CHPh_2$·OH and MgEtBr in Et_2O. MgPhBr and fenchone (**VI**) in Et_2O afford a cryst. *compound*, which has not the expected formula $C_{10}H_{16}O$,MgPhBr,Et_2O (cf. Leroide, A., 1909, i, 596) and contains no MgPhBr, as it does not give Gilman's reaction or form C_6H_6 with H_2O, although it regenerates (**VI**). *p*-NH_2·C_6H_4·COPh and MgEtBr in Et_2O give C_2H_6 corresponding to 1 H of the NH_2 and therefore form the compound COPh·C_6H_4·NH·MgBr. G. A. R. K.

Trimethylsilane and silicon trimethyl chloride. A. G. Taylor and B. V. de G. Walden (*J. Amer. Chem. Soc.*, 1944, **66**, 842—843).—$SiHCl_3$ [prep. from ferrosilicon (95—97% Si)] and MgMeBr in Et_2O give $SiHMe_3$, b.p. 9—11°, which with Cl_2 at −20° yields $SiMe_2Cl$ (75%), f.p. ~−40°, b.p. 57—59·4°/747 mm. [v.p. given for 28·9° (308 mm.) to 56·1° (725 mm.)]. R. S. C.

IX.—PROTEINS.

Precipitation of proteins by synthetic detergents. F. W. Putnam and H. Neurath (*J. Amer. Chem. Soc.*, 1944, **66**, 692—697).—Pptn. of six proteins by *n*-$C_{12}H_{25}$·$NaSO_4$ (**I**) occurs at pH ≯ the isoelectric point; for human carboxyhæmoglobin (isoelectric point 7·1) this pH is 6·4. At > this pH no pptn. occurs and ppts. formed at lower pH are redissolved by adjusting the pH to > the isoelectric point. The following are established for horse serum-albumin. The lower is the pH, the faster is the rate of coagulation, but the wt. of ppt. is const. The wt. of ppt. ∝ concns. of protein and (**I**), and also increases with temp. The pH of protein solutions, previously adjusted to the isoelectric point, is gradually increased from 4·85 to ~6·4 by adding increasing amounts of (**I**). Treating the ppt. with $Ba^{\cdot\cdot}$ yields (*n*-$C_{12}H_{25}$·$SO_4)_2Ba$ and a solution of recovered protein, which is shown by electrophoresis, diffusion, and η to be homogeneous but partly denatured. Possible applications of the pptn. are mentioned. R. S. C.

Diplococcein, antibacterial protein from milk streptococci.—See A., 1944, III, 615.

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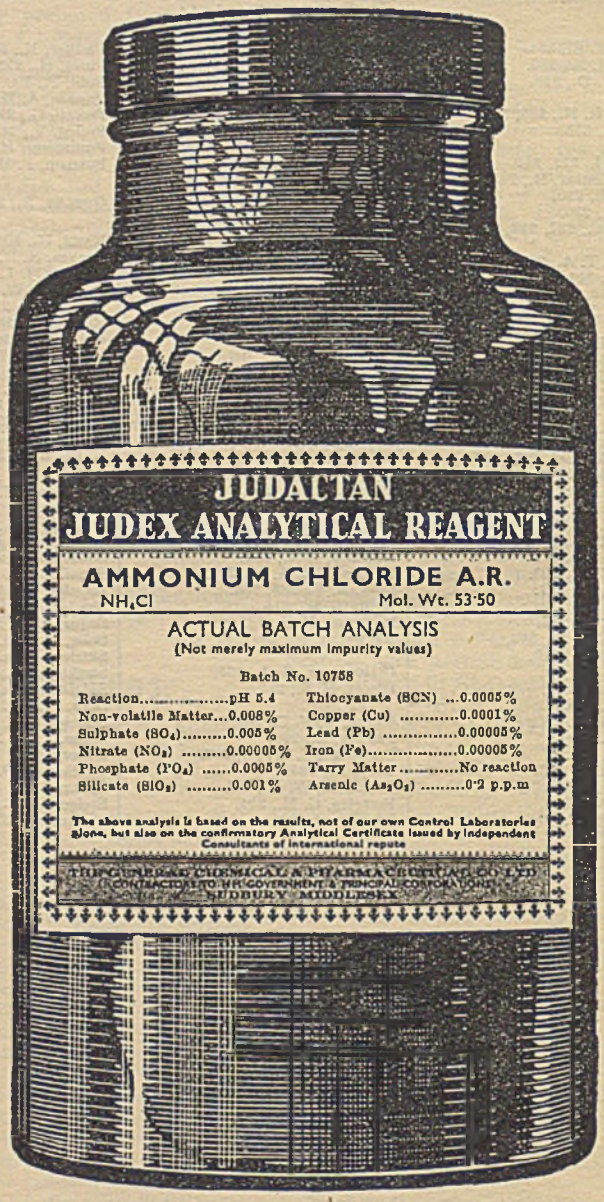

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