BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

NOVEMBER, 1940.

Oxidation of methane. III. T. Ogawa, A. Matsui, H. Nagai, and H. Senoo (J. Soc. Chem. Ind. Japan, 1940, **43**, 116—117B; cf. B., 1938, 353).—The reaction $2CH_4 + O_2 \rightarrow 2CO + 4H_2$ is effected by passing CH_4–air mixtures successively through Fe_2O_3–MgO and Ni–kaolin catalysts in a Ni–Cr tube, at 1220°. R. T.

Mechanism of polymerisation. IV. Experiments relating to the constitution of the solid dimeride and the liquid trimeride of βγ-dimethylbutadiene, and to the separation of the higher polymerides. E. H. Farmer and J. F. Martin (J.C.S., 1940, 1169—1176).—The solid dimeride, $C_{12}H_{20}$, formed by the acid-catalysed (AcOH and 1·8 wt.-% H_2SO_4) polymerisation of $(CH_2{:}CMe)_2$ (cf. Farmer *et al.*, A., 1938, II, 79) yields with $Pb(OAc)_4$ a mixture from which a *monoacetate*, b.p. 128—135°/12 mm., can be separated. This is hydrolysed to a *ketone*, $C_{12}H_{20}O$, m.p. 180° (*oxime*, m.p. 132°) (probably either 1 : 2 : 2 : 3-*tetramethyl*-1 : 3-endo*ethylene*cyclo*hexan*-5-*one* or 1 : 2 : 2 : 4-*tetramethyl*-1 : 4-endo*methylene*cyclo*heptan*-6-*one*, but the 1 : 2 : 4-*Me*$_3$ compound is not excluded), purified through the *semicarbazone*, m.p. 255°. The ketone is oxidised (HNO_3) to a *dibasic acid*, $C_{12}H_{20}O_4$, m.p. 161°, and reduced (NaOEt–EtOH) to a hydrocarbon, m.p. 146°, probably 1:2:2:3-*tetramethyl*-1 : 3-endo*ethylene*cyclo*hexane* or 1 : 2 : 3 : 4-*tetramethyl*-1 : 4-endo*methylene*cyclo*heptane*, although the 1 : 2 : 4-*Me*$_3$ compound is not excluded. Hydrogenation (PtO_2–H_2) of the dimeride gives a *dihydride*, m.p. 78°, which is 1 : 2 : 2 : 3 : 4-*pentamethyl*-1 : 3-endo*ethylene*cyclo*pentane* or 1 : 2 : 2 : 4 : 5-*pentamethyl*-1 : 4-endo*methylene*cyclo*hexane*, but the 1 : 2 : 4 : 5-*Me*$_4$ derivative is not excluded. The trimeric, tetrameric, and pentameric portions of the polymeride have been separated from each other by mol. distillation, leaving as a residue a highly viscous liquid of mainly hexameric complexity. Se-dehydrogenation of the trimeric portion gives an increased yield of the naphthalenic hydrocarbon (I) previously reported, and when the unattacked residue is submitted in the vapour phase to Pd–C–H_2, an isomeric hydrocarbon, $C_{17}H_{22}$ [$C_6H_3(NO_2)_3$ *derivative*, m.p. 181°], is obtained. Oxidation (AcOH–H_2CrO_4) of (I) affords a *quinone*, $C_{17}H_{20}O_2$, m.p. 118°, probably a *tetramethyl*iso*propylnaphthaquinone*. The trimeric fraction probably contains pentamethyl*iso*propenyloctahydronaphthalene. F. R. S.

Preparation of butadiene by catalytic hydrogenation of monovinylacetylene.—See B., 1940, 657.

Mechanism of Wurtz reaction.—See A., 1940, I, 415.

Mercury-photosensitised reactions of propane.—See A., 1940, I, 417.

Nitroparaffins.—See B., 1940, 657.

Leaf-alcohol. IV. *cis* and *trans* problem of leaf alcohol, the natural Δ$^\gamma$-hexenol. S. Takei, M. Ono, and K. Sinosaki (J. Agric. Chem. Soc. Japan, 1940, **16**, 772—780; cf. A., 1939, III, 536).—Hydrogenation (Pd–$BaSO_4$–H_2) of Δ$^\gamma$-hexinol (prepared from Δ$^\gamma$-hexenol by addition of Br and removal of HBr by KOH) in Et_2O at −18° yields *trans*-Δ$^\gamma$-hexenol, whilst in xylene at 100° the *cis*-isomeride (*allophanate*, m.p. 143°; 3 : 5-*dinitrobenzoate*, m.p. 28°; *anthraquinone*-2-*carboxylate*, m.p. 50°) is formed. Hydrogenation at 50° yields a mixture of the two isomerides. Contrary to Stoll and Rouvé (A., 1939, II, 2), leaf-alcohol is the *trans*-isomeride. J. N. A.

Preparation of higher unsaturated alcohols. V. Hydrogenation of methyl erucate. S. Komori (J. Soc. Chem. Ind. Japan, 1940, **43**, 122—125B; cf. A., 1940, II, 202).—Hydrogenation of Me erucate (ZnO–Cr_2O_3 catalyst) affords chiefly docosenol, with a small quantity of behenyl alcohol and docosene. Erucyl and brassidyl alcohols and Δ$^\mu$- and Δ$^\xi$-docosenol are also formed in small amounts, probably by secondary isomerisation of docosenol. R. T.

Synthesis of di*iso*propyl ether. X. Alcoholysis of di*iso*propyl sulphate with *iso*propyl alcohol. M. Katuno (J. Soc. Chem. Ind. Japan, 1940, **43**, 106—109B; cf. B., 1940, 591).—Pr^β_2O is prepared by the reaction $Pr^\beta_2SO_4 + Pr^\beta OH \rightarrow Pr^\beta_2O + Pr^\beta HSO_4$ (I). After Pr^β_2O has distilled off, H_2O is added to decompose (I), and the $Pr^\beta OH$ formed is recovered. R. T.

Mono-halogen derivatives of diethyl sulphone. L. Ramberg and B. Bäcklund (Arkiv Kemi, Min., Geol., 1940, **13**, A, No. 27, 50 pp.).—*α-Bromo-* (I), m.p. 2·5—3°, b.p. 124°/8 mm. (from $SO_2Et{\cdot}CHMe{\cdot}CO_2H$), *β-bromo-* (II), m.p. 19—20°, b.p. 153°/8 mm. (from PBr_5 and $OH{\cdot}[CH_2]_2{\cdot}SO_2Et$), and *α-chloro-diethyl sulphone* (III), m.p. 19·8°, b.p. ~110°/8 mm. (from CHMeCl·SEt), have been prepared. (I) and (II) are salted-in strongly by electrolytes (except KCl and NaCl), (II) having solubilities in N-HI and N-$HClO_4$ 97% and 117% > that in H_2O respectively. (I) and (II) are not attacked by KI or N_2H_4, and (I) [but not (II)] is stable to acid $AgNO_3$ at 100° and NH_3–Ag solutions at room temp. (I) [and similarly (III)] with excess of 2N-KOH at 90—100° (very slowly at 25°) gives: $CHMeBr{\cdot}SO_2Et + 3OH' \rightarrow$ *cis*-Δ$^\beta$-butene (IV) + Br' + SO_3'' + $2H_2O$. 85% of (IV), 75—81% of SO_3'', and 100% of Br' (of the theoretical) are formed. The mechanism of the reaction is discussed. (II) with 0·25N-KOH at room temp. gives rapidly *Et*

vinyl sulphone, m.p. −13° to −12°, b.p. 106·8°/9 mm. (65% yield), which does not polymerise on storage at room temp., and gives with Br *Et αβ-dibromoethyl sulphone*, m.p. 64·8°. With $EtSO_3Na$ (I) gives slowly $4EtSO_3Na,NaBr,H_2O$, decomp. ~200° (also prepared from $EtSO_3Na$ and NaBr), whilst (II) gives $(CH_2{\cdot}SO_2Et)_2$. M. H. M. A.

Separation and identification of fatty acids. Y. Inoue and H. Yukawa (J. Agric. Chem. Soc. Japan, 1940, **16**, 504—512).—Fatty acids can be identified as hydroxamic acids which are prepared from the esters or glycerides by treatment at room temp. with NH_2OH in presence of NaOEt. The following *-hydroxamic acids* are described (m.p. in parentheses): *acet-* (88°), *propion-* (92·5—93°), *butyr-* (syrup), *hexo-* (63·5—64°), *octo-* (78·5—79°), *deco-* (88—88·5°), *dodeco-* (94°), *myrist-* (98—98·5°), *palmit-* (102·5°), *stear-* (106·5—107°), *arachid-* (109·5—110°), *behen-* (112·5°). The solubilities of the acids in EtOH, $COMe_2$, Et_2O, H_2O, and light petroleum are recorded. The corresponding *hydroxamic acids* from oleic, linoleic, and linolenic acids have m.p. 61°, 41—42°, and 37—38°, respectively. The hydroxamic acids are converted into the original fatty acids by boiling with dil. H_2SO_4–EtOH. J. N. A.

Direct esterification of higher fatty acids with glycerol. II. Synthesis of monolaurin. S. Kawai and H. Nobori (J. Soc. Chem. Ind. Japan, 1940, 110B; cf. A., 1940, II, 243).—Lauric acid (1 mol.) and glycerol (1·4 mols.) (30 min. at 240°) give monolaurin in 40% yield. R. T.

Action of sulphuric acid on petroselic acid. A. A. Tschernojarova (J. Gen. Chem. Russ., 1940, **10**, 146—149).—Petroselic acid treated consecutively with H_2SO_4 and H_2O yields *ζ-hydroxystearic acid*, m.p. 82° (*Et* ester, m.p. 45—46°). R. T.

Oxidation of ascorbic acid by oxygen with cupric ion as catalyst.—See A., 1940, I, 416.

Catalytic hydrogenation [of maleic and α-ketoglutaric acid] with deuterium.—See A., 1940, I, 416.

Indium oxalate and oxalatoindates.—See A., 1940, I, 418.

Production of formaldehyde by direct oxidation of methane. A. Matsui and M. Yasuda (J. Soc. Chem. Ind. Japan, 1940, **43**, 117—118B).—CH_4–air–gaseous catalyst (HCl, SO_2, Br, NO_2) mixtures are passed through tubes of various materials (Pyrex, SiO_2, porcelain, Cu) containing solid catalysts (NaCl, KF, H_3BO_3, U_3O_8, BeO). The highest yields of CH_2O are obtained with Pyrex tubes, with NO_2 and U_3O_8 or BeO catalysts, at 600°. R. T.

Distillation of formaldehyde solutions.—See B., 1940, 657.

Photochemical decomposition of acetone.—See A., 1940, I, 417.

Diginin. I. C. W. Shoppee and T. Reichstein (Helv. Chim. Acta, 1940, **23**, 975—991).—Diginin, m.p. (indef.) 155—183°, $[\alpha]_D^{14}$ −223°±4° in $CHCl_3$, gives a well-defined Legal test but does not appear to be a lactone. It is very readily hydrolysed by dil. mineral acids to *diginigenin* (I), $C_{21}H_{28(26)}O_4$, m.p. 115°, $[\alpha]_D^{15}$ −226°±3·5° in $COMe_2$, which does not contain OMe, and *diginose*, $C_7H_{14}O_4$, m.p. 90—92°, $[\alpha]_D^{22}$ +60°±1° (final val. in H_2O), which gives the Keller–Kiliani reaction and contains 1 OMe. It is distinguished from cymarose since when oxidised and treated with $NHPh{\cdot}NH_2$ it gives a non-cryst. phenylhydrazide whereas cymaronephenylhydrazide (micro-prep. described) has m.p. 153·5—154°. (I) probably contains CHO since it readily affords a *semicarbazone*, m.p. 290—292°, and an *oxime*, thin prisms, m.p. 219—220° (decomp.), or octahedra, m.p. 235—236° (decomp.), strongly reduces Ag_2O–$(CH_2{\cdot}NH_2)_2$ at room temp., and gives a strong positive reaction with 1 : 4-$C_{10}H_6(OH)_2$. It contains 1 OH since on mild acetylation it affords a *monoacetate* (II) which becomes cloudy at 181° and melts to a clear liquid at ~185—200°, $[\alpha]_D^{15}$ −210°±4° in $COMe_2$ [*monosemicarbazone*, m.p. 262—263° (decomp.)], which does not appear to contain further primary or *sec.* OH groups since it is relatively stable towards CrO_3. Energetic acetylation of (I) leads to a *diacetate* (III), m.p. 177—178° (*monosemicarbazone*, m.p. 177—178°), which appears to contain an inert CO group or, less probably, a *tert.* OH since it is unchanged when warmed with strong acids. (I) contains a C:C linking since it and (II) give a distinct yellow colour with $C(NO_2)_4$ but this is not conjugated with CO since there is no selective absorption in the region of 240 mμ. This is true also of (III). (I) is hydrogenated (PtO_2 in AcOH) to *tetrahydrodiginigenin* (IV), m.p. 229—231°, $[\alpha]_D^{16}$ +36·6°±1·5° in $CHCl_3$, which has no reducing properties, does not give a yellow colour with $C(NO_2)_4$, and does not react with $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$ so that ·CHO has been reduced. The presence of inert ·CO· is shown by the production under energetic conditions of an amorphous *oxime*, m.p. ~132°. (IV) is transformed by short treatment with boiling Ac_2O into the *monoacetate* (V), m.p. 173—174°, $[\alpha]_D^{14}$ +38·8°±1·5° in $COMe_2$, also obtained by hydrogenation of (II). Prolonged treatment of (IV) with Ac_2O–C_5H_5N at 100° affords non-cryst. *tetrahydrodiginigenin diacetate*. (III) is hydrogenated (PtO_2 in AcOH) to the non-cryst. *diacetate*, hydrolysed to (?) *hexahydrodiginigenin*, m.p. 207°, $[\alpha]_D^{18}$ −13·6°±2° in $CHCl_3$. Attempted partial reduction (Pd in EtOH) of (II) was unsuccessful whilst mild oxidation (CrO_3) of (V) yields an amorphous, neutral substance with aldehydic properties. Similar oxidation of (I) or (IV) leads to extensive degradation with production of acidic and neutral compounds from which only small amounts of homogeneous products can be isolated. Small amounts of CHI_3 are formed from (I) and OI′ in MeOH. (I) and (IV) are stable to HIO_4. It appears probable that (I) is a pregnane derivative. M.p. are corr. H. W.

***o*-Chlorophenylgentiobioside [hepta-acetate, m.p. 207—208·5° (corr.), $[\alpha]_D^{25}$ −49·4° in $CHCl_3$; heptapropionate, m.p. 178·5—179°, $[\alpha]_D^{26}$ −38·0° in $CHCl_3$].**—See A., 1940, III, 831.

Starch. II. Non-homogeneity of starch. K. H. Meyer, W. Brentano, and P. Bernfeld. **III. Fractionation and purification of natural maize.** K. H. Meyer, P. Bernfeld, and E. Wolff. **IV. Methylation and determination of terminal**

groups of amylose and amylopectin of maize. K. H. MEYER, M. WERTHEIM, and P. BERNFELD. **V. Amylopectin.** K. H. MEYER and P. BERNFELD. **VI. Acetates and nitrates of amylose and amylopectin.** K. H. MEYER, P. BERNFELD, and W. HOHENEMSER. **VII. Fine structure of the starch granule and the phenomena of swelling.** K. H. MEYER and P. BERNFELD (Helv. Chim. Acta, 1940, **23**, 845—853, 854—864, 865—875, 875—885, 885—890, 890—897; cf. A., 1929, 799).—II. Treatment of maize starch with H_2O at 70° or 80° or with 33% $CCl_3{\cdot}CH(OH)_2$ at 20° removes ~20% of carbohydrates as limpid solution without causing destruction of the granules, which merely swell. The solutions slowly deposit a flocculent ppt. of amylose (I) which presents cryst. interferences and resists the action of β-amylase (II). If brought into solution by any means (I) is completely saccharified by (II). Prolonged action of the solvent removes ~10% of other fractions but the solutions are turbid and deposit ppts. more slowly or only after addition of precipitants. (II) does not cause complete saccharification but yields small amounts of residual dextrins which give a red colour with I, thus indicating the presence of amylopectin (III). The proportion of (I) varies from sample to sample. Starch therefore contains ~20% of a carbohydrate sharply differentiated from that retained in the swollen granule. The subdivision into (I) and (III) is therefore justified but it is proposed to distinguish (I) as a carbohydrate with non-branched mols. entirely saccharified by (II), and (III) as a carbohydrate with branched mols. degraded by (II) solely to residual dextrins. It should be noted, however, that only 20—30% of the maltose formed from starch by malt extract is derived from (I) whereas 70—80% is derived from (III) which suffers partial degradation. The product extracted by hot H_2O and consisting essentially of (I) is not homogeneous, the first fractions having a lower η and mol. wt. than the less sol. fractions.

III. Four fractions have been separated from crude (I), all of which are free from P. When dried at 105°/vac. (I) is $C_6H_{10}O_5$ and does not show *X*-ray interferences. Over 54% H_2SO_4 (I) becomes $C_6H_{12}O_6$. Native (I) is sol. in H_2O at 70—80° but fractions obtained from it by crystallisation are very slightly sol. or insol. (I) pptd. from H_2O by EtOH is sol. in Et_2O. Insol. (I) can be converted into sol. (I) by dissolution in 33% $CCl_3{\cdot}CH(OH)_2$ and pptn. by $COMe_2$. Sol. (I) does not present cryst. interferences; it loses its solubility after some hr. or days. The solubility of (I) in H_2O depends on its mol. wt., degree of purity, and size of crystallites. (I) migrates towards the anode. Its dissociation const. in 5×10^{-12}. (I) gives limpid solutions in warm $HCO{\cdot}NH_2$ but fractionated (I) readily gels in the course of a few hr. It is sol. in 33% $CCl_3{\cdot}CH(OH)_2$, N_2H_4,H_2O, and $(CH_2{\cdot}NH_2)_2,H_2O$ and in saline solutions which cause starch to swell. It dissolves rapidly in 1% NaOH but a gel of the Na compound is rapidly formed. It gives a blue colour but does not dissolve in CuO–NH_3. It has $[\alpha]_D$ +195—197° in H_2O, +152° in $CCl_3{\cdot}CH(OH)_2$ (calc. for $C_6H_{12}O_6$). The various fractions are readily characterised by their η. The mol. wt. is 13,000—45,000.

IV. Starch or (III) becomes H_2O-sol. when pptd. from 33% $CCl_3{\cdot}CH(OH)_2$ and then give 3% solutions in 1% NaOH, in which they are readily methylated. (II) is sol. in dil. alkali and can be methylated directly. Methylation and hydrolysis gives 3·5%, 0·32%, and 3·7% of tetramethylglucose from starch, (I), and (III), respectively. (II) has one terminal group for ~300 residues whereas starch and (III) have one group for ~30 or 27 residues. As the mol. wt. of the sample of (I) was ~50,000 and mean degree of polymerisation 300, (I) has only one terminal group per mol., which is not branched. (III) has >50 ramifications of its chain. A single treatment of (I) affords *dimethylamylose*, which is sol. in H_2O, $CHCl_3$, and $COMe_2$, does not give a blue colour with I, and is appreciably less viscous than trimethylamylose (IV) in $CHCl_3$. (IV) differs widely from trimethylstarch and trimethylamylopectin (V), more particularly in its ability to form films and threads. The η of (IV) in $CHCl_3$ is $\gg$ that of a branched product of the same mol. wt. and increases less rapidly with concn. than that of (V). The presence of CHO at the other end of the mol. of (I) is established by means of Ag_2O; Fehling's solution is not sufficiently sensitive. This appears true of (III) also. Electrodialysis does not affect (IV) or (V).

V. Starch is dissolved at room temp. by $(CH_2{\cdot}NH_2)_2,H_2O$ and N_2H_4,H_2O, which may possibly cause hydrolysis, and also by 33% $CCl_3CH(OH)_2$, conc. $CCl_3{\cdot}CO_2Na$, $CCl_3{\cdot}CO_2H$, and $CS(NH_2)_2$ with which hydrolysis may be regarded as impossible. The linkings ruptured under these conditions can only be caused by secondary valencies. These facts combined with the observation that (III) separated from aq. solution has the same cryst. interferences as (I) suggest that the giant branched mols. are united one to the other at numerous points by little cryst. micelles representing associations of parts of the chains; inversely, the cryst. micelles are united by loose reticules constituted by parts of the chains not arranged in nets, by mol. threads. (III), pptd. by $COMe_2$ from $CCl_3{\cdot}CH(OH)_2$, is free from P and readily sol. in warm H_2O when fresh. This solubility is rapidly lost when it is dried. Aq. solutions soon become cloudy and deposit (III) quantitatively after several days. They give a pure blue colour with I. In an electric field (III), even when free from P, is transported to the anode, where it is deposited as a gel. After desiccation (III) is practically insol. in H_2O but the particles still swell somewhat in hot H_2O, thereby differing from (I). (III) can be separated into fractions of increasing mol. wt. and diminishing solubility. The simpler fractions are pptd. as flocks by $COMe_2$; the higher fractions form only viscous masses. Only the acetates of the former are sol. in $CHCl_3$ or CCl_4. (III) is converted by (II) into maltose and residual dextrin-I (VI) which gives a red colour with I. The terminal groups not affected by this enzyme are attacked by α- (but not by β-)glucosidase (VII) with formation of glucose. The branching linkings are thus of the α-1 : 6-type; the disaccharide which is the basis of the ramifications is α-gentiobiose, probably identical with Croft Hill's revertose and Fischer's *iso*maltose. By the prolonged action of (VII) (VI) is converted into residual dextrin-II, which is transformed by (II) into maltose and residual

dextrin-III, which is coloured brown-red by I, thus resembling glycogen. The observations are incompatible with the formulæ of Staudinger and Husemann or Hirst and Young and a new scheme is suggested.

VI. (I) is readily converted into its *triacetate* (VII), which is more freely sol. than cellulose triacetate and differs considerably from the acetates of starch and (III), giving very solid films which can be drawn into resistant threads. *Amylopectin triacetate* (VIII) from crude (III) is sol. in $C_2H_2Cl_4$, in which acetates from fractionated (III) are insol. The viscosity–concn. graphs of (VII) and (VIII) differ sharply from one another. This appears also true of the *nitrates* of (I) and (III).

VII. The sub-microscopic structure of the starch grain and the processes of swelling, crystallisation, and gel formation are discussed. H. W.

Nature of bonds in starch. C. E. H. Bawn, E. L. Hirst, and G. T. Young (Trans. Faraday Soc., 1940, **36**, 880—885).—Kinetic experiments on the disaggregation of methylated starch support other evidence in indicating that the linking between repeating units (each of 24—30 glucose units) is of the normal glucosidic type and not due to H-bonding. On the other hand the pasting of native starch with hot H_2O and its subsequent pptn. in granular form are consistent with the formation of H bonds between the macromols. F. L. U.

Carragheen mucilage. E. G. V. Percival and J. Buchanan (Nature, 1940, **145**, 1020—1021; cf. A., 1940, II, 245).—Haas' view (A., 1921, i, 839) that the polysaccharide obtained by extraction of carragheen moss with hot H_2O is essentially the Ca salt of a carbohydrate ethereal sulphate has been confirmed. Attempted acetylation ($C_5H_5N + Ac_2O$) on the hot and other extracts was unsuccessful. Hydrolysis yielded a mixture of sugars containing ~50% of galactose, which appears to be the main unit of the mol. Direct methylation of the hot extract is difficult, and gives a OMe content ≯~15%. Hydrolysis followed by acetylation and vac. distillation gave a dimethylhexose triacetate (~40%) and a monomethylhexose tetra-acetate (~20%), both of which yielded tetramethylgalactopyranoseanilide on suitable treatment. Deacetylation followed by osazone formation gave 6-methyl-*d*-galactosazone and *d*-galactosazone, respectively. L. S. T.

Iodine reaction of glycogen and starch in presence of adrenaline. P. Marquardt (Klin. Woch., 1939, **18**, 1396—1397). M. K.

Cyanic acid. IV. Constitution of cyanic acid. Carbamyl fluoride and bromide. M. Linhard and K. Betz (Ber., 1940, **73**, [*B*], 177—185; cf. A., 1938, I, 517; II, 352).—On electronic grounds, the structure of cyanic acid (I) is regarded as H·N:C:O; (acidic) H easily separates as H^+, and the resulting –N:C:O can electromerise into N:C·O–. Liquid HF at —80° with H_2O-free Et_2O in a Cu vessel, and (I), give *carbamyl fluoride* (II), m.p. 47°, purified by sublimation at 20°/vac. on to a Cu rod at —80° (apparatus described). Dil. NaOH or aq. NH_3 hydrolyses (II) to cyanate and fluoride. With H_2O, (II) gives NH_4F, and thence NH_4HF_2. Cryoscopically in dioxan, (II) shows normal mol. wt. HBr and (I) at —80° give *carbamyl bromide*, m.p. 27—27·5°, purified by sublimation, which is similarly hydrolysed by aq. NaOH. Metallic m.p. apparatus for use with (II) (m.p. determined by the fall of a Cu wire resting on the substance) is described. E. W. W.

Production of hydrocyanic acid and ammonia by the action of the high- and low-frequency electric arc on mixtures of nitrogen, carbon monoxide, and hydrogen at ordinary and low pressure.—See A., 1940, I, 417.

Aliphatic arsinic acids. II. Attempted preparation of di- and tri-arsinoacetic acids. A. R. Marquez (Anal. Asoc. Quím. Argentina, 1940, **28**, 82—86; cf. A., 1940, II, 208).—$CHCl_2·CO_2H$ or $CCl_3·CO_2Et$ with As_2O_3 in excess of NaOH yields only NaOAc and Na_3AsO_4. F. R. G.

Redistribution reaction. R. D. Stiehler and T. L. Gresham (J. Amer. Chem. Soc., 1940, **62**, 2244).—Polemical against Calingaert *et al.* (A., 1940, II, 8). W. R. A.

Isomerisation of polymethylene hydrocarbons in presence of aluminium chloride. V. Isomerisation of *n*-amyl*cyclo*pentane. M. B. Turova-Polak and G. A. Tarasova (J. Gen. Chem. Russ., 1940, **10**, 172—175; cf. A., 1940, II, 159).—*n*-Amyl*cyclo*pentane heated with $AlCl_3$ (20 hr. at 150—155°) yields 55% of *cyclo*hexane derivatives (probably tetramethyl*cyclo*hexanes), together with cracking products of low b.p. R. T.

Catalytic dehydrogenation of representative hydrocarbons.—See A., 1940, I, 416.

Crystalline β-dihydrocarotene. P. Karrer and A. Ruegger (Helv. Chim. Acta, 1940, **23**, 955—959).—Reduction (Al–Hg in Et_2O) of β-carotene leads to *β-dihydrocarotene*, m.p. 182°, shown by its absorption spectrum to have 8 double linkings. Since it is biologically inactive it must be (·CH:CH·CMe:CH·CH:CH·CMe:CH·CH$_2$·C$\lessdot^{\mathrm{CMe_2·CH_2}}_{\mathrm{CMe–CH_2}}\!\!>CH_2$)$_2$. H. W.

Heteropoly-acids as catalysts for vapour-phase partial oxidation of naphthalene.—See A., 1940, I, 416.

Sesquiterpenes. XLV. Synthesis of 1 : 4-dimethylazulene. P. A. Plattner and J. Wyss (Helv. Chim. Acta, 1940, **23**, 907—911).—*o*-$C_6H_4Me·CH_2Cl$ is converted successively into *o*-$C_6H_4Me·CH_2·CH(CO_2Et)_2$, *o*-$C_6H_4Me·CH_2·CH_2·CO_2H$, and 4-methylindanone, m.p. 96°. This is converted by the successive action of MgMeI, $KHSO_4$, and H_2 (Raney Ni) into 1 : 4-*dimethylindane* (I), b.p. 86°/11 mm. Treatment of (I) with $CHN_2·CO_2Et$ at ~135—150° followed by hydrolysis and distillation with Pd–C affords 1 : 4-*dimethylazulene* [additive *compound*, m.p. 177—178°, with $C_6H_3(NO_3)_3$; *picrate*, m.p. 142—143°]. All m.p. are corr. H. W.

Union of aryl nuclei. V. Modification of the Gomberg reaction. J. Elks, J. W. Haworth, and D. H. Hey (J.C.S., 1940, 1284—1286; cf. A., II, 1938,

93).—Increased yields in the Gomberg reaction (A., 1926, 944) are obtained in certain cases by substituting NaOAc for NaOH; *e.g.*, C_6H_6 and *o*-, *m*-, or *p*-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ first at 5—10° and then at room temp. for 48 hr. give 45, 45, or 60% of 2-, 3-, or 4-nitrodiphenyl, respectively. *o*-$C_6H_4Cl{\cdot}N_2Cl$ or β-$C_{10}H_7{\cdot}N_2Cl$ and C_6H_6 similarly afford increased yields (38 and 25%, respectively) of the respective diaryl derivative, but other diazotised amines give decreased yields (cf. also Hodgson *et al.*, A., 1940, II, 126).

[With S. E. Lawton.] β-$C_{10}H_7{\cdot}N_2Cl$ and $PhNO_2$–aq. NaOAc give 2′- and 4′-nitro-2-phenylnaphthalene (total yield, 40%). A. T. P.

Action of selenium at high temperatures on *gem*-methylethyl groups. R. L. Barker and G. R. Clemo (J.C.S., 1940, 1277—1279; cf. A., 1937, II, 142).—$C_{10}H_8$ and α-methyl-α-ethylsuccinic anhydride in $AlCl_3$–$PhNO_2$ afford β-1-*naphthoyl*-α-*methyl*-α-*ethylpropionic acid*, m.p. 135—136°, reduced (Clemmensen) to γ-1-*naphthyl*-α-*methyl*-α-*ethylbutyric acid*, b.p. 190°/1 mm., which is converted by H_2O–H_2SO_4 (1 : 3 vol.) at 100° (bath) into 1-*keto*-2-*methyl*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (I), b.p. 170°/1 mm. (*picrate*, m.p. 85—86°). (I) is reduced (Clemmensen) to 2-*methyl*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, b.p. 160°/1 mm. (*picrate*, m.p. 100—101°), dehydrogenated by Se at 280—300°, then 320°, to 2-methylphenanthrene (Et removed). (I) and MgMeI afford 1-hydroxy-1 : 2-dimethyl-2-ethyl-1 : 2 : 3 : 4-tetrahydrophenanthrene, b.p. 150—160°/1 mm. (some dehydration occurs) (unstable picrate, m.p. 83—84°), converted by Se into 1 : 2-dimethylphenanthrene. A. T. P.

Synthetic œstrogens related to triphenylethylene. A. Schönberg, J. M. Robson, W. Tadros, and (in part) H. A. Fahim (J.C.S., 1940, 1327—1329; cf. A., 1938, III, 908).—4 : 4′-Di-bromo- and -iodobenzophenone with $CH_2Ph{\cdot}MgBr$ yield β-*phenyl*-αα-*di*-p-*bromo*-, m.p. 163—164°, and -*iodo*-*phenylethyl alcohol*, m.p. 198—199°, respectively, dehydrated (H_2SO_4–AcOH) to β-*phenyl*-αα-*di*-p-*bromo*-, m.p. 133—134°, and -*iodo*-*phenylethylene*, m.p. 155—156°, respectively. Bromination of $(p\text{-}C_6H_4Hal)_2C{:}CHPh$ in AcOH yields β-*bromo*-αα-*di*-p-*chloro*-, m.p. 156—157°, -*bromo*-, m.p. 164—165°, and -*iodo*-*phenyl*-β-*phenylethylene* (I), m.p. 173—174°. Of these C_2H_4 derivatives, only (I) induces some œstrogenic activity when injected subcutaneously in mice. $(p\text{-}OMe{\cdot}C_6H_4)_2C{:}CPhBr$ (Koelsch, A., 1932, 848), however, is considerably more active than $CPh_2{:}CPhCl$. 4 : 4′-*Dimethoxystilbenediol diacetate* is obtained by reduction (Zn dust, AcOH–conc. H_2SO_4, ~40°) of anisil. A. Li.

Activation of aromatic halogen by *ortho*-ammonium salt groups. W. S. Emerson, F. B. Dorf, and A. J. Deutschman, jun. (J. Amer. Chem. Soc., 1940, **62**, 2159—2160).—2 : 4 : 6 : 1-$C_6H_2Br_3{\cdot}NH_2$, 40% CH_2O, and Zn–Hg in boiling AcOH give 88% of $p\text{-}C_6H_4Br{\cdot}NMe_2$. Elimination of Br and methylation occur also with 4 : 2 : 6 : 1-$C_6H_2MeBr_2{\cdot}NH_2$ (one Br removed), 3 : 2 : 4 : 6 : 1-$C_6HMeBr_3{\cdot}NH_2$ [gives 3 : 4 : 1-$C_6H_3MeBr{\cdot}NMe_2$ (*hydrochloride*, m.p. 149—150°)], 2 : 4 : 6 : 1-$C_6H_2MeBr_2{\cdot}NH_2$ [gives 2 : 4 : 1-$C_6H_3MeBr{\cdot}NMe_2$, b.p. 120—130°/20 mm. (*hydrochloride*, hygroscopic), also obtained from 2 : 4 : 1-$C_6H_3MeBr{\cdot}NH_2$], and 2 : 4 : 6 : 1-$C_6H_2Me_2Br{\cdot}NH_2$. However, 2 : 4 : 6 : 1-$C_6H_2Cl_3{\cdot}NH_2$ gives 2 : 4 : 6 : 1-$C_6H_2Cl_3{\cdot}NMe_2$. R. S. C.

Restricted rotation in arylamines. I. Preparation and resolution of 3-bromo-2 : 4 : 6 : *N*-tetramethylsuccinanilic acid. R. Adams and L. J. Dankert (J. Amer. Chem. Soc., 1940, **62**, 2191—2193).—Mesidine, b.p. 225—226°, and Br in conc. HCl first at <15° and then at 100° (bath) give bromomesidine (82%), m.p. 40°, and thence *bromo*-N-*methylmesidine* (90%), b.p. 145°/15 mm. (purified by way of the NO-derivative; *Ac* derivative, m.p. 71°; obtained also less readily from 1 : 3 : 5 : 2-$C_6H_2Me_3{\cdot}NHMe$), which with $(CH_2{\cdot}CO)_2O$ and a trace of H_2SO_4 in boiling C_6H_6 gives 3-*bromo*-2 : 4 : 6 : N-*tetramethylsuccinanilic acid* (I), 2 : 4 : 6 : 3 : 1-$C_6HMe_3Br{\cdot}NMe{\cdot}CO{\cdot}[CH_2]_2{\cdot}CO_2H$, m.p. 136°. With brucine in $CHCl_3$, (I) affords the *brucine* salt, $+CHCl_3$, $[\alpha]_D^{27}$ −37·5° in EtOH, and thence the l-*form*, m.p. 132°, $[\alpha]_D^{27}$ −29° in EtOH, of (I); amorphous salt residues afford the d-*form*, m.p. 132°, $[\alpha]_D^{27}$ +27° in EtOH. Mutarotation is very slow, not occurring in aq. alkali or EtOH; in boiling $Bu^{\alpha}OH$ the half-life is 9 hr. *l*- or *dl*-(I) gives the dl-Br_2-derivative, m.p. 171°. *dl*-, *l*-, and *d*-(I) with HNO_3 (*d* 1·5) at room temp. give the 3-*bromo*-5-*nitro*-derivatives, m.p. 165°, $[\alpha]_D^{27}$ 0, −6·3°, +6·0° in EtOH, respectively. 2 : 4 : 6 : N-*Tetramethylsuccinanilic acid*, m.p. 136°, with Br in CCl_4 gives (I). M.p. are corr. R. S. C.

Synthesis of 5-bromo-2-naphthylamine. H. Goldstein and K. Stern (Helv. Chim. Acta, 1940, **23**, 818—820).—5 : 2-$C_{10}H_6Br{\cdot}CO_2Me$ is transformed by $N_2H_4{\cdot}H_2O$ in boiling EtOH into 5-*bromo*-2-*naphthoylhydrazine*, m.p. 214—215°, which yields 5-bromo-2-naphthazide, m.p. ~87° (much decomp.), converted by boiling Ac_2O into *acet*-5-*bromo*-2-*naphthylamide*, m.p. 165°. This is hydrolysed by boiling EtOH–conc. HCl to 5 : 2-$C_{10}H_7Br{\cdot}NH_2$, m.p. 58°. *Et* 5-*bromo*-2-*naphthylcarbamate* has m.p. 86°. M.p. are corr. H. W.

Radical of tri-*p*-tolylamine. S. Granick and L. Michaelis (J. Amer. Chem. Soc., 1940, **62**, 2241—2242).—Potentiometric titration of $(p\text{-}C_6H_4Me)_3N$ by $Pb(OAc)_4$ in 80% (vol.) AcOH and N_2 at 30° shows the blue product (Wieland, A., 1907, i, 1076) to be a singly charged cationic free radical, the absorption spectrum of which is determined. R. S. C.

Zwitterion structures in organic molecules.—See A., 1940, I, 403.

Preparation of amino-sulphonamides. E. Miller, J. M. Sprague, L. W. Kissinger, and L. F. McBurney (J. Amer. Chem. Soc., 1940, **62**, 2099—2103).—*p*-$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}SO_2{\cdot}NH_2$ with H_2–PtO_2 or (better) –Raney Ni in EtOH gives p-*toluidine*-ω-*sulphonamide*, m.p. 171—172°. *p*-$NO_2{\cdot}C_6H_4{\cdot}[CH_2]_2{\cdot}Cl$ and $CS(NH_2)_2$ (I) in EtOH give the *iso*carbamide, which with Cl_2 in H_2O gives *p*-$NO_2{\cdot}C_6H_4{\cdot}[CH_2]_2{\cdot}SO_2Cl$, m.p. 81·5—83°, and thence (conc. aq. NH_3) β-p-*nitrophenylethane*-α-*sulphonamide*, m.p. 120·5—122°, reduced by H_2–Raney Ni in EtOH to the p-NH_2-*amide*, m.p. 181—182°. $ClSO_3H$ and $Ph{\cdot}[CH_2]_2{\cdot}NHAc$ at −10°, later room temp., give p-β-*acetamidoethylbenzenesulphonyl chloride*, m.p. 142·5—144°, and

thence the *sulphonamide*, m.p. 168—169° (oxidised to *p*-$CO_2H{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$), hydrolysed by hot 1 : 3 HCl–H_2O to p-β-*aminoethylbenzenesulphonamide*, m.p. 147·5—149° (*hydrochloride*, m.p. 228—230°). *p*-$CN{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ (prep. described), m.p. 166—167°, and H_2–Pd–C in HCl–EtOH give *benzylamine*-p-*sulphonamide*, m.p. 151—152° (*hydrochloride*, m.p. 249—250°; *Ac* derivative, m.p. 172—173°, also prepared from $CH_2Ph{\cdot}NHAc$ by $ClSO_3H$ etc.). *p*-$CN{\cdot}C_6H_4{\cdot}CH_2Cl$ with (I) gives S-p-*cyanobenzyl*iso*thiocarbamide hydrochloride*, m.p. 204—205°, and thence (Cl_2–H_2O) p-*cyanotoluene-ω-sulphonyl chloride*, m.p. 102—103°, and *-ω-sulphonamide*, m.p. 216—217°, and p-*aminomethyltoluene-ω-sulphonamide*, m.p. 160·5—162° [*hydrochloride*, m.p. 278—280° (decomp.)]. $Cl{\cdot}[CH_2]_3{\cdot}CN$ gives similarly S-*γ-cyanopropyl*iso*thiocarbamide hydrochloride*, m.p. 125—127° (corresponding *picrate*, m.p. 163·5—164·5°), *γ-cyanopropane-*, m.p. 65—66°, and δ-amino-*n*-butane-α-sulphonamide (*hydrochloride*, m.p. 127—129°; *Bz* derivative, m.p. 154—155°). S-β-*Cyanoethyl*iso*thiocarbamide hydrochloride*, m.p. 165—166°, $CN{\cdot}[CH_2]_2{\cdot}SO_2Cl$, b.p. 135—136°/5—6 mm. (*sulphonamide*, m.p. 94—95°), and *γ-aminopropane-α-sulphonamide hydrochloride*, m.p. 159—160°, are similarly prepared. β-Phthalimidoethane-sulphonyl chloride, m.p. 157·5—158·5°, and -sulphonamide, m.p. 207—208°, and thence (N_2H_4) $NH_2{\cdot}[CH_2]_2{\cdot}SO_2{\cdot}NH_2$ (hydrochloride, m.p. 131—133°; *Bz* derivative, m.p. 165—166°) are prepared. $CH_2Cl{\cdot}CN$ and (I) in $COMe_2$ give S-*cyanomethyl*iso*thiocarbamide hydrochloride*, m.p. ~95—105° (decomp.), which is decomposed by Cl_2–H_2O. Separation of $SO_2{\cdot}NH_2$ or NH_2 of sulphanilamide from the Ph nucleus leads to inactive products. R. S. C.

Sulphanilamide derivatives.—See B., 1940, 762.

Substituted sulphanilamides. III. N^1-Hydroxy-N^4-acyl derivatives. M. L. Moore, C. S. Miller, and E. Miller (J. Amer. Chem. Soc., 1940, **62**, 2097—2099; cf. A., 1939, II, 308).—RCO·NHPh (1 mol.) and $ClSO_3H$ (5 mols.), first at 5—20° and later at 55—65°, give acet-, m.p. 147—148°, propion-, m.p. 112—113°, *n*-butyr-, m.p. 118—119°, *n*-valer-, m.p. 111—112°, n-*hexo*-, m.p. 92°, n-*hepto*-, m.p. 85—86°, n-*octo*-, m.p. 69—70°, n-*nono*-, m.p. 72—72·5°, *iso*butyr-, m.p. 131—132·5°, *iso*valer-, m.p. 123—124°, and iso*hexo*-, m.p. 78·5—79·5°, *-amidobenzenesulphonyl chloride*. With NH_2OH,HCl in C_5H_5N or aq. Na_2CO_3 these give acet-, m.p. 194—196°, *propion*-, m.p. 174—178°, n-*butyr*-, (I), m.p. 172—178°, n-*valer*- (II), m.p. 178—179·5°, n-*hexo*- (III), m.p. 175—179°, n-*hepto*- (IV), m.p. 166—169°, n-*octo*- (V), m.p. 160—163°, n-*nono*-, m.p. 168—172°, iso*butyr*-, m.p. 172—176°, iso*valer*-, m.p. 168·5—173°, and iso*hexo*-, m.p. 153—157°, *-amidobenzenesulphonhydroxylamide*. p-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH{\cdot}OH$ (VI), m.p. 170·5—173°, and p-*nitrobenzenesulphonhydroxylamide*, m.p. 145—149°, unstable, are similarly prepared. $(RCO)_2O$ and (VI) in EtOH give β-*carboxy-propion*-, m.p. 170—174°, and *-acryl-amidobenzenesulphonhydroxylamide*, m.p. 184—185°, which are inactive against streptococci. Aq. NaOH hydrolyses (III) to p-n-*hexoamidobenzenesulphinic acid*, m.p. 113—116°, also obtained from the sulphonyl chloride by Na_2SO_3. (I) and (V) are as active as, and (II), (III), and (IV) more active than, sulphanilamide. BzCl and (VI) in C_5H_5N or aq. Na_2CO_3 gave *p*-$NHBz{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$. R. S. C.

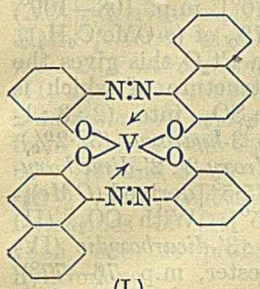
Oxidation of sulphanilic and arsanilic compounds by nascent hydrogen peroxide. G. Barkan (Science, 1940, **92**, 107).—Nascent H_2O_2 formed during the autoxidation of N_2H_4 in presence of $Cu^{\cdot\cdot}$ oxidises sulphanilamide (I) to blue-violet derivatives, extractable with $C_5H_{11}{\cdot}OH$ and BuOH etc. They are stable in these solvents, but not in H_2O, in which they change colour. Arsanilic acid (II) behaves similarly to (I). The blue-violet extracts in BuOH show absorption spectra practically identical in shape with a max. at ~590 mμ., and the compounds from (I) and (II) are probably identical. L. S. T.

Action of nitrous acid on tertiary amines; influence of acidity. G. P. Crowley, G. J. G. Milton, T. H. Reade, and W. M. Todd (J.C.S., 1940, 1286—1289; cf. A., 1935, 337).—Concn. of mineral acid (H_2SO_4, HBr + HCl, HBr + H_2SO_4) has a marked influence on yields of nitration, nitrosation, and fission products obtained from 4 mols. of $NaNO_2$ and 1 mol. of $CH_2(C_6H_4{\cdot}NMe_2\text{-}p)_2$ in N_2. It is confirmed that *p*-$NO_2{\cdot}C_6H_4{\cdot}NMe_2$ (I) is not formed in acid of concn. >3·9N. The nitration/nitrosation ratio, viz., amount of $CH_2[C_6H_3(NO_2){\cdot}NMe_2\text{-}3:4]_2$ (II) : $CH_2(C_6H_4{\cdot}NMe{\cdot}NO\text{-}p)_2$ (III), when (I) is not formed, does not increase as acid concn. increases (contrary to previous conclusions, *loc. cit.*). The above ratio is higher in solutions containing H_2SO_4 than in those containing HCl. In formation of (III) at low concn. of $NaNO_2$, Me eliminated is converted into CH_2O, not into $MeNO_3$ (cf. *loc. cit.*). Mechanisms of reactions are not clear. The yield of (I) is less in H_2SO_4 or mixed acids than in HCl. In H_2SO_4, the yield of (II) has a true max. even when 8 mols. of $NaNO_2$ are used, whereas in HCl the yield increases continuously as normality increases without giving a true max. For 4 mols. of $NaNO_2$, the normalities at which (II) and (III) reach their max. are more widely spaced in H_2SO_4 or mixed acids than in HCl. With H_2SO_4 of high normality, a little $CH_2[C_6H_3(NO_2){\cdot}NMe{\cdot}NO\text{-}3:4]_2$ is formed. Concn. of acid has little effect on yields of products from *p*-$C_6H_4Me{\cdot}NMe_2$ and 3 or 6 mols. of $NaNO_2$ in 2·9—7N-HCl (excess), which give 3 : 1 : 4-$NO_2{\cdot}C_6H_3Me{\cdot}NMe_2$ (83%) and *p*-$C_6H_4Me{\cdot}NMe{\cdot}NO$ (~16%). At higher normalities of HCl, some 3 : 1 : 4-$NO_2{\cdot}C_6H_3Me{\cdot}NHMe$, 3 : 1 : 4-$NO_2{\cdot}C_6H_3Me{\cdot}NMe{\cdot}NO$, and 3 : 5 : 1 : 4-$(NO_2)_2C_6H_2Me{\cdot}NMe{\cdot}NO$ are also formed. With *p*-$NO_2{\cdot}C_6H_4{\cdot}NMeEt$, $NaNO_2$, and 4N-HCl at 15°, Et is eliminated more easily than Me to give *p*-$NO_2{\cdot}C_6H_4{\cdot}NMe{\cdot}NO$ (82·6%) and *p*-$NO_2{\cdot}C_6H_4{\cdot}NEt{\cdot}NO$ (17·4%). A. T. P.

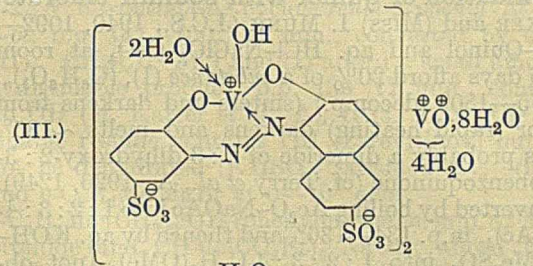
Benzidine; m.p. study. C. Weygand (Z. ges. Naturwiss., 1937, **2**, 408—409; Chem. Zentr., 1937, i, 4095).—Two metastable cryst. forms, m.p. 125° and 122°, are deposited from molten benzidine on cooling to ~100°. The stable form, m.p. 128°, is obtained at temp. nearer the m.p. All three forms, which are described in detail, coexist indefinitely at room temp. A. J. E. W.

Quadrivalent vanadium lakes of azo-dyes. H. D. K. Drew and F. G. Dunton (J.C.S., 1940,

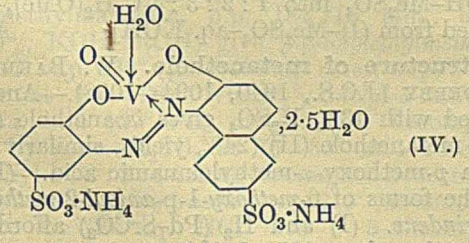
1064—1070; cf. A., 1940, II, 250).—Lakes of V^{IV} with azo-dyes containing reactive substituents (OH, NH_2, CO_2H) in *oo'*-positions with respect to ·N:N· are described. 1-*o*-Hydroxybenzeneazo-β-naphthol and 50% aq. vanadyl chloride–EtOH (reagent *A*) afford the *bisazo-vanadi-complex* (I) (full quadrivalency used), stable to hot conc. HCl; use of moist vanadyl hydroxide–EtOH (reagent *B*) gives (I) and a *vanadyl complex*, $C_{16}H_{10}O_3N_2V,2H_2O$ (similar to Cr^{III} lakes) (loses $2H_2O$ at 130°; regains $1H_2O$ in moist air) (the corresponding C_5H_5N derivative, $C_{16}H_{10}O_3N_2V,C_5H_5N$, loses C_5H_5N at 115° in dry air). 4-*o*-Hydroxybenzeneazoresorcinol and (*B*) afford the *vanadyl complex*, $C_{12}H_8O_4N_2V,2{\cdot}5H_2O$ (aq. mineral acid liberates the azo-dye). 1-*o*-Carboxybenzeneazo-β-naphthol (as Na salt) and (*A*) give an impure *vanadyl complex*, $C_{17}H_{10}O_4N_2V,1{\cdot}5H_2O$ (1 V : 1 azo-dye residue). No lake is obtained from 1 : 2-$PhN_2{\cdot}C_{10}H_6{\cdot}OH$. 1-*o*-Hydroxybenzeneazo-β-naphthylamine and (*B*) yield the anhyd. *bisazo-vanadi-complex*, $C_{32}H_{22}O_2N_6V$ [similar to (I), but less stable to conc. HCl], and an unstable *vanadyl complex*, $C_{16}H_{11}O_2N_3V,2H_2O$. Salicylidene-*o*-aminophenol and (*B*) afford a *vanadyl complex*, $C_{13}H_9O_3NV$ (co-ordinatively unsaturated) [also $+C_5H_5N$, NH_2Ph, (?) $6NH_2Ph$, and $COMe_2$ (loses $COMe_2$ at 130°)]. 1-2'-Hydroxy-5'-sulphobenzeneazo-β-naphthol or 1-2'-hydroxybenzeneazo-β-naphthol-6-sulphonic acid and (*B*) afford glassy complexes; aq. NH_3 or NaOH liberates ionised V and affords the *Na* salt, $C_{16}H_9O_6N_2SNaV,6{\cdot}5H_2O$, or NH_4 salt, $C_{16}H_{13}O_6N_3SV,7{\cdot}5H_2O$, of the respective vanadyl complexes. Similarly, 4-2'-hydroxy-5'-sulphobenzeneazoresorcinol gives the $(NH_4)_2$ salt, $+5H_2O$ (loses $5H_2O$ at 145°; regains $2H_2O$ in moist air), and Na_2 salt, $+7{\cdot}5H_2O$, of the vanadyl complex. 1-2'-Hydroxy-5'-sulphobenzeneazo-β-naphthol-6-sulphonic acid and (*B*) yield a *vanadyl salt* (III) of the vanadyl complex; unco-ordinated V is removed by aq. NH_3



(I.)



(III.)



(IV.)

to give the $(NH_4)_2$ salt (IV). The derivatives of the azo-sulphonic acids are unstable to mineral acids and cannot be prepared from (*A*) in absence of bases. Fastness properties to acids and alkalis of the dyeings with vanadyl lakes, although superior to those of the free dyes, are much inferior to those of the corresponding Cr^{III} lakes. Properties of the lakes suggest that the co-ordination no. of V^{IV} is 6. The stereochemistry of the vanadi- and vanadyl lakes may be regarded as identical with that suggested for the Cr^{III} lakes (cf. A., 1939, II, 309), V having octahedral symmetry.

A. T. P.

New aromatic fluoro-derivatives. III. (SRA.) A. C. DE DEGIORGI and E. V. ZAPPI (Anal. Asoc. Quím. Argentina, 1940, **28**, 72—81; cf. A., 1938, II, 482).—Diazotised 3 : 5-dibromo- and 3 : 4-dinitro-aniline with 40% HBF_4 yield the *-benzenediazonium borofluorides*, decomp. 126° and 161°, respectively, which when heated give 1 : 3-*dibromo*-5-*fluoro*-, b.p. 204—206°/768 mm., and 1-*fluoro*-3 : 4-*dinitro-benzene*, m.p. 34°, respectively. 1 : 3 : 5-$NO_2{\cdot}C_6H_3(OH){\cdot}OEt$ with Me_2SO_4–NaOH yields 3-*nitro*-5-*ethoxyanisole*, m.p. 43—44° (sublimes).

F. R. G.

Decomposition of *p*-hydroxybenzenediazonium salts by alcohols. H. H. HODGSON and C. K. FOSTER (J.C.S., 1940, 1150—1153).—Cameron's results (A., 1898, i, 364) on the decomp. of *p*-$OH{\cdot}C_6H_4{\cdot}N_2Cl$ (= *A*) by MeOH and EtOH are confirmed. Decomp. of the salt $2A,ZnCl_2$ (I) with MeOH or EtOH also gives PhOH (38·4%); some $(p\text{-}OH{\cdot}C_6H_4{\cdot}N{:})_2$ (II) (identified as diacetate or Br_4-derivative) is also formed. Decomp. of (I) with MeOH or EtOH in presence of ZnO affords PhOH (60—63%) and less (II); MeOH–NaOMe gives PhOH (22%) and much (II), whilst $Bu^{\gamma}OH$–Zn dust at 30° gives PhOH (35·7%) and (II) (58·5%). (I)–MeOH–Br give bromoanil and (mainly) 2 : 4 : 6 :1-$C_6H_2Br_3{\cdot}OH$. Decomp. of (I) in presence of excess of HCl also increases the yield of PhOH. Mechanisms of reaction are discussed; oxonium salt formation at the phenolic OH is probably the reason why this group behaves similarly to NO_2 in the above decomp. The salt $2p\text{-}OMe{\cdot}C_6H_4{\cdot}N_2Cl,ZnCl_2$ resists a similar decomp. with MeOH, but in presence of Zn dust some PhOMe is formed. (I) is stable when dry and more convenient to use than (*A*).

A. T. P.

Migration of halogen [*para* to hydroxyl] in a derivative of *m*-cresol. A. B. SEN (Proc. Nat. Acad. Sci. India, 1939, **9**, 89—92).—3 : 4 : 1-$C_6H_3MeBr{\cdot}OH$ (prepared from *m*-$C_6H_4Me{\cdot}NH_2$ via 3 : 4 : 1-$C_6H_3MeBr{\cdot}NHAc$ or from *m*-cresol) with AcOH–HNO_3 (*d* 1·4) yields 4 : 6 : 3 : 2 : 1-$(NO_2)_2C_6HMeBr{\cdot}OH$ (I), m.p. 115° (cf. Walther *et al.*, A., 1915, i, 879) (*p-toluenesulphonate*, m.p. 141°), identical with that prepared by Sane *et al.* (A., 1928, 1130). 2-*Bromo*-4 : 6-*dinitro*-3-*methyldiphenylamine*, m.p. 130°, is obtained from 1 : 3 : 2 : 4 : 6-$C_6HMeClBr(NO_2)_2$ [prep. from (I) and *p*-$C_6H_4Me{\cdot}SO_2Cl$–$NPhEt_2$] and NH_2Ph in EtOH + NaOAc.

A. LI.

Halogeno-4-alkylphenols.—See B., 1940, 762.

Nitrosation of phenols. XVIII. Synthesis of 3-fluoro-4- and -6-nitrosophenol. Comparison of the stabilities of 3-halogeno-4-nitrosophenols. H. H. HODGSON and D. E. NICHOLSON (J.C.S., 1940,

1268—1271; cf. A., 1940, II, 135).—1 : 3 : 4-$OH{\cdot}C_6H_3F{\cdot}NO_2$ and Me_2SO_4–K_2CO_3 give 1 : 3 : 4-$OMe{\cdot}C_6H_3F{\cdot}NO_2$, reduced by Fe–HCl–EtOH to 3-*fluoro*-4-*aminoanisole*, m.p. 50°, converted by Caro's acid into 3-*fluoro*-4-*nitrosoanisole*, m.p. 46°, and thence by HCl (*d* 1·16)–MeOH into 1 : 3 : 4-$OH{\cdot}C_6H_3F{\cdot}NO$ (I), m.p. 161° [*Co* salt, m.p. 130—140°, not co-ordinated], obtained also from *m*-$C_6H_4F{\cdot}OH$–C_5H_5N–$NO{\cdot}SO_4H$ at <10°. (I) is probably a NO-compound rather than a quinoneoxime; it is more stable than other 1 : 3 : 4-$OH{\cdot}C_6H_3Hal{\cdot}NO$. (I) could not be methylated nor converted into 3-fluorobenzoquinone-4-oxime. 1 : 3 : 6-$OMe{\cdot}C_6H_3F{\cdot}NH_2$ (*Ac* derivative, m.p. 132°) and Caro's acid afford 3-*fluoro*-6-*nitroso*-*anisole*, m.p. 150°, and thence (H_2SO_4–MeOH) the *-phenol* (does not melt; does not condense with $NPhMe_2$) [$Co(NO_3)_2$–aq. MeOH give a co-ordinated *Co* salt, m.p. ~105°, also obtained from *m*-$C_6H_4F{\cdot}OH$–aq. H_2SO_4–$Na_3Co(NO_2)_6$]. A. T. P.

Kinetics of oxidation of 2 : 6-dinitrophenol by potassium permanganate.—See A., 1940, I, 415.

Dehydrogenation. III. Formation of naphthols from alcohols and ketones of the hydronaphthalene group. R. P. Linstead and K. O. A. Michaelis (J.C.S., 1940, 1134—1139).—Dehydrogenation in the liquid phase, best using Pd–C prepared in dil. solution, of 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene (I) (46%; in *p*-cymene), *ar*- (55) (quickly dehydrogenated) and *ac*-tetrahydro-β-naphthol (60; in mesitylene), *trans*-α- (19) and *cis*- (28) and *trans*-β-ketodecahydronaphthalene (II) (41; in *p*-cymene), and *cis*- (12) and *trans*-decahydro-β-naphthol (17; only 7% in *p*-cymene), gives the respective $C_{10}H_7{\cdot}OH$ (yield quoted) and $C_{10}H_8$. (II) also affords some $(2\text{-}C_{10}H_7)_2$. Ketones are more readily dehydrogenated than alcohols, and *cis*- more readily than *trans*-compounds. Drastic conditions (leading to elimination of O) are needed to dehydrogenate the substances furthest removed from the aromatic type. Tetrahydronaphthalene is readily dehydrogenated in the liquid phase only when boiling. Rapid catalytic dehydrogenation is effected when the liquid boils at 185° under reduced pressure or on addition of diluent (mesitylene), but none in the tranquil liquid at ~200°. 4-Keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (in *p*-cymene) is dehydrogenated at 240° to 62% of 4-phenanthrol (cf. Mosettig *et al.*, A., 1937, II, 145), phenanthrene, and a compound, m.p. 312°. A. T. P.

Synthesis of dihydrodiethylstilbœstrol. A. M. Docken and M. A. Spielman (J. Amer. Chem. Soc., 1940, **62**, 2163—2164).—Contrary to Dodds *et al.* (A., 1939, II, 312; cf. A., 1940, II, 79), hydrogenation (Pd–C, prepared by Hartung's method; Raney Ni; or Cu chromite) of $(p\text{-}OMe{\cdot}C_6H_4{\cdot}CEt{:})_2$ or of $(p\text{-}OH{\cdot}C_6H_4{\cdot}CEt{:})_2$ (Raney Ni; EtOH) gives only the stereoisomeride of low m.p. The crude product obtained from anethole and HBr (not HCl) in light petroleum (cf. Orndorff *et al.*, A., 1900, i, 289) with Mg (not Na) in boiling Et_2O gives $(p\text{-}OMe{\cdot}C_6H_4{\cdot}CHEt)_2$ m.p. 146° (with polymerides and a little of the isomeride, m.p. 56°), converted by KOH–EtOH at 225° into $(p\text{-}OH{\cdot}C_6H_4{\cdot}CHEt)_2$, m.p. 185—186° (over-all yield 10—15%). R. S. C.

Dibenzofuran [diphenylene oxide]. XIX. Derivatives of 2 : 2′-dihydroxydiphenyl. H. Gilman, J. Swiss, and L. C. Cheney (J. Amer. Chem. Soc., 1940, **62**, 1963—1967; cf. A., 1940, II, 187).—$(o\text{-}OH{\cdot}C_6H_4)_2$ [prep. in 28·6% yield from dibenzofuran (I) by KOH–NaOH at 400—410°], m.p. 108—109°, and 10% NaOH–Me_2SO_4 give 87% of $(o\text{-}OMe{\cdot}C_6H_4)_2$, m.p. 154—155°. With $LiBu^a$ in Et_2O this gives the 3 : 3′-Li_2 derivative (II), the structure of which is proved by conversion by Me_2SO_4 into (2 : 3 : 1-$OMe{\cdot}C_6H_3Me{\cdot})_2$ and by O_2 into 3-*hydroxy*- (32·2%), m.p. 115—116°, and 3 : 3′-*dihydroxy*-2 : 2′-*dimethoxydiphenyl* (1·42%), m.p. 174·5—175·5° [derived $(OMe)_4$-compound (III), m.p. 104—105°]. With CO_2, (II) yields 2 : 2′-*dimethoxydiphenyl*-3 : 3′-*dicarboxylic* (IV) (49·9%), m.p. 208—209° (Me_2 ester, m.p. 76—77°), and -3-*carboxylic acid* (9·3%), m.p. 114·5°. Demethylation of (IV) by HI gives 2 : 2′-*dihydroxydiphenyl*-3 : 3′-*dicarboxylic acid*, m.p. 304° (decomp.), which with HBr (*d* 1·49) or $ZnCl_2$ at 240—250° gives only (I). Veratrole (V) and $LiBu^a$ in Et_2O give the 3-Li derivative [with CO_2 affords 2 : 3 : 1-$(OMe)_2C_6H_3{\cdot}CO_2H$], which with $CuCl_2$ in boiling Et_2O–C_6H_6 affords (III) (1·8%) and (V) (63·5%). The product of Diels *et al.* (A., 1902, i, 219) is 5 : 5′-*dibromo*-2 : 2′-*dihydroxydiphenyl* (VI) (*diacetate*, m.p. 105—106°; *p-toluenesulphonate*, m.p. 198—199°), since with Me_2SO_4–NaOH it gives its *Me*$_2$ *ether* (VII), m.p. 130—131°, which is also obtained from 5 : 1 : 2-$C_6H_3BrLi{\cdot}OMe$ by $CuCl_2$. $LiBu^a$ in Et_2O–C_6H_6 converts (VII) into the 5 : 5′-Li_2 derivative, which yields $[2 : 5 : 1\text{-}OMe{\cdot}C_6H_3(CO_2H)]_2$, m.p. 335—340° (decomp.). Br–AcOH and (VI) give 3 : 5 : 3′ : 5′-*tetrabromo*-2 : 2′-*dihydroxydiphenyl* [previously (*loc. cit.*) unoriented], m.p. 200—201°, the *Me*$_2$ *ether*, m.p. 86—87°, of which with LiPh–Et_2O, followed by CO_2, affords 5 : 5′-*dibromo*-2 : 2′-*dimethoxydiphenyl*-3 : 3′-*dicarboxylic acid*, sinters at 265°, m.p. 274—275° (decomp.), dehalogenated by H_2–Pd–$CaCO_3$ in EtOH at 3 atm. to (IV). R. S. C.

2-Methyl-1 : 4-naphthaquinol di-2 : 4 : 6-trimethylbenzoate, m.p. 204—205°.—See A., 1940, III, 820.

Derivatives of 1 : 2 : 3 : 4-tetrahydroxybenzene VI. Oxidation of quinol with sodium chlorate. W. Baker and (Miss) I. Munk (J.C.S., 1940, 1092—1093).—Quinol and aq. HCl–$NaClO_3$–OsO_4 at room temp./5 days afford 20% of a *substance* (I), $(C_6H_6O_4)_n$, m.p. 175—180° (decomp.) (sinters and darkens from 155°), or (rapid heating) darkens and melts ~185°, which is probably a dimeride of 2 : 3-dihydroxy-2 : 3-dihydrobenzoquinone (cf. Terry *et al.*, A., 1926, 1249). It is converted by boiling Ac_2O–NaOAc into 1 : 2 : 3 : 4-$C_6H_2(OAc)_4$, m.p. 134—136°, and thence by aq. KOH–EtOH–Me_2SO_4 into 1 : 2 : 3 : 4-$C_6H_2(OMe)_4$ [not obtained from (I)–Me_2SO_4–aq. KOH]. A. T. P.

Structure of metanethole. W. Baker and J. Enderby (J.C.S., 1940, 1094—1098).—Anethole refluxed with 43% H_2SO_4 gives *iso*anethole (I) (70%) and metanethole (II) (24% yield), similarly obtained from *p*-methoxy-α-methylcinnamic acid. (II) is one of the forms of 6-*methoxy*-1-*p*-*anisyl*-2-*methyl*-3-*ethylhydrindene*. (I) and H_2 (Pd–$SrCO_3$) afford the H_2-derivative, b.p. 187—188°/0·06 mm., converted by HBr (*d* 1·5)–AcOH into αγ-di-*p*-hydroxyphenyl-β-

methyl-*n*-pentane. (II) with Br–AcOH gives a Br_2-derivative, m.p. 135°, with HBr (*d* 1·5)–AcOH affords "*metanethol*" (6-*hydroxy*-1-p-*hydroxyphenyl*-2-*methyl*-3-*ethylhydrindene*), m.p. 156—157° (anhyd.) or ~83° (+$x$$H_2O$), and with HNO_3 (*d* 1·4)–AcOH yields a $(NO_2)_2$-derivative (III), m.p. 190°. (III) and aq. $KMnO_4$–AcOH give 3-nitroanisic acid and 5(or 3)-*nitro*-2-(3′-*nitroanisoyl*)*anisic acid*, m.p. 221—222°. (II) and CrO_3–AcOH–H_2SO_4 at 40° afford anisic and 2-*anisoylanisic acid*, m.p. 208°; the latter is prepared from 4 : 1 : 2-OMe·$C_6H_3(CO)_2O$, PhOMe, and $AlCl_3$ at 80°. (I) and $SnCl_4$–$CHCl_3$ (not HCl–MeOH) give (II) (10% yield), together, probably, with liquid stereoisomerides of (II). "Methronol" (Erdmann, A., 1885, 528) is probably 1-phenyl-2-methyl-3-ethylhydrindene. A. T. P.

p-Phenoxytriphenylmethane and the corresponding free radical. D. L. Clarke and S. T. Bowden (J.C.S., 1940, 1334).—*p*-OPh·C_6H_4·COPh with MgPhBr yields an oily carbinol (I) which gives a cryst. additive compound when the reddish-brown solution in liquid SO_2 is slowly evaporated. AcCl or HCl + $CaCl_2$ in C_6H_6 or light petroleum converts (I) into the chloride, which with mol. Ag gives a deep orange colour, discharged by O_2. Reduction (Zn dust in AcOH) of (I) yields p-*phenoxytriphenylmethane*, m.p. 142°. A. Li.

Interaction of β-ionone with halides in presence of lithium, and a synthesis of 1 : 6-dimethylnaphthalene. F. B. Kipping and F. Wild (J.C.S., 1940, 1239—1242).—β-Ionone (I)–MeI–Et_2O added to Li–Et_2O (+ trace of LiMe) give δ-2 : 6 : 6-*trimethyl*-Δ^1-cyclo*hexenyl*-β-*methyl*-Δ^γ-*buten*-β-*ol*, b.p. 89—90°/0·2 mm. [ozonolysis product, geronic acid (II)], dehydrated ($KHSO_4$ at 135°, then at 170—180°/15 mm. in N_2) to δ-2 : 6 : 6-*trimethyl*-Δ^1-cyclo*hexenyl*-β-*methyl*-$\Delta^{\alpha\gamma}$-*butadiene* (III), b.p. 113—115°/15 mm. [maleic anhydride gives a crude product, m.p. 155° (decomp.)]. Ozonolysis of (III) gives (II), whilst CrO_3–aq. H_2SO_4 affords AcOH (1 mol.). Se dehydrogenation of (III) at 320—350° in a sealed tube gives 1 : 6-$C_{10}H_6Me_2$. (I) and PhBr–Li–Et_2O (+ a trace of LiPh) afford δ-2 : 6 : 6-*trimethyl*-Δ^1-cyclo*hexenyl*-β-*phenyl*-Δ^γ-*buten*-β-*ol*, b.p. 147—150°/0·1 mm., converted by O_3 into (II). CH_2:CH·CH_2I and (I) afford a small amount of a distillable product, b.p. 139°/12 mm., containing no OH (cf. Karrer *et al.*, A., 1932, 852); the undistillable residue contains OH (Zerevitinov) but could not be dehydrated ($KHSO_4$) satisfactorily. $(CH_2)_2O$ and *o*-C_6H_4Me·MgBr at 0—10° give *o*-C_6H_4Me·$[CH_2]_2$·OH (phenylurethane, m.p. 82·5°); the bromide and $CHMe(CO_2Et)_2$–NaOEt afford Et β-*o*-tolylethylmethylmalonate, b.p. 184°/10 mm., and thence (20% KOH–EtOH) give β-*o*-*tolylethylmethylmalonic acid*, m.p. 138° (p-*nitrobenzyl* ester, m.p. 86°). The latter at 160—200° yields γ-*o*-*tolyl*-α-*methylbutyric acid*, b.p. 157°/0·12 mm. (slight decomp.), converted by conc. H_2SO_4 at 75—80° into 1-keto-2 : 5-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, m.p. 47° [2 : 4-*dinitrophenylhydrazone*, m.p. 219° (decomp.)], and thence by Zn–aq. HCl into 2 : 5-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 115°/14 mm., which with Se at 320—350° affords 1 : 6-$C_{10}H_6Me_2$, identical with the dehydrogenation product of ionene. A. T. P.

Synthesis of phenylacetylenylhexylcarbinol [γ-hydroxy-α-phenyl-Δ^α-noninene]. N. Malenok and I. Sologub (J. Gen. Chem. Russ., 1940, **10**, 150—153).—CPh:CH and heptaldehyde condense (Grignard) to *phenylacetylenylhexylcarbinol*, b.p. 144—145°/1 mm. (*acetate*, b.p. 147·5°/1·5 mm.), dehydrated by distillation from $H_2C_2O_4$ to α-*phenyl*-Δ^γ-*nonen*-Δ^α-*inene*, b.p. 110—111°/1 mm. This is oxidised (AcO_2H) to γδ-*oxido*-α-*phenyl*-Δ^α-*noninene*, b.p. 133·5—134·5°/0·5 mm. R. T.

Enediols. IV. *cis–trans* Isomerism. R. C. Fuson, S. L. Scott, E. C. Horning, and C. H. McKeever (J. Amer. Chem. Soc., 1940, **62**, 2091—2094; cf. A., 1940, II, 169).—Hydrogenation (PtO_2) of hindered $(COAr)_2$ for the min. time gives *cis*-(:CAr·OH)$_2$, but after a longer period gives the *trans*-compound, which is also obtained from the pure *cis*-form by H_2–PtO_2. The form of higher m.p. is assumed to be *trans*. The *trans*-form is more stable in air. Thus are obtained cis- (I), m.p. 123—124° (*diacetate*, m.p. 166—167°), and trans-αβ-*dihydroxy*-2 : 6 : 2′ : 6′-*tetramethylstilbene* (II), m.p. 151—152° (*diacetate*, m.p. 196—197°), trans-αβ-*dihydroxy*-2 : 4 : 6 : 2′ : 4′ : 6′-*hexa-ethyl*-, m.p. 181·5—183·5°, and -*methyl*-*stilbene*, m.p. 157—165° (air), 166—168° (N_2). (I) and (II) give the same *dibenzoate*, m.p. 261—263° (uncorr.). 2 : 6 : 1-$C_6H_3Me_2$·COCl gives (method: *loc. cit.*) 2 : 6 : 2′ : 6′-*tetramethyl*-*benzil* (III), m.p. 153—154°, and some -*benzoin*, m.p. 127—128° [*acetate*, m.p. 104—105°; with $CuSO_4$–C_5H_5N–H_2O gives (III)]. Unless otherwise stated, m.p. are corr. R. S. C.

Polycyclic aromatic hydrocarbons. XXIV. J. W. Cook and R. H. Martin (J.C.S., 1940, 1125—1127).—A more detailed account of work previously reviewed (A., 1939, II, 413). Photo-oxides of the anthracene hydrocarbons are peroxides involving both *meso*-C atoms. Their formation appears to be unrelated to carcinogenic activity. 9-*Methyl*-, m.p. 122—123°, 10-*methyl*-, m.p. 129—130°, and 10-iso*propyl*-, m.p. 166—167°, -1 : 2-*benzanthracene photo-oxides* are prepared. 5 : 6 : 9 : 10-Tetramethyl-1 : 2-benzanthracene photo-oxide is unchanged by boiling 8% KOH–EtOH for 2 hr. 9 : 10-*Dimethyl*-1 : 2-*benzanthracene photo-oxide* (I), m.p. 193—194°, or 188—189° (+1$CHCl_3$), is hydrogenated (Pd-black, $COMe_2$; 20 hr. in the dark) to 9 : 10-dihydroxy-9 : 10-dimethyl-9 : 10-dihydro-1 : 2-benzanthracene (Bachmann *et al.*, A., 1937, II, 497), but a similar hydrogenation (24 hr.) of (I) (+$CHCl_3$, whereby HCl is probably liberated) affords (probably) 10-hydroxy-9 : 10-dimethyl-9 : 10-dihydro-1 : 2-benzanthracene, m.p. 185°, converted by MeOH–HCl into 9 : 10-dimethyl-1 : 2-benzanthracene. 1 : 2-Dimethylchrysene does not give a photo-oxide. A. T. P.

Acetylation of *d*-ψ-ephedrine and *l*-ephedrine. W. Mitchell (J.C.S., 1940, 1153—1155).—Gentle acetylation (Ac_2O at 70°) of the corresponding bases gives acetyl-*d*-ψ-ephedrine, m.p. 103—104° (lit. 101°), $[\alpha]_D^{20}$ +110·0° in EtOH [hydrochloride, new m.p. 187°; *hydrobromide* (I), m.p. 181—182°], and *acetyl*-*l*-*ephedrine* (+2H_2O), m.p. 52°, $[\alpha]_D^{20}$ +5·0° in EtOH;

(anhyd.) m.p. 87°, $[\alpha]_D^{20}$ +7·0° in EtOH. Since these compounds form NO-derivatives, they must be *O*-Ac derivatives (cf. Schmidt, A., 1914, i, 989): *nitroso-acetyl-d-ψ-ephedrine* (II) has m.p. 51—52°, $[\alpha]_D^{20}$ +148·0° in EtOH, but the *l*-compound, m.p. ~85°, was not obtained pure. Hydrolysis (boiling aq. 5% NaOH) of (II) affords nitroso-*d-ψ*-ephedrine, m.p. 86°, $[\alpha]_D^{20}$ +124·5° in EtOH, also obtained directly from the base, as is *nitroso*-l-*ephedrine*, m.p. 93°, $[\alpha]_D^{20}$ +80·5° in EtOH. The compound described as "phenylmethylacetylaminobromopropane" (Schmidt, A., 1914, i, 989) has been shown to be (I). The equilibrium between *l*-ephedrine and *d-ψ*-ephedrine on heating with aq. HCl is discussed with particular reference to the hydrolysis of the acetylephedrines. M.p. are corr. F. R. S.

Local anæsthetics derived from tetrahydronaphthalene. Esters of [I] 2-dialkylamino-3-hydroxy-1 : 2 : 3 : 4-tetrahydronaphthalene, [II] 1-dialkylamino-2-hydroxy-1 : 2 : 3 : 4-tetrahydronaphthalene. E. S. Cook and A. J. Hill (J. Amer. Chem. Soc., 1940, **62**, 1995—1998, 1998—1999).—I. 1 : 4-Dihydronaphthalene (improved prep.) with, best, NaOCl–AcOH gives 26·5% of 2-chloro-3-hydroxy- (I) and with BzO_2H–$CHCl_3$ affords 2 : 3-epoxy-1 : 2 : 3 : 4-tetrahydronaphthalene (II) [also obtained from (I) by KOH–EtOH]. With the appropriate NHR_2, (I) or (II) gives 2-diethylamino-, b.p. 138—145°/3 mm. [*hydrochloride*, m.p. 168—170°; *phenylurethane* (III), forms m.p. 125—126° and 79—80° (*hydrochloride*, m.p. 179—180°); p-*nitro*-, m.p. 110—111°, and p-*amino-benzoate*, m.p. 150—150·5°], 2-*dibutylamino*-, b.p. 155—157°/3 mm. [*phenylurethane*, m.p. 110—111° (*hydrochloride*, m.p. 198—200°); *benzoate hydrochloride*, m.p. 191—192°; p-*nitro*-, m.p. 157—160°, and p-*amino-benzoate*, m.p. 192—195°], and 2-piperidino-, new m.p. 51—52°, b.p. 170—172°/3 mm. {*hydrochloride*, m.p. 235—237°; *phenylurethane*, m.p. 81—82° [*hydrochloride*, m.p. 204—206° (decomp.)]; *benzoate*, m.p. 154—156° (*hydrochloride*, m.p. 245—246°)}, -3-hydroxy-1 : 2 : 3 : 4-tetrahydronaphthalene. Of these products, (III) is the most potent local anæsthetic (rabbit's cornea), but is irritant.

II. 2-Bromo-1-hydroxy-1 : 2 : 3 : 4-tetrahydronaphthalene and the appropriate NHR_2 give 1-diethylamino-, b.p. 181°/18 mm. [*benzoate hydrochloride*, m.p. 192—193°; *phenylurethane*, m.p. 104—104·5° (*hydrochloride*, m.p. 206—206·5°)], 1-*di*-n-*butylamino*-, b.p. 206—208°/17 mm., and 1-piperidino-, new m.p. 74—75° {benzoate, m.p. 81—82° [hydrochloride, m.p. 208—209° (lit. 176·5—177·5°)]; *phenylurethane*, m.p. 145—146° (*hydrochloride*, m.p. 203—204°); p-*nitro-benzoate hydrochloride*, m.p. 238·5—239·5°}, -2-hydroxy-1 : 2 : 3 : 4-tetrahydronaphthalene. R. S. C.

Action of formic acid on triphenylmethyl ethyl ether and on triphenylmethyl chloride. S. T. Bowden and T. F. Watkins (J.C.S., 1940, 1333—1334).—Reduction of CPh_3·OEt to $CHPh_3$ by HCO_2H (measured by rate of evolution of CO_2 when the solid is added to anhyd. HCO_2H at 100±0·02°) is as rapid as that of CPh_3·OH, and more complete, whilst that of CPh_3Cl is complete but slower. A. Li.

α-Dihydro-theelin [-œstrone] from human pregnancy urine. M. N. Huffman, D. W. Macorquodale, S. A. Thayer, E. A. Doisy, G. V. Smith, and O. W. Smith (J. Biol. Chem., 1940, **134**, 591—604; cf. A., 1940, III, 582).—*Œstroneoxime O-carboxymethyl ether* (+0·5EtOH), m.p. 188° (obtained in quant. yield from œstrone, CO_2H·CH_2·O·NH_2, HCl, and KOAc in boiling Pr^aOH), is sol. in aq. $NaHCO_3$ and hence is separable from non-ketonic œstrogens. *Œstriol* 3-*monobenzoate*, m.p. 225°, is oxidised by AcOH–$Pb(OAc)_4$ apparently to the corresponding dialdehyde. A micro-modification of the procedure of Whitman *et al.* (A., 1937, II, 289) is applied to the isolation (from urine collected during spontaneous labour and delivery) of small amounts of α-dihydrocestrone as its di-α-naphthoate. W. McC.

Sulphonated arylstearic acids.—See B., 1940, 724.

Attempted synthesis of papaverine. J. F. Kefford (J.C.S., 1940, 1209).—6-Nitro-3 : 4-dimethoxycinnamic acid, new m.p. 286° (decomp.), and $FeSO_4$–aq. NH_3 afford the 6-NH_2-compound (I), m.p. 175—177°, converted by conc. HCl into 6 : 7-*dimethoxycarbostyril*, m.p. 229°. (I) gives (diazo-reaction) 6-*cyano*-3 : 4-*dimethoxycinnamic acid*, m.p. 273—274°, converted over Br in a desiccator into αβ-*dibromo*-6-*carboxy*-3 : 4-*dimethoxyphenylpropionic acid*, m.p. 282°, and cis-ω-*bromo*-6-*cyano*-3 : 4-*dimethoxystyrene*, m.p. 155°. Mg veratryl bromide could not be prepared. A. T. P.

Synthesis of thyronine. C. R. Harington and R. V. P. Rivers (J.C.S., 1940, 1101—1103).—*p*-OH·C_6H_4·CO_2Et and *p*-C_6H_4Br·OMe–KOH–Cu-bronze at 150°, then 240°, give *Et* 4-p-*methoxyphenoxybenzoate*, m.p. 23—24°, converted by N_2H_4,H_2O in EtOH at 100° into 4-p-*methoxyphenoxybenzhydrazide*, m.p. 136—136·5° [p-*toluenesulphonyl* derivative (I), m.p. 172—173°]. (I) and $(CH_2$·$OH)_2$–Na_2CO_3 at 160° (1 min.) afford 4-*p*-methoxyphenoxybenzaldehyde (II), m.p. 60·5° (semicarbazone, new m.p. 212—213°). (II) and hippuric acid give the azlactone, converted by HI (*d* 1·7)–Ac_2O–red P into thyronine [4-*p*-hydroxyphenoxyphenylalanine] (cf. A., 1927, 961). Its *Me* ester *hydrochloride*, m.p. 215°, with $NHEt_2$–BzCl–C_5H_5N yields ON-*dibenzoylthyronine Me* ester, m.p. 132—134°, with $NHEt_2$–C_5H_5N–*p*-C_6H_4Me·SO_2Cl gives N-p-*toluenesulphonylthyronine*, m.p. 141° (after sintering), and with $CHCl_3$–aq. Na_2CO_3–$ClCO_2CH_2Ph$ at 0°, then at room temp., affords N-*carbobenzyloxythyronine*, m.p. 105—106°. A. T. P.

Dialkylaminoalkyl furoates and benzoates as topical anæsthetics. E. S. Cook and C. W. Kreke (J. Amer. Chem. Soc., 1940, **62**, 1951—1953).—The following are prepared. β-Diethylaminoethyl 2-furoate hydrochloride, new m.p. 130·4—131·9°, and benzoate hydrochloride, new m.p. 125·2—126·2°, and *hydrobromide*, m.p. 119·2—120·2°; γ-*diethylamino*-n-*propyl* 2-*furoate hydrochloride*, m.p. 132—134°, and *benzoate hydrochloride*, m.p. 110·9—114·9°, and *hydrobromide*, m.p. 120—122°; β-*dibutylaminoethyl* 2-*furoate hydrobromide*, m.p. 90·9—91·9°, and *benzoate hydrochloride*, m.p. 100·7—104·2°, and *hydrobromide*, m.p. 113·8—115·8°; γ-*dibutylamino*-n-*propyl* 2-*furoate hydrobromide*, m.p. 93·6—95·6°, and *benzoate hydrochloride*, m.p. 98·6—102·6°, and *hydro-*

bromide, m.p. 121·1—124·6°; β-*phenylethylaminoethyl 2-furoate hydrobromide*, m.p. 119·5—122·5°. The products have no or weak anæsthetic properties. M.p. are corr. R. S. C.

Bromination of 2-naphthyl benzoate. S. E. Hazlet (J. Amer. Chem. Soc., 1940, **62**, 2156—2157).—2-$C_{10}H_7$·OBz with Br and a trace of Fe powder in AcOH gives 1-*bromo-2-naphthyl benzoate*, m.p. 98·5—99·5°, hydrolysed to and obtained from 1 : 2-$C_{10}H_6Br$·OH (acetate, m.p. 55—56°). R. S. C.

Kolbe synthesis with alkyl-*o*-xenols. S. Harris and J. S. Pierce (J. Amer. Chem. Soc., 1940, **62**, 2223—2225).—By conversion of *o*-C_6H_4Ph·OH into the esters, Fries rearrangement ($AlCl_3$), reduction, and interaction with CO_2–K_2CO_3 at 110°, later 225°, are obtained 2-*hydroxy-5-ethyl-*, m.p. 161—164° (*acetate*, m.p. 156—160·5°), -5-n-*propyl-*, m.p. 137—143·5° (*acetate*, m.p. 148—151°), and -5-n-*hexyl-diphenyl-3-carboxylic acid*, m.p. 131—134°. *o*-Xenyl acetate, m.p. 63—63·5°, b.p. 139—141°/1 mm., propionate, b.p. 153—155°/2 mm., and n-*hexoate*, b.p. 174—177°/1·5 mm., 2-hydroxy-5-acetyl-, m.p. 167—168·5°, -5-propionyl-, m.p. 147·5—148°, and -5-n-*hexoyl-diphenyl*, m.p. 86—88°, 2-hydroxy-5-ethyl-, b.p. 141—143°/1 mm., -5-*n*-propyl-, b.p. 150—152°/0·9 mm., and -5-n-*hexyl-diphenyl*, b.p. 190—194°/2 mm., are described. Bactericidal properties are noted. R. S. C.

Stereochemistry of diphenyls. L. Comparison of the interference of a methoxyl and hydroxyl group. R. Adams and H. M. Teeter (J. Amer. Chem. Soc., 1940, **62**, 2188—2190; cf. A., 1939, II, 547).—1 : 2 : 5-C_6H_3MeBr·CN, m.p. 54—55°, b.p. 107—110°/3 mm., and H_2SO_4–HNO_3 at <15° give 6-*bromo-5-nitro-*m-*toluonitrile* (I), m.p. 100—103°, converted by NH_2Ac–NaOAc at 200° into 6-*hydroxy-5-nitro-*m-*toluonitrile*, m.p. 125—126°, which with boiling HCl–MeOH gives 5 : 1 : 6 : 3-NO_2·$C_6H_2Me(OH)$·CO_2Me, m.p. 102—103° (derived acid, m.p. 238—240°). Boiling 1 : 1 (vol.) H_2SO_4–H_2O hydrolyses (I) to 5 : 1 : 6 : 3-NO_2·C_6H_2MeBr·CO_2H, m.p. 212—213° (lit., 175—176°), the *Me* ester, m.p. 81—81·5°, of which with *o*-C_6H_4I·OMe and Cu-bronze at 240—250°, later 270°, gives 28% of 6-*nitro-2'-methoxy-2-methyldiphenyl-4-carboxylic acid* (II), m.p. 227—229°, converted by 40% HBr in AcOH into the 2'-*OH-acid* (III), m.p. 180—181° (*brucine*, softens at 169°, m.p. 205°, $[\alpha]_D^{25}$ —22·4° in $CHCl_3$, and *strychnine* salt, m.p. 223—227°, $[\alpha]_D^{25}$ —14·2° in $CHCl_3$). (II), but not (III), is resolved. Brucine and (II) in EtOH give only the *brucine* salt, +EtOH, m.p. 145—147°, $[\alpha]_D^{25}$ —7·8° in $CHCl_3$, of the l-*acid*, m.p. 227—228°, $[\alpha]_D^{25}$ —7·55° in AcOH, half-life 215 min. at 25°, ~11 min. in boiling AcOH; probably the *l*-base *l*-acid salt is stabilised by co-ordination with the solvent EtOH. The *l*-acid is also obtained by way of the *strychnine*, $[\alpha]_D^{25}$ —13·4° in $CHCl_3$, and *cinchonine*, $[\alpha]_D^{25}$ +140·0° in $CHCl_3$, salts. M.p. are corr. R. S. C.

Synthesis of hydroxymandelonitrile dibenzoates. K. E. Hamlin, jun., and W. H. Hartung (J. Amer. Pharm. Assoc., 1940, **29**, 357—360).—BzCl (slight excess), C_5H_5N (1 mol.), and OH·C_6H_4·CHO (I) (1 mol.) yield *o*- (phenylhydrazone, m.p. 137—138°), *m*-, m.p. 48·5—49°, and *p*-benzoyloxybenzaldehyde, m.p. 90—90·5 (lit. 72°; cf. Kopp, A., 1894, i, 128) (phenylhydrazone, m.p. 173—174°), which with saturated aq. NaCN and C_5H_5N followed by successive treatment with BzCl and dil. HCl afford o-, m.p. 92—92·5°, and m-*hydroxymandelonitrile dibenzoate*, m.p. 118·5—119·5°, and the *p*-isomeride, m.p. 144·5—145·5°, respectively. The latter are also obtained directly from (I), aq. NaCN (slight excess), and BzCl (2 equivs.) in C_5H_5N (2 equivs.). F. O. H.

5 : 8-Dibromo-2-naphthoic acid and 5 : 8-dibromo-2-naphthylamine. H. Goldstein and K. Stern (Helv. Chim. Acta, 1940, **23**, 809—817; cf. A., 1938, II, 99).—5 : 8-*Dibromo-2-naphthoic acid* (I), m.p. 287° [*Et* ester (II), m.p. 94°], is obtained by the gradual addition of Br to β-$C_{10}H_7$·CO_2H (simplified prep. from β-$C_{10}H_7$·NH_2) in warm AcOH containing I and is purified through the *Me* ester, m.p. 152°. With PCl_5 or $SOCl_2$ it affords the *chloride*, m.p. 130°, which is transformed into the *amide*, m.p. 242°, and *anilide*, m.p. 217°. (II) and N_2H_4,H_2O in boiling EtOH afford 5 : 8-*dibromo-2-naphthoylhydrazine* (III), m.p. 231—235° [*Ac* derivative, m.p. 306° (decomp.)], which yields the corresponding *hydrazones* with $COMe_2$, PhCHO, and *p*-NO_2·C_6H_4·CHO, m.p. >180° after softening at 150°, 260°, and 275°, respectively. $NaNO_2$ and (III) in AcOH yield 5 : 8-dibromo-2-naphthazide (IV), m.p. ~112°, transformed by 50%, 70%, 80%, or 90% H_2SO_4 exclusively into (I). (IV) and the requisite boiling alcohol afford *Me*, m.p. 168—170°, and *Et* (V), m.p. 155°, 5 : 8-*dibromo-2-naphthylcarbamate*; (V) and boiling EtOH–conc. HCl give (I). In boiling glacial AcOH or in boiling C_6H_6 with subsequent exposure to moist air (IV) passes into s-*di-5 : 8-dibromo-2-naphthylcarbamide*, chars, without melting, at ~300°. With boiling C_6H_6 followed by NH_2Ph, (IV) gives N-*phenyl*-N'-5 : 8-*dibromo-2-naphthylcarbamide*, m.p. ~238° after shrinking at 228°. Successive treatments of carefully dried (IV) with boiling Ac_2O, H_2O, and EtOH–HCl lead to 5 : 8-*dibromo-2-naphthylamine*, m.p. 105° (yield 80—90%) [hydrochloride (VI); *picrate*, m.p. 221—228°; *formyl*, m.p. 226°, *Ac*, m.p. 215°, and *Bz*, m.p. 216°, derivatives], also obtained from (V) and boiling AcOH–H_2SO_4–H_2O. Diazotisation (*iso*-C_5H_{11}·O·NO) of (VI) in EtOH–conc. H_2SO_4 gives 1 : 4-$C_{10}H_6Br_2$. M.p. are corr. H. W.

5-Nitro-6-methyl-2-naphthoic acid. C. C. Price (J. Amer. Chem. Soc., 1940, **62**, 2245).—2 : 6 : 1-$C_{10}H_5Me_2$·NO_2 and boiling HNO_3–H_2O give 5-*nitro-6-methyl-2-naphthoic acid*, m.p. 258—259°. 1 : 6 : 2-NO_2·$C_{10}H_5Me$·CO_2H has m.p. 238—239°. R. S. C.

Constituents of natural phenolic resins. XVII. Synthesis of *l*-matairesinol. R. D. Haworth and F. H. Slinger (J.C.S., 1940, 1098—1101; cf. A., 1939, II, 122).—*O*-Benzylvanillin, $(CH_2$·$CO_2Et)_2$, and NaOEt in Et_2O afford a non-cryst. product, reduced (Na–Hg, H_2O, CO_2) to meso-αβ-*di*-(4-*benzyloxy*-3-*methoxybenzyl*)*succinic acid* (I), m.p. 203° (pyrolysis at 220° or AcCl does not give the anhydride), converted by Ac_2O into a product, m.p. 90—110°, or by P_2O_5–C_6H_6 into a *substance*, m.p. 148°, hydrolysed by alkali to a *substance*, m.p. 129—130°. (I) and boiling

conc. HCl–AcOH afford meso-αβ-*di*-(4-*hydroxy*-3-*methoxybenzyl*)*succinic acid* (II), m.p. 228—229°; MeOH–HCl then gives the *Me* ester, m.p. 169—170°, but Me_2SO_4–aq. NaOH gives *meso*-αβ-di-(3 : 4-dimethoxybenzyl)succinic acid and its Me ester (cf. A., 1939, II, 476). (II) and Ac_2O afford an oil [probably *trans*-αβ-di-(4-acetoxy-3-methoxybenzyl)-succinic anhydride], which with boiling H_2O gives dl-αβ-*di*-(4-*acetoxy*-, m.p. 129—130°, or with N-HCl affords dl-αβ-*di*-(4-*hydroxy*-3-*methoxybenzyl*)*succinic acid* (III), m.p. 194—195°. (III) and strychnine in $CHCl_3$ give the *strychnine* salt (IV), $+9H_2O$, shrinks at 145°, m.p. 247°, $[\alpha]_D^{17}$ −18° in $CHCl_3$, and thence ($NaHCO_3$) the l-*acid* (V), m.p. 109°, $[\alpha]_D^{17}$ −47° in EtOH. The acid recovered ($NaHCO_3$) from the mother-liquors from (IV) gives a brucine salt, $[\alpha]_D^{15}$ −54° in $CHCl_3$, and thence the d-*acid*, m.p. 106—108°, $[\alpha]_D^{16}$ +40° in EtOH. (V) and Ac_2O afford a gum, converted by Al–Hg in C_6H_6–Et_2O–H_2O at room temp. into an oil, which with KOH–MeOH, followed by aq. HCl at 100°, gives *l*-matairesinol, m.p. 116—117°, $[\alpha]_D^{16}$ −46° in $COMe_2$, identical with that from *Podocarpus spicatus*. Its *di*-p-*nitrobenzoate*, m.p. 95—156° (MeOH–$CHCl_3$; solvated) or 157—158° (from aq. AcOH), $[\alpha]_D^{18}$ +9° in $CHCl_3$, is also obtainable from natural *l*-matairesinol. The *d*- and *dl*-forms obtained similarly are not pure, but yield the respective Me_2 ethers with Me_2SO_4–aq. NaOH. A. T. P.

Constituents of natural phenolic resins. XVIII. 1 : 2 : 3 : 4-Tetrahydronaphthalene-2 : 3-dicarboxylic acid and the 1-phenyl derivative. R. D. Haworth and F. H. Slinger (J.C.S., 1940, 1321—1327).—Reduction (Na–Hg in hot aq. NaOH) of 2 : 3-$C_{10}H_6(CO_2H)_2$ gives acids converted by AcCl into a mixture of *cis*- (I), m.p. 183° (identical with that of Perkin *et al.*, J.C.S., 1888, **53**, 12), and trans-1 : 2 : 3 : 4-*tetrahydronaphthalene*-2 : 3-*dicarboxylic anhydride* (II), m.p. 225—226°. Hydrolysis of (I) and (II) gives respectively the *cis*-, m.p. 195° (*loc. cit.*), and trans-*acid*, m.p. 226—227°; the latter is resolved by strychnine into the d-, $[\alpha]_D^{16}$ +85·5°, and l-trans-*acids*, m.p. 182—183°, $[\alpha]_D^{16}$ −85° in $CHCl_3$ (*strychnine* salts, m.p. 195—240° and 170—180°, respectively). Dehydration (Ac_2O) of the mixed *cis*- and *trans*-acids yields only (I), also produced by boiling (II) with Ac_2O for 15 min. Esterification (Fischer–Speier or Ag salt method) of the *cis*- and *trans*-acids yields *Me* esters, m.p. 68—68·5° and 44·5—45°, respectively. The former ester with EtOH–NaOEt gives the latter. Reduction (Al–Hg) of (I) and (II) yields the cis- and trans-*lactones*, m.p. 133—134° and 156°, respectively, of 2-hydroxymethyl-1 : 2 : 3 : 4-tetrahydronaphthalene-3-carboxylic acid, hydrolysis (MeOH–NaOH) and acidification of which gives the original lactones without change of configuration. Mixed 1-phenyl-1 : 2 : 3 : 4-tetrahydronaphthalene-2 : 3-dicarboxylic acids, m.p. 170—180° (A., 1939, II, 476) [form, m.p. 218—219° (decomp.), isolable], with AcCl give a mixture of 1-*phenyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-2 : 3-*dicarboxylic anhydrides*, *A*, m.p. 240—241°, *B*, m.p. 155—156°, *C*, m.p. 171—172°, and *D*, m.p. (crude) 193—199°. Cautious hydrolysis of anhydrides *A*, *B*, and *C* gives the *acids*, *A*, m.p. 236—237°, *B*, m.p. 218—219° (cf. above), and *C*, m.p. 162—163°, converted by CH_2N_2 into the Me_2 esters, *A*, m.p. 108—109°, *B*, m.p. 102—103°, and *C*, m.p. 113—114°, or by AcCl into the original anhydrides. The crude anhydride *D* with CH_2N_2 gives Me_2 esters *B* (80%) and *D* (20%), m.p. 127°. With boiling Ac_2O, anhydrides *B* and *C* are unaffected, but *A* and *D* yield anhydrides *C* and *B*, respectively. With MeOH–HCl acids *A* and *C* yield the corresponding Me_2 esters, but *B* gives a mixture of esters *B* and *D*. All four esters with NaOH or NaOEt yield acid *A*. It is concluded that the configurations of the acids are : *A trans*(1 : 2)-*trans*(2 : 3)-, *B cis*(1 : 2)*cis*(2 : 3)-, *C trans*(1 : 2)*cis*-(2 : 3)-, *D* (unstable) *cis*(1 : 2)*trans*(2 : 3)-. The relative stabilities of these configurations are discussed. Anhydrides *A*, *B*, and *C* are sulphonated by cold conc. H_2SO_4, but with $AlCl_3$ in $PhNO_2$ yield 3 : 4-*benzo*-1 : 2 : 10 : 11-*tetrahydrofluorenone*-1-*carboxylic acids*, *A* [*trans*(10 : 11)*trans*(1 : 10)], m.p. 203—204°, *B* [*cis*-(10 : 11)*cis*(1 : 10)], m.p. 220—221°, and *C* [*trans*-(10 : 11)*cis*(1 : 10)], m.p. 163—164°, respectively. All of these with Se yield 3 : 4-benzfluorenone. On decarboxylation *A* and *C* yield trans(10 : 11)-3 : 4-*benzo*-1 : 2 : 10 : 11-*tetrahydrofluorenone*, m.p. 161—163°, whilst *B* gives the cis(10 : 11)-*form*, m.p. 131—134°. From these results it is suggested that naturally occurring 1-phenylnaphthalene-lignans have the stable *trans*(1 : 2)*trans*(2 : 3)-structure. A. Li.

Behaviour of oximino- and *iso*nitro-compounds under the conditions of Van Slyke's determination of amino-nitrogen. M. Schenck and J. Reschke (Ber., 1940, **73**, [*B*], 200—205).—The behaviour of acet- (I) and benz-hydroxamic acid (II), and of the diketo- (III), oximino-keto- (IV) and -lactam- (V), and nitro-keto- (VI), -oximino- (VII), and -lactam-hydroxamic acid (VIII) from cholic acid, deoxybilianic acid oxime (IX), and dehydrocholic acid trioxime (X) in Van Slyke's apparatus is studied. Except for (I), and NH_2OH,HCl, both of which give some N_2O, the gas is largely N_2 : (II) gives 19%, (III) 17%. (IV) 114%. (V) 128%, (VI) 6—9%, (VII) 19%, (VIII) 12%, (IX) 23%, and (X) 117% of the theoretical for evolution of $1N_2$ per mol. of hydroxamic acid. This shows the strong influence of position and substitution on evolution of N_2, which seems particularly favoured by N·OH at $C_{(7)}$. Possible explanations of the results are discussed. E. W. W.

Effect of substitution on thermal decomposition of gaseous benzaldehyde.—See A., 1940, I, 414.

Decomposition of benzylidene diacetate, *o*-chlorobenzylidene diacetate, and benzylidene dibutyrate.—See A., 1940, I, 414.

Schiff bases from *p*-aminothymol. W. T. Sumerford, W. H. Hartung, and G. L. Jenkins (J. Amer. Chem. Soc., 1940, **62**, 2082—2083).—4-Benzylidene-, m.p. 149°, 4-2′-*hydroxy*- (I), m.p. 170°, 4-2′-*hydroxy*-4′-*methyl*-, m.p. 155°, 4-4′-*methoxy*- (II), m.p. 160°, 4-4′-*hydroxy*-3′-*methoxy*-, m.p. 194°, and 4-3′ : 4′-*methylenedioxy-benzylidene*-, m.p. 161—162°, and 4-*cinnamylidene-aminothymol* (OH = 1), m.p. 154°, are prepared. (I) and (II) are antipyretic for cats. (I) is not toxic. M.p. are corr. R. S. C.

Reaction of aldoximes with diazomethane. A. F. Thompson, jun., and M. Baer (J. Amer. Chem. Soc., 1940, **62**, 2094—2096).—Contrary to Forster *et al.* (J.C.S., 1909, **95**, 425), the appropriate $NO_2{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}OH$ with CH_2N_2 in Et_2O gives α-*o*-, m.p. 59°, α-*m*-, m.p. 61°, β-*m*-, m.p. 72°, and α-*p*- (I), m.p. 101·5°, -nitrobenzaldoxime *O*-Me ether together with small amounts of the α-*o*- [hydrochloride, m.p. 128—132° (lit., 125—134°)], α-*m*-, m.p. 117°, β-m-, m.p. 86—88°, α-*p*- (II), m.p. 201° (lit., 205°), and β-p- (III), m.p. 147—149°, *-nitrobenzaldoxime* N-*Me ether*. The β-*p*-aldoxime *O*-Me ether was not obtained. The structure of the *N*-Me ethers is proved by ready acid hydrolysis to the aldehyde and NHMe·OH and by conversion of (III) into (II) when melted. CH_2N_2 has no effect on (I). Only (I) is formed from the oxime, KOH, and MeI in Et_2O. R. S. C.

Kinetic study of the reaction of acetophenone with benzaldehyde.—See A., 1940, I, 414.

Addition of βγ-unsaturated alcohols to the active methylene group. II. Action of ethyl acetoacetate on cinnamyl alcohol and phenylvinylcarbinol. M. F. Carroll (J.C.S., 1940, 1266—1268; cf. A., 1940, II, 266).—$CHPh{:}CH{\cdot}CH_2Cl$ (convenient prep.) and KOAc–AcOH at 90—100° give mixed acetates, hydrolysed by 40% aq. NaOH–EtOH to $CH_2{:}CH{\cdot}CHPh{\cdot}OH$ (I) and $CHPh{:}CH{\cdot}CH_2{\cdot}OH$ (II). $CH_2Ac{\cdot}CO_2Et$, (II), and NaOAc at 165°, then at 185—240°, afford γ-phenyl-Δ$^{\alpha}$-hexen-ε-one (III) and cinnamyl acetoacetate and acetate. (I) similarly (220°; KOAc) yields cinnamylacetone; no transposition occurs. (III) and $KMnO_4$–aq. NaOH give α-phenyl-lævulic acid, also obtained from $CHBrPh{\cdot}CO_2Et$–$CH_2Ac{\cdot}CO_2Et$–K_2CO_3–$COMe_2$. A. T. P.

Substances with odour of violets. VIII. Synthesis of 1 : 1 : 6-trimethyl-3-γ-keto-Δ$^{\alpha}$-butenyl*cyclo*heptene. M. Stoll and W. Scherrer (Helv. Chim. Acta, 1940, **23**, 941—948; cf. Barbier, A., 1940, II, 217).—Addition of dihydro*iso*phorone (I) followed by LiCl in MeOH to CH_2N_2 in Et_2O gives a mixture of ketones which is partly purified through the semicarbazones, which are hydrolysed and treated with conc. aq. $NaHSO_4$, whereby 3 : 3 : 5-trimethyl-*cyclo*heptanone (II), b.p. 87—88°/12·5 mm. (semicarbazone, m.p. 192—193°), remains unattacked (yield 21%). The $NaHSO_3$ compound yields 3 : 5 : 5-trimethyl*cyclo*heptanone, b.p. 86—88°/12 mm. (yield 12%) [semicarbazone, m.p. 196—197° (varies with rate of heating); picrate, m.p. 214—215°, of compound with aminoguanidine; *p*-nitrophenylhydrazone, m.p. 154—155°]. A third product of the change is the *oxide*, $CH_2{<}\begin{matrix}CMe_2{-}CH_2\\CHMe{\cdot}CH_2\end{matrix}{>}C{<}\begin{matrix}CH_2\\O\end{matrix}$, b.p. 67—69°/13 mm. (yield 46%). (II) is converted by NaOEt and *iso*amyl formate into 3 : 3 : 5-trimethyl-7-hydroxymethylene*cyclo*heptanone, b.p. 108—110°/10 mm., oxidised ($KMnO_4$ in alkaline solution) to ββδ-trimethylpimelic acid, the Th salt of which at 320—350° passes into (I). Anhyd. HCN and a little KCN transform (II) into the *cyanohydrin*, b.p. 103°/0·2 mm. (corresponding amide, m.p. 131°), hydrolysed and esterified to *Me* 1-*hydroxy*-3 : 3 : 5-*trimethyl*cyclo*heptane*-1-*carboxylate*, b.p. 123—128°/14 mm., which is converted by $SOCl_2$ followed by $BaCl_2$ at 250°/0·8 mm. into *Me* 3 : 3 : 5-*trimethyl*-Δ^1-cyclo*heptenecarboxylate*, b.p. 118—122°/18 mm. This is hydrolysed to solid, m.p. 116—117° (chloride, b.p. 130—131°/18 mm.), and liquid acids (chloride, b.p. 123—129°/15 mm.). The two chlorides are catalytically reduced (Fröschl) to 3 : 3 : 5-trimethyl-Δ^1-*cyclo*heptenaldehyde (III) (*semicarbazone*, m.p. 172—174°) and the corresponding saturated *alcohol*, b.p. 122—126°/16 mm. $COMe_2$ and (III) condense to 1 : 1 : 6-trimethyl-3-γ-keto-Δ$^{\alpha}$-butenyl*cyclo*heptene, b.p. 157—160°/17 mm. (*semicarbazone*, m.p. 208—209°), which does not resemble irone in odour. The *cyclo*heptane ring is not sufficient in itself to give the irone perfume. H. W.

Substances with odour of violets. IX. Synthesis of nuclear-methylated homologues of ionone, 1 : 1 : 3 : 6-tetramethyl-2-γ-keto-Δ$^{\alpha}$-butenyl*cyclo*hexene. L. Ruzicka and H. Schinz (Helv. Chim. Acta, 1940, **23**, 959—974).—Methylheptenone (I), purified through the semicarbazone, is condensed with Zn and $CH_2Br{\cdot}CO_2Et$ in C_6H_6 to the OH-ester, b.p. 130—132°/12 mm., which is smoothly dehydrated by PBr_3–C_5H_5N but not by AcOH and fused $ZnCl_2$ to nearly homogeneous Et geranate (II), hydrolysed to geranic acid (III), b.p. 111—112°/0·25 mm. (I) purified through its $NaHSO_3$ derivative is converted by similar treatment into (II) accompanied by a considerable proportion of Et *cyclo*geranate (IV), b.p. 100—101°/12 mm., separated from (II) by using its more difficult hydrolysis. (III) is transformed by $SOCl_2$ into the chloride, b.p. 95—105°/0·6 mm., and thence the anilide, b.p. 180°/0·2 mm. This is converted by PCl_5 in C_6H_6 into the imino-chloride, which gives citral in very poor yield when acted on by $CrCl_2$. (III) is not successfully cyclised by H_2SO_4 or H_3PO_4 but is readily converted by HCO_2H at 100° into α-*cyclo*geranic acid (V), m.p. 104—106° after softening at 97°, identical with that obtained by treating (IV) with KOH–MeOH at 150—170°. (V) is readily converted (Merling's method, A., 1908, i, 653) through the chloride, b.p. 87—88°/12 mm., and *o*-toluidide, m.p. 150°, into citral. The prep. of βγ-dimethyl-Δ$^{\beta}$-hepten-ζ-one (VI), b.p. 76°/13 mm. (semicarbazone, m.p. 161—163°), from $(CH_2{:}CMe)_2$ is described. The Reformatsky condensation of (VI) leads to the OH-ester, b.p. 139—143°/12 mm., transformed by PBr_3 and C_5H_5N in light petroleum followed by distillation into Et methylgeranate, b.p. 116—121°/12 mm., hydrolysed by KOH–EtOH at 100° to methylgeranic acid (VII), b.p. 122—125°/0·35 mm., with about 25% of Et methyl*cyclo*geranate, b.p. 105—108°/12 mm., hydrolysed (KOH–EtOH at 160—170°) to methyl*cyclo*geranic acid (VIII), m.p. 65—70°. The cyclisation of (VII) to (VIII) by 100% HCO_2H at 100° is described. (VIII) is transformed by $SOCl_2$ in light petroleum into the chloride, b.p. 100—102°/14 mm., which gives the *o*-toluidide (IX), m.p. 156—157°, and the *anilide* (X), m.p. 131—132°. (IX) and (X) are reduced (Merling) to a mixture of at least two *methyl*cyclo*citrals*, b.p. 94—97°/12 mm. (*semicarbazones*, m.p. 214—215° and 140—145°), which are condensed with $COMe_2$ to 1 : 1 : 3 : 6-*tetramethyl*-2-γ-*keto*-Δ$^{\alpha}$-*butenyl*-Δ^2- or -Δ^3-cyclo*hexene* (XI), b.p. 105—108°/0·75 mm., which is allied by its odour

to the ionones but not to irone. (XI) gives a non-cryst. *p*-bromophenylhydrazone and a *phenylsemicarbazone* (divisible into fractions, m.p. 130—135° to 165—166°). (XI) is hydrogenated (H_2–Pd–EtOAc) to the H_4-ketone [*semicarbazone*, m.p. 183—186° (not const.)]. H. W.

***p*-Phenylphenacyl esters.** H. E. Carter (J. Amer. Chem. Soc., 1940, **62**, 2244—2245).—p-*Phenylphenacyl* β-*phenyl*iso*butyrate*, m.p. 71—72°, γ-*phenyl*-α-*methyl*-n-*butyrate*, m.p. 62—63°, and δ-*phenyl*-β-*methyl*-n-*valerate*, m.p. 66—67°, are prepared. R. S. C.

Trimerisation of mesityl vinyl ketone. R. C. Fuson and C. H. McKeever (J. Amer. Chem. Soc., 1940, **62**, 2088—2091).—$AlCl_3$ added to $Cl{\cdot}[CH_2]_2{\cdot}COCl$ and *s*-$C_6H_3Me_3$ in CS_2 at 10° gives *mesityl vinyl ketone* (I) (63%), b.p. 99—101°/3·5 mm.; under other conditions at room temp. 25% of (I) and (?) β-*mesitylpropiomesitylene*, m.p. 80—81°, are obtained. Hydrogenation (Raney Ni; room temp./2 atm.; EtOH) of (I) gives 1 : 3 : 5 : 2-$C_6H_2Me_3{\cdot}COEt$ [$(NO_2)_2$-derivative, m.p. 143·5—144·5°]. With Br, (I) gives αβ-*dibromopropiomesitylene*, m.p. 78·5—79·5°, reconverted into (I) by NaI. MgMeI converts (I) into 1 : 3 : 5 : 2-$C_6H_2Me_3{\cdot}COPr^a$, b.p. 120—121°/7 mm. [$(NO_2)_2$-derivative, m.p. 133—135°], also obtained by the Friedel–Crafts reaction. HCl adds to (I) giving β-*chloropropiomesitylene*, m.p. 46—47·5°. (I) is stable to heat alone or with Bz_2O_2 or ascaridole, but with K_2CO_3 in boiling MeOH gives 65—70% of 1 : 3 : 5-*trimesitoyl*cyclo*hexane* (II), m.p. 210—212°, with some *dimeride*, m.p. 83—83·5°, and also a *trimeride* [? stereoisomeride of (II)], m.p. 150—151°. 1 : 3 : 5-$C_6H_3(CO_2Me)_3$ (from the acid and H_2SO_4–MeOH) with H_2–Raney Ni in dioxan at 175°/2750 lb. gives stereoisomeric H_6-esters, b.p. 163—164°/2·5 mm. (yields a form, m.p. 42—44°). Hydrolysis by boiling 15% NaOH, interaction with $SOCl_2$, and then *s*-$C_6H_3Me_3$–$AlCl_3$–CS_2 gives (II). R. S. C.

Synthesis of baeckeol. B. A. Hems and A. R. Todd (J.C.S., 1940, 1208—1209).—Phlori*so*butyrophenone and MeI–$COMe_2$–K_2CO_3 afford 2-hydroxy-4 : 6-dimethoxy-3-methyli*so*butyrophenone, m.p. 103—104° [acetate, two forms, m.p. 73° (prisms from aq. MeOH at low temp.) and 79—80° (needles from hot aq. MeOH or from other form at 75°)], identical with baeckeol (cf. Ramage *et al.*, A., 1940, II, 223). A. T. P.

Phenanthrene derivatives. X. Acetylation of 4-methylphenanthrene. W. E. Bachmann and R. O. Edgerton (J. Amer. Chem. Soc., 1940, **62**, 2219—2223; cf. A., 1938, II, 184).—2-$C_{10}H_7{\cdot}[CH_2]_3{\cdot}COCl$ and $SnCl_4$ in C_6H_6 give 4-keto- (88%), m.p. 69—70°, converted by MgMeI into 4-hydroxy-4-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene (80%), m.p. 109—110°, which with Pd–C at 310—320° gives 4-methylphenanthrene (I) (85%), m.p. 49—50°. With AcCl and $AlCl_3$ in $PhNO_2$ at −10° this gives 1-*acetyl*-4- (II) (50%), m.p. 84—85° and 71—72·5° (picrate, m.p. 142—143°), and 3-*acetyl*-5-*methylphenanthrene* (III) (15%), m.p. 98—99° (picrate, m.p. 107—110°). Structures are proved as follows. α-1-*Naphthylethyl bromide* (prep. from the carbinol by PBr_3 in Et_2O at −10°), unstable, m.p. 37—40°, with $CHNa(CO_2Et)_2$ in EtOH gives an ester, whence by hydrolysis and heating at 160—180° 1-$C_{10}H_7{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2H$ (90%), m.p. 108—110°, is obtained. The Arndt–Eistert procedure then yields γ-1-*naphthylvaleric acid* (68%), m.p. 78—80°, the chloride of which is cyclised ($SnCl_4$–C_6H_6) to 1-*keto*-4-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (IV) (91%), m.p. 81·5—83°. MgMeI converts (IV) into a carbinol, which with Pd–C at 300—320° gives 1 : 4-dimethylphenanthrene, m.p. 50—51·5° (lit., 50—51°, 77°) [picrate, m.p. 143—143·5° (lit., 143·5°, 155°)]. Zn–Hg–HCl–AcOH–PhMe and dehydrogenation convert (IV) into (I). The product from (IV) and MgEtBr–Et_2O treated with Pd–C at 300—320° gives 4-*methyl*-1-*ethylphenanthrene*, an oil (*picrate*, m.p. 104—106°), obtained also by Clemmensen reduction of (II). PhEt, $(CH_2{\cdot}CO)_2O$, and $AlCl_3$ at <0° and then at room temp. give *p*-$C_6H_4Et{\cdot}CO{\cdot}[CH_2]_2{\cdot}CO_2H$ (57%), new m.p. 107—109°, reduced (Martin–Clemmensen) to *p*-$C_6H_4Et{\cdot}[CH_2]_3{\cdot}CO_2H$, new m.p. 72·5—74°, which yields ($SOCl_2$–C_5H_5N; then $AlCl_3$–CS_2 at <0°) 1-keto-7-ethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (87%), b.p. 108—110°/0·6 mm. With NaOMe and $Me_2C_2O_4$ in C_6H_6–N_2 this gives *Me* 1-*keto*-7-*ethyl*-1 : 2 : 3 : 4-*tetrahydro*-2-*naphthylglyoxylate* (82%), m.p. 35·5—37°, which with powdered soft glass at 190—200° gives CO and *Me* 1-*keto*-7-*ethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-2-*carboxylate* (85%), b.p. 168—170°/1·5 mm. Condensation with Na–Br·$[CH_2]_3{\cdot}CO_2Me$–C_6H_6 and later hydrolysis by conc. HCl–AcOH gives γ-1-*keto*-7-*ethyl*- (68%), m.p. 74—75·5°, reduced (Martin–Clemmensen) to γ-7-*ethyl*-1 : 2 : 3 : 4-*tetrahydro*-2-*naphthylbutyric acid* (V), m.p. 108·5—110°. The Me ester (prep. by CH_2N_2) of (V) is dehydrogenated by Pd–C at 235—255° and then hydrolysed to to γ-7-*ethyl*-2-*naphthylbutyric acid* (90%), m.p. 105·5—106·5°. Conversion thereof by PCl_5 in C_6H_6 into the chloride and cyclisation ($SnCl_4$) gives 4-*keto*-6-*ethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (80%), m.p. 52·5—53·5°, whence MgMeI and later Pd–C yields 5-methyl-3-ethylphenanthrene [picrate, new m.p. 113·5—115°; *s*-$C_6H_3(NO_2)_3$, new m.p. 127—128°, and 1 : 2 : 4 : 6-$C_6H_2Me(NO_2)_3$ compound, m.p. 78—79·5°], also obtained by reduction of (III). R. S. C.

Biochemistry of filamentous fungi. VI. Mycelial constituents of *Oospora sulphureo-ochracea*. Trimethylsulochrin and its fission products. H. Nishikawa (Bull. Agric. Chem. Soc. Japan, 1940, **16**, 97—99; cf. A., 1940, II, 92).—Repeated methylation (Me_2SO_4) of sulochrin [Me 2 : 6 : 4′-trihydroxy-6′-methoxy-4-methylbenzophenone-2′-carboxylate] yields *trimethylsulochrin* (I), m.p. 157°, which with conc. H_2SO_4 at 100° (bath) gives dimethyl-*p*-orsellinic acid and Me dimethyl-α-resorcylate. Hydrolysis (KOH–MeOH) of (I) yields 2 : 6 : 4′ : 6′-*tetramethoxy*-4-*methylbenzophenone*-2′-*carboxylic acid*, m.p. 194°. J. N. A.

Lignin and related compounds. XLVIII. Identification of vanillin and vanilloyl methyl ketone as ethanolysis products from spruce wood. L. Brickman, W. L. Hawkins, and H. Hibbert (J. Amer. Chem. Soc., 1940, **62**, 2149—2154; cf. A., 1940, II, 254).—Separation of vanillin and *vanilloyl Me ketone* [4-*hydroxy*-3-*methoxyphenyl*

Me diketone] (I) from the ethanolysis products from spruce wood by methods involving distillation and fractionation of 2 : 4-dinitrophenylhydrazones is detailed. (I), m.p. 72—73°, b.p. 125°/0·2 mm., gives a *quinoxaline* derivative, m.p. 162—163°, *mono-*, m.p. 215—216°, and *di-semicarbazone*, m.p. 241°, and 2 : 4-*dinitrophenylhydrazone*, m.p. 226—227° (*Me ether*, m.p. 194—195°). 3 : 4 : 1-$(OMe)_2C_6H_3$·COMe, HCO_2Et, and Na wire in C_6H_6 give *veratroylacetaldehyde*, an oil (Na salt; 2 : 4-*dinitrophenylhydrazone*, m.p. 189—190°). Addition of 3 : 4 : 1-$OMe·C_6H_3(OH)·CO·CHMe·OH$ to $CuSO_4$ in aq. C_5H_5N at 100° gives (I), but other methods of synthesis failed. (I) may form one member of an oxidation–reduction system functioning in plant respiration.

R. S. C.

Preparation of 4 : 4′-dicyanodiphenyl and diphenyl diketones. (Misses) C. de Milt and M. Sartor (J. Amer. Chem. Soc., 1940, **62**, 1954—1955). —$(p\text{-}CN·C_6H_4)_2$ [obtained in 66% yield from neutralised $(p\text{-}N_2Cl·C_6H_4)_2$ (1 mol.), $NiCl_3$ (1 mol.), and KCN (4 mols.)] with MgRCl gives ketimine hydrochlorides, hydrolysed by boiling, very dil. AcOH to 4 : 4′-dibenzoyl-, m.p. 218° (*dioxime*, m.p. 247°), *-di*(*phenylacetyl*)-, m.p. 208—210° (*dioxime* m.p. 202—205°), and *-dipropionyl-diphenyl*, m.p. 163—165° (*dioxime*, m.p. 226—229°).

R. S. C.

Substances with odour of violets. VII. Synthetic problems in the irone series. Synthesis of 3 : 5 : 5-trimethyl*cyclo*heptanone. L. Ruzicka, H. Schinz, and C. F. Seidel (Helv. Chim. Acta, 1940, **23**, 935—941; cf. A., 1935, 672).—Addition of dihydro*iso*phorone and *iso*amyl formate to NaOEt under Et_2O yields hydroxymethylenedihydro*iso*phorone, b.p. 99—101°/13 mm., converted by successive oxidation with $KMnO_4$–NaOH, esterification with conc. H_2SO_4 and MeOH, and reduction by Na in abs. EtOH into βδδ-*trimethylhexane-αζ-diol*, b.p. 150°/12 mm. This is converted by HBr at 120—130° into the corresponding *dibromide*, b.p. 135°/12 mm., which gives the *dinitrile*, b.p. 144—145°/0·3 mm. The dry Th salt of the dicarboxylic acid when distilled in a vac. yields 3 : 5 : 5-trimethyl*cyclo*heptanone, b.p. 87°/11 mm. (*semicarbazone*, m.p. 187—189°; *p*-nitrophenylhydrazone, m.p. 153—154°; picrate, m.p. 212—213°, of the aminoguanidine compound).

H. W.

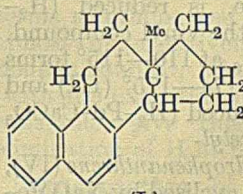
[Attempted] synthesis of Wieland's $C_{13}H_{20}O_6$ acid from bile acids. S. K. Ranganathan (Current Sci., 1940, **9**, 276—277; cf. Wieland *et al.*, A., 1933, 609; Baker *et al.*, *ibid.*, 935).—Et aconitate, $CH_2(CO_2Et)_2$, and a trace of EtOH-free NaOEt (no solvent) give Et *n*-butane-ααβγδ-pentacarboxylate, b.p. 195°/3 mm., hydrolysis and decarboxylation of which affords *meso-* (I), m.p. 189°, and *dl-*, m.p. 236°, -butane-αβγδ-tetracarboxylic acid. The Et ester, b.p. 180°/2 mm., of (I) is cyclised to Et_3 *cyclo*pentanone-2 : 3 : 4-tricarboxylate, b.p. 171°/2 mm. (hydrolysed to *cyclo*pentanone-3 : 4-dicarboxylic acid), the K derivative of which with $CHMeBr·[CH_2]_2·CO_2Et$ (excess) yields Et γ-2-keto-1 : 4 : 5-tricarbethoxy-*cyclo*pentylvalerate (II), b.p. 218°/2 mm. Attempted hydrolysis, with or without decarboxylation, of (II) was unsuccessful. Et β-methylbutane-αβγγδ-pentacarboxylate, b.p. 207°/3 mm., affords β-methylbutane-αβγδ-tetracarboxylic acid, m.p. 193° (anhydride, m.p. 187°), the Et ester, b.p. 186°/2 mm., of which is cyclised to Et_3 3-methyl*cyclo*pentanone-2 : 3 : 4-tricarboxylate, b.p. 176—178°/2 mm.

A. Li.

Asymmetry of the aliphatic nitro-group. Resolution of 9-nitro-2-benzoylfluorene. F. E. Ray and S. Palinchak (J. Amer. Chem. Soc., 1940, **62**, 2109—2113).—The *aci*-form (I) of 9-nitro-2-benzoylfluorene is resolvable only when the lone pair of electrons on $C_{(9)}$ is co-ordinated with a solvent mol. The *K* salt, prepared (83—88%) from 2-benzoylfluorene, KOEt, and $EtNO_3$ in EtOH–Et_2O, is stable when dry, but in solution gives 2-benzoylfluorenone (II) and HNO_2, and with aq. acid gives (I), yellow, m.p. 80—84° (decomp.). In boiling EtOH (I) gives a red dimeride, 9 : 9′-*dinitro*-2 : 2′-*dibenzoyl*-9 : 9′-*difluorenyl* (III), m.p. 135—137°. The menthyl ester of (I) is obtained as an oil, $[\alpha]_D^{24}$ −218° in EtOH, containing EtOH, removal of which causes decomp. to menthol, (II), and (III). The K salt gives the *brucine* salt, + EtOH (IV), sinters at 160°, m.p. 175—185° (decomp.). When this is treated with KOH–EtOH, the freshly prepared mixture has $[\alpha]_D$ −65°, changing in 30 hr. to the $[\alpha]_D$ of brucine; the difference (18°) is the approx. $[\alpha]_D$ of the ion of (I). When aq. KOH is used, racemisation occurs at once and there is no change in α. When KOAc–EtOH is added to (IV), there is an immediate change in [α], probably due to replacement of the co-ordinated EtOH by KOAc; later the inactive K salt is pptd. Dil. HCl at −10° ppts. inactive (I) from (IV), but in AcOH (IV) gives $[\alpha]_D$ +5·54° → −4·04° in 0·5 hr.; probably active (I) exists temporarily, co-ordinated with AcOH. With Br–$CHCl_3$, (IV) gives an active bromide, which rapidly racemises and decomposes. Kinetic studies show that racemisation and decomp. of (IV) occur simultaneously in $CHCl_3$ or BuOH (co-ordinates), but in C_5H_5N racemisation at first occurs alone. 9-Nitro-2 : 7-dibenzoylfluorene (V), m.p. 194—195°, gives a *K* salt, solvent-free and +BuOH, and thence a brucine salt, [α] +67° in $CHCl_3$, +78° in C_5H_5N, unchanged for 2 hr. (later decomp.), the symmetry of (V) accounting for absence of resolution. Prep. (Friedel–Crafts) of (V) gives also some (?) 2 : 3-dibenzoylfluorene, m.p. 119—120°.

R. S. C.

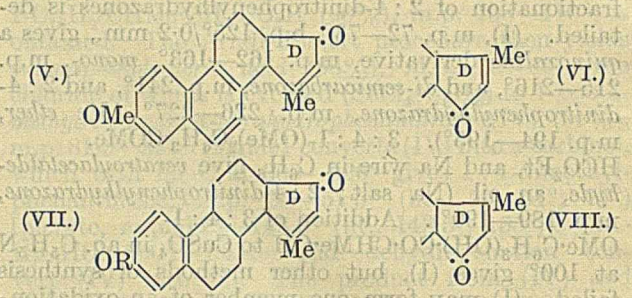
Synthesis of *cis-* and *trans*-17-equilenone. W. E. Bachmann and A. L. Wilds (J. Amer. Chem. Soc., 1940, **62**, 2084—2088; cf. A., 1940, II, 225).—Equilenin derivatives are named on the basis of equilenane for (I). 1-Keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (improved prep.), $Me_2C_2O_4$, and NaOMe in C_6H_6–N_2 give *Me* 1-*keto*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-2-*glyoxylate*, ? dimorphic, m.p. 90—91° and 106—108°, which in presence of powdered glass at 180—200° gives *Me* 1-*keto*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-2-*carboxylate*, m.p. 88—90° after softening. With MeOH–NaOMe and MeI in boiling C_6H_6 this gives *Me* 1-*keto*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-



(I.)

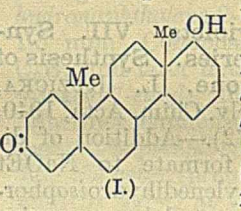
2-*carboxylate* (I), m.p. 79·5—80·5°, which by the Reformatsky reaction gives *Me*$_2$ 1-*hydroxy*-2-*methyl*-1 : 2 : 3 : 4 - *tetrahydrophenanthrene* - 2 - *carboxylate* - 1 - *acetate*, m.p. 131—133° (with 40% KOH gives 1-keto-2-methyl-1: 2 : 3 : 4-tetrahydrophenanthrene). Dehydration then yields anti-2-*carboxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*phenanthrylideneacetic* acid (II), m.p. 220—221° [*Me*$_2$ ester (III), m.p. 110—111°], and the *anhydride*, m.p. 188·5—189·5°, of the *syn*-acid. Boiling NaOH–MeOH–H_2O converts (III) into the 2-Me$_1$ ester, m.p. 197—199°, which with $KMnO_4$–H_2O–C_6H_6 at 0° gives (I), thus proving that the Me has not migrated. 2% Na–Hg in H_2O reduces the K salt of (II) to 2-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-2-*carboxylic*-1-*acetic acid*, stereoisomeric α-, m.p. 228—229° [*Me*$_2$ ester (IV), m.p. 106—107°], and β-*form* (V), m.p. (+ solvent) 160—165° (gas), (anhyd.) 182—183°. With NaOH–MeOH–H_2O, (IV) gives the 2-*Me*$_1$ α-ester, m.p. 133—134°, which yields (Arndt–Eistert) *Me* α-2-*carbomethoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-1-*propionate*, m.p. 98—99° [derived dicarboxylic *acid* (VI), m.p. 213—213·5°], cyclised by NaOMe–C_6H_6–N_2 to *Me* α-dl-17-*equilenone*-16-*carboxylate*, m.p. 124—125°, sublimes at 200°/0·4 mm. Boiling conc. HCl–AcOH–H_2O–N_2 then gives α-dl-17-*equilenone* (VII), m.p. 100—101° (*picrate*, m.p. 109·5—110·5°), obtained also less well from (VI) by Ac_2O or by pyrolysis of the Pb salt, and converted by reduction and dehydrogenation into 1 : 2-*cyclo*pentenophenanthrene. Similarly, (V) yields the 2-*Me*$_1$ ester, m.p. 156—158°, *Me* β-dl-17-*equilenone*-16-*carboxylate*, m.p. 134—134·5° (vac.), and β-dl-17-*equilenone* (VIII), m.p. 188·5—189·5° (vac.). (VII) and (VIII) do not induce œstrus in 0·5-mg. doses. R. S. C.

Steroids and sex hormones. LXIII. Attempted synthesis of œstrogens with use of αβ-diacetylethylene. M. W. Goldberg and P. Müller (Helv. Chim. Acta, 1940, **23**, 831—840).—Contrary to Dane *et al.* (A., 1937, II, 500), 1-acetylenyl-1 : 2 : 3 : 4-tetrahydro-1-naphthol (I), b.p. 104°/0·2 mm., is the sole product of the action of CH:C·MgBr (II) on 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene. Partial reduction (H_2–Pd–$CaCO_3$–EtOH) of it gives 1-vinyl-1 : 2 : 3 : 4-tetrahydro-1-naphthol, dehydrated by Al_2O_3 at 160°/high vac. to 1-$C_{10}H_7$Et (picrate, m.p. 98°). Under identical conditions (I) is dehydrogenated to 1-acetylenyl-3 : 4-dihydronaphthalene, b.p. 118°/10 mm. 6-Methoxy-1-acetylenyl-3 : 4-dihydronaphthalene, b.p. 120°/0·1 mm., obtained by distilling in a high vac. the product of the interaction of (II) and 1-keto-6-methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene, is reduced (H_2–Pd–$CaCO_3$ in EtOH–dioxan) to the vinyl compound, which with (:CHAc)$_2$ in abs. C_6H_6 at 110—115° forms isomeric *adducts*, $C_{19}H_{22}O_3$, m.p. 174—175° (III) and 107—108°, both of which are reduced (H_2–Pd–$CaCO_3$ in EtOAc) to 7-*methoxy*-1 : 2-*diacetyl*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydrophenanthrene* (IV), m.p. 127—128°. (III) in C_6H_6 is cyclised by NaOMe–MeOH to 15-*methyl*-15-*dehydro*-x-*norequilenin Me ether* (V) or (VI), m.p. 116—117°, whereas (IV) yields 15-*methyl*-15-*dehydro*-x-*norœstrone Me ether* (VII; R = Me), m.p. 181—183° (*oxime*, m.p. 185—186°), or its isomeride (VIII). (VII) or (VIII) is hydrolysed to 15-*methyl*-15-*dehydro*-x-*norœstrone*, m.p. ~180°, or



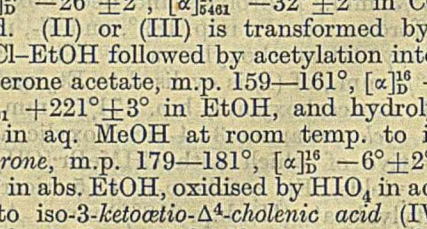
its isomeride [(VII) and (VIII) with R = H] which has œstrogenic activity. H. W.

Steroids and sex hormones. LXIV. Preparation of *D*-homodihydrotestosterone. M. W. Goldberg and R. Monnier (Helv. Chim. Acta, 1940, **23**, 840—845).—3-*trans*-Acetoxy-*D*-homoandrostan-17*a*-one is reduced (H_2–PtO_2 in AcOH at room temp.) to D-*homoandrostane*-3-trans-17a-*diol* 3-*acetate*, m.p. 160—167° (mixture of *cis*–*trans* isomerides at $C_{(17a)}$), which with BzCl in C_5H_5N affords the 17a-*benzoate*, m.p. 201—202°. This is hydrolysed by $KHCO_3$ in MeOH to D-*homoandrostane*-3-trans-17a-*diol* 17a-*benzoate*, m.p. 230—233°, oxidised (CrO_3 in AcOH) to D-*homoandrostan*-17a-*ol*-3-*one* 17a-*benzoate*, m.p. 194—195°, hydrolysed (KOH–MeOH) to D-*homoandrostan*-17a-*ol*-3-*one* (D-*homodihydrotestosterone*) (I), m.p. 187—189°. All m.p. are corr. (vac.). The physiological activity of (I) is equal to that of dihydrotestosterone. H. W.



(I.)

Constituents of the adrenal cortex and related substances. XL. 17-*iso*Deoxycorticosterone. C. W. Shoppee (Helv. Chim. Acta, 1940, **23**, 925—934).—Δ^4-Pregnene-17β : 20 : 21-triol-3-one is converted by Ac_2O and C_5H_5N at room temp. into the 20 : 21-*diacetate* (I), m.p. 170—172° and, after re-



(II.)

solidification, m.p. 193—194°. With Zn dust in boiling C_5H_5N, (I) gives 17-iso*deoxycorticosterone acetate* (II), m.p. 137—138°, $[\alpha]_D^{16}$ −21°±3° in $COMe_2$, whereas in boiling PhMe a *polymorph* (III), m.p. 174°, $[\alpha]_D^{17}$ −26°±2°, $[\alpha]_{5461}^{17}$ −32°±2° in $COMe_2$, is produced. (II) or (III) is transformed by boiling conc. HCl–EtOH followed by acetylation into deoxycorticosterone acetate, m.p. 159—161°, $[\alpha]_D^{16}$ +182°±4°, $[\alpha]_{5461}^{16}$ +221°±3° in EtOH, and hydrolysed by $KHCO_3$ in aq. MeOH at room temp. to iso*deoxycorticosterone*, m.p. 179—181°, $[\alpha]_D^{16}$ −6°±2°, $[\alpha]_{5461}^{16}$ −9°±2° in abs. EtOH, oxidised by HIO_4 in aq. MeOH at 20° to iso-3-*ketoœtio*-Δ^4-*cholenic acid* (IV), m.p. 194—196°, $[\alpha]_D^{18}$ +47·5°±2°, $[\alpha]_{5461}^{19}$ +54°±3° in $COMe_2$ [*Me* ester (V), m.p. 115—116°, $[\alpha]_D^{18}$ +36°±2°,

$[\alpha]^{19}_{5461}$ +46°±3° in $COMe_2$]. Isomerisation does not occur when (IV) is heated with conc. HCl–AcOH (1 : 9) at 100° or when (V) is boiled with KOH–MeOH. M.p. are corr. H. W.

Nature of the by-product in the synthesis of vitamin-K_1. M. Tishler, L. F. Fieser, and N. L. Wendler (J. Amer. Chem. Soc., 1940, **62**, 1982—1991).—The by-product isomeric with 2-methyl-3-phytyl-1 : 4-naphthaquinol (I) (A., 1939, II, 513; 1940, II, 96) is 2-*methyl*-2-*phytyl*-2 : 3-*dihydro*-1 : 4-*naphthaquinone* (II). Figures given in parentheses below are log $E_{mol.}$. Variations in the synthesis lead to 15—24% of (I) and 20—22% of (II). (II) is not formed from (I) (cf. *loc. cit.*), since >90% of (I) is recovered after heating with $H_2C_2O_4$ in dioxan for 34 hr. at 75°. (II) is insol. in Claisen's alkali, does not reduce $AgNO_3$–EtOH, gives neither the Furter–Meyer nor the Craven test, absorbs ~2 H_2 in presence of PtO_2, absorbs Br in CCl_4, does not react with CH_2N_2, MgMeBr at 180°, $AlBr_3$, or various other reagents, and is unchanged by HCl–AcOH at 100°. It gives a 2 : 4-*dinitrophenylhydrazone*, m.p. 107—108°, is pyrolysed (best) in boiling decahydronaphthalene and N_2 to vitamin-K_1 (5%) and 2-methyl-1 : 4-naphthaquinol (10%), and has absorption max. at 253 (3·97) and 300 mμ. (3·27). It is oxidised by $Pb(OAc)_4$ or SeO_2. With CrO_3–AcOH at 60—70° it gives 2-*methyl*-2 : 3-*dihydro*-1 : 4-*naphthaquinone*-2-*acetic acid*, m.p. 126°, and ζκξ-trimethylpentadecan-β-one (identified as semicarbazone). It is reduced by $Al(OPr^\beta)_3$–$Pr^\beta OH$–CCl_4–$HgCl_2$ to 1 : 4-*dihydroxy*-2-*methyl*-2-*phytyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. ~40—50° (*diacetate*, an oil; *bis*-2 : 5-*dinitrobenzoate*, *forms*, m.p. 74—75° and 120°; 2 active H), dehydrated by conc. HCl–AcOH at room temp. to a mixture including a little 2-$C_{10}H_7Me$. Vitamin-K_1 with $SnCl_2$ in boiling HCl–AcOH gives the *naphthotocopherol* (III), b.p. 155° (liquid)/10^{-5} mm. [p-*nitrobenzoate*, m.p. 84—85°; absorption max. 246 (4·54) and ~320 mμ. (3·6)]; this is oxidised by $FeCl_3$–H_2O–MeOH–Et_2O to 2-*methyl*-3-γ-*hydroxy*-βγ-*dihydrophytyl*-1 : 4-*naphthaquinone* (IV) [*quinol di-* (V), m.p. ~20°, and *tri-acetate*, m.p. 65°]. 2 : 3 : 1 : 4-$C_{10}H_4Me_2(OH)_2$, phytol, and $H_2C_2O_4$ in dioxan at 75° give 2 : 3-*dimethyl*-2-*phytyl*-2 : 3-*dihydro*-1 : 4-*naphthaquinone*, b.p. 140—150°/10^{-4} mm. [absorption max. 253 (3·96) and ~300 mμ. (3·2); consumes 2 MgMeI; absorbs 4 H with $Al(OPr^\beta)_3$]. The by-product, $C_{19}H_{20}O_2$, m.p. 73° (A., 1940, II, 17) is probably 2-*methyl*-2-βγ-*dimethylbutenyl*-2 : 3-*dihydro*-1 : 4-*naphthaquinone*; it has absorption max. at 253 (3·98) and 298 mμ. (3·31) [cf. (II)]; its solubility in alkali is ascribed to enolisation. The following absorption max. are recorded: 2-*methyl*-1 : 4-*naphthaquinol* Et_1 *ether*, m.p. 115—116°, 243 (4·26) and ~320 mμ. (3·7); 1-hydroxy-4-keto-1-phenyl-2 : 3-dimethyl-1 : 4-dihydronaphthalene (Crawford, A., 1940, II, 82) 251 (4·07) and 281 mμ. (3·91); 2-methyl-3-phytyl-, 248 mμ. (4·26), and 2 : 3-diallyl-1 : 4-naphthaquinone, 249 mμ. (4·24); vitamin-K_1 248 mμ. (4·24—4·27) in EtOH. (III) has vitamin-*E* activity in 25-mg. and -*K* activity in 0·3—0·6-mg. doses (18 hr.); (IV) and (V) have no -*K* activity. (II) has -*K* activity in 5×10^{-5}-g. doses. R. S. C.

Pigments from sea-urchins and syntheses of related compounds. C. Kuroda and H. Ohshima (Proc. Imp. Acad. Tokyo, 1940, **16**, 214—217).—The spines of *Pseudocentrotus depressus* ("Aka-uni") when treated with mineral acid and org. solvent give the pigment *spinochrome-Aka*, sublimes at 285—295°, identified as 2 : 3 : 5 : 7 : 8-*pentahydroxy*-6-*methyl*-1 : 4-*naphthaquinone* (2 : 3 : 7-Me_3 *ether*, m.p. 160°; *penta-acetate*, m.p. 182°). The spines of *Heterocentrotus mammilatus* and *Anthocidaris crassispina* give the pigments *spinochrome-F*, m.p. 229°, and -*M*, m.p. 193°, respectively. 2 : 3 : 1 : 4-$(OMe)_2C_6H_2(OH)_2$ with methylmaleic anhydride and $AlCl_3$–NaCl gives 2 : 3 : 5 : 8-*tetrahydroxy*-6-*methyl*-1 : 4-*naphthaquinone*, m.p. 230° (*tetra-acetate*, m.p. 178—179°; 2 : 3-Me_2 *ether*, m.p. 117°); similarly, $(CH{\cdot}CO)_2O$ gives 2 : 3 : 5 : 8-tetrahydroxy-1 : 4-naphthaquinone, m.p. 265° (cf. A., 1939, II, 513) (*tetra-acetate*, m.p. 207°; 2 : 3-Me_2 *ether*, m.p. 129°). E. W. W.

Preparation of halogenoaminoanthraquinones.—See B., 1940, 726.

Application of the diene synthesis to terpenoid compounds. Eucarvone and maleic anhydride. T. F. West (J.C.S., 1940, 1162—1164).—Eucarvone [2 : 4-*dinitrophenylhydrazone*, m.p. 152—153° (decomp.)] with $(CH{\cdot}CO)_2O$ forms an *adduct*, $C_{14}H_{16}O_4$, m.p. 165—167° (Me_2, m.p. 102—103°, and Et_2 esters, m.p. 93—95°). These results invalidate one of the arguments used by Goodway and West (A., 1939, II, 79) to criticise Rydon's seven-membered ring structure for caryophyllene. F. R. S.

Dehydrogenation. IV. Catalytic disproportionation and dehydrogenation of some terpenes and terpene ketones. R. P. Linstead, K. O. A. Michaelis, and S. L. S. Thomas (J.C.S., 1940, 1139—1147).—The results of the action of Pd and Pt catalysts on the compounds are in harmony with the known structures and under mild conditions give clear evidence of the skeleton structure and the no. of double bonds. All the unsaturated substances undergo disproportionation into aromatic and saturated compounds at comparatively low temp. (140—205°), the proportions formed being those predictable from the no. of double bonds in the original terpene. Limonene gives a mixture of *p*-cymene and *p*-menthane in mol. ratio ~2 : 0·9 at 140° (Pt–C). Pinene at 156° with Pt–C affords equimol. proportions of *p*-cymene and pinane. Cadinene at 180° (Pt–C) yields cadalene and tetrahydrocadinene, but under vigorous conditions 1 : 6-$C_{10}H_6Me_2$ is obtained. At 205° with Pd–C, selinene is converted into eudalene and tetrahydroselinene. Pulegone with Pd–C at 175° forms menthone and thymol. Carvone is isomerised almost quantitatively to carvacrol. All the compounds studied, whether unsaturated or saturated (with the exception of camphor, which is completely resistant), give their aromatic counterparts with elimination of H at higher temp. F. R. S.

Mutarotation of α-nitrocamphor in chlorobenzene solution.—See A., 1940, I, 416.

Triterpene resinols and related acids. IX. Oxidation of α-amyradienyl acetate. E. S. Ewen and F. S. Spring. **X. β-Amyradienol.** C. W.

PICARD and F. S. SPRING (J.C.S., 1940, 1196—1198, 1198—1202).—IX. Ozonisation of α-amyradienyl acetate (I) at 0° gives a mixture of α-amyrenonyl acetate and epi(iso)-*α-amyrenonyl acetate* (II), $C_{32}H_{50}O_3$, m.p. 199—200°, $[\alpha]_D^{20}$ +56° in $CHCl_3$, which is reduced (Na–C_5H_{11}·OH) followed by treatment with Ac_2O to (I). Ozonisation of (I) at 22° affords a mixture containing an amorphous acid fraction, (II), and *α-amyradionyl acetate*, $C_{32}H_{50}O_4$, m.p. 257—258°, $[\alpha]_D^{21}$ +120° in $CHCl_3$.

X. Prolonged treatment of β-amyrenonyl benzoate, $[\alpha]_D^{20}$ +156° in $CHCl_3$, with KOH (cf. Beynon *et al.*, A., 1938, II, 416; Ruzicka *et al.*, A., 1939, II, 330) gives a low-melting β-amyrenonol, probably contaminated with an isomeric αβ-unsaturated ketone. Purification cannot be achieved by crystallisation but is effected by acetylation, pure β-amyrenonyl acetate, $[\alpha]_D^{20}$ +116° in $CHCl_3$, then being readily isolated. Reduction of β-amyrenonol with Na–EtOH gives an addition–reduction *compound*, $C_{32}H_{56}O_2$, m.p. 236·5—239·5°, and with Na–C_5H_{11}·OH affords a similar *compound*, $C_{35}H_{62}O_3$, m.p. 238—239°; with Ac_2O these compounds yield β-amyradienyl acetate. Hydrolysis of the latter leads to *β-amyradienol*, m.p. 213·5—214·5°, $[\alpha]_D^{20}$ +319° in $CHCl_3$ (*benzoate*, m.p. 250°, $[\alpha]_D^{20}$ +317° in $CHCl_3$), which is oxidised (AcOH–CrO_3) to *β-amyradienone*, m.p. 206—208°. The benzoate on reduction with Na–C_5H_{11}·OH and treatment with Ac_2O gives an *acetate*, $C_{35}H_{62}O_3$, m.p. 223—224°, which is a mixed crystal containing β-amyradienyl acetate and β-amyrenyl acetate and corresponds with the "dehydro-β-amyrenyl acetate *b*" of Simpson (cf. A., 1940, II, 137). F. R. S.

Constituents of *Helenium* species. IV. The compound, m.p. 233—234°, obtained from *H. tenuifolium*. E. P. CLARK (J. Amer. Chem. Soc., 1940, **62**, 2154—2156; cf. A., 1940, II, 184).—Rast's method of determining mol. wt. is unreliable in the tenulin series. The substance, $C_{16}H_{22}O_5$, m.p. 233—234° (A., 1939, II, 435), is really *tenulin β-methoxyethyl ether*, $C_{19}H_{26}O_6$. It gives an *ethoxyacetyl* derivative, m.p. 119°, analysis of which indicates the mol. wt. With H_2O_2–NaOH–H_2O–$COMe_2$ or $KMnO_4$–$COMe_2$–H_2O it gives an *acid*, $C_{19}H_{26}O_9$, m.p. 239° (*Me* ester, m.p. 283°), hydrolysed by boiling, dil. acid to OMe·$[CH_2]_2$·OH and acetyltenulinic acid, m.p. 239° or (? anhyd.) 319°. The OH and Ac of tenulin are sterically proximate. R. S. C.

Constituents of the leaves of certain *Leucadendron* species. III. Oxidations of leucodrin derivatives with periodic acid and lead tetra-acetate. W. S. RAPSON (J.C.S., 1940, 1271—1274).—Oxidation of leucodrin Me ether (I) in the lactonic form in acid media with either $Pb(OAc)_4$ or HIO_4 results in absorption of 2 equivs. of O and formation of 1 equiv. of CH_2O. In 0·1N-NaOH, oxidation of (I) or leucodrin (II) with excess of HIO_4 leads to absorption of 8 equivs. of O and gives 1 equiv. of CH_2O and anisylsuccinic acid in optically active form; with $Pb(OAc)_4$ and (I), 15 equivs. of O are absorbed. Oxidation of leucodrin Me_4 ether with $Pb(OAc)_4$ in alkaline solution affords a monobasic *acid*, $C_{18}H_{26}O_8$ (+H_2O), m.p. 73—76·5°, and the Br-ether similarly gives a substance, $C_{18}H_{25}O_8Br$, m.p. 178° (decomp.). Mutarotation of (II) in aq. or aq.-EtOH media has not been observed, indicating that the lactone ring systems are fairly stable; acidification of alkaline solutions of (I) or (II) causes the [α] to revert during 80—100 hr. to that of the corresponding lactonic forms. Interpretation of the results in terms of a full structure for (II) has not been possible but the partial structure *p*-OH·C_6H_4·CH(CH_2·CO·O·)·$C_5H_8O_3$·CO·O· is suggested. F. R. S.

Hydroxy-lactone from *d*-pimaric acid. E. E. FLECK and S. PALKIN (J. Amer. Chem. Soc., 1940, **62**, 2044—2047).—*d*-Pimaric acid (I) and conc. H_2SO_4 at −20° to −30° give a saturated OH-*lactone*, $C_{20}H_{32}O_3$, m.p. 181—182°, b.p 200—250° (bath)/1 mm., $[\alpha]_D^{20}$ −4° in abs. EtOH, only partly hydrolysed by NaOH–EtOH but converted by KOH–Bu^{a}OH into the corresponding *acid*, +0·66H_2O, m.p. 150—151°, and anhyd. (*Me* ester, m.p. 156—157°). Known tests are used to detect dihydro-*l*-pimaric and -abietic and *l*-abietic (II) acid in (I). When freed (method described) from (II) but still containing H_2-acids, (I) has m.p. 218—219°, $[\alpha]_D^{20}$ +75° in abs. EtOH. (I) has never been obtained pure. On the assumption that H_2SO_4 converts (I) into 50% each of acid and neutral material, and by isolation of the latter, it is shown that >10% and >14% of (I) is present in the oleoresin and rosin of *P. palustris* and *P. caribæa*, respectively. Analysis of mixtures of (I) and *l*-pimaric acid gives slightly high results (within 5—10%) for (I). R. S. C.

Kikyo root. X. Constitution of platycodigenin. Properties of double linking and oxygen atoms of platycodigenin. M. TSUJIMOTO (J. Agric. Chem. Soc. Japan, 1940, **16**, 613—620; cf. A., 1939, II, 556).—Platycodigenin contains one double linking which cannot be reduced catalytically, and of the 7 O, two are present as CO_2H, and four as OH. J. N. A.

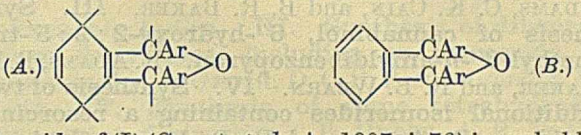
Lignin and related compounds. I. Hydrogenation of soft-wood lignin. Y. HACHIHAMA, S. ZYODAI, and M. UMEZU (J. Soc. Chem. Ind. Japan, 1940, **43**, 127B).—Lignin (from *Picea jezoensis*) was hydrogenated (NiO catalyst in dioxan; 35—55 hr. at 260—270°/95—230 atm.); the Et_2O-sol. products included 1 : 4 : 3-$C_6H_3Pr(OH)$·OMe (I), 1 : 2 : 4-$C_6H_3(OH)_2$·CO_2H, *o*-$C_6H_4(OH)_2$, and *p*-OH·C_6H_4·CO_2H. (I) is an important constituent of soft-wood lignin. R. T.

Lignin. XXXIV. Formation of vanillin from spruce lignin. K. FREUDENBERG, W. LAUTSCH, and K. ENGLER (Ber., 1940, **73**, [*B*], 167—171).—Spruce lignin (I), or, better, deresinated spruce-wood powder, in 2N-NaOH with $PhNO_2$ at 160° (3 hr.) gives, after removal of $PhNO_2$, NH_2Ph, and Ph_2N_2O, neutralisation and treatment with $NaHCO_3$, and extraction with C_6H_6, vanillin (II) ≡ 20—25% of original (I). Other products include phenols, vanillic and veratric acids, AcOH, $H_2C_2O_4$, and *vanillin-5-carboxylic acid*, m.p. 250° (decomp.); taking account of these, 50% of the original (I) is isolated as (II) or its breakdown products. Sulphite waste liquor may be successfully used as a source of (I) and thus of (II). E. W. W.

Esters of 2-furylacetic acid. J. F. RYAN, J. PLUCKER, tert., and E. D. AMSTUTZ (J. Amer. Chem. Soc., 1940, **62**, 2037).—*Me*, b.p. 87—88°/21 mm., *Et*, b.p. 88°/15 mm., *Pr*$^{\alpha}$, b.p. 115—116°/34 mm., Pr$^{\beta}$, b.p. 92—93°/17 mm., *Bu*$^{\alpha}$, b.p. 110—111°/13 mm., and *Bu*$^{\beta}$ 2-*furylacetate*, b.p. 112—113°/21 mm., are prepared. R. S. C.

***N'*-Aryl-*N*-alkylfuramidines.** W. M. DEGNAN and F. B. POPE (J. Amer. Chem. Soc., 1940, **62**, 1960—1962).—Heating 2-furoyl chloride with NH_2R and dil. KOH (15—20% excess) gives 2-*furo*-n-*propyl*-, m.p. 39—40°, -n-, m.p. 40—41°, -sec.-, m.p. 122—123°, and -tert.-*butyl*-, m.p. 99°, -n-*amyl*-, m.p. 31—32°, -β-*amyl*-, m.p. 48—56°, -β-*methyl*-sec.-*butyl*-, m.p. 68—69°, -iso*amyl*, m.p. 53—54°, -δ-*methyl*-β-*amyl*-, m.p. 54—55°, -cyclo*hexyl*-, m.p. 108·5—109°, and -β-*ethyl*-n-*hexyl*-, an oil, -*amide*. Addition of the appropriate amide and then of NH_2R' to PCl_5 in C_6H_6 gives N'-*phenyl*-N-n-*propyl*-, m.p. 63·5—64° (139—140°), -N-n-*butyl*-, m.p. 67—68° (141—142°), and -N-cyclo*hexyl*-2-*furamidine*, m.p. 78·5—79° (174°), N'-p-*phenetyl*-N-n-*propyl*-, m.p. 81·0—81·5° [(+H_2O) 78·5—79·5°], -N-n-*butyl*-, m.p. 65·5—66° [(+H_2O) 78·5—79·5°, (anhyd.) 135—136°], -N-sec.-*butyl*-, m.p. 52·0—52·5° (132—133°), -N-n-*amyl*-, m.p. 61·0—61·5° [(+H_2O) 75—76°], -N-β-*amyl*-, m.p. 75—76° (125·5—126·5°), -N-iso*amyl*-, m.p. 77° (120—121°), -N-δ-*methyl*-β-*amyl*-, m.p. 77° (120—121°), and -N-cyclo*hexyl*-2-*furamidine*, m.p. 108—109° (170—171°), N'-p-*carbethoxyphenyl*-N-n-*propyl*-, m.p. 86—87° (167—168°), -N-n-*butyl*-, m.p. 75·5—76° (128—129°), and -N-cyclo*hexyl*-2-*furamidine*, m.p. 114—115° (188—189°), N'-α-, m.p. 54·5—55·5° (99—101°), and N'-β-*naphthyl*-N-n-*butyl*-2-*furamidine*, m.p. 61·5—62° (91·5—92.5°). Figures in parentheses are m.p. of the *hydrochlorides*, which are potent local anæsthetics. R. S. C.

Absorption and fluorescence spectra of dihydro*iso*benzfurans and *iso*benzfurans. R. ADAMS and M. H. GOLD (J. Amer. Chem. Soc., 1940, **62**, 2038—2042; cf. A., 1940, II, 280).—*trans*-(*p*-$C_6H_4Ph{\cdot}CH{:})_2$ (I) (modified prep.) and $(CH_2{:}CH)_2$ in C_6H_6 at 100° give 4 : 5-*dixenoyl*cyclo*hexene*, m.p. 267—268°, converted by boiling H_2SO_4–Ac_2O into 1 : 3-*dixenyl*-4 : 7-*dihydroisobenzfuran*, m.p. 238—239° [absorption max. 2440 (4·4), 2720 (4·45), 3620 (4·8), fluorescence max. 4290, 4845, 4965, and 5160 A.] (figures in parentheses are log ϵ), which with Br–NaOAc–AcOH gives o-*dixenoylbenzene*, m.p. 191—192°. With KOH–EtOH–H_2O–C_6H_6–Zn dust this gives 1 : 3-*dixenyl*iso*benzfuran*, m.p. 247—249° [absorption max. 2400 (4·4), 2920 (4·6), 3350 (3·95), and 4360 (4·55), fluorescence max. 5250 A.]. $(CH_2{:}CMe)_2$ and (I) yield similarly 4 : 5-*dixenoyl*-1 : 2-*dimethyl*-cyclo*hexene*, m.p. 280—281° (decomp.), 1 : 3-*dixenyl*-5 : 6-*dimethyl*-iso*benzfuran*, m.p. 245—247° [absorption max. 2440 (4·4), 2960 (4·6), 3400 (4·0), and 4350 (4·6); fluorescence max. 5250 A.], and -4 : 7-*dihydro*-iso*benzfuran*, m.p. 239—241° [absorption max. 2450 (4·4), 2710 (4·45), and 3670 (4·5); fluorescence max. 4290, 4915, 5025, and 5250 A.], and 4 : 5-*dixenoyl*-1 : 3-*dimethylbenzene*, m.p. 218—219°. The following absorption (*a*) and fluorescence max. (*b*) are recorded. 1-3-Diphenyl-4 : 7-dihydro*iso*benzfuran (*a*) 2300 (4·4), 3320 (4·7), 3480 (4·55), (*b*) 3840 and 4050, and -*iso*benzfuran 2610 (4·5), 2700 (4·5), 3100 (3·95), and 4150 (4·45), (*b*) 4860, 1 : 3-diphenyl-5 : 6-dimethyl-4 : 7-dihydro*iso*benzfuran (*a*) 2300 (4·4), 3330 (4·65), and 3490 (4·5), (*b*) 3840, 4080, and 4590, and -*iso*benzfuran (I) (*a*) 2490 (4·3), 2580 (4·4), 2690 (4·5), 2770 (4·55), 3100 (3·95), 4150 (4·4), (*b*) 4860 A. The optical data indicate existence of free radicals [as (*A*) and (*B*)], which is confirmed by the absorption of O_2 by *iso*benzfurans and by addition of αβ-unsaturated CO-compounds preceded by a transitory red colour. The



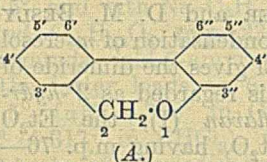
dimeride of (I) (Guyot *et al.*, A., 1907, i, 76) is probably formed by union of 2 mols. of (*B*). M.p. are corr. R. S. C.

Condensation products of phenols and ketones. V. Structure of the dimeric forms of *o-iso*propenylphenols. W. BAKER and D. M. BESLY (J.C.S., 1940, 1103—1106).—Condensation of *m*-cresol with $COMe_2$ in presence of HCl gives the dimeride of 4-*iso*propenyl-*m*-cresol, which is regarded as 2'-*hydroxy*-2 : 4 : 4 : 7 : 4'-*pentamethylflavan* (I), the Et_2O addition product, $C_{20}H_{24}O_2,Et_2O$, having m.p. 76—77°. (I) with Ac_2O forms 2'-*acetoxy*-2 : 4 : 4 : 7 : 4'-*pentamethylflavan*, m.p. 108°; it is oxidised ($KMnO_4$–Ac_2O) to 2 : 4 : 4 : 7-*tetramethylchroman*-2-*carboxylic acid*, m.p. 148—149°. The oxidation and a consideration of the mechanism of its formation lead to the structure assigned. 2-Hydroxy-5-methylacetophenone, C_5H_5N, and *o*-OMe·C_6H_4·COCl followed by HCl give 2-(2'-*methoxybenzoyloxy*)-5-*methylacetophenone*, m.p. 85°, which with K_2CO_3 affords ω-2'-*methoxybenzoyl*-2-*hydroxy*-5-*methylacetophenone*, m.p. 106°, converted by AcOH–NaOAc into 2'-*methoxy*-6-*methylflavone*, m.p. 110°. Hydrolysis (HBr) of this compound leads to 2'-*hydroxy*-6-*methylflavone*, m.p. 255—256° (*Ac* derivative, m.p. 101°). *o*-OH·C_6H_4·COMe, C_5H_5N, and *o*-OMe·C_6H_4·COCl give 2-(2'-*methoxybenzoyloxy*)*acetophenone*, m.p. 79°, similarly successively converted into ω-2'-*methoxybenzoyl*-2-*hydroxyacetophenone*, m.p. 80°, 2'-methoxy- and 2'-hydroxyflavone. The last compound and the 6-Me derivative give mixtures on catalytic reduction. F. R. S.

Isolation of cannabinol, cannabidiol, and quebrachitol from red oil of Minnesota wild hemp. R. ADAMS, D. C. PEASE, and J. H. CLARK (J. Amer. Chem. Soc., 1940, **62**, 2194—2196).—Steam-distillation of marihuana red oil (I) (Adams *et al.*, A., 1940, II, 80), fractional distillation in vac., removal of cannabinol (II) as bisdinitrobenzoate (III) (47%) and later by pyrolysis with C_5H_5N,HCl at 225—230°/75—100 mm., conversion of the non-volatile, alkali-insol. part of the residue by 3 : 5 : 1-$(NO_2)_2C_6H_3{\cdot}CON_3$ into urethanes, and fractional crystallisation and decomp. of the least sol. fraction by NH_3–EtOH, gives cannabinol, m.p. 75—76° (corr.), b.p. 185°/0·5 mm. (lit., an oil) [3 : 5-*dinitrophenylurethane*, m.p. 221—222° (decomp.); *p*-nitrobenzoate, new m.p. 165—166°; *m*-nitrobenzenesulphonate, new m.p. 127—129°; acetate, new m.p. 76—77°]. Ammonolysis of (III)

gives (II), m.p. 66—67° (corr.) (lit., an oil), $[\alpha]_D^{27}$ —125° in EtOH. Extraction of (I) with H_2O gives quebrachitol. R. S. C.

Structure of cannabinol. I. Preparation of an isomeride, 3-hydroxy-6 : 6 : 9-trimethyl-1-*n*-amyl-6-dibenzopyran [4″-hydroxy-2 : 2 : 5′-trimethyl-6″-*n*-amyldibenzopyran]. R. ADAMS, D. C. PEASE, J. H. CLARK, and B. R. BAKER. **II. Synthesis of two isomerides, 4″-hydroxy-2 : 2 : 5′-trimethyl-3″- and -5″-*n*-amyldibenzopyran.** R. ADAMS, C. K. CAIN, and B. R. BAKER. **III. Synthesis of cannabinol, 6″-hydroxy-2 : 2 : 5′-trimethyl-3″-*n*-amyldibenzopyran.** R. ADAMS, B. R. BAKER, and R. B. WEARN. **IV. Synthesis of two additional isomerides containing a resorcinol residue.** R. ADAMS and R. B. BAKER (J. Amer. Chem. Soc., 1940, **62**, 2197—2200, 2201—2204, 2204—2207, 2208—2215).—I. *o*-$C_6H_4Br{\cdot}CO_2H$ (I), *m*-$C_6H_4(OH)_2$ (II), $CuSO_4$, and aq. NaOH give 4″-hydroxydibenzopyrone (numbering as *A*) (52%), new m.p. 247° (Me ether, new m.p. 143°; *acetate*, m.p. 177°), converted by MgMeI into 4″-*hydroxy*-2:2-*dimethyldibenzopyran* (40%), m.p. 128° (*acetate*, m.p. 96°). Orcinol and (I) similarly give 4″-*hydroxy*-6″-*methyldibenzopyrone*, softens at 143°, m.p. 150°, and 4″-*hydroxy*-2 : 2 : 6″-*trimethyldibenzopyran*, m.p. 144° (*acetate*, m.p. 85°). 4 : 2 : 1-$C_6H_3MeBr{\cdot}CO_2H$ (IV) and (II) give 4″-*hydroxy*-5′ : 6″-*dimethyldibenzopyrone*, m.p. 311° (block) (*acetate*, m.p. 175—176°). Orcinol and (IV) give 4″-*hydroxy*-5′-*methyl*-6″-n-*amyldibenzopyrone* (V) (25%), m.p. 206° (*acetate*, m.p. 126°), and 4″-*hydroxy*-2 : 2 : 5′-*trimethyl*-6″-n-*amyldibenzopyran* (VI), m.p. 83° [*acetate* (VII), m.p. 62°; p-*nitrobenzoate*, m.p. 92°; m-*nitrobenzenesulphonate*, m.p. 118°]. The orientation of (V) and (VI) depends on non-identity with cannabinol (see below).



(*A*.)

II. 7-Hydroxy-4-methylcoumarin and Bu^tCOCl in boiling C_5H_5N give the 7-*valeroxy*-compound, m.p. 75—76°, which with $AlCl_3$ at 80° and later 150° gives 7-*hydroxy*-8-n-*valeryl*-4-*methylcoumarin*, m.p. 98—103°, which in 16% aq. NaOH–N_2 gives 2 : 6-*dihydroxyvalerophenone*, m.p. 85—86°. Zn–Hg–HCl–H_2O–EtOH then gives 2-n-*amylresorcinol* (VIII), m.p. 55—56°, but in absence of EtOH the BuCO is eliminated. (IV), (VIII), aq. NaOH, and $CuSO_4$ give 4″-*hydroxy*-5′-*methyl*-3″-n-*amyldibenzopyrone*, m.p. 238—239° (decomp.), converted by MgMeI into 4″-*hydroxy*-2 : 2 : 5′-*trimethyl*-3″-n-*amyldibenzopyran*, m.p. 87·5—88·5° [p-*nitro*-, m.p. 120—121°, and thence (H_2–PtO_2; EtOH; 2—3 atm.) p-*amino*-*benzoate*, m.p. 165·5—166·5°; m-*nitrobenzenesulphonate*, m.p. 122·5—123°; acetate, an oil]. 4-*n*-Amylresorcinol and (IV) give similarly 4″-*hydroxy*-5′-*methyl*-5″-n-*amyldibenzopyrone*, m.p. 226°, and 4″-*hydroxy*-2 : 2 : 5′-*trimethyl*-5″-n-*amyldibenzopyran*, m.p. 86—88° [*acetate* (IX), m.p. 68—69°; 4″-m-*nitrobenzenesulphonate*, m.p. 100—101°; *p*-nitrobenzenesulphonate, an oil]. Similarity in the absorption spectra of (VII), (IX), and cannabinol acetate confirms the dibenzopyran structure of cannabinol.

III. Menthone, (IV), NaOEt, and $Cu(OAc)_2$ in boiling EtOH give 6″-*keto*-4″ : 4″-*dimethyl*-3″ : 4″ : 5″ : 6″-*tetrahydrodibenzopyrone*, m.p. 145—146°. *n*-$C_5H_{11}{\cdot}CHO$ (X), $COMe_2$, and 10% NaOH give $COMe{\cdot}CH{:}CH{\cdot}C_5H_{11}$-*n* (46%), b.p. 124—125°/32 mm., which with $CH_2(CO_2Et)_2$ and NaOEt–EtOH gives an ester, converted by hydrolysis (KOH) and heating in HCl into 5-n-*amyl*cyclo*hexane*-1 : 3-*dione* (XI), m.p. 70—71°, also obtained from olivetol by H_2–Raney Ni in aq. NaOH at 125°/2800 lb. (XI), (IV), and NaOEt–$Cu(OAc)_2$–EtOH give 6″-*keto*-5′-*methyl*-4″-n-*amyl*-3″ : 4″ : 5″ : 6″-*tetrahydrodibenzopyrone* (78%), m.p. 95—96°, dehydrogenated by S at 250° to 6″-*hydroxy*-5′-*methyl*-4″-n-*amyldibenzopyrone* (34%), m.p. 186°, which with MgMeI affords cannabinol [6″-hydroxy-2 : 2 : 5′-trimethyl-4″-*n*-amyldibenzopyran], m.p. 76—77°. Commercial (X) contains $CHEt_2{\cdot}CHO$ and leads by the above methods to 5-α-*ethyl*-n-*propyl*cyclo*hexane*-1 : 3-*dione*, m.p. 104—105°, 6″-*keto*-5′-*methyl*-4″-α-*ethyl*-n-*propyl*-3″ : 4″ : 5″ : 6″-*tetrahydrodibenzopyrone*, m.p. 111—112°, 6″-*hydroxy*-5′-*methyl*-4″-α-*ethyl*-n-*propyldibenzopyrone*, m.p. 217—218° (*acetate*, m.p. 128—130°), and 6″-*hydroxy*-2 : 2 : 5′-*trimethyl*-4″-α-*ethyl*-n-*propyldibenzopyran*, m.p. 133—134° (*acetate*, m.p. 103°; p-*nitrobenzoate*, m.p. 171°).

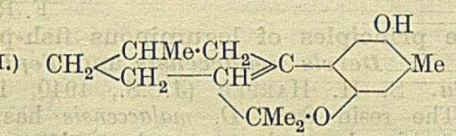
IV. 4-n-*Amyldihydroresorcinol* (prep. by H_2–Raney Ni at 125°/2800 lb.), m.p. 67°, (IV), NaOEt, and $Cu(OAc)_2$ in EtOH give 6″-*keto*-5′-*methyl*-3″- (XII) (20%), m.p. 97—99°, and -5″-n-*amyl*-3″ : 4″ : 5″ : 6″-*tetrahydrodibenzopyrone* (XIII) (33%), m.p. 65—66°, separated by solvents. Reactions below show (XII) and (XIII) to be equilibrated by acid or alkali. When (XII) or (XIII) is treated with Br–$CHCl_3$ and the product is heated in quinoline at 200°, 6″-*hydroxy*-5′-*methyl*-3″- (XIV), m.p. 176—177°, and -5″-n-*amyldibenzopyrone* (XV), m.p. 182—183°, respectively, are obtained. (XIV), but not (XV), is obtained also by S at 250—255°. MgMeI converts (XV) into 2′ : 6′-*dihydroxy*-5-*methyl*-2-α-*hydroxy*isopropyl-3′-n-*amyldiphenyl*, m.p. 103—104°. With N-NaOMe and Me_2SO_4, (XIV) or (XV) gives 6″-*methoxy*-5′-*methyl*-3″-n-*amyldibenzopyrone* (XVI), m.p. 96°, and with CH_2PhCl–NaOMe–MeOH either gives 6″-*benzyloxy*-5′-*methyl*-3″-n-*amyldibenzopyrone* (XVII), m.p. 121—121·5°, hydrolysed by boiling conc. HCl–AcOH to (XIV). However, by condensation by K_2CO_3 in $COMe_2$ (XIV) and (XV) give distinct derivatives, (XV) thus yielding 6″-*methoxy*- (XVIII), m.p. 45—46°, and 6″-*benzyloxy*-5′-*methyl*-5″-n-*amyldibenzopyrone* (XIX), m.p. 86°. 6″-*Benzenesulphonoxy*-5′-*methyl*-3″-, m.p. 103—104°, and -5″-n-*amyldibenzopyrone*, m.p. 139°, are obtained by $PhSO_2Cl$ in boiling C_5H_5N. If crude mixed (XII) and (XIII) are subjected to Br–quinoline, 37% of (XV) is readily isolated and the mother-liquors yield 23% of (XVII). MgMeI converts (XVI) in boiling Et_2O–C_6H_6 into a carbinol, dehydrated by anhyd. $MgSO_4$ in boiling C_6H_6 to 6″-*methoxy*-2 : 2 : 5′-*trimethyl*-3″-n-*amyldibenzopyran* (XX), m.p. 75—76°. (XVII) gives similarly 6″-*benzyloxy*-2 : 2 : 5′-*trimethyl*-3″-n-*amyldibenzopyran* (XXI), m.p. 74—75°, by way of 2′-*hydroxy*-6′-*benzyloxy*-5-*methyl*-3′-n-*amyl*-2-α-*hydroxy*isopropyl-3-n-*amyldiphenyl*, m.p. 73—74°, which with Me_2SO_4–KOH–MeOH gives 6′-*benzyloxy*-2′-*methoxy*-5-*methyl*-3′-n-*amyl*-2-iso*propenyldiphenyl*, m.p.

76—77°. Hydrolysis of (XX) by HBr–AcOH or of (XXI) by conc. HCl–AcOH gives 6″-*hydroxy*-2 : 2 : 5′-*trimethyl*-3″-n-*amyldibenzopyran*, m.p. 62—63° (*acetate*, m.p. 72—73°; p-*nitrobenzoate*, m.p. 144°). MgMeI converts (XVIII) and (XIX) into 6′-*hydroxy*-2′-*methoxy*- (XXII), m.p. 102—103°, and -2′-*benzyloxy*- (XXIII), m.p. 106·5—107·5°, -5-*methyl*-2-α-*hydroxyisopropyl*-3′-n-*amyldiphenyl*. 48% HBr–C_6H_6 cyclises (XXIII) to 6″-*benzyloxy*- (XXIV), m.p. 67—68°, and (XXII) to 6″-*methoxy*-2 : 2 : 5′-*trimethyl*-5″-n-*amyldibenzopyran* (XXV), b.p. 182°/3 mm.

p-NO_2·C_6H_4·COCl and (XXIII) in C_5H_5N give 2′-*benzyloxy*-6′-p-*nitrobenzyloxy*-5-*methyl*-3′-n-*amyl*-2-iso*propenyldiphenyl*, m.p. 100—101°. 6″-*Hydroxy*-2 : 2 : 5′-*trimethyl*-5″-n-*amyldibenzopyran*, b.p. 203—205°/3 mm. (p-*nitrobenzoate*, m.p. 129—130°), is obtained from (XXIV) by HCl–AcOH or from (XXV) by HBr–AcOH. M.p. (all parts) are corr. R. S. C.

Structure of cannabidiol. V. Position of the alicyclic ethylenic linkings. R. Adams, H. Wolff, C. K. Cain, and J. H. Clark (J. Amer. Chem. Soc., 1940, **62**, 2215—2219; cf. A., 1940, II, 304).—Hydrogenation (PtO_2) of cannabidiol Me_2 ether (I) in EtOH gives *dihydrocannabidiol Me₂ ether* (II), b.p. 158–161°/2 mm., $[\alpha]_D^{28}$ −133° in 95% EtOH. Addition of *m*-$C_6H_4(OH)_2$ and then of pulegone to $LiBu^a$ in Et_2O–N_2 gives a partly dehydrated carbinol, converted by $KHSO_4$ at 140° into 2-3′-*methyl*-6′-iso*propylidene*-$\Delta^{1:2}$-cyclo*hexenylresorcinol Me₂ ether* (III), m.p. 75—76°, $[\alpha]_D^{27}$ +56° in 95% EtOH, which with H_2–PtO_2 in EtOH (or by partial hydrogenation in AcOH) gives 2 : 3′-*methyl*-6′-iso*propylidene*cyclo*hexylresorcinol Me₂ ether* (IV), m.p. 53—54°, $[\alpha]_D^{32}$ +60° in 95% EtOH. 1 : 3 : 5-$C_6H_3Me(OMe)_2$ yields similarly 2-3′-*methyl*-5′-iso*propylidene*-$\Delta^{1:2}$-cyclo*hexenyl*- (V), m.p. 81—82°, $[\alpha]_D^{27}$ +37° in 95% EtOH, and -cyclo*hexyl-orcinol Me₂ ether* (VI), m.p. 114—115°, $[\alpha]_D^{30}$ +44° in 95% EtOH. Doeuvre's method (ozonisation and determination of CH_2O formed) of determining CH_2:̈ is not quant., but a modification (described) is a reliable qual. test. It gives 63% of CH_2O from eugenyl cinnamate, 49% from cannabidiol (VII), 41% from (I), 0 from (II) or tetrahydrocannabidiol Me_2 ether. (VII) thus contains CHMe:CH_2 and not :CMe_2. The absorption spectrum of (II) resembles that of (IV) and (VI), but not that of (III), (V), 2-5′-methyl-2′-*iso*propyl-$\Delta^{1:2}$-*cyclo*hexenylresorcinol or orcinol Me_2 ether. The endocyclic ethylenic linking of (VII) is thus not conjugated with the aromatic nucleus. R. S. C.

Conversion of cannabidiol into a product with marihuana activity. Type reaction for synthesis of analogous substances. Conversion of cannabidiol into cannabinol. R. Adams, D. C. Pease, C. K. Kain, B. R. Baker, J. H. Clark, H. Wolff, and R. B. Wearn (J. Amer. Chem. Soc., 1940, **62**, 2245—2246).—C_5H_5N,HCl, HCl–EtOH, HCl–Et_2O, NH_2·SO_3H, H_3PO_4–EtOH, or $ZnCl_2$–EtOH isomerises cannabidiol to *tetrahydrocannabinol* (I), b.p. 188—190°/2·5 mm. α varies (*e.g.*, $[\alpha]_D^{27}$ −160° or $[\alpha]_D^{32}$ −240°) owing to stereoisomeric differences according to the method of prep. Dehydrogenation of (I) gives cannabinol and reduction gives *hexahydrocannabinol*, b.p. 153—155°/0·1 mm., $[\alpha]_D^{27}$ (always) −70°. Et 5-methyl*cyclo*hexanone-2-carboxylate, orcinol, and

(II.) 

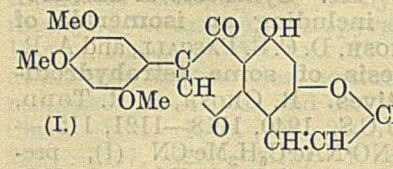
$POCl_3$ give the pyrone, converted by MgMeI into the *substance* (II), m.p. 115·5—116°. (I) has marihuana activity. R. S. C.

***Cannabis Indica*. III. Synthesis of dibenzopyran derivatives, including an isomeride of cannabinol.** R. Ghosh, D. C. S. Pascall, and A. R. Todd. **IV. Synthesis of some tetrahydrodibenzopyran derivatives.** R. Ghosh, A. R. Todd, and S. Wilkinson (J.C.S., 1940, 1118—1121, 1121—1125).—III. 3 : 1 : 4-NO·NAc·C_6H_3Me·CN (I), prepared from 3 : 1 : 4-NHAc·C_6H_3Me·CN and NO_2 (decomposed on keeping in C_6H_6 to 2-*cyano*-5-*methyldiphenyl*, m.p. 87—88°), with *p*-$C_6H_4(OMe)_2$ gives 2′-*cyano*-2 : 5-*dimethoxy*-5′-*methyldiphenyl*, m.p. 97° [-2 : 5-(*OEt*)$_2$-compound, m.p. 72—73°], which with HBr affords 6-*hydroxy*-5′-*methyl*-3 : 4-*benzocoumarin*, m.p. 233—234° (decomp.) (*acetate*, m.p. 155°). The acetate with MgMeI and PhOMe affords 5″-*hydroxy*-2 : 2 : 5′-*trimethyldibenzopyran*, m.p. 118° (*acetate*, m.p. 86—87°; 3 : 5-*dinitrobenzoate*, m.p. 169°). A corresponding series of reactions with 1 : 2 : 5-*n*-C_5H_{11}·$C_6H_4(OMe)_2$ (2-*acetoxy*-5-*methoxyvalerophenone*, m.p. 72—73°, and its *semicarbazone*, m.p. 159—160°, and *ketazine*, m.p. 161—162°) affords 2′-*cyano*-2 : 5-*dimethoxy*-5′-*methyl*-4-n-*amyldiphenyl*, b.p. 95—100°/0·036 mm., 6-*hydroxy*-5′-*methyl*-7-n-*amyl*-3 : 4-*benzocoumarin*, m.p. 191—192° (*acetate*, m.p. 138—139°), and 5″-*hydroxy*-2 : 2 : 5′-*trimethyl*-4″-n-*amyldibenzopyran*, m.p. 110—111°; the last-named substance is an isomeride of cannabinol. Orcinol Me_2 ether and (I) give 2-*cyano*-2′ : 6′-*dimethoxy*-4′ : 5-*dimethylazobenzene*, m.p. 126°.

IV. Condensation of quinol with Et *cyclo*hexanone-2-carboxylate (H_2SO_4) gives 6-*hydroxy*-3 : 4-cyclo*hexenocoumarin*, m.p. 239—240°; the -5′-*Me* compound, m.p. 246°, is obtained with Et 1-methyl*cyclo*hexan-3-one-4-carboxylate, and the 7-hydroxy-5′-methyl derivative, m.p. 199—200° (lit. 142°), from *m*-$C_6H_4(OH)_2$. 5-*Hydroxy*-5′-*methyl*-7-n-*amyl*-3 : 4-cyclo*hexenocoumarin*, m.p. 177°, is prepared from olivetol monohydrate. The following Ac derivatives are obtained from the OH-compound and Ac_2O in C_5H_5N : 7-*acetoxy*-, m.p. 185—186°, and 7-*acetoxy*-5′-*methyl*-, m.p. 132°, 6-*acetoxy*-, m.p. 139—140°, 5-*acetoxy*-7-*methyl*-, m.p. 124°, and 5-*acetoxy*-5′-*methyl*-7′-n-*amyl*-, m.p. 82—83°, -3 : 4-cyclo*hexenocoumarin*. By condensation of the appropriate coumarin with MgMeI the following are prepared: 4″-*hydroxy*-2 : 2-*dimethyl*-, m.p. 135° (*Ac* derivative, m.p. 66°), 4″-*hydroxy*-2 : 2 : 5′-*trimethyl*-, m.p. 144—145° (*Ac* derivative, m.p. 58°), 5″-*hydroxy*-2 : 2-*dimethyl*-, m.p. 130°, 6″-*hydroxy*-2 : 2 : 4″-*trimethyl*-, m.p. 138° (*Ac* derivative, m.p. 107—108°), 6″-*hydroxy*-2 : 2 : 5′ : 4″-*tetramethyl*-, m.p. 112—113° (*Ac* derivative, m.p. 124°), and 6″-*hydroxy*-2 : 2 : 5′-*trimethyl*-4″-n-*amyl*-, b.p. 165—175°/0·02 mm., -3′ : 4′ : 5′ : 6′-*tetrahydrodibenzo*-

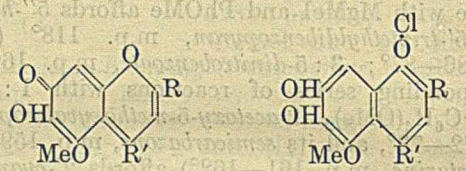
pyran; dehydrogenation (Pd–C) of the Ac derivative of the last compound gives cannabinol. F. R. S.

Active principles of leguminous fish-poison plants. V. *Derris malaccensis* and *Tephrosia toxicaria*. S. H. HARPER (J.C.S., 1940, 1178—1184).—The resin from *D. malaccensis* has been fractionated by chemical means and pure *l*-α-toxicarol has been obtained. In addition rotenone, elliptone, deguelin, malaccol, sumatrol, and a *phenol* (I), $C_{23}H_{22}O_7$, m.p. 219°, α_D ±0° in $CHCl_3$ (O-*Ac*, m.p. 210°, O-*Bz*, m.p. 193°, and O-*Me* derivatives, m.p. 178°), have been isolated. As a working hypothesis structure (I) is suggested. The resin from *T. toxicaria* has been similarly fractionated, and rotenone, *l*-α-toxicarol, and sumatrol have been isolated. F. R. S.



(I.)

Constitution of santalin. J. B. LAL (Proc. Nat. Acad. Sci. India, 1939, **9**, 83—88).—Previous work on santalin is reviewed, and reasons are given for assigning to it and its hydrochloride the appended formulæ:



R = 3-hydroxy-4-methoxyphenyl; R′ = 4-(5-hydroxy-6-methoxy-2-*p*-methoxyphenyl-1 : 4-benzopyranyl). A. LI.

Spectrographic study of rottlerin and its derivatives.—See A., 1940, I, 402.

Benzene-*o*-bisthioindoxyl.—See B., 1940, 726.

Synthesis of emetine and its analogues. Oxidation of 3-carbalkyloxy-1-β-phenylethylpyridinium salt [bromide]. S. SUGASAWA, K. SAKURAI, and T. OKAYAMA (Proc. Imp. Acad. Tokyo, 1940, **16**, 225—228).—3-*Carbomethoxy*-, decomp. 197°, 3-*carbethoxy*-, m.p. 193—194°, and 3-*carboxylamido*-1-β-*phenylethylpyridinium bromide*, m.p. 209° (all prepared by addition), are oxidised by alkaline $K_3Fe(CN)_6$ to 1-β-*phenylethyl*-2-*pyridone*-, m.p. 190—191°, reduced catalytically, or better by Na–Hg, to -2-*piperidone*-5-*carboxylic acid* (I), m.p. 140°. $Ph{\cdot}[CH_2]_2{\cdot}NH_2$ (II) and $CO_2Et{\cdot}CH(CHO){\cdot}CH_2{\cdot}CO_2Et$ at room temp. give a product which after catalytic reduction in EtOH yields (with spontaneous ring-closure) the *Et* ester, b.p. 170—180°/4 mm., of 1-β-*phenylethyl*-2-*pyrrolidone*-4-*carboxylic acid*, m.p. 192—193°. (II) and $CO_2Et{\cdot}CH(CHO){\cdot}[CH_2]_2{\cdot}CO_2Et$ similarly give the *Et* ester, an oil, of (I). E. W. W.

Action of diazomethane on acid chlorides of the pyridine series. A. DORNOW (Ber., 1940, **73**, [*B*], 185—188).—Nicotinyl chloride hydrochloride with CH_2N_2 in Et_2O, followed by HCl, gives, after heating with H_2O, 3-*hydroxyacetylpyridine*, m.p. 41—42° (*picrate*, m.p. 142—143°), which has a hyperæmic action. The 3-diazoacetylpyridine, intermediately formed, with cold conc. HCl gives the *hydrochloride*, decomp. 245—250° (darkening from 200°), of 3-*chloroacetylpyridine*, m.p. 51—52° (*picrate*, m.p. 132°). With C_5H_5N in $PhNO_2$, this gives 1-(3′-*pyridoylmethyl*)*pyridinium chloride*, m.p. 129—130° [*product*, $C_{18}H_{11}O_7N_5$, m.p. ~125—130° (decomp.), with picryl chloride]. *iso*Nicotinic acid with $SOCl_2$ gives the chloride hydrochloride, which with CH_2N_2 in Et_2O gives 4-*diazoacetylpyridine*, m.p. (+0·5H_2O) 35—36° (*picrate*, m.p. 244°), converted by conc. HCl into 4-*chloroacetylpyridine*, m.p. (+MeOH) 103° (decomp.), and by AcOH into 4-*acetoxyacetylpyridine*, m.p. 68—69° [*picrate*, m.p. 148° (decomp.)]. E. W. W.

Arylpyridines. IV. 3- and 4-Pyridyldiphenyls. I. M. HEILBRON, D. H. HEY, and A. LAMBERT (J.C.S., 1940, 1279—1284).—Diazotised $3\text{-}C_6H_4Ph{\cdot}NH_2$ and C_5H_5N give a mixture of 3-α-, b.p. 75—85°/0·002 mm., and 3-γ-*pyridyldiphenyl*, m.p. 81—82°, separated by fractional crystallisation of the *picrates*, m.p. 169° (I) and 231° (II), respectively. Reduction ($SnCl_2$–HCl) of α-3-nitrophenylpyridine gives the NH_2-derivative, which with Ac_2O affords the 3-α-*NHAc*-compound, m.p. 141—142°, converted through the NO-derivative (NOCl) and treatment with $C_6H_2(NO_2)_3{\cdot}OH$ into (I). A similar series of reactions leads to β-3-*amino*-, m.p. 77—78°, and -*acetamido-phenylpyridine*, m.p. 135—136°, and 3-β-*pyridyldiphenyl*, b.p. 75—85°/0·002 mm. (*picrate*, m.p. 178—179°), and γ-3-*amino*-, m.p. 165—166°, and -*acetamido-phenylpyridine*, m.p. 171—172°, and (II). Diazotised $4\text{-}C_6H_4Ph{\cdot}NH_2$ and C_5H_5N yield a mixture of 4-γ-, m.p. 215° and 4-α-*pyridyldiphenyl picrates*, m.p. 186—187°, the identity of which is similarly proved by the prep. of α-4-*acetamido*-, m.p. 135—136°, and -*nitrosoacetamido-phenylpyridine*, m.p. 88—89° (decomp.), 4-α-*pyridyldiphenyl* (III), m.p. 141—142°, β-4-*acetamidophenylpyridine*, m.p. 181—182°, 4-β-*pyridyldiphenyl* (IV), m.p. 151—152° (*picrate*, m.p. 208—210°), γ-4-*acetamidophenylpyridine*, m.p. 210—211°, and 4-γ-*pyridyldiphenyl* (V), m.p. 209°. Nitration (HNO_3–AcOH) of (III) gives a mixture of 4′-*nitro*-, m.p. 213° (*NH*$_2$-compound, m.p. 191—192°, and its *Ac* derivative, m.p. 236—237°), and 2′-*nitro*-4-α-*pyridyldiphenyl*, m.p. 136—137° [*nitrate*, m.p. 188—190° (decomp.); *NH*$_2$-compound, m.p. 98—99°, and its *Ac* derivative, m.p. 146—147°). Similar nitration of (IV) affords 4′-, m.p. 192—193°, and 2′-*nitro*-4-β-*pyridyldiphenyl*, m.p. 124—125°, and of (V) yields 4′-, m.p. 196—197°, and 2′-*nitro*-4-γ-*pyridyldiphenyl*, m.p. 99—100°. The constitution of the nitration products is proved by oxidation to the corresponding $NO_2{\cdot}C_6H_4{\cdot}CO_2H$. F. R. S.

Antiplasmodial action and chemical constitution. III. Carbinolamines derived from naphthalene and quinoline. H. KING and T. S. WORK. **IV. Synthesis of complex carbinolamines and polyamines.** T. S. WORK (J.C.S., 1940, 1307—1315, 1315—1320; cf. A., 1938, II, 163). —III. α-*Naphthoyldiazomethane* (from $\alpha\text{-}C_{10}H_7{\cdot}COCl$ and CH_2N_2 in Et_2O), m.p. 56°, with HCl in Et_2O gives $\alpha\text{-}C_{10}H_7{\cdot}CO{\cdot}CH_2Cl$, which when treated with the appropriate NHR_2 in Et_2O and reduced (H_2, Pd–C, MeOH–aq. HCl) yields 1-naphthyldimethyl- (*picrate*,

m.p. 178—180°), -diethyl- (*picrate*, m.p. 136°), -di-β-hydroxyethyl- (*picrate*, m.p. 127—128°), and -di-*n*-propyl-amino- (*picrate*, m.p. 149—150°), and -piperidino-methylcarbinol (*hydrochloride*, m.p. 270°). 7-*Methoxy*-1-*naphthacyl bromide* (from $OMe{\cdot}C_{10}H_6{\cdot}COCl$ as above; prep. starting from 1 : 7-$CN{\cdot}C_{10}H_6{\cdot}SO_3H$ described), b.p. 165—170°/1 mm., similarly gives 7-methoxy-1-naphthylpiperidinomethylcarbinol (*hydrochloride*, m.p. 225—227°). 4-*Quinolyl* CH_2Cl *ketone*, m.p. 101°, is prepared from the CHN_2 *ketone*, m.p. 83—84°. 4-Quinolyl CH_2Br ketone hydrobromide [from Et 4-quinoloylacetate (improved prep.)] similarly yields (as above) 4-quinolyl-diethyl- (*dipicrate*, m.p. 168°), -di-*n*-propyl- (*dipicrate*, m.p. 153°), and -di-*n*-amyl-amino- (*dipicrate*, m.p. 142°), -piperidino- [dipicrate, new m.p. 168° (decomp.); hydrochloride, m.p. 160°], and -4′ : 4″-piperidylpiperidino-methylcarbinol [using *N*-benzoyl-4 : 4′-dipiperidyl (hydrobromide, m.p. 233°; *perchlorate*, m.p. 268°), obtained (together with the Bz_2 compound, m.p. 167°) from dipiperidyl and BzCl in $COMe_2$–H_2O at p_H 3·8] [trihydrochloride, m.p. >300° (decomp.); *tripicrate*, m.p. 195°]. 6-Methoxy-4-quinolyl CH_2Br ketone hydrobromide similarly yields 6-methoxy-4-quinolyl-diethyl- (*dihydrochloride*, m.p. 182—183°), -di-*n*-butyl- (I) (dihydrochloride, m.p. 142°; *dipicrate*, m.p. 169°), -di-*n*-amyl- (II) (*dipicrate*, m.p. 155°), -di*iso*amyl- (*dipicrate*, m.p. 156°), -di-*n*-hexyl- (III) (*dipicrate*, m.p. 173°), and -di-*n*-heptyl- (*dipicrate*, m.p. 130°), -piperidino- (*hydrochloride*, m.p. 164°), and -4′ : 4″-piperidylpiperidino-methylcarbinol (*trihydrochloride*, anhyd. and $+2H_2O$, decomp. >300°). 6-*Methoxy*-4-*quinolylmethylcarbinol hydrochloride*, m.p. 217°, was obtained in an attempt to prepare the NBu^{β}_2-compound. Of these carbinolamines, (I), (II), and (III) show weak antiplasmodial activity (*P. relictum*) in canaries, the others none. Di-*n*-hexyl-, (IV), b.p. 122°/15 mm. (*tetrahydrate*, b.p. 114—116°/14 mm.; *hydrochloride*, m.p. 270°), and -heptylamine (V), m.p. 1° (lit. 30°) (*trihydrate*, m.p. 32—33°; hydrochloride, new m.p. 255°), are prepared by catalytic reduction (H_2, PtO_2, AcOH) of *di*-n-*hexyl*-, b.p. 185°/14 mm., and -*heptyl-benzylamine*, b.p. 205°/16 mm., respectively. n-*Hexyl*-, b.p. 146—148°/14 mm. (*hydrochloride*, m.p. 217—218°), and -heptylbenzylamine (*hydrochloride*, m.p. 196°) are obtained as by-products in the prep. of (IV) and (V) from $CH_2Ph{\cdot}NH_2$ and the alkyl bromide.

IV. *p*-$C_6H_4Ph{\cdot}CO{\cdot}CH_2Cl$ with piperidine (I) in $COMe_2$ yields *p*-diphenylyl piperidinomethyl ketone, m.p. 86° (*picrate*, m.p. 188°), reduced (H_2, PtO_2, EtOH–aq. HCl) to the corresponding carbinol, m.p. 120° [hydrochloride, m.p. 243° (decomp.); *methiodide*, m.p. 205°]. 4 : 4′-*Di*(*chloroacetyl*)*diphenyl*, m.p. 226—227° (from the acid chloride with CH_2N_2 followed by HCl in C_6H_6), with (I) in boiling $CHCl_3$ yields 4 : 4′-*di*(*piperidinoacetyl*)*diphenyl*, m.p. 140°, reduced (as above) to 4 : 4′-*bis*-(β-*piperidino*-α-*hydroxyethyl*)*diphenyl*, m.p. 158°. Sebacyl chloride with CH_2N_2 in Et_2O gives the *bis*(*diazo-ketone*), m.p. 91°, converted by HCl in C_6H_6 into αμ-*dichloro*-β*λ*-*diketododecane*, m.p. 92°; this with (I) in $COMe_2$ yields the αμ-dipiperidino-derivative, m.p. 43°, reduced (as above) to αμ-dipiperidino-β*λ*-dihydroxydodecane, m.p. 78° (*dipicrate*, m.p. 152°), and with $NHEt_2$ and similar reduction yields αμ-bisdiethylamino-β*λ*-dihydroxydodecane (an oil) (*dipicrate*, m.p. 121°). $[CH_2]_{10}(COCl)_2$ similarly yields the *bis*(*diazo-ketone*), m.p. 96°, αξ-*dichloro*-, m.p. 97°, and -dipiperidino-β*ν*-diketotetradecane (II), m.p. 48°, which is not reduced by H_2–PtO_2, and with Al–Hg in neutral solution gives β*ν*-*diketotetradecane*, m.p. 75°, and a base from which no cryst. derivative could be obtained. $MgPr^{\alpha}Br$ and (II) yield αξ-*dipiperidino*-β*ν*-*dihydroxy*-β*ν*-*dipropyltetradecane*, b.p. 230—240°/0·3 mm. *NN′*-Di-*p*-toluenesulphonylbenzidine (III) with $NEt_2{\cdot}[CH_2]_3{\cdot}Cl$ (IV), new b.p. 75—76°/29 mm., in boiling aq. EtOH–NaOH gives a product hydrolysed by AcOH–conc. HCl at 180° under pressure to *NN′*-bis-(γ-diethylaminopropyl)benzidine, b.p. 230—250°/0·9 mm. [*tetrahydrobromide*, m.p. 260° (decomp.)]. $NHBz{\cdot}[CH_2]_5{\cdot}Cl$, (III), and NaOH in H_2O–$COMe_2$ at 150—160° under pressure yield NN′-*di*-p-*toluenesulphonyl*-NN′-*di*-ε-*benzamidoamylbenzidine*, m.p. 192°, hydrolysed to *NN′*-di-ε-aminoamylbenzidine, m.p. 270° (decomp.) [*tetrahydrochloride* (hygroscopic)]. 4 : 4′- and 2 : 4′-Dipiperidyl with $NEt_2{\cdot}[CH_2]_2{\cdot}Cl$ in EtOH at 100° under pressure yield 1 : 1′-bis-β-diethylaminoethyl-4 : 4′-, b.p. 200—230°/0·3 mm. [*tetrapicrate*, m.p. 250° (decomp.)], and -2 : 4′-dipiperidyl, b.p. 205—210°/0·5 mm. (*tetrapicrate*, m.p. 170°). Tetrahydroquinoline with (IV) at 100° under pressure yields 1-γ-diethylaminopropyltetrahydroquinoline, b.p. 192°/10 mm. (*dipicrate*, m.p. 147°). αζ-*Di*-p-*toluenesulphonamidohexane*, m.p. 152° (from $NH_2{\cdot}[CH_2]_6{\cdot}NH_2$, *p*-$C_6H_4Me{\cdot}SO_2Cl$, and aq. NaOH), with (IV) in aq. EtOH–NaOH at 100° gives a product hydrolysed (AcOH–HCl at 180°) to αζ-di-(γ-diethylaminopropylamino)hexane, b.p. 135—140°/0·5 mm. (*tetrahydrobromide*, m.p. 64°). α*κ*-*Di*-p-*toluenesulphonamidodecane* (V), m.p. 129°, similarly yields α*κ*-*di*-(γ-*diethylaminopropylamino*)*decane*, b.p. 178—184°/1·5 mm. [crude hydrobromide (hygroscopic), m.p. 142—143°]. *iso*-$C_5H_{11}Br$ and (V) under similar conditions give α*κ*-di*iso*amylaminodecane (*dihydrochloride*, m.p. 318°). None of the compounds described has antiplasmodial activity, thus showing the importance of the quinoline nucleus. A. Li.

Nitrogen compounds in petroleum distillates. XVIII. Isolation, ozonisation, and synthesis of 2 : 4-dimethyl-8-*sec*.-butylquinoline. L. M. Schenck and J. R. Bailey (J. Amer. Chem. Soc., 1940, **62**, 1967—1969; cf. A., 1940, II, 24).—Cumulative, followed by countercurrent, extraction of the residual bases from 2 : 3 : 4-trimethyl-8-ethyl- and -8-*n*-propyl-quinoline (I) (A., 1933, 1305) gives a further amount of (I) and 2 : 4-*dimethyl*-8-sec.-*butylquinoline* (II), b.p. 310° (*picrate*, m.p. 148—150°). $K_2Cr_2O_7$–dil. H_2SO_4 oxidises (II) to 2 : 4-dimethylquinoline-8-carboxylic acid. Ozonisation of (II) in CCl_4 and oxidation of the product by H_2O_2 gives $CHMeEt{\cdot}CO_2H$ (III). 70% of (II) is obtained from CH_2Ac_2 and *o*-$CHMeEt{\cdot}C_6H_4{\cdot}NH_2$. CH_2Ac_2 and *p*-$CHMeEt{\cdot}C_6H_4{\cdot}NH_2$ give 2 : 4-dimethyl-6-*sec*.-butylquinoline, b.p. 321° (*picrate*, m.p. 141—142°), giving (III) by O_3 and then H_2O_2. Successive treatment with O_3, 3% H_2O_2, and boiling aq. K_2CO_3 converts (I) into NH_3, $H_2C_2O_4$, HCO_2H, AcOH, $Pr^{\alpha}CO_2H$, and a little CO_2. R. S. C.

Carbazolecarboxyl chlorides.—See B., 1940, 762.

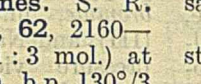
Sulphanilamides. I. 3-(*p*-Aminobenzenesulphonamido)carbazole. A. Novelli (Anal. Asoc. Quím. Argentina, 1940, **28**, 87—90).—3-Aminocarbazole (modified prep.) with *p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ in $COMe_2$ boiled in presence of C_5H_5N yields the *Ac* derivative, m.p. 252—255°, of 3-(*p-aminobenzenesulphonamido*)*carbazole*, m.p. 256—257°. F. R. G.

Effect of p_H and irradiation on the ultra-violet absorption spectrum of barbituric acid.—See A., 1940, I, 402.

Barbituric acids.—See B., 1940, 702

Synthesis of tetrahydropyrimidines. S. R. Aspinall (J. Amer. Chem. Soc., 1940, **62**, 2160—2162).—$NH_2{\cdot}[CH_2]_3{\cdot}NH_2$ and EtOAc (1 : 3 mol.) at 165° give 60% of the Ac_1 derivative (I), b.p. 130°/3 mm. (*picrate*, m.p. 197°), which with CaO at 250° gives 90% of 2-methyl-3 : 4 : 5 : 6-tetrahydropyrimidine (II), b.p. 91°/4 mm., m.p. 75° (lit., 72—74°) [*phenylcarbamido*-derivative, m.p. 147°; picrate, m.p. 157° (lit., 152°)]. Acetylation at 150° (or 250°) gives a mixture of (I) and (II), but dehydration of this crude product gives 70% of (II). $NHBz{\cdot}[CH_2]_3{\cdot}NH_2$ (*phenylcarbamido*-derivative, m.p. 166°) and 2-phenyl-3 : 4 : 5 : 6-tetrahydropyrimidine, m.p. 87° (lit., 72—78°), b.p. 155—165°/5 mm. (*picrate*, m.p. 181°), are similarly obtained. R. S. C.

Attempts to find new antimalarials. XVII. Derivatives of 5 : 6 : 3′ : 2′-pyridoquinoline. W. O. Kermack and (Miss) A. P. Weatherhead (J.C.S., 1940, 1164—1169).—2-*Hydroxy*-4-*methyl*-5 : 6 : 3′ : 2′-*pyridoquinoline*, m.p. 330°, prepared from 6-amino-2-hydroxy-4-methylquinoline (Skraup reaction), with PCl_5 gives the 2-*Cl*-compound, m.p. 204°, which with the appropriate reagent affords 2-*piperidino*-, m.p. 104° (*hydrobromide*, m.p. >400°), 2-*piperazino*-($+2H_2O$), m.p. 110°, anhyd., m.p. 125°, 2-β-*diethylaminoethylamino*-, m.p. 123° (*hydrobromide*, m.p. 229°), and 2-γ-*diethylaminopropylamino*-4-*methyl*-5 : 6 : 3′ : 2′-*pyridoquinoline hydrobromide* ($+2H_2O$), m.p. 265°. 2-Chloro-6-nitro-4-methylquinoline and $NEt_2{\cdot}[CH_2]_2{\cdot}NH_2$ yield 6-*nitro*-2-β-*diethylaminoethylamino*-4-*methylquinoline hydrochloride*, m.p. 165°, and *picrate*, m.p. 210°. 4-*Hydroxy*-2-*methyl*-5 : 6 : 3′ : 2′-*pyridoquinoline*, m.p. 358°, obtained from 6-amino-4-hydroxy-2-methylquinoline, in a similar series of reactions, leads to 4-*chloro*-, m.p. 149°, 4-*piperidino*-, m.p. 163° (*picrate*, m.p. 225°), and 4-β-*diethylaminoethylamino*-2-*methyl*-5 : 6 : 3′ : 2′-*pyridoquinoline* ($+H_2O$), m.p. 68°. *p*-$NH_2{\cdot}C_6H_4{\cdot}NHAc$ and Et oxaloacetate condense to *Et* α-p-*acetamidoanilinofumarate*, m.p. 122°, cyclised to *Et* 6-*acetamido*-4-*hydroxyquinoline*-2-*carboxylate*, m.p. 309°, which is hydrolysed (HCl) to 6-*amino*-4-*hydroxyquinoline*-2-*carboxylic acid* (I), m.p. 308° (*hydrochloride*, m.p. >400°). NH_2Ph and Et oxaloacetate give *Et* 4-*hydroxyquinoline*-2-*carboxylate*, m.p. 212°, which is nitrated (H_2SO_4–HNO_3) to the 6-NO_2-compound, m.p. 286°; reduction of this with $SnCl_2$–HCl affords (I). The *sulphate*, m.p. 275°, of 6-amino-4-hydroxyquinoline (*dihydrochloride*, m.p. 305°) gives (Skraup reaction) 4-*hydroxy*-5 : 6 : 3′ : 2′-*pyridoquinoline* (II) ($+0{\cdot}5H_2O$), m.p. 298°, which is converted successively into the 4-*Cl*-, m.p. 147°, 4-β-*diethylaminoethylamino*-, m.p. 235°, and 4-γ-*diethylaminopropylamino*-compounds (*picrate*, m.p. 231°). (II) has the angular structure. F. R. S.

Colour in relation to chemical constitution of the organic and inorganic salts of oximinomalonylguanidine. I. N. D. Dass and S. Dutt (Proc. Nat. Acad. Sci. India, 1939, **9**, 93—98).—Oximinomalonylguanidine (I) [from guanidine carbonate with $CH_2(CO_2Et)_2$ at 150—160°, followed by HNO_2] in H_2O is violet and has an absorption spectrum almost identical with those of its *K*, *Na*, NH_4, NH_3Me, NH_3Et, NH_2Me_2, NH_2Et_2, $NHMe_3$, NH_3Pr, NH_3Bu, and *piperidinium* salts. (I) does not form salts with very weak bases, and probably has the structure  . A. Li.

Phthalocyanines and related compounds. XVII. Intermediates for the preparation of tetrabenzporphins : acids derived from phthalimidine. R. P. Linstead and G. A. Rowe. **XVIII. Intermediates for the preparation of tetrabenzporphins : Thorpe reaction with phthalonitrile.** P. A. Barrett, R. P. Linstead, and (in part) J. J. Leavitt and G. A. Rowe. **XIX. Tetrabenzporphin, tetrabenzmonazaporphin, and their metallic derivatives.** P. A. Barrett, R. P. Linstead, F. G. Rundall, and G. A. P. Tuey (J.C.S., 1940, 1070—1076, 1076—1079, 1079—1092).—XVII. Condensation of iminophthalimidine with $CH_2Ac{\cdot}CO_2Et$ at 140° (no catalyst) gives *Et phthalimidyl*-3-*acetoacetate*, m.p. 101°, with evolution of heat and NH_3; with $CH_2(CO_2Et)_2$, a smaller yield (at 199°) of 3-*dicarbethoxymethylenephthalimidine* (I), m.p. 104—105°, is obtained. Both products are readily oxidised ($KMnO_4$) to phthalimide. Hydrolysis [$Ba(OH)_2$] of (I) affords 3-carboxymethylenephthalimidine (II), m.p. 220° (*Me* ester, m.p. 124—125°). This acid is also obtained from phthalylacetic acid and aq. NH_3 after acidification at room temp. but if acidified at 0—5°, the monohydrate of *o-carbamylbenzoylacetic acid* (III), m.p. 120° (*Me* ester, m.p. 116—117°), is formed; this is identical with the "dihydrate" of (II). Reduction of (II) with Na–Hg gives 3-carboxymethylphthalimidine (*Me* ester, m.p. 139—140°), identical with *iso*indolinone-3-acetic acid. This substance is also formed by reduction (Na–Hg) of (III) at room temp. but at 0°, β-*hydroxy*-β-*o-carbamylphenylpropionic acid*, m.p. 180°, is obtained; this, when heated under reduced pressure at 105°, yields the phthalimidine. *o*-$CN{\cdot}C_6H_4{\cdot}[CH_2]_2{\cdot}CO_2H$ (*Me* ester, b.p. 290—295°) is prepared by reduction (Na–Hg) of the corresponding cinnamic acid.

XVIII. Condensation (Thorpe reaction) of *o*-$C_6H_4(CN)_2$ with $CH_2Ph{\cdot}CO{\cdot}CN$ gives 1-*imino*-3-*cyanobenzylidenephthalimidine*, m.p. 207—209°, isolated as the *hydrochloride*, m.p. 299°, and hydrolysed (HCl–EtOH) to 3-*cyanobenzylidenephthalimidine*, m.p. 228—230°. Similar condensation with $CN{\cdot}CH_2{\cdot}CO_2Et$ affords 3-*cyanocarbethoxymethylenephthalimidine*, m.p. 170°, and with $CH_2(CO_2Et)_2$ yields 1-*imino*-3-*dicarbethoxymethylenephthalimidine*, m.p. 97° (*hydrochloride*, m.p. 210°). Hydrolysis of this acid with NaOH–

EtOH leads to the *imino-acid* (IV), m.p. 280—300° (decomp.); with HCl–H_2O, 3-*dicarbethoxymethylene-phthalimidine*, m.p. 108°, is obtained, which is hydrolysed to (II).

XIX. Zn and (IV) when heated at 330—340° and treated with HCl give *tetrabenzmonazaporphin*, green crystals with a bluish-purple lustre, which forms Cu, Fe^{II}, and *Mg* derivatives; its structure is proved by quant. oxidation. The substance is also produced from MgMeI and *o*-$C_6H_4(CN)_2$ (17% yield). 3-Amino-1 : 1-dimethyl-*ψ-iso*indole and Ac_2O yield 2-*acetyl*-3 : 3-*dimethylphthalimidine*, m.p. 105—106°, hydrolysed to 3 : 3-*dimethylphthalimidine*, m.p. 162°, which gives only a trace of pigment with $Zn(OAc)_2$. 3-Carboxymethylphthalimidine and Zn afford Zn tetrabenzporphin, converted by HCl into tetrabenzporphin (Mg derivative), of which the structure is proved by quant. oxidation. *o*-CN·C_6H_4·COMe may be used for the prep. of Cu derivatives of tetrabenz-monaza-, -diaza-, and -triaza-porphin. The absorption spectra of all these compounds have been measured quantitatively and the results are compared with those for the analogous phthalocyanine and tetrabenztriazaporphin derivatives. The various methods available for their prep. are reviewed and possible mechanisms are discussed. F. R. S.

Phthalocyanines.—See B., 1940, 660.

Preparation of biliverdin. R. Lemberg and J. W. Legge (Austral. J. Exp. Biol., 1940, **18**, 95—98).—The "blue stable stage" in the oxidation of bilirubin by H_2O_2 in acid-EtOH solution (method of Malloy and Evelyn) is biliverdin (I) (dehydrobilirubin). A new method for the prep. of (I) based on this yields about 40% of pure cryst. product. Prolonged oxidation by H_2O_2 attacks the unsaturated side-chains of (I) but not the tetrapyrrole nucleus; there are no marked changes in the absorption spectrum. D. M. N.

Cyanine dyes.—See B., 1940, 703.

Electron-sharing ability of organic radicals. XI. 2-Thienyl- and 2-mesityl-pyrrolidines. J. G. Kirchner and I. B. Johns (J. Amer. Chem. Soc., 1940, **62**, 2183—2184).—Mg 2-thienyl iodide and Cl·$[CH_2]_3$·CN in boiling Et_2O and then in xylene give 2-2′-*thienylpyrroline* (27·5%), m.p. 57°, b.p. 111·1—112·1°/4 mm. (picrate, m.p. 197·7°), reduced by Sn–HCl (Na–EtOH causes decomp.) to 2-2′-*thienylpyrrolidine* (I), b.p. 88—89°/3 mm., $-\log K_B$ 6·47 in MeOH, 4·65 in H_2O (picrate, m.p. 187·6°). 1 : 3 : 5 : 2-$C_6H_2Me_3Br$ gives similarly 2-*mesityl-pyrroline*, b.p. 101—102° (corr.)/2 mm. [*picrate*, m.p. 180° (corr.)], and -*pyrrolidine*, b.p. 124·2° (corr.)/3·5 mm., $-\log K_B$ 6·73 in MeOH (picrate, m.p. 194·6°; resists resolution). (I) gives a camphorate, m.p. 128—129°, $[\alpha]_D^{21}$ +15·54° in EtOH, and thence a partly resolved base, $[\alpha]_D^{23}$ −3·12° in EtOH. R. S. C.

Chemotherapy. I. Substituted sulphanilamidopyridines. R. O. Roblin, jun., and P. S. Winnek. **II. Heterocyclic sulphanilamido-compounds.** R. O. Roblin, jun., J. H. Williams, P. S. Winnek, and J. P. English (J. Amer. Chem. Soc., 1940, **62**, 1999—2002, 2002—2005).—Products marked (*A*) below are more active chemotherapeutically than sulphanilamide and sulphapyridine; those marked (*S*) are slightly active; others are inactive. Solubility in H_2O and max. blood levels are recorded. The importance of the latter as indicating presence in the blood of a reasonable amount of the drug is stressed. M.p. are corr.

I. The following are prepared. 2- (*A*), m.p. 190—191°, and 3-sulphanilamidopyridine (*A*), m.p. 258—259° (decomp.); 2-*chloro-* (*A*), m.p. 186—187°, 2-*bromo-* (*A*), m.p. 196—197°, 2-*amino-*, m.p. 207—208°, 2-*hydroxy-*, m.p. 243—244° (decomp.), and 2-*ethoxy-*, m.p. 207—208°, -5-*sulphanilamidopyridine*; 5-*bromo-*, m.p. 199—200°, 5-*iodo-*, m.p. 220—221°, 5-*nitro-* (*A*), m.p. 220—221°, 5-*amino-* (*A*), m.p. 157—158°, and 3-*ethoxy-* (*S*), m.p. 198—200°, -2-*sulphanilamidopyridine*; 2 : 5-*disulphanilamidopyridine* (*S*), m.p. 215—216°. The effect of substituents is remarkable. Hydrogenation [$Pd(OH)_2$–$CaCO_3$] of 2-*p*-nitrobenzenesulphonamido-3-ethoxypyridine in 95% EtOH at 50°/3—4 atm. gives 2-p-*hydroxylaminobenzenesulphonamido*-3-*ethoxypyridine*, m.p. 189—190°.

II. Addition of malic acid and then of NH:$C(NH_2)_2$,H_2SO_4,0·5H_2O to 20% fuming H_2SO_4 at 0° gives *iso*cytosine sulphate (69%), converted by boiling $POCl_3$ into 4-chloro-2-aminopyrimidine (71%), which was H_2–$Pd(OH)_2$–$CaCO_3$ in MeOH or EtOH at 50°/3—4 atm. gives 2-aminopyrimidine. By the usual methods are obtained: 2-*sulphanilamido-thiazole* (*A*), m.p. 201—202°, -4-*methylthiazole* (*A*), m.p. 237—238°, -*benzthiazole*, m.p. 304—305° (decomp.), -4-p-*diphenylylthiazole*, m.p. 216—217°, -1 : 3 : 4-*thiadiazole*, *p*-NH_2·C_6H_4·SO_2·NH·C$\lessgtr^{S\cdot CH}_{N\cdot N}$, m.p. 216—218° (decomp.), -*pyrimidine* (I) (*A*), m.p. 255—256° (decomp.) (*Na* salt; $N^{4'}$-*Ac* derivative, m.p. 258—259°), and -4-*methylpyrimidine* (II) (*A*), m.p. 235—236° (decomp.) ($N^{4'}$-*Ac* derivative, m.p. 248—249°); 1-*sulphanilyl*-3-*methyl-* (*S*), m.p. 166—167°, and 4-*sulphanilamido*-1-*phenyl*-2 : 3-*dimethyl-*, m.p. 260—261° (decomp.), -5-*pyrazolone*; 5-p-*nitrobenzenesulphanilamidotetrazole* (III), m.p. 185—186° (decomp.); *sulphanilylguanidine* (IV) (*S*), m.p. 189—190° (decomp.); 5-*sulphanilamidouracil*, m.p. 277—279° (decomp.). Attempts to reduce the NO_2 of (III) led to (IV) or its NO_2-derivative. (I) and (II) show promise clinically. To avoid confusion it is proposed to call (I), (II), etc. "sulphadiazines." R. S. C.

Synthesis of ωω′-bis-2′-amino-4′-thiazolylalkanes and N^4-2′-thiazolylsulphanilamides. J. Walker (J.C.S., 1940, 1304—1307).—Adipoyl chloride and CH_2N_2 give *αδ-bis-diazo-*, m.p. 69—71°, converted by HCl into the -*chloro-acetyl*-n-*butane*, m.p. 81—82°, which with $CS(NH_2)_2$ yields *αδ-bis*-2-*aminoyl*-4-*thiazol*-n-*butane*, m.p. 220—221° [*dihydrochloride*, m.p. 284—285° (efferv.)]. Similarly *αζ-bischloroacetyl*-n-*hexane*, m.p. 85—86°, prepared from suberoyl chloride, with $CS(NH_2)_2$ forms *αζ-bis*-2-*amino*-4-*thiazolyl*-n-*hexane*, m.p. 204—205° (*dihydrochloride*, m. p. 308—310°). *α0-Bis*-2-*amino*-4-*thiazolyl*-n-*octane*, m.p. 180—181° [*dihydrochloride*, m.p. 309—311° (efferv.)], and *ακ-bis*-2-*amino*-4-*thiazolyl*-n-*decane*, m.p. 168—171° (*dihydrochloride*, m.p. 274—276°), are similarly obtained. The Arndt–

Eistert method has been applied to the bis-homologation of sebacic and adipic acids. 4-*Sulphonamidophenylthiocarbamide*, m.p. 209°, prepared from sulphanilamide and NH_4CNS, condenses with CH_2Cl·COMe and COMe·CHBr·$[CH_2]_2$·OAc to give respectively N^4-4′-*methyl*-, m.p. 234—235°, and N^4-5′-β-*hydroxyethyl*-4′-*methyl*-2′-*thiazolylsulphanilamide*, m.p. 211—212°. F. R. S.

Anthraquinonylthiazoles.—See B., 1940, 727.

Minor alkaloids of *Duboisia myoporoides*. III. Valeroidine. W. F. Martin and W. Mitchell (J.C.S., 1940, 1155—1157).—Valeroidine (I) and Ac_2O give the Ac derivative, isolated as the *hydrobromide*, m.p. 197°, and with $Bu^{\beta}COCl$, *diisovaleryldihydroxytropan hydrobromide*, m.p. 176—177°, is obtained. Dihydroxytropan also forms a Ac_2 derivative, isolated as the hydrobromide, m.p. 219—220°. The hydrobromide of (I) is demethylated by $SOCl_2$ to *norvaleroidine hydrobromide*, m.p. 270°, $[\alpha]_D^{20}$ +1·0° in H_2O. Attempts to orient the OH groups have given obscure results. F. R. S.

Synthesis of formylphenacetyltropeine. Y. Asahina and H. Nogami (Proc. Imp. Acad. Tokyo, 1940, **16**, 229—230).—Homotropine hydrochloride with NaOAc–Ac_2O gives *acetylhomotropine*, an oil [*picrate*, m.p. 229° (decomp.)], the *hydrochloride*, m.p. 67°, of which is catalytically reduced in EtOH (Pd–C) (cf. Rosenmund *et al.*, A., 1928, 1005) to *phenacetyltropeine*, an oil (*picrate*, m.p. 169°). This with HCO_2Et–Na–Et_2O, followed by H_2O, gives *formylphenacetyltropeine* (" *atropanal* ") (I), m.p. 214° (decomp.) [*hydrochloride*, m.p. 204° (decomp.); *oxime*, m.p. 139° (decomp.) (*hydrochloride*, m.p. ~165°)]. This has no mydriatic action, and is weaker than atropine (II) in its paralysing action on parasympathetic endings, but is a strong respiratory stimulant causing small rise of blood pressure. It is suggested that (II) injected into the portal vein is (at least partly) oxidised to (I) in the liver. E. W. W.

Gelsemine. I. Reduction of gelsemine. T. T. Chu and T. Q. Chou (J. Amer. Chem. Soc., 1940, **62**, 1955—1957).—Gelsemine (I) absorbs 2 H in presence of PtO_2 in MeOH, giving *dihydrogelsemine*, $C_{20}H_{24}O_2N_2$, + $COMe_2$, m.p. 224—225°, $[\alpha]_D^{17}$ +78·5° in $CHCl_3$ [*hydrochloride*, m.p. 318—320° (decomp.); *hydrobromide*, m.p. 328—330° (decomp.); *hydriodide*, m.p. 294—295°; *nitrate*, m.p. 285° (decomp.); *methiodide*, m.p. 301—302° (decomp.)]. Zn–HCl in presence of a little $PtCl_4$ or $PdCl_2$ isomerises (I) to iso*gelsemine*, +$COMe_2$, froths at 105°, resolidifies, melts at 198—202°, or solvent-free at 200—202°, $[\alpha]_D^{19}$ +38·8° [*methiodide*, m.p. 279—280° (decomp.)], and gives also a small amount of a *substance*, $C_{18}H_{22}O_4N$, sinters at 261°, decomp. 265—267°, $[\alpha]_D^{18}$ −14·9° in MeOH [*hydrobromide*, m.p. 305—308° (decomp.); methiodide, decomp. 262—265°]. R. S. C.

Alkaloids of fumariaceous plants. XXIX. Constitution of cryptocavine. R. H. F. Manske and L. Marion (J. Amer. Chem. Soc., 1940, **62**, 2042—2044).—Cryptocavine methosulphate and Na–Hg in hot dil. H_2SO_4 give tetrahydromethylcryptocavine, converted by AcCl into anhydrotetrahydromethyl-cryptocavine (-cryptopine), m.p. 111°, which with $KMnO_4$–$COMe_2$ gives 5 : 6 : 2 : 1-CH_2O_2:C_6H_2Me·CHO and 4 : 5 : 1 : 2-$(OMe)_2C_6H_2(CHO)$·$[CH_2]_2$·NMe_2. Cryptocavine is thus cryptopine (J.C.S., 1916, **109**, 815) in which the positions of the CO and CH_2 are reversed. R. S. C.

Sulphophenylarsinic acids and their derivatives. III. *p*-Sulpho- and *p*-sulphonamidodiphenylarsinic acids. J. F. Oneto and E. L. Way (J. Amer. Chem. Soc., 1940, **62**, 2157—2158).—The Bart reaction in EtOH, applied to *p*-SO_3H·C_6H_4·NH_2 (I) and $AsPhCl_2$, gives (I) (64%) and $PhAsO_3H_2$ (84%), but diazotisation of (I) in H_2O, addition of $AsPhCl_2$ in EtOH and then of a little CuBr, and finally heating at 80° gives *phenyl*-p-*sulphophenylarsinic acid*. Addition of AsPhO, NaOH, and a little $CuSO_4$ in H_2O to diazotised sulphanilamide gives 11% of *phenyl*-p-*sulphonamidophenylarsinic acid* (II), m.p. 229—231°, obtained in 23 and 28—30% yields by the Sakellarios and Scheller methods, respectively. $NaNO_2$–H_2SO_4–EtOH–H_2O converts $AsPhCl_2$ into $PhAsO_3H_2$ (86%). HCl–HI–SO_2 converts (II) into *phenyl*-p-*sulphonamidophenylchloroarsine*, m.p. 106—107°. The *bromoarsine*, m.p. 100—101°, similarly obtained, with aq. NH_3 at 100° gives *diphenyldi*-p-*sulphonamidophenylarsyl oxide*. HI–AcOH converts (II) into the *iodoarsine*, m.p. 121—122°, and NaOCl gives *phenyl*-p-*sulphonchloroamidophenylarsinic acid*, m.p. 160—161°. R. S. C.

Colour tests for organo-lithium compounds. H. Gilman and J. Swiss (J. Amer. Chem. Soc., 1940, **62**, 1847—1849).—(*a*) When a solution of LiAlk is treated successively with *p*-C_6H_4Br·NMe_2–C_6H_6, $COPh_2$–C_6H_6, H_2O, and HCl, a red colour develops in the aq. layer owing to the reactions: LiAlk + *p*-C_6H_4Br·NMe_2 (I) → Li·C_6H_4·NMe_2-*p* (II) + AlkBr; (II) + $COPh_2$ → (HCl) CPh_2:C_6H_4:NMe_2Cl. LiAr does not react. MgRHal does not react with (I) and with $COPh_2$ gives colourless CPh_2R·OH. LiMe and LiC:CR do not react. (*b*) When LiR is added to $CHPh_3$ in C_6H_6 or Et_2O, a yellow colour develops in 0·5—2 min., but Grignard reagents do not react. R may be alkyl or aryl. LiMe and Li 4-dibenzfuryl give no colour. For $LiBu^{\alpha}$ the limit is 0·02—0·03M. R. S. C.

Hydrogen bond in protein structure.—See A., 1940, I, 404.

Hydrogen bridge models for globular proteins.—See A., 1940, I, 404.

[Apparatus for] micro-analysis of gases.—See A., 1940, I, 420.

Micro-Kjeldahl apparatus.—See A., 1940, I, 421.

Identification of alcohols by means of optical properties of esters of carbanilic acid. B. T. Dewey and N. F. Witt (Ind. Eng. Chem. [Anal.] 1940, **12**, 459—460).—The phenylurethanes of *n*-alcohols C_1—C_{12}, and of CH_2Ph·OH, Ph·$[CH_2]_2$·OH, and Ph·$[CH_2]_3$·OH have been prepared and their m.p. and optical crystallographic data recorded. The optical properties provide a means of identifying the urethanes even when they are mixed with $CO(NHPh)_2$. J. D. R.