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JUNE, 1943

A., II.—ORGANIC CHEMISTRY

CONTENTS

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CONTENTS

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A., II.—Organic Chemistry

JUNE, 1943.

I.—ALIPHATIC.

Photochemical reactions of the halogens with aliphatic compounds.—See A., 1943, I, 159.

Production of *iso*octane.—See B., 1943, II, 70.

Progress of butadiene production.—See B., 1943, II, 69.

Kinetics and energetics of the high-temperature cracking of methane to acetylene.—See A., 1943, I, 156.

Polymerisation of acetylene to benzene. P. Pascal and C. Coupard (*Compt. rend.*, 1942, **214**, 757—759).—C_2H_2 passed over C–Al_4C_3 at 700—725° yields C_6H_6 (50—60), PhMe, PhEt, xylene, and $CHPh{:}CH_2$ (together 10—15), $C_{10}H_8$ (10—15), Ph_2 (5—10), and anthracene hydrocarbons (5—10%). A. LI.

Alkyl halides containing a quaternary carbon atom.—See B., 1943, II, 70.

Action of halogen acids on alcohols in presence of benzene. S. P. Walvekar, N. L. Phalnikar, and B. V. Bhide (*J. Indian Chem. Soc.*, 1942, **19**, 409—413).—In the absence of C_6H_6 the rate of action with HCl of EtOH, Pr$^{\alpha}$OH, Bu$^{\alpha}$OH, and CH_2Bu$^{\beta}$·OH follows the sequence Et > Pr$^{\alpha}$ > Bu$^{\alpha}$ > CH_2Bu$^{\beta}$. The rate, however, increases when C_6H_6 is present and this increase is explained by solubility considerations. H. W.

Aliphatic trisulphonylmethanes. E. Samén (*Arkiv Kemi, Min., Geol.*, 1942, **15**, **B**, No. 15, 8 pp.).—Pr$^{\alpha}$SH and boiling HCO_2H give $CH(SPr^{\alpha})_3$, b.p. 150—151°/9 mm., oxidised (Et_2O–*o*-CO_2H·C_6H_4·CO_3H at −10°) to *tri*-n-*propanesulphonyl-methane*, m.p. 235—237°, converted (halogen in H_2O or dil. NaOH) into the *-methyl bromide*, m.p. 142—143°, and *chloride*, m.p. 123—124°. Similarly prepared are $CH(SO_2Bu^{\alpha})_3$, m.p. 228—230°, *tri*-n-*butanesulphonylmethyl bromide*, m.p. 83—84°, and *chloride*, m.p. 57—58°. SO_2Et·$CH(SO_2Me)_2$, m.p. 276—278°, affords *bismethanesulphonylethanesulphonylmethyl bromide*, m.p. 136—137°, and *chloride*, m.p. 149—150°. M.p. are corr. $CH(SO_2Alk)_3$ are strong acids; conductivity data are given. A. T. P.

Kinetics of the reaction between γ-ethylsulphonylbutan-β-one and bromine in aqueous hydrobromic acid.—See A., 1943, I, 156.

Photochemical chlorination and sulpho-chlorination of paraffin hydrocarbons in carbon tetrachloride solution.—See A., 1943, I, 159.

Peroxides in *iso*propanol. C. E. Redemann (*J. Amer. Chem. Soc.*, 1942, **64**, 3049—3050).—Pr$^{\beta}$OH rapidly forms peroxides in air in bright light, up to 0·36 mol. per l. being found in an old sample. R. S. C.

Batyl alcohol. N. Kornblum and H. N. Holmes (*J. Amer. Chem. Soc.*, 1942, **64**, 3045—3046).—$CH_2{:}CH{\cdot}CH_2{\cdot}ONa$ (**I**) and *n*-$C_{18}H_{37}I$ at 60—65° give 70—79% of *n*-$C_{18}H_{37}{\cdot}O{\cdot}CH_2{\cdot}CH{:}CH_2$, m.p. 28·5—29°, b.p. 150—152°/2 mm. (cf. Davies *et al.*, A., 1931, 62), converted by 30% H_2O_2 in AcOH at 80—85° into batyl alcohol (55—67%), sinters 69°, m.p. 70—71° (corr.). $CH_2{:}CH{\cdot}CH_2{\cdot}OH$ and (**I**) at the b.p. condense to give high-boiling, unsaturated neutral and acidic products. R. S. C.

Further attempted purification of vitamin-A_2. P. Karrer and E. Bretscher (*Helv. Chim. Acta*, 1942, **25**, 1650—1653; cf. A., 1942, II, 185).—In pike-liver oil of the winter of 1941 the ratio vitamin-A_2 : -*A* is greatly displaced in favour of -A_2 in comparison with the summer oils of 1941 and 1942. After threefold chromatography over $Ca(OH)_2$ followed by mol. distillation a product is obtained in which the -*A* band at 620 mμ. cannot be detected with certainty. It appears that the ratio of the max. extinction coeff. of the blue spectrum of the $SbCl_3$ reaction and the ultra-violet spectrum differs in the cases of -A_2 and -*A*. Degradation of the purest products with O_3 gives a substance which yields CHI_3 but is not identified with certainty as $COMe_2$. H. W.

Preparation of pentaerythritol.—See B., 1943, II, 71.

Diacetone- [**di*iso*propylidene-**]xylitol.** R. S. Tipson and L. H. Cretcher (*J. Org. Chem.*, 1943, **8**, 95—98).—Xylitol is converted by $COMe_2$ containing anhyd. $CuSO_4$ and a little conc. H_2SO_4 into *diiso*propylidenexylitol, m.p. 34—34·5°, $[\alpha]_D^{25}$ ±0° in $COMe_2$, transformed by *p*-$C_6H_4Me{\cdot}SO_2Cl$ in dry C_5H_5N into the p-*toluenesulphonate*, m.p. 70—71°, $[\alpha]_D^{25}$ ±0° in abs. EtOH. When treated with NaI in $COMe_2$ at 100° this affords *p*-$C_6H_4Me{\cdot}SO_3Na$ (**I**) in 94% yield. This reaction in the sugar series is characteristic of *p*-$C_6H_4Me{\cdot}SO_2$ attached to a primary alcoholic group (cf. Oldham *et al.*, A., 1932, 254). Erythritol is converted by *p*-$C_6H_4Me{\cdot}SO_2Cl$ in C_5H_5N into the *tetra*-p-*toluenesulphonate*, m.p. 165—166°, which with NaI in $COMe_2$ gives (**I**) in 91% yield with apparently $(CH_2{:}CH)_2$. Oldham's rule does not therefore apply to the sugar alcohols. H. W.

βγδε- and a second dimethylene-*D*-mannitol. W. T. Haskins, R. M. Hann, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1943, **65**, 67—70).—*D*-Mannitol, 37% CH_2O, and conc. HCl at 100° give trimethylene-, m.p. 232° (cf. Schulz *et al.*, A., 1894, i, 438; 1896, i, 115; named mannitol triformacetal), and αγδζ- or αγεζ-*dimethylene*-D-*mannitol* (**I**), m.p. 204—208°, [α] −91·0° in H_2O. *D*-Mannitol αζ-dibenzoate with 37% CH_2O and dry HCl in dioxan at 0—5° gives βγδε-*dimethylene*-D-*mannitol* αζ-*dibenzoate*, m.p. 120—122°, [α] +47·5° in $CHCl_3$, converted by NaOMe–MeOH in $CHCl_3$ at 5° into βγδε-*dimethylene*-D-*mannitol* (**II**) (85%), m.p. 139°, [α] +71·7° in H_2O (αζ-*diacetate*, m.p. 105—106°, [α] +98·3° in $CHCl_3$). (**II**) gives a αζ-*di*-p-*toluenesulphonate*, m.p. 164—165°, [α] +68·1° in $CHCl_3$, converted by NaI in $COMe_2$ at 100° into the αζ-di-iodide (**III**) (98%), m.p. 196—197°, [α] +49·7° in $CHCl_3$ (Micheel, A., 1932, 834). With Raney Ni–H_2–NaOH in MeOH, (**III**) gives βγδε-dimethylene-αζ-dideoxy-*D*-mannitol, m.p. 59—60°, [α] +54·9° in $CHCl_3$ (cf. *loc. cit.*), and thence (boiling 10% HCl) αζ-*dideoxy*-D-*mannitol*, m.p. 147—148°, [α] −22·5° in H_2O, which with HIO_4 gives 1·90 MeCHO, proving the αζ-position of the deoxy-groups. (**II**) does not reduce HIO_4, gives a *diacetate*, m.p. 166°, [α] −64·4° in $CHCl_3$, *dibenzoate*, m.p. 180°, [α] +9·5° in $CHCl_3$, and *di*-p-*toluenesulphonate*, m.p. 147°, [α] −37·3° in $CHCl_3$ (unaffected by NaI in $COMe_2$ at 100° or in Ac_2O at 140°). M.p. are corr. [α] are $[\alpha]_D^{20}$. R. S. C.

Ring structure of polygalitol. N. K. Richtmyer and C. S. Hudson (*J. Amer. Chem. Soc.*, 1943, **65**, 64—67).—Polygalitol (**I**) (prep. from roots of *Polygala senega*, N.F.; sucrose also present), m.p. 141—142°, $[\alpha]_D^{20}$ +42·5° in H_2O (tetra-acetate, dimorphic, m.p. 65—67° and 73—74°), is crystallographically identical with aceritol. (**I**) and styracitol (**II**) consume 2 equivs. of $NaH_5I_2O_6$, giving 1 HCO_2H, and consume 2 HIO_4, giving a dialdehyde, converted by Br–Sr$(OH)_2$ into *Sr* D-*hydroxymethyldiglycollate*, +4H_2O, $[\alpha]_D^{20}$ −13·9 ± 0·4° (anhyd.) in H_2O, +45·4—45·6 ± 0·4° (calc. for acid) in N-HCl. (**I**) and (**II**) are isomeric αε-anhydro-*D*-hexitols. R. S. C.

β-Sulphinopropionic acid and related compounds. J. A. Reuterskiöld (*Arkiv Kemi, Min., Geol.*, 1941, **14**, **B**, No. 16, 6 pp.).—Cl·$[CH_2]_2$·CO_2H and $(CH_2{\cdot}SH)_2$ in slightly alkaline solution at 0° give *ethane-αβ-di(thiol-β′-propionic acid)*, $(CO_2H{\cdot}[CH_2]_2{\cdot}S{\cdot}CH_2)_2$, m.p. 158·5—159·5°. Oxidation with 5% aq. $KMnO_4$ gives the corresponding *disulphone*, m.p. 300° (decomp.), converted by aq. NaOH (1 day), followed by $SrCl_2,6H_2O$ (neutralise with 0·5N-HCl), into the *Sr* salt (+3H_2O), and thence into the Ag_2 salt, and finally *β-sulphinopropionic acid*, m.p. 73—76°, resolidifies at ~100° and re-melts at 122—124°. A. T. P.

Reactions of atoms and free radicals in solution. IV. Decomposition of acetyl peroxide in aliphatic acids. Synthesis of succinic acid and its substitution derivatives. M. S. Kharasch and M. T. Gladstone (*J. Amer. Chem. Soc.*, 1943, **65**, 15—17; cf. A., 1942, II, 393).—Ac_2O_2 (0·144) in AcOH at 85—95° gives CO_2 (0·22), CH_4 (0·212), MeOAc (0·0072), and $(CH_2{\cdot}CO_2H)_2$ (0·072 mol.), in $Pr^{\beta}CO_2H$ 0·066 mol. gives CO_2 (0·088), CH_4 (0·08), MeOAc (0·0072), and $(CMe_2{\cdot}CO_2H)_2$ (0·028 mol.), m.p. 191—192° (anil, m.p. 85°), and in $CH_2Cl{\cdot}CO_2H$ gives CO_2, CH_4, and *meso*-$(CHCl{\cdot}CO_2H)_2$. Reaction is postulated as $Ac_2O_2 \rightarrow Me{\cdot} + AcO' + CO_2$, $AcOH + Me{\cdot} \rightarrow CH_4 + {\cdot}CH_2{\cdot}CO_2H \rightarrow (CH_2{\cdot}CO_2H)_2$ etc., also $AcO{\cdot} \rightarrow MeOAc + CO_2$. Ac_2O_2 in AcCl gives $COCl{\cdot}[CH_2]_2{\cdot}CO_2Ac$ (no details). R. S. C.

Fats. CIII. Reaction of tetranitromethane with fatty acids and fats. H. P. Kaufmann [with P. Kirsch, B. W. King, and L. S. Huang] (*Ber.*, 1942, **75**, [*B*], 1201—1214).—Fatty acids with a triple linking, like other compounds of the C_2H_2 series, do not give a colour with $C(NO_2)_4$. Fatty acids and fats with isolated double linkings give colours which darken as the I val. increases. Glycerides and fatty acids with conjugated unsaturated linkings give in 10% solution a blood-red colour which weakens and tends towards

orange with increasing dilution. With trebly conjugated-unsaturated compounds the colour persists but fades to rose. The limit of detection of elæostearic acid in CCl_4 is 0·03% whilst recognisable reaction is observed with tung oil (1 in 1000). All conjugated-unsaturated systems do not give a colour with $C(NO_2)_4$. Great differences are observed between the behaviour of *cis–trans* isomeric fatty acids. For the development of full colour a very large excess of $C(NO_2)_4$ is required. The Lambert–Beer law is obeyed. The relationship between I val. and extinction val. for solutions of oleic acid in $CHCl_3$ is approx. rectilinear but its use for the photometric determination of the I val. of unknown fats is not considered sufficiently accurate. The possibility that the action of $C(NO_2)_4$ on fatty acids may cause elaidinisation is established by the observed conversion of oleic (**I**) into elaidic (**II**) and of erucic into brassidic acid. Olive oil yields palmitodielaidin. Polymerisation phenomena are observed with linoleic and linolenic acid, chaulmoogra and cod-liver oil but it is undecided whether the action is a true polymerisation or a ring formation with co-operation of O (dioxan system). (**II**) is oxidised by $C(NO_2)_4$ in boiling CCl_4 to nonaldehyde (**III**) and nonoic (**IV**), θ_t-diketostearic, and azelaic acid with unidentified polymerised material. Under similar conditions stilbene affords benzil, BzOH, and PhCHO and $(CHMe:)_2$ yields AcOH, MeCHO, and Ac_2. (**I**) gives the same products as (**II**) possibly by reason of preliminary elaidinisation. Erucic acid is converted into (**III**), (**IV**), brassylic acid (Me ester, m.p. 35—36°), and $\mu\nu$-diketobehenic acid, m.p. 91—92°. Attempts to isolate the primary adducts on which the colour changes depend were unsuccessful. The reaction products include $CH(NO_2)_3$, NO, and CO_2. Not infrequently the reaction leads to explosions for no obvious reason. H. W.

Fatty acids. XI. Isolation of linoleic acid from vegetable oils by low-temperature crystallisation. J. S. Frankel, W. Stoneburner, and J. B. Brown (*J. Amer. Chem. Soc.*, 1943, **65**, 259—262).—Sesamé, cotton-seed, grape-seed, and poppy-seed oil yield, by crystallisation from $COMe_2$ (cf. A., 1941, II, 239), 97—100%-pure α-linoleic acid, but olive oil gives mixed stereoisomerides R. S. C.

Course of autoxidation reactions in polyisoprenes and allied compounds. IV. Isolation and constitution of photochemically formed methyl oleate peroxide. V. Observations on fish-oil acids. E. H. Farmer and D. A. Sutton. **VI. Peroxidation of rubber.** E. H. Farmer and A. Sundralingam (*J.C.S.*, 1943, 119—122, 122—125, 125—133).—IV. Mol. distillation or chromatographic analysis of the product of autoxidation at 35° of Me oleate yields an unsaturated *mono-* (with a small amount of di-)*hydroperoxide*, reduced (H_2, PtO_2 in EtOH) to Me hydroxystearate or (Al–Hg in Et_2O) to Me hydroxyoleate; $Fe(NH_4)_2(SO_4)_2$ effects partial reduction.

V. Me dodecahexaenoate rapidly absorbs O_2, giving peroxides which decompose spontaneously into oxygeno-compounds (some of which contain only 1 atom of absorbed O per C_{23} chain) and scission products (responsible for the fishy odour). These products and those from ling oil show increased light absorption.

VI. Peroxide formation is 80—90% in the early stages of oxidation (O_2) of rubber at 35° in C_6H_6, but steadily decreases as oxidation proceeds. Determinations of I val. and active H val. show that O_2 initially enters active CH_2 groups as O_2H groups, secondary reactions giving OH-compounds. Oxidative scission occurs from the outset, the final products being neutral, mol. wt. a few thousand, and acidic substances, mol. wt. 700—800, the quantity of O_2 absorbed being > adequate to account for the scissions. Small quantities of H_2O and CO_2 are formed at all stages, elimination of H_2O continuing after the oxidation products have been isolated. A. Li.

High polymerides and new rules. S. Weiner (*J. Chem. Educ.*, 1942, **19**, 514—516). L. S. T.

Configurative relationship between optically active lactic and thiolactic acids.—See A., 1943, I, 154.

Synthesis of the *cis*- and *trans*-form of an *iso*ambrettolide and of civetone. H. Hunsdiecker (*Naturwiss.*, 1942, **30**, 587).—Aleuritic acid (A., 1927, 447) when heated with AcOH–HBr affords θ_{iso}-tribromopalmitic acid, which with Zn–EtOH gives o-bromo-Δ^9-hexadecenoic acid in the olein and *elaidin* (**I**), m.p. 42°, forms. On heating with K_2CO_3 in COMeEt these yield the corresponding hexadecenolides differing from ambrettolide only in the position of the double linking. The *elaidin* form (**II**) of *iso*ambrettolide is a viscous fluid, b.p. 131°/0·7 mm., yielding with H_2 o-hexadecanolide. On hydrolysis (**II**) affords a *o-hydroxy-*Δ^8*-hexadecenoic acid*, m.p. 70°. The olein form was not obtained pure. The synthesis of natural civetone was similar. (**I**) was converted via the acid chloride into *Me p-bromo-β-keto-*Δ^κ*-hexadecenoate*, m.p. 25°. The corresponding *l*-compound, m.p. 35°, on intramol. acetoacetic ester condensation gives *Me civetone-α-carboxylate*, b.p. 175°/0·2 mm., which on hydrolysis and elimination of CO_2 yields natural civetone, which is thus the elaidin form. J. H. B.

Isolation and constitution of an acid from the root bark of *Ixora coccinea* (Linn.). A. R. S. Kartha and K. N. Menon (*Proc. Indian Acad. Sci.*, 1943, **17**, **A**, 11—15).—The light petroleum extract of the fresh root bark consists of a liquid, $\Delta^{9\kappa}$*-heptadecadienoic acid* (*Me* ester, b.p. 195—196°/5 mm.; *Et* ester, b.p. 215—216°/5 mm.). which may be that obtained by Chonowsky (A., 1909, i, 760). The residue from the bark extracted with EtOH yielded mannitol. F. R. G.

Structure of arachidonic and linoleic acids. C. L. Arcus and I. Smedley-Maclean (*Biochem. J.*, 1943, **37**, 1—6).—Ozonolysis and oxidation of methyl arachidonate with $KMnO_4$ in $COMe_2$ confirm that arachidonic acid is $\Delta^{\beta\eta\kappa\nu}$-eicosatetraenoic acid (cf. Dolby *et al.*, A., 1941, II, 4). Contrary to the results of Takahashi, ozonolysis of Et linoleate shows that the acid is $\Delta^{9\lambda}$-octadecadienoic acid. J. N. A.

Maleic anhydride as reagent for conjugated diolefines. R. F. Robey (*Science*, 1942, **96**, 470).—Certain dienes fail to respond to this reagent. E. R. R.

Determination of 2 : 3-diketo-*l*-gulonic acid.—See A., 1943, III, 448.

Molecular compound of optically active di-(α-carboxyethyl) disulphide and αα′-dithioladipic acid.—See A., 1943, I, 153.

Production of aldehydes and ketones from nitro-paraffins. K. Johnson [with E. F. Degering] (*J. Org. Chem.*, 1943, **8**, 10—11).—The NO_2-paraffin is dissolved in dil. aq. NaOH and the solution is added dropwise to ice-cold, dil. H_2SO_4 with good stirring. N_2O is immediately evolved. $Ca(OH)_2$ may replace NaOH but more time must be given for the initial reaction. The prep. of $COMe_2$, MeCHO, EtCHO, Pr$^\alpha$CHO, Pr$^\beta$CHO, and COMeEt is described. The reaction is generally applicable for the synthesis of aldehydes and ketones. H. W.

Structural effects of unsaturation and hyperconjugation in aldehydes, nitriles, and chlorides.—See A., 1943, I, 144.

Catalytic reduction by formic acid under pressure. I. Preparation of aldehydes from carboxylic acids with titanium dioxide as catalyst. R. R. Davies and H. H. Hodgson (*J.C.S.*, 1943, 84—86).—Nonoic, undecenoic, lauric, benzoic, salicylic, and *p*-chloro- and *p*-sulphobenzoic acids are reduced by HCO_2H at 250—260 (TiO_2) in a special apparatus to the aldehydes (22, 25, 31, 37, 92, 41, and 22% yield respectively). Butyric and heptoic acids do not react, and p-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$ gives chiefly $PhNO_2$. A reaction mechanism is suggested. A. Li.

Electrolytic oxidation. XIII. Formaldehyde.—See A., 1943, I, 159.

Hydrogenation of formaldehyde.—See B., 1943, II, 71.

Ketone alcohols. I. Derivatives of β-methylpentan-β-ol-δ-one. C. E. Miller. **II. Derivatives of polymerisation of pentan-γ-one.** K. C. Odney and C. E. Miller (*J. Amer. Pharm. Assoc.*, 1942, **31**, 516—518, 518—519).—I. $OH{\cdot}CMe_2{\cdot}CH_2{\cdot}COMe$ (**I**) (1 mol.) shaken with HCl (*d* 1·175; 3 mols.) at room temp. gives $CMe_2Cl{\cdot}CH_2{\cdot}COMe$, b.p. 45—47°/25 mm., which, refluxed with o-$C_6H_4(CO)_2NK$, did not yield the corresponding amine. (**I**) with AcCl affords *β-acetyl-β-methylpentan-δ-one*, b.p. 46—47°/15 mm. In attempts to prepare a SH analogue, (**I**) was saturated with H_2S at room temp. to yield a S-containing product, b.p. 36—42°/18 mm.; refluxed with K_2S_3–C_6H_6, (**I**) gives a product, b.p. 70—72°/22 mm., which is unsaturated, contains S, and, on degradation, yields $COMe_2$, S, and Pr$^\beta$SH.

II. Vals. of n^{20} (1·3929—1·3951) indicate that, when $COEt_2$ is refluxed in presence of $Ba(OH)_2$, polymerisation is not complete. Distillation after 100 hr. yields 34% of a product, b.p. 98°, 24°/27 mm., I val. 91—139 (*phenylurethane*, m.p. 232—233°; *α-naphthylurethane*, m.p. 217°; *dinitrophenylosazone*, m.p. 148°). F. O. H.

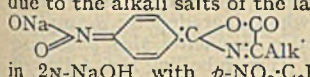
γ-Ethylsulphonylbutan-β-one and its bromo-derivatives. L. Ramberg and B. Bäcklund (*Arkiv Kemi, Min., Geol.*, 1941, **15**, **A**, No.3, 22 pp.).—$CHMeBr{\cdot}COMe$ (from Br and COMeEt) and $EtSO_2Na$ (**I**) in EtOH give (54% yield) *γ-ethylsulphonylbutan-β-one* (**II**), m.p. −1·3°, b.p. 135°/8 mm. [p-*nitrophenylhydrazone*, *A*, orange plates, m.p. 138·8—139·4° (corr.), *B*, yellow needles, m.p. 133·5—134·5° (corr.); $A \rightarrow B$ slowly at room temp., $B \rightarrow A$ in several hr. above the m.p.]. (**II**) with hot dil. KOH gives Et_2SO_2 (98% yield) and KOAc. (**II**) gives in H_2O or 1—2N-HBr at room temp. with 1 mol. of Br (62% yield) *γ-bromo-* (**III**), m.p. 26·0—26·7°, b.p. 140—141°/8 mm., and with excess of Br (5—6 days; 80% yield) *αααγ-tetrabromo-* (**IV**), m.p. 131·9°, but in EtBr with 1 mol. of Br (64% yield) *α-bromo-γ-ethylsulphonyl-butan-β-one* (**V**), m.p. 66·3°, b.p. ~170°/8 mm. (**III**) rearranges to (**V**) at room temp. rapidly in presence of dry HBr > conc. aq. HBr ≫ conc. aq. HCl > alone (several months); dry HCl or Bz_2O_2 has no effect, but the rearrangement is accelerated by ultra-violet light. (**III**) probably oxidises HBr to Br, which then brominates in the α-position. (**III**) reacts with alkalis: (**III**) + $4OH' \rightarrow$ *cis*-$(CH_2{\cdot}CH{:})_2 + SO_3'' + OAc' + Br' + H_2O$ (cf. A., 1940, II, 335), but (**V**) gives Et_2SO_2 and undergoes a complex decomp. (**V**) with (**I**) gives *αγ-bisethylsulphonylbutan-β-one* (**VI**), m.p. 65·3—65·9°, titratable as an acid ($K_{25°}$ = 4·07 × 10^{-7}), but decomposed by hot dil. KOH to Et_2SO_2 and $EtSO_2{\cdot}CH_2{\cdot}CO_2K$ (converted by Br–KBr into $EtSO_2{\cdot}CHBr_2$), with $PhSO_2Na$ (**VII**) *α-phenylsulphonyl-γ-ethylsulphonylbutan-β-one*, m.p. 95·6°, a stronger acid than (**VI**), and with NaSPh (**VIII**)

SO_2Et·CHMe·CO·CH_2·SPh (not characterised), hydrolysed (hot dil. KOH) to Et_2SO_2 (84%) and SPh·CH_2·CO_2K; (**I**), (**VII**), and (**VIII**) are oxidised by (**III**) without coupling. (**IV**) oxidises KI, SO_2, N_2H_4, etc., the γ-Br atom probably being reduced, but the *aaa*-Br_3-derivative could not be isolated. With alkali in MeOH at room temp. (**IV**) gives SO_2Et·$CBrMe·CO_2'$ (77% yield) and $CHBr_3$ (60% yield). M. H. M. A.

***tert.*-Alkyl primary amines, CRR'R''·NH_2. II.** H. R. Henze, B. B. Allen, and W. B. Leslie (*J. Amer. Chem. Soc.*, 1943, **65**, 87—89).—The abnormal reaction of CH_2:CH·CH_2·MgCl (**I**) (2 mols.) with OEt·CH_2·CN (**II**) (1 mol.) to give a *tert.* amine (A., 1939, II, 409) is not confined to (**II**). Thus, the appropriate nitrile yields 30—59% of *aa-diallyl-*Δ$^{\gamma}$-n-*butenylamine* [*triallylcarbinylamine*] (**III**), b.p. 182—183·5°/741 mm. (*picrate*, m.p. 173·5—174·5), *aa-diallyl-*n-*butyl-* (**IV**), b.p. 190—191°/742 mm. (*picrate*, m.p. 149—149·5°), and -n-*amyl-amine*, b.p. 205—206°/742 mm. (*picrate*, m.p. 121·5—122°), *α-benzyl-*, b.p. 268·5° (decomp.)/742 mm. (*picrate*, m.p. 139·5—140°), and *α-*n-*butoxy-*, b.p. 233—234°/742 mm. (*picrate*, m.p. 106·5—107°), *-α-allyl-*Δ$^{\gamma}$-n-*butenylamine*. OBu^{a}·CH_2·CN (prep. from CH_2Cl·OBu^{a} and CuCN) (0·28), b.p. 79°/30 mm., with $MgBu^{a}Br$ (0·28) and then (**I**) (0·37 mol.) in Et_2O gives *α-*n-*butoxymethyl-α-allyl-*n-*amylamine* (54%), b.p. 247·5—248·5°/742 mm. (*picrate*, m.p. 79—80°). H_2–PtO_2 reduces (**III**) in $COMe_2$ or (**IV**) in EtOH to *aa-di-*n-*propyl-*n-*butylamine*, b.p. 190·5—191·5°/742 mm. (*picrate*, m.p. 154—154·5°). Temp. are corr. R. S. C.

Utilisation of aliphatic nitro-compounds. V. Reduction of nitro-alcohols and -glycerols to the corresponding amines. K. Johnson and E. F. Degering (*J. Org. Chem.*, 1943, **8**, 7—9).—NO_2-alcohols and -glycols are unstable under most reducing conditions but are reduced to the corresponding NH_2-compounds by catalytic hydrogenation (Raney Ni) with fair yields. Some decomp. causes the simultaneous formation of other bases. The method has been applied to the prep. of β-amino-β-methyl-, -β-ethyl-, -β-*n*-propyl-, and -β-*iso*propyl-propane-αγ-diol, NH_2·CMe_2·CH_2·OH, NH_2·CHEt·CHMe·OH, NH_2·CHEt·$CHBu^{a}$·OH, NH_2·CHEt·CH_2·OH, and NH_2·CMeEt·CH_2·OH (for details of these compounds see Vanderbilt and Hass, A., 1940, II, 62). H. W.

Nature of Waser's specific colour reaction for α-amino-acids. P. Karrer and R. Keller (*Helv. Chim. Acta*, 1943, **26**, 50—54; cf. A., 1924, i, 1068).—The intense blue-violet colour formed by the action of *p*-NO_2·C_6H_4·COCl (but not *o-* or *m*-NO_2·C_6H_4·COCl or BzCl) on α-NH_2-acids in presence of Na_2CO_3 or, better, C_5H_5N is due to the alkali salts of the lactones of the *p*-nitrobenzamido-acids,



. Agitation of a solution of *l*-leucine in 2N-NaOH with *p*-NO_2·C_6H_4·COCl in Et_2O gives r-N-p-*nitrobenzoyl-leucine*, m.p. 222—223°, and 2-p-*nitrophenyl*-4-iso*butyloxazol-5-one* (p-*nitrobenzoyl-leucine lactone*), m.p. 76°. H. W.

Biological formation of acetylcholine.—See A., 1943, III, 262.

Magnetic behaviour of complexes of nitrilotriacetic acid, ethylenediaminetetra-acetic acid, and imines of salicylaldehyde.—See A., 1943, I, 119.

Manufacture and application of acid amide derivatives.—See B., 1943, II, 72.

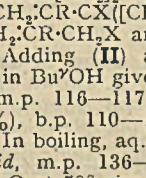
Acrylonitrile. III. Cyanoethylation of αβ-unsaturated compounds. IV. Cyanoethylation of active hydrogen groups. H. A. Bruson and T. W. Riener (*J. Amer. Chem. Soc.*, 1943, **65**, 18—23, 23—27; cf. A., 1943, II, 122).—III. CMeR:CHX (*A*) (X = COMe, $CO·NH_2$, or CN) and CH_2:CH·CN (**I**) in presence of CH_2Ph·NMe_3·OH (**II**) or KOH give CMeR:CX·$[CH_2]_2$·CN and, as main product, by rearrangement of (*A*), CH_2:CR·CX$[CH_2]_2$·CN (*B*). (*A*) exists in equilibrium with CH_2:CR·CH_2X and equilibrium is disturbed by formation of (*B*). Adding (**II**) at 25° and then (**I**) at 5—10° to CMe_2:CH·COMe in $Bu^{\gamma}OH$ gives *γ-acetyl-γ-*iso*propenylpimelodinitrile* (**III**) (73·5%), m.p. 116—117°, and *δ-keto-γ-*iso*propylidene-*n-*hexonitrile* (10—15%), b.p. 110—115°/2 mm. [with (**I**) and (**II**) gives 50% of (**III**)]. In boiling, aq. KOH, (**III**) gives *γ-acetyl-γ-*iso*propylidenepimelic acid*, m.p. 136—137°, which with $Ca(OCl)_2$–KOCl–KOH–K_2CO_3–H_2O at 50° gives $CHCl_3$ and *γ-carboxy-γ-*iso*propenyl-*, m.p. 160°, hydrogenated (Raney Ni) as Na salt in H_2O at 135°/115 atm. to *γ-carboxy-γ-*iso*propyl-pimelic acid* (**IV**), m.p. 160°. COMe·CH_2Pr^{β} with (**I**) and (**II**) in $Bu^{\gamma}OH$ at 32—35° gives *γ-acetyl-γ-*iso*propylpimelodinitrile* (poor yield), m.p. 101° (and much tar), converted, as above, into *γ-acetyl-γ-*iso*propylpimelic acid*, m.p. 148°, and thence (**IV**) [proof of structure of (**III**) etc.]. CH_2:CH·CH_2·CN (**V**) (1) with (**I**) (1 mol.) and (**II**) in $Bu^{\gamma}OH$ at 10—15° (later room temp.) gives *γ-cyano-γ-vinylpimelodinitrile* (**VI**), m.p. 60—61°, and a smaller amount of *γ-cyano-*Δ$^{\gamma}$-n-*hexenonitrile*, b.p. 134—137°/10 mm. [with (**I**) and (**II**) in $Bu^{\gamma}OH$ at 20—30° gives (**VI**)], hydrolysed to *γ-carboxy-γ-vinylpimelic acid* (**VII**), m.p. 153°, and CHMe:C(CO_2H)·$[CH_2]_2$·CO_2H, m.p. 151—153° (lit. 152°). Hydrogenation of (**VII**) gives CO_2H·CEt$([CH_2]_2$·$CO_2H)_2$ (*loc. cit.*), m.p. 171—172°. CHMe:CH·CN gives the same products as does (**V**), proving the existence of the equilibrium. CMe_2:CH·CN (prep. by exothermic rearrangement of CH_2:CMe·CH_2·CN by (**II**) at 30—55°), b.p. 140—142°, with (**I**) and (**II**) in $Bu^{\gamma}OH$ at 30—40° gives *γ-cyano-δ-methyl-*Δ$^{\gamma}$-n-*hexenonitrile*, b.p. 150°/10 mm., and *γ-cyano-γ-*iso*propylidenepimelodinitrile*, m.p. 67—68° (hydrolysed by boiling 10% aq. NaOH to *γ-cyano-γ-*iso*propylidenepimelic acid*, m.p. 167—168°). *cyclo*Hexylideneacetonitrile (prep. from *cyclo*hexanone, CN·CH_2·CO_2H, and C_5H_5N at 10—20° and later 100—105°), b.p. 105—110°/21 mm., with (**I**)–(**II**)–$Bu^{\gamma}OH$ at 28—37° gives mainly *γ-cyano-γ-*Δ$^{\alpha}$-cyclo*hexenylpimelodinitrile*, m.p. 81—82°. CHMe:CH·$CO·NH_2$ with (**I**) and (**II**) in MeCN at 25—30° gives mainly *γ-carbamyl-γ-vinyl-pimelodinitrile*, m.p. 77°, b.p. 235—240°/2 mm.

IV. CH_2 in CH_2Ar·CN, $MeNO_2$, CN·CH_2·CO_2R, $CH_2(CO·NH_2)_2$, $CH_2(CO_2R)_2$, CN·CH_2·$CO·NH_2$, or CH_2Ar·SO_2·NH_2 is substituted by (**I**) in presence of strong alkali [(**II**) or 30% KOH–MeOH] in the solvent named below. Thus are obtained *γ-nitro-γ-β'-cyanoethyl-* (in dioxan; 25—35°), m.p. 114°, *γ-cyano-γ-phenyl-* (in $Bu^{\gamma}OH$; 10—25°; 94%), m.p. 70°, *γ-cyano-γ-*p-*nitrophenyl-* (in dioxan), m.p. 147—148°, *γ-cyano-γ-carbethoxy-* (in dioxan; 30—35°; nearly 100%), m.p. 37°, *γγ-dicarbethoxy-* (in dioxan; 30—35°; 82%), m.p. 62°, *γ-cyano-γ-carbamyl-* (in H_2O; 35—40°), m.p. 118°, *γγ-dicarbamyl-* (in H_2O; 35—38°), m.p. 210°, and *γ-sulphonamido-γ-phenyl-*, m.p. 103—104°, *-pimelodinitrile*, *Et γ-cyano-α-carbethoxy-α-ethyl-*, m.p. 47°, and *-α-benzyl-*n-*butyrate* (in dioxan; 30—35°), m.p. 47°, b.p. 175—180°/1 mm., and *Et α-carbethoxy-α-β'-cyanoethyl-*n-*hexoate* (in dioxan; 30—35°), b.p. 145—150°/1 mm. OH-compounds give the CN·$[CH_2]_2$ ethers. Thus, the appropriate glycol with (**I**) and a little 40% aq. KOH or NaOMe at 25—35° gives 80—95% of *ethylene*, b.p. 158°/2 mm., *αβ-propylene*, b.p. 165°/2 mm., *trimethylene*, b.p. 165°/1 mm., *βγ-butylene*, m.p. 53—54°, b.p. 170°/2 mm., *pentamethylene*, b.p. 185°/1 mm., and *decamethylene glycol di-β-cyanoethyl ether*, b.p. 225°/1 mm', *ββ'-di-(β''-cyanoethoxyethyl) ether*, b.p. 190°/1 mm., and *sulphide*, b.p. 225°/2 mm., *ethylene glycol di-β-β'-cyanoethoxyethyl ether*, b.p. 215°/1 mm., and *αβγ-tri-β'-cyanoethoxyethyl-propane*, b.p. 260°/1 mm. The appropriate oxime with (**I**) and NaOMe, NaOH, or (**II**) at 25—35° to 50—60° gives *acet-*, b.p. 85°/10 mm., *Me Et ket-*, b.p. 109°/21 mm., *acetophenone-*, m.p. 44°, and *furfurald-oxime β-cyanoethyl ether*, m.p. 116°, and *glyoxime*, m.p. 123°, and *benzoin oxime di-β-cyanoethyl ether*, m.p. 72—73°. R. S. C.

Manufacture of α-cyano-Δ$^{\alpha\gamma}$-butadiene.—See B., 1943, II, 72.

II.—SUGARS AND GLUCOSIDES.

Diginin. II. Constitution of diginose. C. W. Shoppee and T. Reichstein (*Helv. Chim. Acta*, 1942, **25**, 1611—1623; cf. A., 1940, II, 336).—Diginonolactone, $[\alpha]_D^{14}$ −29·8°±1° in $COMe_2$, does not give cryst. derivatives with *p*-C_6H_4Br·$NH·NH_2$ or NPh_2·NH_2 at 100°. It is transformed by successive treatments with $Ba(OH)_2$ and *S*-benzylthiuronium sulphate into *S-benzylthiuronium diginonate*, m.p. 137—138°, $[\alpha]_D^{12}$ −9·2°±2° in MeOH. The corresponding *salts* of cymaronic, sarmentonic, and oleandronic acid have m.p. 130—130·5°, $[\alpha]_D^{12}$ 0°±2° in MeOH, m.p. 46°, $[\alpha]_D^{18}$ +6·5°±2°, $[\alpha]_{5461}^{18}$ +10·6°±2°, and 128—130°, $[\alpha]_D^{14}$ +5·8°±2° in MeOH. A ready method for the differentiation of diginose (**I**), cymarose (**II**), sarmentose, and oleandrose is thus afforded. (**II**) is oxidised by $KMnO_4$ (≡4 O) to AcOH and *l*(−)-methoxysuccinic acid, isolated as the diamide (**III**), m.p. 183—184°, $[\alpha]_D^{18}$ −57·2°±2° in MeOH. In the attempted prep. of (**III**) Me_2 *l*(−)-malate was treated successively with CH_2N_2 (which did not cause methylation) and NH_3, thus giving an unstable *form*, m.p. 149—150° after becoming opaque, of *l*(−)-maldiamide; it has $[\alpha]_D^{15}$ −37°±2° in H_2O and solidifies to the stable variety, m.p. 162°. When oxidised similarly (**I**) yields AcOH and *d*(+)-methoxy-succinic acid, identified as the *diamide*, m.p. 183—184°, $[\alpha]_D^{17}$ +56·8°±4° in MeOH. (**I**) is most probably *A*. In acid medium (**II**) reacts relatively slowly with HIO_4 and does not give a well-defined end-point. (**I**) reacts more rapidly but consumes >1 O. In presence of K_2CO_3 oxidation proceeds appreciably more rapidly whereby (**II**) consumes O uniformly up to 1 equiv. and then more slowly but without giving a sharp end-point whilst (**I**) consumes uniformly ~2 equivs., after which a slight retardation is observed. M.p. are corr. (block). H. W.


(*A*.)

Amino-aldehyde linkings. G. Ågren and A. Taylor (*Arkiv Kemi, Min., Geol.*, 1941, **14**, **B**, No. 14, 6 pp.).—*o-* or *p*-NH_2·C_6H_4·CO_2H and glucose (**I**) in H_2O at 70°, then at 0° for 12 hr., followed by evaporation in a vac., give *compounds*, $C_{13}H_{19}O_8N$, m.p. 126° or 122°, respectively. Reaction with (**I**) is facilitated by using CO_2Et·C_6H_4·NH_2,HCl in H_2O (evaporate rapidly in a vac. at 15°) thus affording *compounds*, $C_{15}H_{24}O_8NCl$. It is probable that some azo-derivative is formed as a secondary reaction. Esterification of CO_2H in NH_2-acids and peptides facilitates reaction between NH_2 and CHO groups. A. T. P.

Crystalline 4-methyl-*D*-mannose and its derivatives. W. T. Haskins, R. M. Hann, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1943, **65**, 70—73).—4-Methyl-2 : 3-*iso*propylidene-*D*-mannosan-<1 : 5>β<1 : 6 (**I**) and N-HCl at 100° give 4-*methyl*-D-*mannose*

(**II**), *α-form*, m.p. 127—128°, $[\alpha]$ +34°→+22·6° in H_2O (*k* 0·020 at 20°) (*phenylhydrazone*, m.p. 158—159°, $[\alpha]$ +46·2°→+17·8° in C_5H_5N in 6 days; phenylosazone, m.p. 157—158°, $[\alpha]$ −36°→−14·4° in C_5H_5N in 24 hr.). With boiling dry 3% HCl–MeOH, (**I**) gives *α-methyl-4-methyl*-D-*mannopyranoside* (55%), m.p. 101—102°, $[\alpha]$ +83·9° in H_2O [in 0·05N-HCl gives (**II**)]. (**II**) gives *tetra-acetates*, m.p. 75—76°, $[\alpha]$ +59·2° in $CHCl_3$, and m.p. 63—64°, $[\alpha]$ +20·2° in $CHCl_3$. Br–$CaCO_3$–H_2O gives 4-*methyl*-D-*mannono-δ-lactone*, m.p. 165—166°, $[\alpha]$ +163·8°→+94·2° in H_2O in 6 days, and thence 4-*methyl*-D-*mannono-phenylhydrazide*, m.p. 146—147°, $[\alpha]$ +10·6° in H_2O, and *-amide*, m.p. 171—172°, $[\alpha]$ +11·9° in H_2O (1 : 2 : 3 : 5 : 6-*penta-acetate*, m.p. 98—99°, $[\alpha]$ +11·4° in $CHCl_3$). H_2–Raney Ni in H_2O at 100°/167 atm. gives 4-*methyl*-D-*mannitol*, m.p. 86—87° (foams), resolidifies, remelts at 133—134°, $[\alpha]$ +16·7° in H_2O [*penta-acetate*, m.p. 85—86°, $[\alpha]$ +35·4° in $CHCl_3$; $(CMe_2)_2$ derivative, m.p. 57—58°, $[\alpha]$ +9·0° in EtOH]. Relations of (**II**) to *D*-mannose are discussed. $[\alpha]$ are $[\alpha]_D^{20}$.
R. S. C.

Synthesis of amino-sugars. I. W. H. Myers and G. J. Robertson (*J. Amer. Chem. Soc.*, 1943, **65**, 8—11).—Aminoglucosides are prepared by ring-fission of benzylidene-2 : 3-anhydroglucosides by NH_3, two *trans*-isomerides being formed, of which one is in large excess (cf. Peat *et al.*, A., 1939, II, 7). 4 : 6-Benzylidene-2 : 3-anhydro-α-methylalloside and conc. aq. NH_3 at 100° (sealed tube) give mixed NH_2-derivatives (*A*) (100%), m.p. 168°, $[\alpha]_D^{18}$ +104·7° in $CHCl_3$, whence Ac_2O–C_5H_5N yields 60% of 2-acetamido-4 : 6-benzylidene-α-methylaltroside 3-acetate (1) (cf. *loc. cit.*). With boiling 0·5% HCl–MeOH, (**I**) gives 2-*acetamido-α-methylaltroside* 3-*acetate* (60%), m.p. 189° (decomp.), $[\alpha]_D^{16}$ +7·3° in MeOH, and with boiling Ac_2O–NaOAc gives the corresponding *triacetate* (**II**) (65%), m.p. 176°, $[\alpha]_D^{20}$ +110° in $CHCl_3$. With conc. HCl in cold $COMe_2$, (*A*) give 2-*amino*-4 : 6-*benzylidene-α-methylaltroside hydrochloride*, m.p. 96°, $[\alpha]_D^{21}$ +85·5° in $CHCl_3$. 4 : 6-Benzylidene-2 : 3-anhydro-α-methylmannoside and conc. aq. NH_3 at 100° give a mixture (*B*), m.p. 188°, $[\alpha]_D^{19}$ +88·9° in $CHCl_3$, separated by acetylation into 3-*acetamido*-4 : 6-*benzylidene-α-methylaltroside* 2-*acetate* (**III**) (60%), m.p. 201°, $[\alpha]_D^{12}$ +14·6° in $CHCl_3$, and 2-*acetamido*-4 : 6-*benzylidene-α-methylglucoside* 3-*acetate* (1%), m.p. 235°, $[\alpha]_D^{12}$ +45·5° in $CHCl_3$. With conc. HCl in $COMe_2$, (*B*) gives 3-*amino*-4 : 6-*benzylidene-α-methylaltroside hydrochloride* (88%), m.p. 183° (decomp.), $[\alpha]_D^{19}$ +83·5° in H_2O. With 0·5% HCl–MeOH at 55°, (**III**) gives 3-*acetamido-α-methylaltroside* 2-*acetate* (60%), m.p. 174°, $[\alpha]_D^{16}$ +106·2° in $CHCl_3$, which by acetylation gives the *triacetate* (**IV**), m.p. 177°, $[\alpha]_D^{18}$ +34·1° in $CHCl_3$. With 2N-HCl (19 c.c.) in boiling H_2O (400 c.c.), (*A*) gives, according to the method, 2-*amino-α-methylaltroside*, m.p. 193°, $[\alpha]_D^{20}$ +107° in $CHCl_3$, or its *hydrochloride*, a syrup, $[\alpha]_D^{22}$ +39·7° in $CHCl_3$. In boiling 1% HCl, (*B*) gives 3-amino-β-methylaltroside hydrochloride (=methyl*epi*glucosamine hydrochloride), m.p. 209° (decomp.), $[\alpha]_D^{18}$ −149° in H_2O. 2 : 3-Anhydro-α-methylalloside and NH_3 give a syrup whence 68% of (**II**) is obtained. 4 : 6-Benzylidene-2 : 3-anhydro-α-methylmannoside and boiling aq. $H_2C_2O_4$ give 2 : 3-*anhydro-α-methylmannoside* (80%), m.p. 67°, $[\alpha]_D^{20}$ +44·6° in $CHCl_3$, which with NH_3 gives a syrup, yielding (**IV**) (65%) and 2-*acetamido-α-methylglucoside triacetate*, m.p. 132°, $[\alpha]_D^{20}$ +44·6° in $CHCl_3$. 2-Amino-4 : 6-benzylidene-β-methylglucoside and Ac_2O–C_5H_5N give the N-*Ac* derivative 3-*acetate* (75%), m.p. 158°, $[\alpha]_D^{20}$ −12·9° in $CHCl_3$, which with NH_3 gives a syrup and thence 2-*acetamido-β-methylglucoside triacetate* (70%), m.p. 238° (decomp.). 4 : 6-Benzylidene-2 : 3-anhydro-α-methyl-guloside (or -taloside) and NH_3 give a mixture (80%), m.p. 128—130°, $[\alpha]_D^{20}$ +60·6° in $CHCl_3$, yielding 2- (or 3-)*acetamido*-4 : 6-*benzylidene-α-methyl-idoside* 3- (or 2-)*acetate* (**V**) (55%), m.p. 188°, $[\alpha]_D^{12}$ +43·4° in $CHCl_3$, and *-galactoside* 3- (or 2-)*acetate* (8%), m.p. 260°, $[\alpha]_D^{12}$ +70·3° in $CHCl_3$. Warm HCl converts (**V**) into 2- (or 3-)*acetamido-α-methylidoside* 3- (or 2-)*acetate* (81%), a syrup, $[\alpha]_D^{16}$ −36·0° in MeOH. R. S. C.

Alkaline degradation of phenylglucosides. New method for determining the configuration of glucosides and sugars. (Miss) E. M. Montgomery, N. K. Richtmyer, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1943, **65**, 3—7).—β-Phenylglucosides etc. are degraded to anhydro-compounds by alkali much faster than are the α-isomerides, thus confirming existing allocations of structure and affording a method of determining structures of arylglucosides and compounds with which they can be correlated. β-Phenyl-*D*-glucoside is completely hydrolysed by 1·3N-$Ba(OH)_2$ or -KOH at 100° in 9 hr., yielding 88% of *D*-glucosan<1 : 5>β<1 : 6> (**I**), whereas 85% of the α-isomeride is recovered after boiling for 2 weeks in 2·6N-KOH, there having been no change in $[\alpha]$. β-Phenyl-*D*-galactoside in 1·3N-KOH at 98° gives 91% of *D*-galactosan<1 : 5>β<1 : 6> (**II**) in 9 hr.; 4% of the α-galactoside is recovered after 16 weeks in 2·6N-KOH at 100° whilst 97% of PhOH (determined by I) is liberated, yielding 85% of (**II**). α-Phenyl-*D*-mannoside in boiling 1·3N-KOH gives a syrup, whence a little *D*-mannosan<1 : 5>β<1 : 6> is isolated as CMe_2 derivative, whereas the β-mannoside gives 57% (A., 1942, II, 351). α-Phenyl-*D*-xyloside is unaffected, whereas the β-xyloside gives a decomposed syrup. β-*o*-Tolyl-, β-*o*-hydroxymethylphenyl-, β-*p*-xenyl-, β-*p*-acetylphenyl-, β-*o*- (stable *form*, m.p. 168—169°; tetra-acetate, new m.p. 160—162°) and β-*p*-nitrophenyl-*D*-glucoside give 60—90% of (**I**), but α- + β-methyl-, β-*cyclo*hexyl-, β-*n*-decyl-, and β-allyl-glucosides are unchanged and the α-*o*- and α-*p*-nitrophenylglucosides give tars. R. S. C.

Synthesis of βββ-trichloroethyl-*d*-glucoside, and its isolation from maize and dandelion plants treated with chloral hydrate. L. P. Miller (*Contr. Boyce Thompson Inst.*, 1942, **12**, 465—470).—*βββ-Trichloroethyl-d-glucoside*, m.p. 152·5—153·5° (corr.), $[\alpha]_D^{25}$ −39·7° in H_2O [from the synthetic tetra-acetate with $Ba(OMe)_2$ in MeOH], is isolated as tetra-acetate from the tops and roots of maize or dandelion grown in a medium containing $CCl_3{\cdot}CH(OH)_2$, or directly, by Pb pptn. and Et_2O extraction of aq. extracts, from the leaves of dandelion so grown, together with a trichloroethylglycoside isolated as the *hexa-acetate*, $C_{25}H_{33}O_{18}Cl_3$, m.p. 158—159° (or 170—171° after partial melting and resolidification), $[\alpha]_D^{25}$ −47·2° in $CHCl_3$.
A. Li.

Steroids. XXXIV. Saccharides of deoxycorticosterone. K. Miescher and C. Meystre (*Helv. Chim. Acta*, 1943, **26**, 224—233).—Gradual addition of acetobromo-*d*-galactose in $CHCl_3$ to a mixture of Ag_2CO_3 and deoxycorticosterone (**I**) in this solvent at 40—45° followed by hydrolysis (K_2CO_3 in MeOH) of the non-cryst. tetra-acetate gives *deoxycorticosterone-β*-d-*galactoside*, m.p. 195—198°, $[\alpha]_D^{20}$ +136°±4° in $COMe_2$. Under similar conditions but with C_6H_6 as solvent acetobromolactose yields *deoxycorticosterone-β-lactoside*, m.p. 202—208°, $[\alpha]_D^{20}$ +80°±4° in MeOH (*hepta-acetate*, m.p. 194—195°, $[\alpha]_D^{20}$ +52°±4° in $COMe_2$). *Deoxycorticosterone-maltoside hepta-acetate* has m.p. 183—185°. (**I**) is shaken with acetobromolactosido-*d*-glucose and Ag_2CO_3 in $CHCl_3$ at 40—45° and the product is transformed by Ac_2O–C_5H_5N into the *hendeca-acetate*, m.p. (indef.) 120—130°, of *deoxycorticosterone*-6-*β-lactosido*-d-*glucoside* (+$2H_2O$), m.p. (indef.) ~160°. 6-*β-Lactosido*-d-*glucose hendeca-acetate*, m.p. 192—194°, is obtained by shaking glucose tetra-acetate with acetobromolactose and $CaCl_2$ in EtOH-free $CHCl_3$ and continuing the process after addition of Ag_2CO_3 and I; it is converted by HBr–AcOH into 6-*β-lactosidoacetobromo*-d-*glucose hepta-acetate*, m.p. 138—142°. The prep. of permanent supersaturated 1% and 2% aq. solutions of deoxycorticosterone-*β-d*-glucoside is described; this compound is less freely sol. in H_2O than are the new saccharides. M.p. are corr. H. W.

Cerberin and cerberoside.—See A., 1943, III, 343.

Starch. XXIV. Composition of various starches. K. H. Meyer and P. Heinrich (*Helv. Chim. Acta*, 1942, **25**, 1639—1650; cf. A., 1942, II, 303).—Extraction of starch (**I**) with H_2O at a suitable temp. (between 50° and 80°) which must be determined for each variety causes dissolution solely of amylose (**II**) since the sol. portion does not give residual dextrin (**III**) when degraded by β-amylase (**IV**); at a higher temp. the branched components also pass into solution and yield (**III**). Treatment of (**I**) with boiling H_2O followed by electrodialysis brings the greater part of the amylopectin (**V**) to the anode side but part remains dissolved; the proportion increases with the temp. of extraction. Complete elimination of (**II**) is effected by solubilising (**I**) in conc. $CaCl_2$ and removing the salt by dialysis. After electrodialysis of the solution thus obtained the greater part of the branched components is deposited on the anodic side. A great part of the polysaccharides, certainly containing all of (**II**), remains in solution. Evidence is brought in favour of the view that the main part of this dissolved fraction is a slightly ramified (**V**) of low mol. wt.; this is termed the "intermediate fraction." The results of the examination of starches from maize, rice, tubers, leaves, and shoots of potatoes, sago, tapioca, and peas are tabulated. (**I**) from rice contains a small proportion of a freely sol. polysaccharide of low mol. wt. giving 52% of (**III**) when degraded by (**IV**). The principal part of the grain is composed of a very sparingly sol. polysaccharide which scarcely swells and should therefore have a very high mol. wt.; it gives 42% of (**III**). A similar variety of (**I**) occurs in "waxy maize." H. W.

Application of the mercaptalation assay to synthetic starch. M. L. Wolfrom, C. S. Smith, and A. E. Brown (*J. Amer. Chem. Soc.*, 1943, **65**, 255—259).—Synthetic starch (prep. from α-, not β-, glucopyranose 1-phosphate by potato phosphorylase) is hydrolysed by conc. HCl at 0° in presence of EtSH. *k* (determined by $[\alpha]$) for depolymerisation is 0·032 hr.$^{-1}$ (cf. 0·027 for natural potato starch). The initial average degree of polymerisation is 32±1 glucose units.
R. S. C.

Multiple amylose concept on starch. III. Isolation of an amylose in crystalline form. R. W. Kerr and G. M. Severson (*J. Amer. Chem. Soc.*, 1943, **65**, 193—198; cf. A., 1942, II, 219).—Attempts to isolate γ-amylose (**I**) from the fraction of maize starch (**II**) less sol. in EtOH failed. Fractionation of potato starch (**III**) by aq. EtOH reveals a greater solubility and smaller tendency to gel, compared with (**II**). Extraction of (**II**) by H_2O at < the gelatinisation temp. gives a solution [5·1% of the (**II**) dissolved], which at 0° deposits 94% of its solids as a gelatinous mass but with a little BuOH it deposits 79·5% of its solids as a cryst. amylose (photomicrograph). The amorphous ppt. has a conversion limit (barley diastase) 86% and alkali no. 35·4. Cryst. amylose has a conversion limit 93% and alkali no. 35·0, gives a purple colour with I and a very sharp "V" type *X*-ray pattern, and contains essentially linear 1 : 4-α-glucosidically linked glucopyranose units. (**III**) yields

a similar, but crystallographically slightly different, cryst. amylose, having conversion limit 97% and alkali no. 21·3. The conversion limit of (**I**) is raised to 70% by working in more dil. solution. The part (~25%) of whole (**II**) pptd. by BuOH has alkali no. 22 and conversion limit 81%. Cryst. amylose is part of the starch ingredients adsorbed on cotton. It is concluded that starch contains amylose varying from the almost wholly linear to fairly highly branched, the proportion of the latter being higher in (**III**) than in (**II**). R. S. C.

Significance of the degradation of starch by *macerans* amylase. R. W. Kerr (*J. Amer. Chem. Soc.*, 1943, **65**, 188—193).—Gelatinisation of dioxan-extracted maize starch in aq. NaOH and treatment with *B. macerans* amylase (**I**) at 45° and pH 6 gives 9·9% of insol. matter (resembling γ-amylose) and a further ~0·3% when kept, and then by pptn. by C_2HCl_3 etc. 25·2—25·3% of mixed dextrins, in which the β- : α-dextrin ratio is 0·26. Potato starch gives similarly first only 0·43% and then ~0·3% of insol. matter and 30·6% of mixed dextrins, in which the β : α ratio is 0·28. The mixed dextrins are unaffected by barley diastase. Hydrolysis of maize starch by acid progressively decreases the amount of insol. matter and rapidly that of the dextrins obtained by later treatment with (**I**). Limit dextrins, prepared by barley diastase, give no Schardinger dextrins by treatment with (**I**). The fraction (55%) of starch more sol. in aq. EtOH gives 43·6% of cryst. dextrins. It is concluded that these dextrins are formed enzymically by rearrangements of simpler configurations. R. S. C.

Action of *macerans* enzyme on a component of maize starch.—See A., 1943, III, 427.

Amylose and amylopectin content of starches determined by their iodine complex formation. F. L. Bates, D. French, and R. E. Rundle (*J. Amer. Chem. Soc.*, 1943, **65**, 142—148).—Potentiometric titration of amylose (**I**) (dispersed in alkali) with I–KI shows complex formation, followed by adsorption; amylopectin shows only adsorption. The following (**I**) contents of the starches are thus determined: waxy rice, waxy sorghum, waxy maize, waxy barley 0; tapioca, rice 17; banana 20·5; maize 21; potato 22; popcorn 23; wheat 24; sago 27; lily bulb 34%. These results agree with those obtained by pptn. by BuOH. The amount of I bound by (**I**) ∝ inversely [I]. The affinity for I probably increases with the length of the straight chains and decreases with the degree of branching. The (**I**) of any one starch is probably homogeneous but is different for different starches. Hassid's synthetic starch (A., 1943, II, 25) is essentially (**I**). R. S. C.

Diffraction of electrons in cellulose ethers and esters.—See A., 1943, I, 146.

Simplified preparation of Schweitzer's reagent. A. Breslau (*J. Chem. Educ.*, 1942, **19**, 356). L. S. T.

III.—HOMOCYCLIC.

Thallous salts as derivatives of sulphonic acids. H. Gilman and R. K. Abbott, jun. (*J. Amer. Chem. Soc.*, 1942, **65**, 123—124).—Tl sulphonates are useful for identification, being readily prepared from the acid by TlOH (titration) or from the Na salt by HCO_2Tl in approx. quant. yield and giving large crystals of high m.p. *Tl sulphamate*, m.p. 139—140°, *sulphanilate*, m.p. 207—209°, o-, m.p. 213—216°, and p-*toluene*-, m.p. 226—228°, p-*bromobenzene*-, m.p. 274—276°, m-*nitrobenzene*-, m.p. 307—309°, 2-*bromotoluene*-4-, m.p. 220—222°, o-*toluidine*-4-, m.p. 101—103°, 1 : 2-*naphthaquinone*-4-, m.p. 228—232° (decomp.), d-*camphor*-, m.p. 267—269°, 1 : 2 : 3 : 4-*tetramethylbenzene*-5-, m.p. 260—262° (very sol.), 1 : 2 : 3 : 5-*tetramethylbenzene*-4-, m.p. 283—285° (fairly sol.), and 1 : 2 : 4 : 5-*tetramethylbenzene*-3-, m.p. 340—341° (decomp.) (insol. in H_2O), and *pentamethylbenzene*-, m.p. 325—326°, -*sulphonate* are described. R. S. C.

Preparation of aromatic sulphonyl fluorides.—See B., 1943, II, 70.

Phenylmethanesulphinic acid. B. Holmberg (*Arkiv Kemi, Min., Geol.*, 1940, **14**, **A**, No. 8, 13 pp.).—*β-Benzylsulphonyl-propionic*, m.p. 177—178°, and -*succinic*, m.p. 193—194°, *acids*, and $CH_2Ph{\cdot}SO_2{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2H$, are hydrolysed (N-NaOH, 100°) via the *HgCl* salt to $CH_2Ph{\cdot}SO_2H$ (**I**), m.p. 61—63°, and the appropriate unsaturated acid, the reaction being reversed in acid solution. (**I**) is stable to hot N-NaOH and cold. conc. HCl, and contrary statements (A., 1880, 811; 1906, i, 819) are due to its great sensitivity to atm. O_2. (**I**) with Br–AcOH gives *benzylsulphonyl bromide*, m.p. 79—80°. Chlorination of $CH_2Ph{\cdot}CNS$ in H_2O (cf. A., 1939, II, 498) gives solutions containing only traces of (**I**). M. H. M. A.

Bromination of diphenylalkanes and preparation of stilbene derivatives. II. βγ-Diphenyl-*n*-butane. H. J. Barber, R. Slack, and A. M. Woolman (*J.C.S.*, 1943, 99—101; cf. A., 1943, II, 92).—CHPhMeCl and Mg–Et_2O give *meso*- (**I**), m.p. 124°, and *r*-$(CHPhMe)_2$ (**II**), b.p. 153—156°/14 mm. (**I**) and Br in 95% AcOH afford 4 : 4′ : *βγ-tetrabromo*- (**III**), m.p. 178—185° (decomp.), and meso-4 : 4′-*dibromo-βγ-diphenyl*-n-*butane* (**IV**), m.p. 160—161°. The mother-liquors from (**II**) and Br–95% AcOH, after separation of (**III**), are diluted with H_2O, treated with Zn dust, and the product is hydrogenated (PtO_2; 50 lb. per sq. in.) to dl-4 : 4′-*dibromo-βγ-diphenyl*-n-*butane* (**V**), b.p. 166—171°/0·3—0·4 mm. A low yield of (**IV**) is obtained from *p*-$C_6H_4Br{\cdot}CHMeCl$ and Na–C_6H_6 (no reaction with Mg–Et_2O). Unsuccessful attempts were made to dehydrogenate the 4 : 4′-Br_2-compound with Pd–C at 300° or Cu chromite in $PhNO_2$, or to reduce (**III**) with CuCl in C_5H_5N or CuCN in quinoline, but (**III**) and Zn–AcOH (15 min.) readily yield cis- (**VI**), m.p. 90—92°, and trans-4 : 4′-*dibromo-αβ-dimethylstilbene* (**VII**), m.p. 125—128°, both of which are oxidised by CrO_3–AcOH to *p*-$C_6H_4Br{\cdot}CO_2H$. (**VI**) is converted into (**VII**) in boiling $PhNO_2$–I (trace). (**VI**) and HBr–$CHCl_3$ at 0° afford 4 : 4′ : *β-tribromo-βγ-diphenyl*-n-*butane*, m.p. 112—115° (decomp.), converted at 150—200° (10 min.) into (**VII**). Hydrogenation (Pt; $COMe_2$) of (**VI**) [(**VII**) is not similarly reduced] affords (**IV**); addition of 2 Br gives (**III**). (**IV**) or (**V**) and CuCN–C_5H_5N at 190—205° give meso-, m.p. 196—198°, or dl-4 : 4′-*dicyano-βγ-diphenyl*-n-*butane*, b.p. 190—200°/1 mm., respectively. (**VII**) and CuCN in quinoline yield 4 : 4′-*dicyano-αβ-dimethylstilbene*, sublimes at 240°/1 mm., m.p. 216°. *meso*- (*dihydrochloride*, $+H_2O$) and *r*-4 : 4′-diamidino-βγ-diphenyl-*n*-butane (*dihydrochloride*), and trans-4 : 4′-*diamidino-αβ-dimethylstilbene dihydrochloride*, $+2H_2O$, are obtained in the usual manner through the iminoether hydrochloride. A. T. P.

The ascorbic acid–dehydroascorbic acid system in synthesis and inactivation of sympathomimetic amines. K. H. Beyer (*J. Pharm. Exp. Ther.*, 1942, **76**, 149—155).—Various amines were oxygenated at pH 7 in presence of ascorbic acid for 18—24 hr. Solutions were made basic and NH_3 was determined. Those having no OH group in the ring and NH_2 in the side-chain were deaminated with recovery of 30—54% of theoretical yield of NH_3. Side-chain OH β to NH_2 decreased deamination to ~10%. NHMe in addition to side-chain OH did not affect deamination as compared with the corresponding primary amine; a *tert.* amine did not undergo deamination. *p*-OH-amines were oxidised to the 3 : 4-$(OH)_2$-compounds. V. J. W.

Properties of *p*-hydroxylaminobenzenesulphonamide and a related molecular complex. M. G. Sevag (*J. Amer. Chem. Soc.*, 1943, **65**, 110—113).—*p*-$NO_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ and Zn dust in aq. NH_4Cl give *p*-$OH{\cdot}NH{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ (**I**), m.p. 141·5° (cf. Bratton *et al.*, A., 1940, III, 436), and a substance, m.p, 161·5° (cf. Burton, A., 1941, II, 220), shown to be a 2 : 1 *complex* of (**I**) and *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ (**II**) by analysis, solubility, absorption of O_2, colorimetric determination of (**II**), and isolation of (**II**) as sulphate and hydrochloride. R. S. C.

***p*-Aminobenzenesulphonylcyanamide.**—See B., 1943, II, 145.

Azo-compounds and their intermediate products. XXIII. *o*-(Benzeneazo)azobenzene. P. Ruggli and J. Rohner (*Helv. Chim. Acta*, 1942, **25**, 1533—1542; cf. A., 1938, II, 318).—Gradual addition of solid PhNO to *o*-$NH_2{\cdot}C_6H_4{\cdot}N_2Ph$ (prep. from *o*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$ described) in cold AcOH gives o-(*benzeneazo*)*azobenzene* (**I**), m.p. 106—108°, in 83% yield; it is converted by reductive fission into *o*-$C_6H_4(NH_2)_2$ and NH_2Ph. (**I**) and $CPh_2{:}CO$ in light petroleum or preferably in C_6H_6 in presence or absence of light afford an *adduct*, $C_{32}H_{24}ON_4$, m.p. 162—163°. (**I**) is reduced by Zn dust and NH_3–EtOH to o-*benzeneazohydrazobenzene* (**II**), m.p. 98·5—100°, converted by H_2–PtO_2–EtOH into *o*-$C_6H_4(NH_2)_2$ and NH_2Ph. Cryst. (**II**) is stable in air but in C_5H_5N is slowly dehydrogenated to (**I**). (**II**) is transformed by boiling AcOH under N_2 into (**I**) and 2-phenylbenzotriazole (**III**). Addition of (**II**) to Ac_2O in Et_2O gives the *Ac* derivative, *o*-$PhN_2{\cdot}C_6H_4{\cdot}NH{\cdot}NPhAc$, m.p. 102—103·5°, which passes at 180—200° into (**III**) and NHPhAc. (**I**) is reduced by Zn dust in C_5H_5N–conc. aq. NH_3 to o-(*phenylhydrazino*)*hydrazobenzene*, m.p. 132° (yellow-orange at 122° and softens at 128°). It is rapidly dehydrogenated to (**I**) by air in C_5H_5N, disproportionated in CO_2 to NH_2Ph and *o*-$NH_2{\cdot}C_6H_4{\cdot}N_2Ph$, and converted by Ac_2O at 70° into *o*-$NHAc{\cdot}C_6H_4{\cdot}N_2Ph$. H. W.

Action of cuprous oxide on diazotised amines. II. Reactions in solutions of various alcohols and organic solvents. Preparation of 1 : 6-dinitronaphthalene. H. H. Hodgson and H. S. Turner (*J.C.S.*, 1943, 86—89; cf. A., 1943, II, 59).—1 : 6 : 2-$(NO_2)_2C_{10}H_5{\cdot}N_2HSO_4$ [from the 2-*p*-toluenesulphonamide (improved prep.) and conc. H_2SO_4 at 30—40°, followed by $NO{\cdot}SO_4H$ and then AcOH at <20°] with EtOH yields 21, with Cu_2O 18, but with Cu_2O in MeOH, EtOH, $Pr^{\alpha}OH$, $Pr^{\beta}OH$, $Bu^{\alpha}OH$, $Bu^{\beta}OH$, $(CH_2{\cdot}OH)_2$, $Cl{\cdot}[CH_2]_2{\cdot}OH$, $COMe_2$, and EtOAc yields 60·2, 57·6, 40·6, 59·7, 30, 51·2, 48·3, 69·5, 35·5, and 39·8%, respectively, of 1 : 6-$C_{10}H_6(NO_2)_2$ (**I**). $CH_2Ph{\cdot}OH$, $Bu^{\gamma}OH$, and *cyclo*hexanone give no isolable product. 2 : 4 : 1-$(NO_2)_2C_{10}H_5{\cdot}N_2HSO_4$ with Cu_2O in $Cl{\cdot}[CH_2]_2{\cdot}OH$ gives 75% of 1 : 3-$C_{10}H_6(NO_2)_2$. For the more anionoid alcohols an appreciable induction period occurs before a rapid decomp., suggesting a two-stage reaction, viz., complex formation between ArN_2X and org. solvent, followed by decomp. facilitated by Cu_2O. Prep. of (**I**), m.p. 166·5° (lit. 161°, 166—167°), is improved. A. Li.

Amino-aldehyde linkings.—See A., 1943, II, 154.

Tautomerism of benzoquinone–*p*-nitrosophenol systems. II. 3-Fluoro-4-nitrosophenol. H. H. Hodgson (*J.C.S.*, 1943, 89—90; cf. A., 1937, II, 251).—The ultra-violet absorption spectrum of 1 : 3 : 4-OH·C_6H_3F·NO (**I**) has unique features in comparison with those of its 3-halogeno-analogues (*A*). There is only one band (eliminated by acid; intensified by alkali), with peak at 3700 A. Compared with (*A*) there is a large displacement of the band towards shorter λλ; this supports the fact that (**I**), unlike (*A*), is not convertible into a quinonoid isomeride. A. T. P.

Amine–formaldehyde condensation in the formation of aniline–formaldehyde resins and of aminoplastics. I. H. von Euler and H. Nyström (*Arkiv Kemi, Min., Geol.*, 1941, **14**, **B**, No. 26, 7 pp.).—Partly an account of work previously abstracted (A., 1942, II, 309). 2 : 3 : 5 : 1-OH·$C_6H_2Me_2$·CH_2·OH and NH_2Ph,HCl in boiling aq. HCl (pH 2) give 4 : 6-*dimethyl-2-anilinomethylphenol*, m.p. 85° (*N-NO*-derivative, m.p. 118·5°) (2-p-*toluidino*-analogue, m.p. 99°), also obtained from 2 : 3 : 5 : 1-OH·$C_6H_2Me_2$·CH_2Br and NH_2Ph in PhMe. 1 : 4 : 2 : 3 : 5 : 6-$(OH)_2C_6(CH_2·OH)_4$ (**I**) and boiling aq. NH_2Ph,HCl, followed by boiling 4N-HCl, give an amorphous condensation product formed from 2 mols. of NH_2Ph and 1 mol. of (**I**). A. T. P.

***p*-Toluidine salts of monoaryl sulphates.** A. D. Barton and L. Young (*J. Amer. Chem. Soc.*, 1943, **65**, 294—295).—KArSO$_4$ and *p*-$C_6H_4Me·NH_2$,HCl in H_2O give p-*$C_6H_4Me·NH$ Ph*, m.p. 145—146°, o-, m.p. 135·5—136·5°, m-, m.p. 133—134°, and p-*tolyl*, m.p. 162—163°, p-*bromophenyl*, m.p. 193—194°, and p-*nitrophenyl sulphate*, m.p. 167—168° (cf. Burkhardt *et al.*, A., 1926, 511). R. S. C.

Chlorination of *p*-diphenylyl acetate in acetic acid. H. R. Schmidt, (Miss) C. M. S. Savoy, and J. L. Abernethy (*J. Amer. Chem. Soc.*, 1943, **65**, 296—297).—*p*-$C_6H_4Ph·OAc$ and Cl_2 in AcOH give the 4′-Cl-derivative (cf. A., 1943, II, 28). R. S. C.

Equilibrium between borate ion, pyrocatechol, and pyrocatechol borate ion in aqueous solution, and the preparation of monopyrocatechol borates.—See A., 1943, I, 160.

Synthesis of polyenes. III. Synthesis of diethylstilbœstrol. M. S. Kharasch and M. Kleiman (*J. Amer. Chem. Soc.*, 1943, **65**, 11—15; cf. A., 1940, II, 362).—Adding $NaNH_2$ to CHPhMeCl (prep. from CHPh:CH_2 by dry HCl at −80°; 68% yield), b.p. 73°/11 mm., in liquid NH_3 gives CHPhMe·CPhMeCl, b.p. 147—148°/11 mm., which when repeatedly distilled in vac., gives HCl and *trans*-(CPhMe:)$_2$; the reverse addition gives 40% of *cis*-(CPhMe:)$_2$ and high-boiling oils. Adding CHPhEtCl (0·1) (prep. from CHPhEt·OH by dry HCl at 0°; 55% yield), b.p. 85—87°/15 mm., in PhMe to $NaNH_2$ (0·3 mol.) in liquid NH_3 gives a mixture, b.p. (mostly) 162—164°/12 mm., of CHPhEt·CPhEtCl + (?) (CPhEt:)$_2$, which with H_2–Pt-black–EtOH or Na–NH_3 gives (CHPhEt)$_2$, m.p. 88·5—89°, and with Br–CCl_4 gives a *dibromide*, $C_{18}H_{20}Br_2$ [? (CPhEtBr)$_2$], m.p. 166·5°. Adding *p*-OMe·C_6H_4·CHEtBr (**I**) [prep. from anethole (**II**)–PhMe by dry HBr at −80°] in PhMe to an excess of $NaNH_2$ in NH_3 gives a substance (γδ-di-*p*-anisyl-Δ^{α}-*n*-hexene or 1 : 2-di-*p*-anisyl-3-methyl-1-ethyl*cyclo*propane) (**III**) (34—40%), m.p. 120·5°, and high-boiling products, including a hexameride, m.p. 209—210°, of (**II**). (**III**) depresses the m.p. of *trans*-(*p*-OMe·C_6H_4·CEt:)$_2$ (**IV**), m.p. 124°, absorbs 1 H_2 (Pt-black; MeOH) to give (*p*-OMe·C_6H_4·CHEt)$_2$ (**V**), m.p. 142°, and with KOH in $(CH_2·OH)_2$ (vac.) at 224° gives (*p*-OH·C_6H_4·CEt:)$_2$ (55·5% if the residual oil is re-treated), m.p. 165—166°, identified by mixed m.p., as diacetate and dibenzoate, and by its absorption spectrum. Non-identity of (**III**) and (**IV**) and identity of (**V**) with an authentic specimen are confirmed by crystallo-optical data. Adding (**I**) (2 mols.) and then Na (1 atom) to $NaNH_2$ (1 mol.) in NH_3 gives 80% of *p*-OMe·C_6H_4·CHEt·NH_2 [hydrochloride, m.p. 215° (decomp.); Bz derivative, m.p. 120°]. R. S. C.

Structures of 4 : 4′-dihydroxy- [and 4 : 4′-dimethoxy-]αβ-diethylstilbene.—See A., 1943, I, 118.

Auroxanthin, a carotene pigment which absorbs light of short wave-length. P. Karrer and J. Rutschmann (*Helv. Chim. Acta*, 1942, **25**, 1624—1627; cf. Kuhn *et al.*, A., 1931, 491).—In addition to violaxanthin (**I**) the mixture of carotenoids from *Viola tricolor* contains flavoxanthin and *auroxanthin*, $C_{40}H_{60(62)}O_5$, m.p. 191—192° (vac.). The absorption spectrum of auroxanthin lies more in the region of short λ than does that of any other carotenoid, whence it follows that it has only 8 conjugated double linkings. Micro-hydrogenation indicates the presence of 8 or 9 double linkings. The colour reactions of auroxanthin and violaxanthin with HCl are very closely similar. Of the 5 O, ⩽4 and probably all are present as OH; CO: is absent. H. W.

Attempted asymmetric syntheses employing choleic acids. C. C. Reid and J. M. Sturtevant (*J. Amer. Chem. Soc.*, 1943, **65**, 125).—Bromination of the crotonic–choleic acid complex and prep. of CHPhMe·OH from COPhMe by hydrogenation in aq. Na deoxycholate give inactive products. The *complex*, 1COPhMe + 3deoxycholic acid (**I**), m.p. 167—168° (corr.), could not be reduced [catalyst or Al(OPr$^{\beta}$)$_3$–C_6H_6]. CHPhMe·OH could not be obtained from the *complex*, PhCHO + 2(**I**), m.p. 164—165°, by MgMeBr. R. S. C.

Vinyl alcohols. IV. Oxidative cleavage. R. C. Fuson, D. J. Byers, A. I. Rachlin, and P. L. Southwick. **V. Isomeric bromo-αβ-dimesityl-Δ^{α}-propen-α-ols.** R. C. Fuson, R. V. Lindsey, jun., and P. B. Welldon (*J. Amer. Chem. Soc.*, 1942, **64**, 2886—2888, 2888—2891; cf. A., 1942, II, 92).—IV. Mes·CMe:CMes·OH (Mes = mesityl) is stable in absence of air but in air gives MesCOMe, MesOH, and CO, with small amounts of $MesCO_2H$ (**I**), CH_2:CMes·COMes, H_2, and a *phenol*, $C_{18}H_{22}O_2$, m.p. 169·5—171·5° (*diacetate*, m.p. 148—149°). 2 : 3 : 5 : 6 : 1-C_6HMe_4·C(OH):CMeMes with O_2 in $COMe_2$ gives similarly MesCOMe, durenol, and CO with small amounts of 2 : 3 : 5 : 6 : 1-$C_6HMe_4·CO_2H$, 2 : 3 : 5 : 6 : 1-C_6HMe_4·CO·CMes:CH_2, and H_2.

V. (**I**) and Br (no Fe) give 2 : 4 : 6 : 3 : 1-$C_6HMe_3Br·CO_2H$ (74%), m.p. 162—165°, the chloride (prep. by $SOCl_2$), b.p. 175—178°/28 mm., of which with $CH_2Mes·MgCl$ in Et_2O at 0° gives 3′-*bromodeoxymesitoin* (**II**) (45%), m.p. 91—92° [or sometimes mainly $(CH_2Mes)_2$]. $CH_2Mes·COCl$, 1 : 3 : 5 : 2-$C_6H_2Me_3Br$ (**III**), and $AlCl_3$ in CS_2 at 0—17° give, by migration of Br, 3-*bromodeoxymesitoin* (**IV**) (90%), m.p. 98—99°. Condensation of (**II**) and (**IV**) with CH_2O yields 3-*bromomesityl α-mesitylvinyl* (**V**), m.p. 150—151°, and *mesityl α-3-bromomesitylvinyl ketone* (**VI**), m.p. 149—150° [mixed with (**V**), 131—134°], respectively. H_2–PtO_2 in AcOH reduces (**V**) and (**VI**) to unstable solid propenols; that from (**V**) with Na followed by Me_2SO_4 in hot C_6H_6 gives *α-methoxy-α-3-bromomesityl-β-mesityl-Δ^{α}-propene*, m.p. 117·5—119°, and with O_2 in $COMe_2$ gives MesCOMe and 2 : 4 : 6 : 3 : 1-$C_6HMe_3Br·OH$; that from (**VI**) with O_2 gives 2 : 4 : 6 : 3 : 1-$C_6HMe_3Br·COMe$ and MesOH. (**II**) is unchanged by $AlCl_3$ in CS_2. $(CH_2O)_3$, (**III**), $ZnCl_2$, and conc. HCl at 65—70° give 3-*bromomesitylmethyl chloride*, m.p. 44—45°, b.p. 126—129°/2 mm., converted by NaCN in aq. EtOH at 55—60° into 3-*bromomesitylacetonitrile*, m.p. 113—114°; hydrolysis (boiling 55% H_2SO_4) to the *acid*, m.p. 168·5—169·5° (some *amide*, m.p. 231—232°, also obtained), conversion thereof into the chloride, b.p. 146—148°/4 mm., by $SOCl_2$, and Friedel–Crafts reaction with *s*-$C_6H_3Me_3$ gives (**IV**). R. S. C.

5-Amino-2-methoxybenzyl alcohol.—See B., 1943, II, 145.

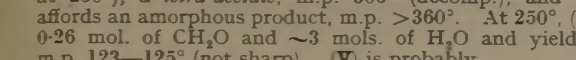
Phenol–formaldehyde resins. III. Condensation with dihydroxybenzenes and dihydroxybenzene alcohols: a principle of Bakelite production from wood-tar phenols. H. von Euler, E. Adler, S. de Kispéczy, and A. M. Fagerlund (*Arkiv Kemi, Min., Geol.*, 1941, **14**, **A**, No. 10, 20 pp.).—*o*-$C_6H_4(OH)_2$ and 40% CH_2O in 10% aq. NaOH and N_2 at room temp. for 2 days, followed by Me_2SO_4–aq. NaOH, afford 1 : 2 : 3 : 6-$(OMe)_2C_6H_2(CH_2·OH)_2$, m.p. 92°, oxidised by $KMnO_4$–aq. NaOH, to 2 : 3-*dimethoxyterephthalic acid*, m.p. 206—208° (sinters at 195°) [48% HBr then gives the 2 : 3-$(OH)_2$-acid, new m.p. 293—293·5° (decomp.)]. 1 : 4 : 2 : 3 : 5 : 6-$(OH)_2C_6(CH_2·OH)_4$ and *m*-4-xylenol (**I**) or *p*-cresol in boiling EtOH–conc. HCl give 2 : 3 : 5 : 6-*tetra*-(2′-*hydroxy*-3′ : 5′-*dimethylbenzyl*)-*quinol*, m.p. 271—272° (C_5H_5N compound, m.p. 89°; *hexa-acetate*, m.p. 275·5—276·5°), or 2 : 3 : 5 : 6-*tetra*-(2′-*hydroxy*-5′-*methylbenzyl*)-*quinol*, m.p. 265—267° (*hexa-acetate*, m.p. 222—222·5°), respectively. (**I**) and CH_2O–aq. NaOH give 4 : 1 : 3 : 5-OH·$C_6H_2Me_2$·CH_2·OH (**II**), m.p. 56—57°, which with quinol–EtOH–HCl yields $CH_2(C_6H_2Me_2·OH-1:3:5:2)_2$ and 2 : 5-*di*-(2′-*hydroxy*-3′ : 5′-*dimethylbenzyl*)*quinol*, m.p. 293—296° (*tetra-acetate*, m.p. 212·5—213°); the latter is also obtained from 1 : 4 : 2 : 5-$(OH)_2C_6H_2(CH_2·OH)_2$ and (**I**) in EtOH–HCl. (**II**) and *o*-$C_6H_4(OH)_2$–HCl–EtOH give a *di*-(2′-*hydroxy*-3′ : 5′-*dimethylbenzyl*)*pyrocatechol*, m.p. 190·5° (*tetra-acetate*, m.p. 147°), different from the 3 : 6-disubstituted *isomeride*, m.p. 227°, obtained from 1 : 2 : 3 : 6-$(OH)_2C_6H_2(CH_2·OH)_2$ and (**I**). (**II**) and *m*-$C_6H_4(OH)_2$ yield 2 (or 6)-2′-*hydroxy*-3′ : 5′-*dimethylbenzylresorcinol*, m.p. 226—227°. Resols are formed during condensation (alkali) of a mixture of a bifunctional phenol and *o*- or *p*-$C_6H_4(OH)_2$ with CH_2O; these can be hardened by heat. Such a condensation can be applied to the mixed phenols from wood tar. A. T. P.

Phenol–formaldehyde resins. IV. Mechanism of hardening of resols. Hardening of di-*p*-tolylmethane monoalcohol. V. Constitution of hardening product of di-*p*-tolylmethane monoalcohol. E. Adler, H. von Euler, and H. G. Hasselquist. **VI. Hardening of di-*p*-tolylmethane dialcohol. VII. Cyclic ether from di-*p*-tolylmethane dialcohol.** H. von Euler, E. Adler, and B. Bergström (*Arkiv Kemi, Min., Geol.*, 1941, **14**, **A**, No. 23, 7 pp.; No. 24, 8 pp; No. 25, 6 pp.; No. 30, 6 pp).—IV. (2 : 5 : 1-OH·$C_6H_3Me)_2CH_2$ and CH_2O–aq. NaOH give 2-*hydroxy*-3-(2′-*hydroxy*-5′-*methylbenzyl*)-5-*methylbenzyl alcohol* (**I**), m.p. 136—136·5°, and some 2 : 2′-dihydroxy-5 : 5-dimethyl-3 : 3′-di(hydroxymethyl)diphenylmethane (**II**), m.p. 151—151·5°, also obtained from (**I**) and CH_2O–aq. NaOH. Elimination of 1 mol. of H_2O from 2 mols. of (**I**) during hardening at 125—127° affords *di*-[2-*hydroxy*-3-(2′-*hydroxy*-5′-*methylbenzyl*)-5-*methylbenzyl*] *ether* (**III**), m.p. 179—179·5°.

V. The constitution of (**III**) is discussed and confirmed. (**III**) affords a *tetrabenzoate*, m.p. 173—175°, and a *tetra*-p-*nitrobenzoate*, m.p. 255°. (**I**) and HBr–C_6H_{14} give 2-*hydroxy*-3-(2′-*hydroxy*-5′-*methylbenzyl*)-5-*methylbenzyl bromide* (**IV**), dimorphic, m.p. 139·5—140°, also obtained similarly from (**III**). (**IV**) is converted by AcOH–NaOAc into the -*benzyl acetate*, m.p. 109·5—110°. *Di*-(3-*bromo*-4-*methoxy*-2 : 5-*dimethylbenzyl*) *ether*, m.p. 71—72°, is prepared from the 4 : 4′-$(OH)_2$-compound and Me_2SO_4–aq. NaOH.

VI. (**II**) at 150° (30 min.) loses 0·9—1 mol. of H_2O and ~0·2 mol. of CH_2O, giving a cryst. compound (**V**) and resin (*A*). (*A*) or (**V**) with HBr–$CHCl_3$ at −20° affords 2 : 2′-*dihydroxy*-5 : 5′-*dimethyl*-3 : 3′-*di*(*bromomethyl*)*diphenylmethane* (**VI**), m.p. 151° (decomp.), also obtained from (**II**) and HBr–EtOH at −20°.

VII. (**V**) gives (CH_2N_2) a *Me*$_4$ *ether*, m.p. 260—262° (immersed at 250°), a *tetra-acetate*, m.p. 306° (decomp.), and when heated affords an amorphous product, m.p. >360°. At 250°, (**V**) eliminates 0·26 mol. of CH_2O and ~3 mols. of H_2O and yields a product, m.p. 123—125° (not sharp). (**V**) is probably



2 : 3 : 5 : 1-OH·$C_6H_2Me_2$·CH_2·OH at 140° probably gives 4 : 6-dimethyl-2-hydroxymethylphenyl 2-hydroxy-3 : 5-dimethylbenzyl ether.

A. T. P.

Phenol–formaldehyde resins. XI. Mechanism of the hardening of resols. Formation of dihydroxydibenzyl ethers. H. von Euler, E. Adler, G. Eklund, and O. Törngren (*Arkiv Kemi, Min., Geol.*, 1942, **15**, **B**, No. 9, 8 pp.).—Very gradual addition of 40% CH_2O to an aq. solution of *p*-cresol and NaOH gives 2 : 5 : 1-OH·C_6H_3Me·CH_2·OH, m.p. 106—107°, converted at 150° for 30 min. in a sealed tube into *di*-2-*hydroxy*-5-*methylbenzyl ether* (**I**), m.p. 101—102°, in 10% yield; it gives an unstable, pale violet colour with $FeCl_3$–EtOH. (**I**) is transformed by HBr in $CHCl_3$ at 0° into the very unstable bromide, which can be converted by immediate treatment with aq. $NaHCO_3$ into the (? trimeric) *quinonemethide*, m.p. 150—151°, which is insol. in alkali and does not give a colour with $FeCl_3$. 2 : 3 : 5 : 1-OH·$C_6H_2Me_2$·CH_2·OH (**II**) is transformed by NaOH and *p*-C_6H_4Me·SO_2Cl into 2 : 4-*dimethyl*-6-*hydroxymethylphenyl* p-*toluenesulphonate*, m.p. 59—60°, which requires a temp. of 200° for conversion into the corresponding *ether* di-p-*toluenesulphonate*, m.p. 105—106°, hydrolysed to (2 : 3 : 5 : 1-OH·C_6H_2Me·CH_2)$_2$O, m.p. 99—100°. (**II**) and *p*-NO_2·C_6H_4·COCl (Schotten–Baumann) afford 2 : 4-dimethyl-6-hydroxymethylphenyl *p*-nitrobenzoate, m.p. 122°, but mainly the *di*-p-*nitrobenzoate*, m.p. 166—167°.

H. W.

Phenol–formaldehyde resins. XII. Mechanism of the hardening of resols. Hardening of 3-bromo-2-hydroxy-5-methylbenzyl alcohol. E. Adler, S. Tingstam, and O. Caspersson (*Arkiv Kemi, Min., Geol.*, 1942, **15**, **B**, No. 10, 8 pp.).—4 : 2 : 1-C_6H_2MeBr·OH is slowly converted by NaOH and CH_2O at room temp. into 3-*bromo*-2-*hydroxy*-5-*methylbenzyl alcohol* (**I**), m.p. 35—36°, which gives a pure blue colour with $FeCl_3$ in EtOH. (**I**) at 150° (sealed tube) for 2 hr. gives a little CH_2O, (mainly) *di*-3-*bromo*-2-*hydroxy*-5-*methylbenzyl ether*, m.p. 75·5—76·5° (*Me*$_2$ *ether*, m.p. 86—87°), which gives a violet colour with $FeCl_3$, and a small proportion of the (probably trimeric) *quinonemethide* (**II**), $(C_8H_7OBr)_3$, m.p. 259°. (**I**) differs from 2 : 3 : 5 : 1-OH·$C_6H_2Me_2$·CH_2·OH (**III**) in that it does not yield a diphenylmethane derivative under these conditions. At 180° (**III**) gives mainly the corresponding trimeric quinonemethide as main component of the crystallisable material whereas (**I**) gives little (**II**) and mainly *αβ-di*-3-*bromo*-2-*hydroxy*-5-*methylphenylethane*, m.p. 148—149°. (**I**) and HBr in well-cooled $CHCl_3$ afford 3-*bromo*-2-*hydroxy*-5-*methylbenzyl bromide*, m.p. 51—51·5°, which gives (**II**), m.p. 262—262·5°, when dissolved in Et_2O and shaken with 2N-Na_2CO_3.

H. W.

Arylacetonitrile derivatives.—See B., 1943, II, 145.

Derivatives of aminobenzamides.—See A., 1943, II, 175.

Antispasmodics. I. Basic esters of arylacetic acids. R. R. Burtner and J. W. Cusic (*J. Amer. Chem. Soc.*, 1943, **65**, 262—267).—Fluorene with $LiBu^{\alpha}$ (prep. described) in boiling Et_2O or NaPh (prep. described) in C_6H_6–N_2 (later adding Et_2O) and pouring on to solid CO_2 gives fluorene-9-carboxylic acid. *Diphenylacetehydrazide hydrochloride*, m.p. 298°, with $NaNO_2$–H_2O–PhMe at 5° and then NEt_2·$[CH_2]_2$·OH (**I**) at 100° gives β-diethylaminoethyl diphenylmethylcarbamate [hydrochloride, m.p. 184—185° (lit. 179°)]. α- or β-Naphthil with KOEt–EtOH–Et_2O at room temp. gives 1-, m.p. 133—134° (decomp.) (lit. 137°), or 2-*naphthilic acid*, m.p. 175° (decomp.) (scarlet colour in conc. H_2SO_4), respectively, reduced by HI–aq. AcOH to di-α-, m.p. 224° (lit. 223°), or *di*-β-*naphthylacetic acid*, m.p. 190°, respectively. CN·CPh_2·CO_2Me with H_2–Raney Ni in EtOH at room temp./45 lb. gives *Me* β-*amino*-αα-*diphenylpropionate hydrochloride*, m.p. 202° (decomp.) (derived *acid*, m.p. 360°), converted by $NaNO_2$–HCl–H_2O at 0° into *Me* β-*hydroxy*-αα-*diphenylpropionate*, m.p. 103° (derived *acid*, m.p. 167—168°). 2-Nitrofluorene-9-carboxylic acid with, successively, PCl_5 at 100°, (**I**)–C_6H_6 at room temp., and Raney Ni–H_2–EtOH–C_6H_6 gives β-*diethylaminoethyl* 2-*aminofluorene*-9-*carboxylate hydrochloride*, m.p. 92—94° (decomp.). Anthracene-9-carboxylic acid is best obtained from the aldehyde by Ag_2O–NaOH–H_2O–EtOH. 9-Formylfluorene, $CH_2(CO_2H)_2$, and piperidine at 85° give γ-2 : 2-*diphenylenecrotonic acid*, m.p. 202—203°. (CHPh·OH)$_2$ (prep. from benzoin by Raney Ni–H_2 in dioxan; not $SnCl_2$–EtOH) and $H_2C_2O_4$ give $CHPh_2$·CHO, which with $CH_2(CO_2H)_2$ and piperidine at 85° gives γγ-*diphenylcrotonic acid* (73%), m.p. 115—116°. Et tropate and thence the acid are best prepared from CHO·CHPh·CO_2Et by Raney Ni–H_2–EtOH. The following *ester hydrochlorides* are prepared from the alcohol and acid chloride or dialkylaminoalkyl chloride and acid in, *e.g.*, Pr^{α}OH : NEt_2·$[CH_2]_2$, tropine (sulphate), and NEt_2·CMe_2·$[CH_2]_2$ tropate (phosphate); NEt_2·$[CH_2]_2$, m.p. 98—99°, and 4-hydroxy-1-methylpiperidine atropate; NEt_2·$[CH_2]_2$ α-*phenyltropate*, m.p. 143—144°, *diphenylacetate*, m.p. 112°, *benzilate*, m.p. 177—178°, β-*hydroxy*-β-*phenylpropionate*, m.p. 141—142°, *anisilate*, m.p. 172°, α-*chloro*-*diphenylacetate*, m.p. 149—151°, ββ-*diphenylacrylate*, m.p. 159—160°, γγ-*diphenylcrotonate*, hygroscopic, m.p. 114—118°, *fluorene*-9-*carboxylate* (**II**), m.p. 143—144°, 9-*hydroxyfluorene*-9-*carboxylate*, m.p. 204°, 9-*fluorenylacetate*, m.p. 130—132°, γ-2 : 2-*diphenylenecrotonate*, m.p. 205°, *di*-α-, m.p. 211°, and -β-*naphthylacetate*, m.p. 151°, 1-, m.p. 143—144°, and 2-*naphthilate*, m.p. 195°, α-*phenyl*-β-2-*furylacrylate*, m.p. 157°, *anthracene*-9-*carboxylate*, m.p. 162°, and *hydrindene*-2-*carboxylate*, m.p. 132—133°; $(NEt_2$·$[CH_2]_2)_2$ dl-*camphorate*, hygroscopic; NMe_2·$[CH_2]_2$, m.p. 164°, 4-*hydroxy*-1-*methyl*-, hygroscopic, -1-n-*butyl*-, m.p. 162°, -1-β-*phenylethyl*-, m.p. 218—219°, and -1 : 2 : 6-*trimethyl*-*piperidine diphenylacetate*, hygroscopic; NEt_2·$[CH_2]_3$, m.p. 220°, NEt_2·$CHMe$·CH_2, m.p. 177°, NBu^{α}·$[CH_2]_2$, m.p. 165°, $NHBu^{\beta}$·$[CH_2]_2$, m.p. 160°, 4-*hydroxy*-1-*methyl*-, m.p. 218°, -1-β-*phenylethyl*-, m.p. 157—158°, and -1 : 2 : 6-*trimethyl*-*piperidine fluorene*-9-*carboxylate*, m.p. 217—218°. *Diphenylacet*-, m.p. 145°, and fluorene-9-carboxyl-, a syrup, -β-diethylaminoethylamide hydrochloride are also prepared. Of these esters and amides, (**II**) has the most favourable therapeutic index as an antispasmodic.

R. S. C.

Optically active nitro- and amino-mandelic acids. I. A. Fredga and E. Andersson (*Arkiv Kemi, Min., Geol.*, 1941, **14**, **B**, No. 18, 7 pp.).—*r*-*m*-Nitromandelic acid (**I**) is resolved into (−)-, m.p. 133—134°, $[\alpha]_D^{25}$ −122·4° in H_2O (*brucine* salt, +0·5H_2O, decomp. 148—150°), and (+)-m-*nitromandelic acid*, m.p. 133—134°, $[\alpha]_D^{25}$ +122·6° in H_2O (*cinchonine* salt, +0·5H_2O or anhyd.). Reduction by aq. $FeSO_4$–$Ba(OH)_2$ affords (−)- (+H_2O) (**II**), m.p. 128—128·5° (decomp. >129°), $[\alpha]_D^{25}$ −98·1° in H_2O (also by H_2–Pd–C–H_2O), and (+)-m-*aminomandelic acid*, m.p. 128—128·5° (decomp. >129°), $[\alpha]_D^{25}$ +98·2° in H_2O, respectively. (**I**) is reduced H_2–Pd–H_2O) to *r*-*m*-aminomandelic acid, m.p. 130°, converted by the diazo-reaction (aq. NaH_2PO_2–H_2SO_4–$CuSO_4$) into *r*-mandelic acid, m.p. 117—118°; (**II**) similarly gives (−)-mandelic acid, m.p. 131·5—132·5°, $[\alpha]_D^{25}$ −152° in H_2O.

A. T. P.

Optical activity of nitro- and amino-mandelic acids. E. Grimsell (Andersson) (*Arkiv Kemi, Min., Geol.*, 1942, **15**, **B**, No. 17, 11 pp.).—Conductivity data are given for *o*-, *m*-, and *p*-nitromandelic acid and their *K* salts (cf. McKenzie *et al.*, A., 1935, 356), and optical data for *l*(+)-mandelic acid, its *o*-, *m*-, and *p*-NO_2- and -NH_2-derivatives in various solvents. *r*-*o*-Nitromandelic acid is reduced (Na salt–H_2O–H_2–Pd–C) to *r*-*o*-aminomandelic acid, m.p. 144°, deaminated to mandelic acid. (−)-*o*-Aminomandelic acid similarly gives (−)-mandelic acid.

A. T. P.

Synthesis of cinnamic acids from methyl acrylate or acrylonitrile and diazonium salts. C. F. Koelsch (*J. Amer. Chem. Soc.*, 1943, **65**, 57—58).—Adding aq. ArN_2Cl to CH_2:CH·CN–NaOAc–$CuCl_2$–$COMe_2$ (pH ~6) gives 34—48% of α-*chloro*-β-*phenyl*-, m.p. 18—21°, b.p. 137—140°/15 mm., α-*chloro*-β-m- (impure), m.p. 83—84°, b.p. 215—225°/13 mm., and -p-*nitrophenyl*-, m.p. 111—112°, and α-*chloro*-β-p-*tolyl*-, b.p. 140—145°/11 mm., -*propionitrile*, converted in boiling NPhEt_2 into CHAr:CH·CN. CH_2:CH·CO_2Me reacts similarly but gives rather poorer yields. p-*Nitrocinnamonitrile*, m.p. 200—201°, and impure *Me* α-*chloro*-β-p-*tolylpropionate*, b.p. 135—145°/11 mm., are described.

R. S. C.

Condensation of malonanilic acid with aldehydes. V. With *o*- and *p*-chlorobenzaldehydes and *m*-bromobenzaldehyde; influence of the halogens. K. C. Pandya and (Miss) R. B. Pandya (*Proc. Indian Acad. Sci.*, 1943, **17**, **A**, 1—6).—NHPh·CO·CH_2·CO_2H with RCHO gives CHR:C(CO_2H)·CO·NHPh with a little CHR:CH·CO·NHPh (**I**). In presence of C_5H_5N, (**I**) is predominant. The following were prepared: p-*chloro*-, m.p. 190°, o-*chloro*-, m.p. 225°, and m-*bromobenzylidenemalonanilic acid*, m.p. 186—188°; p-*chloro*-, m.p. 180°, o-*chloro*-, *forms*, m.p. 176—177° and 153—154°, and m-*bromo*-*cinnamanilide*, *forms*, m.p. 128—129° and (probably) 162°.

F. R. G.

Fatty derivatives of salicylic acid and α-naphthol. D. Price and (Miss) E. L. May (*J. Amer. Chem. Soc.*, 1943, **65**, 297).—*o*-OH·C_6H_4·CO_2Me and *n*-C_9H_{19}·COCl at 220—225° give *Me* o-*decoyloxybenzoate*, b.p. 217—219°/12 mm., converted (Fries; light petroleum) into *Me* 4(? 5)-*decoylsalicylate*, m.p. 66·5—67·5°, b.p. 180—190°/1·5 mm. (derived *acid*, m.p. 120·5—121·5°). α-$C_{10}H_7$·n-*octoate*, b.p. 156—157°/1 mm., and 2-*octoyl*-1-*naphthol*, m.p. 68—68·5°, are also prepared.

R. S. C.

Sulphonyl derivatives of amidines and imino-ethers. H. J. Barber (*J.C.S.*, 1943, 101—104).—*p*-NO_2·C_6H_4·SO_2Cl (**I**) (prep. described), b.p. 143—144°/1·5 mm., with NH:CPh·OEt (2 mols.) (**II**) in $COMe_2$ at 30—35° affords p-*nitrobenzenesulphonylbenzimino Et ether* (**III**), m.p. 129—130°, or with NH:CPh·NH_2,HCl in aq. NaOH–$COMe_2$ gives N-p-*nitrobenzenesulphonylbenzamidine* (**IV**), m.p. 179° (decomp.). (**III**) and NH_3–EtOH give an *isomeride*, m.p. 159—165° (previous softening) (decomp. ~195—200°), of (**IV**), converted by prolonged boiling in EtOH into (**IV**). (**IV**) loses SO_2 at 200° to

give p-*nitrophenylbenzamidine*, m.p. 167—168°. (**II**) (as hydrochloride) and *p*-NHAc·C_6H_4·SO_2Cl (**V**)–C_5H_5N at 70° yield p-*acetamidobenzenesulphonylbenzimino Et ether*, m.p. 100—102°, converted at 110—120° into a *form*, m.p. 136—137°. Either form with NH_3–EtOH yields p-*acetamidobenzenesulphonylbenzamidine*, α-, m.p. 185—187° (pre-heated), or β-form, m.p. 208—210° [formed by more prolonged action of EtOH–NH_3; also obtained from (**V**) and NH:CPh·NH_2]. Hydrogenation (PtO_2, 2 atm.) of (**III**) in $COMe_2$ at room temp. gives p-*aminobenzenesulphonylbenzimino Et ether*, m.p. 98°, converted by NH_3–EtOH into the corresponding *benzamidine*, α-, m.p. 155—160°, or β-*form*, m.p. 205—207°. NH:CMe·OEt and (**I**) in Et_2O at ~25° give p-*nitrobenzenesulphonylacetimino Et ether*, m.p. 87—88°; in 1 case (in boiling Et_2O) *p*-NO_2·C_6H_4·SO_2·NHAc was the main product. *p*-NO_2·C_6H_4·SO_3Na and NPh:CPhCl heated gradually to 180° yield BzCl and NN′-*diphenylbenzamidine* p-*nitrobenzenesulphonate*, m.p. 240—241°, converted by cold aq. NaOH into NPh:CPh·NHPh. N-p-*Nitrobenzenesulphonylbenzimino Ph ether*, m.p. 173—174° (decomp. 280—285°, with some evolution of SO_2), is obtained from *p*-NO_2·C_6H_4·SO_2·N:CPhCl, new m.p. 164—165°, and PhOH–NaOH (10 : 1) at 40°, then at 100°. (**I**) and *p*-NO_2·C_6H_4·SO_2·NNaPh at 150—200° give *di*-p-*nitrobenzenesulphanilide*, m.p. 264°. A. T. P.

β-Cyano-β-phenylpropionic acid. S. Wideqvist (*Arkiv Kemi, Min., Geol.*, 1941, **14**, **B**, No. 19, 6 pp.).—CHPh:$C(CO_2Et)_2$ and KCN–aq. EtOH give CN·CHPh·CH_2·CO_2H, m.p. 75° (lit. 150°), converted by conc. HCl at 115° into CO_2H·CHPh·CH_2·CO_2H, or by conc. H_2SO_4 at room temp. (12 hr.) or H_2O at 25° (10 days) into CO_2H·CH_2·CHPh·CO·NH_2. A. T. P.

Urethanes. VII. Reactions of acyl diurethanes with ammonia and primary amines. Stabilising effect of the phenyl radical in phenylmalonyl- and phenylsuccinyl-diurethane. S. Basterfield and A. J. Dyck (*Canad. J. Res.*, 1942, **20**, **B**, 240—245).—Introduction of Ph increases the stability of the mol. CHPh(CO·NH·CO_2Et)$_2$ (**I**) and 25% aq. NH_3 at room temp. slowly give CHPh(CO·NH_2)$_2$, m.p. 232°, NH_2·CO_2Et (**II**), and some (?) NH_4 phenylbarbiturate. Under similar conditions (**I**) and 25% NH_2Et afford *phenylmalonethylamide*, m.p. 154°, (**II**), and, probably, NH_3Et phenylbarbiturate. With NH_2Ph and (**I**) at 150° the products are *phenylmalonanilide* (**III**), m.p. 204—205°, *phenylmalonyldiphenylcarbamide*, m.p. 234—235° [converted by NH_2Ph at 150—160° into (**III**) and CO(NHPh)$_2$], and *phenylcarbamidophenylmalonylurethane*, m.p. 151°; at 180—190° (**III**) and CO(NHPh)$_2$ are produced. CO_2H·CH_2·CHPh·CO_2H, (**II**), and $POCl_3$ at room temp., then at 40°, and finally at 50° afford *phenylsuccinyldiurethane* (**IV**), m.p. 162°, slowly transformed by 25% NH_3 at room temp. into NH_2·CO·CHPh·CH_2·CO·NH_2 and (**II**). Similarly NH_2Et gives *phenylsuccinethylamide*, m.p. 179—180°, and (**II**). With NH_2Ph at 180° the main product is (?) *phenylsuccinyldiphenylcarbamide* (**V**), m.p. 235°, with CO(NHPh)$_2$ and a gum, whereas at 180—200° (**V**), (?) *phenylcarbamidophenylsuccinanilide*, m.p. 234°, and CO(NHPh)$_2$ result. Malonyldiurethane and *cyclo*hexylamine rapidly give *malon*cyclo*hexylamide*, m.p. 174°, and (**II**). H. W.

β-Arylglutaconic acids. VII. Constitution of the so-called hydroxy-anhydrides. G. R. Gogte (*Proc. Indian Acad. Sci.*, 1942, **16**, **A**, 240—243).—Earlier work on α-acyl- and αγ-diacyl-β-arylglutaconic anhydrides (cf. A., 1938, II, 284; 1939, II, 133; 1941, II, 103) is reviewed. Contrary to Limaye *et al.* (A., 1940, II, 130), no α-Me derivative is obtained from *p*-OMe·C_6H_4·C(:CH·CO_2Et)·CH_2·CO_2Et by NaOEt–MeI. Reduction or attempted esterification of *p*-OMe·C_6H_4·C(:CH·CO_2H)·CHAc·CO_2Et gives only the lactone, CAr<CH——CO / C(CO$_2$Et):CMe>O. Decomp. occurs before CO_2Et·CH_2·CO·CHMe·CO_2Et can be condensed with ArOAlk by H_2SO_4. R. S. C.

Preparation of aldehydes from carboxylic acids with titanium dioxide as catalyst.—See A., 1943, II, 152.

Condensation of chlorodinitrotoluenes with *p*-nitrosodimethylaniline. D. S. Mittal (*J. Indian Chem. Soc.*, 1942, **19**, 408).—The requisite $C_6H_2MeCl(NO_2)_2$ with *p*-NO·C_6H_4·NMe_2 in presence of EtOH and Na_2CO_3 and hydrolysis of the resulting products with 2*N*-HNO_3 leads to 5-chloro-2 : 4-dinitro-, m.p. 150—152° (phenylhydrazone, m.p. 217°; oxime, m.p. >280°), 4-chloro-3 : 5-dinitro-, m.p. 79—80° (phenylhydrazone, m.p. 109°; anil, m.p. 108°; oxime, m.p. >290°); and 2-chloro-3 : 5-dinitro-benzaldehyde, m.p. 78° (oxime, m.p. >290°; anil, m.p. 138°). The corresponding benzoic and cinnamic acids have been prepared from these aldehydes. H. W.

Gallaldehyde tribenzyl ether. R. O. Clinton and T. A. Geissman (*J. Amer. Chem. Soc.*, 1943, **65**, 85—87).—Benzylation is more effectively carried out in COPhMe. 3 : 4 : 5 : 1-$(OH)_3C_6H_2$·CO_2Me, CH_2PhCl, and K_2CO_3 in COPhMe at 140—150° give *Me gallate* (*CH_2Ph*)$_3$ *ether* (81%), m.p. 89·5—90°. The acid gives similarly *CH_2Ph gallate* (*CH_2Ph*)$_3$ *ether* (47%), m.p. 90—90·5°. Either ester with NaOH–EtOH–H_2O gives 3 : 4 : 5 : 1-$(CH_2Ph·O)_3C_6H_2$·CO_2H, m.p. 196—196·5° (lit. 187°) (resists decarboxylation), the *hydrazide*, m.p. 137—137·5°, of which with $PhSO_2Cl$ in C_5H_5N at 20—25° gives α-*benzenesulphon-β-gallhydrazide* (*CH_2Ph*)$_3$ *ether* (88%), m.p. 165—165·5°. With Na_2CO_3 in $(CH_2·OH)_2$ at 160°, this gives *gallaldehyde* (*CH_2Ph*)$_3$ *ether* (94%), m.p. 104—104·5° (*oxime*, m.p. 140—140·5°; 2 : 4-*dinitrophenylhydrazone*, m.p. 214—214·5°), which with 2 : 4 : 1-$(OH)_2C_6H_3$·COMe and 50% aq. KOH in boiling EtOH gives 2 : 4-*dihydroxyphenyl* 3 : 4 : 5-*tribenzyloxystyryl ketone* (28%), m.p. 160—161°. R. S. C.

Formylation of methyl γ-resorcylate by Gattermann's reaction; synthesis of methyl 2 : 6-dihydroxy-3-formylbenzoate. (Miss) K. S. Radha and R. C. Shah (*J. Indian Chem. Soc.*, 1942, **19**, 393—395).—2 : 6 : 1-$(OH)_2C_6H_3$·CO_2Me is converted by $Zn(CN)_2$ and dry HCl in well-cooled Et_2O followed by H_2O into *Me* 2 : 6-*dihydroxy-3-formylbenzoate* (**I**), m.p. 113—115°; no recognisable product could be isolated after addition of $AlCl_3$; the 2 : 4-*dinitrophenylhydrazone* and *semicarbazone* have m.p. 272—275° (decomp.) and 220—222°, respectively. (**I**), $CH_2Ac·CO_2Et$, and piperidine in C_5H_5N at 100° give *Me* 7-*hydroxy*-3-*acetylcoumarin*-8-*carboxylate*, m.p. 245—246°; $CH_2(CO_2Et)_2$ affords *Et* 7-*hydroxy*-8-*carbomethoxycoumarin*-3-*carboxylate*, m.p. 255—256°. Reduction (Zn–Hg, EtOH, dil. HCl) of (**I**) gives *Me* 2 : 4-*dihydroxy*-m-*toluate*, m.p. 62—63°. 2 : 6-*Dihydroxy*-3-*formylbenzoic acid*, m.p. 215—216°, is decarboxylated by dil. HCl at 180—190° to 2 : 4 : 1-$(OH)_2C_6H_3$·CHO. (**I**) and conc. H_2SO_4–HNO_3 give the 5-NO_2-, m.p. 148—150°, and Br in AcOH affords the 5-*Br*-derivative, m.p. 143—145°. CO_2Me in the γ-position has no deactivating effect on the reactivity of the resorcinol nucleus. H. W.

***p*-Alkylation of benzoyldurene by the Grignard reagent.** R. C. Fuson and B. C. McKusick (*J. Amer. Chem. Soc.*, 1943, **65**, 60—64).—2 : 3 : 5 : 6 : 1-C_6HMe_4·COPh (**I**) [prep. from durene by BzCl–CS_2–$AlCl_3$ (77%) or from 2 : 3 : 5 : 6 : 1-C_6HMe_4·COCl (**II**) by $CdPh_2$], m.p. 119—120°, with CH_2Ph·MgCl in Et_2O gives 4′-*benzyl*-2 : 3 : 5 : 6-*tetramethylbenzophenone* (**III**), *forms*, m.p. 128·5—129·5° (stable) and 119—120°, and with $MgBu^{\gamma}Cl$ gives 2 : 3 : 5 : 6-*tetramethyl*-4′-tert.-*butylbenzophenone* (**IV**) (33%), m.p. 127—128° [(*NO_2*)$_2$-derivative, m.p. 212—213°, prepared by HNO_3 (*d* 1·5)]. These reactions correspond to 1 : 6-addition of MgRCl followed by loss of a mol. of H_2 or its equiv. Na–EtOH reduces (**III**) to 4′-*benzyl*-2 : 3 : 5 : 6-*tetramethyldiphenylmethane* (**V**), m.p. 69—70°. The Grignard reagent from *o*-C_6H_4Br·CH_2Ph (prep. from the ketone by Martin–Clemmensen reduction) with (**II**) in Et_2O gives 2′-*benzyl*-2 : 3 : 5 : 6-*tetramethylbenzophenone* (49%), m.p. 118·5—119·5°, reduced (Na–EtOH) to 2′-*benzyl*-2 : 3 : 5 : 6-*tetramethyldiphenylmethane*, m.p. 126·5—127·5°. 2 : 3 : 5 : 6 : 1-C_6HMe_4·CH_2Ph [prep. from (**I**) by Na–EtOH but not by Clemmensen reduction], m.p. 57—58° (lit. 60·5°, 145°), with BzCl–$AlCl_3$–CS_2 gives 4-*benzyl*-2 : 3 : 5 : 6-*tetramethylbenzophenone* (**VI**) (77%), m.p. 173—174°. BzCl, $AlCl_3$, and (**I**) at 155° give 2 : 3 : 5 : 6 : 1 : 4-$C_6Me_4(COPh)_2$ (39%), m.p. 273—275°, reduced, as also is (**VI**), by Na–*n*-C_5H_{11}·OH to 4-*benzyl*-2 : 3 : 5 : 6-*tetramethyldiphenylmethane*, m.p. 176—177°. With boiling syrupy H_3PO_4, (**III**) gives durene and *p*-CH_2Ph-C_6H_4-CO_2H (also obtained from *p*-$C_6H_4Bz·CO_2H$ by Martin–Clemmensen reduction). *p*-CH_2Ph-C_6H_4-COCl, durene, and $AlCl_3$ in CS_2 give impure (**III**), identified by reduction to (**V**). Reduction (Clemmensen or Na–EtOH) of (**IV**) gives 2 : 3 : 5 : 6-*tetramethyl*-4′-tert.-*butyldiphenylmethane*, m.p. 116—117°. In syrupy H_3PO_4, (**IV**) gives *p*-$C_6H_4Bu^{\gamma}$·CO_2H and durene. (**IV**) is also obtained (20%) from *p*-$C_6H_4Bu^{\gamma}Br$ by successive treatment with Mg–Et_2O, anhyd. $CdCl_2$, and (**II**). Br and a trace of I in boiling CCl_4 convert (**I**) into 4-*bromo*-2 : 3 : 5 : 6-*tetramethylbenzophenone*, m.p. 116—117°, better obtained from bromodurene by BzCl–$AlCl_3$ in CS_2. (**IV**) gives similarly 4-*bromo*-2 : 3 : 5 : 6-*tetramethyl*-4′-tert.-*butylbenzophenone*, m.p. 182—183°, also obtained (40%) from 2 : 3 : 5 : 6 : 4 : 1-C_6Me_4Br·COPh by $MgBu^{\gamma}Cl$. R. S. C.

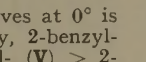
Friedel–Crafts reaction with cinnamic, crotonic, and β-chlorocrotonic acids. C. F. Koelsch, H. Hochmann, and C. D. Le Claire (*J. Amer. Chem. Soc.*, 1943, **65**, 59—60).—CHPh:CH·CO_2H and $AlCl_3$ in boiling C_6H_6 give 3-phenylhydrindone (39%) and $CHPh_2$·CH_2·CO_2H (25%). Adding CHMe:CH·CO_2H in C_6H_6 to $AlCl_3$ (3 mols.) and boiling gives 3-methylhydrindone (**I**) (81·5%), b.p. 132—137°/15 mm., and CHPhMe·CH_2·CO_2H (**II**) (4%); use of 2 mols. of $AlCl_3$ gives 50—56% of (**I**) and 29—32% of (**II**). CMeCl:CH·CO_2H and $AlCl_3$ in C_6H_6 give 36·5% of CPh_2Me·CH_2·CO_2H (**III**), 58% being obtained from CPhMe:CH·CO_2H, C_6H_6, and $AlCl_3$. Adding PCl_5 and then $AlCl_3$ to (**III**) in C_6H_6 gives 78% of 3-phenyl-3-methylhydrindone (*oxime*, m.p. 167—168°), converted by OBu·NO–conc. HCl–EtOH at 40—45° (later room temp.) into the 2-*oximino*-derivative (63%), m.p. 168—168·5°, which with $AcCO_2H$ (less well, CH_2O) and conc. HCl in aq. AcOH gives 3-*phenyl*-3-*methylindane*-1 : 2-*dione*, m.p. 115—116°. With *o*-$C_6H_4(NH_2)_2$ in EtOH, this gives the *quinoxaline*, m.p. 129—130°, and with H_2O_2–NaOH gives α-*phenyl*-α-*methylhomophthalic acid*, m.p. 170—172°. R. S. C.

Steric hindrance to ketonic function. II. Velocity of oximation of *cyclo*hexanone and of its monomethyl derivatives. A. R. Poggi [with M. Müller]. **III. Velocity of oximation of 2-benzylidene-derivatives of *cyclo*hexanone and its homologues.** A. R. Poggi [with A. M. Rossi and A. Maurizi]. **IV. Velocity of oximation of 2-benzyl derivatives of *cyclo*hexanone and its homologues.** A. R. Poggi

[with E. Wiechmann] (*Gazzetta*, 1942, **72**, 262—273, 274—281, 282—287; cf. A., 1943, I, 132).—II. Oximes of 3- and 4-methyl*cyclo*hexanone are formed at about the same rate as that of *cyclo*hexanone, but that of 2-methyl*cyclo*hexanone (**I**) is formed more slowly.

III. The oxime of 2-benzylidene*cyclo*hexanone (**II**) is formed much more slowly than that of (**I**); oxime formation in the 4-, 5-, and 6-Me derivatives of (**II**) is still slower (4- > 5- > 6-).

IV. Velocity of oxime formation in CH_2Ph derivatives at 0° is intermediate between those of (**I**) and (**II**); in velocity, 2-benzyl-4-methyl- (**III**) > 2-benzyl-5-methyl- (**IV**) > 2-benzyl- (**V**) > 2-benzyl-6-methyl-*cyclo*hexanone (**VI**). At 13°, the order is (**III**) and (**V**) > (**IV**) > (**VI**). 2- or 6-Substitution thus exerts steric hindrance. E. W. W.

Synthesis of 2-keto*cyclo*hexylsuccinic acid and related substances. I. Syntheses involving *cyclo*hexene oxide. J. A. McRae, E. H. Charlesworth, and D. S. Alexander (*Canad. J. Res.*, 1943, **21**, **B**, 1—12).—*cyclo*Hexene oxide (**I**) with $CHNa(CO_2Et)_2$ and $CH_2Br{\cdot}CO_2Et$ in EtOH yields a product hydrolysed and decarboxylated to *2-hydroxycyclohexylsuccinolactone*, m.p. 130°, oxidised [Br–$Mg(OH)_2$ at <10° or alkaline $KMnO_4$ at >40—50°] to *2-keto*cyclo*hexylsuccinic acid*, m.p. 154—155°, which at 200° under reduced pressure yields *2-ketohexahydrobenzfuran-3-acetic acid*, $[CH_2]_4$  , m.p. 116—118°, and with EtOH–NH_3 under pressure gives *2-ketohexahydroindole-3-acetic acid*, m.p. 201°, decomposed by cold 1·25N-NaOH. 2-Hydroxy*cyclo*hexylacetolactone (Coffey, A., 1923, i, 695) is oxidised (as above) to 2-keto*cyclo*hexylacetic acid, m.p. 73—74° (lit. 39—41°), which at 200° under reduced pressure gives *2-ketohexahydrobenzfuran*, b.p. 160—165°/25 mm., m.p. 7—8° (readily hydrolysed by hot 0·1N-NaOH), and with EtOH–NH_3 gives a N-containing oil (**II**). 2-Hydroxy-α-carbethoxy*cyclo*hexylacetolactone with 5N-NaOH followed by Br–$Mg(OH)_2$ yields *2-keto*cyclo*hexylmalonic acid* (**III**), m.p. 163° (decomp.) [semicarbazone, m.p. 271° (decomp.)], and with aq. NaOH–$KMnO_4$ gives (**III**) and 2-hydroxy*cyclo*hexylmalonolactone, m.p. 121—122°. With EtOH–NH_3 (**I**) yields a product (? **II**) (N 21·8%). *α-2-Hydroxycyclohexyl-α-benzylacetolactone*, b.p. 202—204°/10 mm. [from (**I**), $CHNa(CO_2Et)_2$, and CH_2PhCl as above], is oxidised [Br–$Mg(OH)_2$] to *α-2-ketocyclohexyl-α-benzylacetic acid*, which when distilled loses 1 H_2O and gives the unsaturated *lactone*, b.p. 220—240°/16 mm. (**I**) with $CHNa(CO_2Et)_2$ in EtOH, followed by MeI in C_6H_6, yields a product hydrolysed and decarboxylated to *α-2-hydroxycyclohexylpropiolactone*, b.p. 148—150°/21 mm., oxidised [Br–$Mg(OH)_2$] to *α-2-ketocyclohexylpropionic acid*, m.p. 133—135°. A. Li.

Action of diazo-compounds on quinones. II. Reaction between diazo-compounds and naphthaquinones: preparation of phenylnaphthalenes. G. B. Marini-Bettòlo and C. Rossi (*Gazzetta*, 1942, **72**, 208—215).—Naphthaquinone in AcOH with *p*-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ at 60°, or better at room temp. with a trace of Cu powder, gives *2-p-nitrophenyl-1 : 4-naphthaquinone* (cf. Hey *et al.*, A., 1940, II, 211), which with Zn and Ac_2O–NaOAc gives the 1 : 2 : 4-Ac_3 derivative, m.p. 184°, of 1 : 4-*dihydroxy-2-p-aminophenylnaphthalene*, m.p. 165° (*hydrochloride*, m.p. 250°). Similarly *m*-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ gives *2-m-nitrophenyl-1 : 4-naphthaquinone*, m.p. 214°. Starting with 2-methyl-1 : 4-naphthaquinone, 3-p-, m.p. 182°, and 3-m-*nitrophenyl-2-methyl-1 : 4-naphthaquinone*, m.p. 225°, are obtained. The last gives the Ac_3 derivative, m.p. 172°, of 1 : 4-dihydroxy-3-*m*-aminophenyl-2-methylnaphthalene, m.p. indefinite, owing to oxidisability [*hydrochloride*, m.p. 170°, which when diazotised and coupled with *m*-$C_6H_4(OH)_2$ and β-$C_{10}H_7{\cdot}OH$ gives compounds, m.p. 208°, and 182°, respectively]. 3-p-*Anisyl-2-methyl-1 : 4-naphthaquinone*, m.p. 176° (whence 1 : 4-*diacetoxy-3-p-anisyl-2-methylnaphthalene*, m.p. 115°), and 3-p-*tolyl-2-methyl-1 : 4-naphthaquinone*, m.p. 158°, are prepared similarly. E. W. W.

Effects of solvents on absorption spectra of dyes.—See A., 1943, I, 114.

Derivatives of *o*-3′-acenaphthoylbenzoic acid. A. T. Peters and F. M. Rowe (*J. Soc. Dyers and Col.*, 1943, **59**, 52—54).—*o-3′-Acenaphthoylbenzoic acid* (**I**) and $AlCl_3$–NaCl at 134—135° (bath) give 3 : 4-*phthaloylacenaphthene* (**II**), m.p. 194—195° [p-*nitro-*, m.p. 255—256°, and 2 : 6-*dichloro-4-nitro-phenylhydrazone*, m.p. 248—249° (decomp.)], oxidised by $Na_2Cr_2O_7$–AcOH to a 1 : 1 *compound*, melts partly at 258—260°, with subsequent shrinking and darkening, melting finally at 330—350°, of (**II**) and 4 : 5-*phthaloylnaphthalic anhydride* (**III**), m.p. 368° (decomp.) [*di*-p-*nitro-*, m.p. 287—288° (decomp.), and *di*-2 : 6-*dichloro-4-nitro-phenylhydrazone*, m.p. ~200°; *imide*, decomp. >390°; N-*methylimide*, m.p. 315—316°; N-p-*nitrophenylimide*, m.p. ~400°]; (**III**) is the sole product of a more vigorous similar oxidation. (**III**) and *o*-$C_6H_4(NH_2)_2$ in AcOH afford 9′-*keto*-3′ : 4′-*phthaloyl-8′-aza-phenalino*(7′ : 8′ : 2 : 3)-ψ-*indole* [1 : 2-4′ : 5′-*phthaloyl-1′* : 8′-*naphthoylenebenziminazole*] (**IV**), m.p. 380°. (**I**) is reduced by Zn–aq. NaOH–EtOH to *o-3′-acenaphthylmethylbenzoic acid* (**V**), m.p. 201—202°, and the *lactone*, m.p. 211—212°, of *o*-carboxyphenyl-3-acenaphthylcarbinol; (**V**) only is formed using Zn–aq. NaOH–$CuSO_4$–NH_3, but subsequent cyclisation was not achieved. 4-*o*-Carboxybenzoylnaphthalic anhydride and 20% oleum–H_3BO_3 at 150°, or conc. H_2SO_4 at 180—185°, afford 3 : 4-phthaloylnaphthalic anhydride (**VI**), m.p. 315° [p-*nitrophenylhydrazone*, m.p. 350—353° (decomp.); *imide* (**VII**), m.p. 360° (decomp.) (darkens from 345°); *N*-methylimide, m.p. 276—277°, also obtained from 4-*o*-carboxybenzoyl-1 : 8-naphthal-*N*-methylimide, m.p. 238—239°, and conc. H_2SO_4 at 180—190°; N-p-*nitrophenylimide*, m.p. >380°]. 4-*o*-Carboxybenzoyl-1 : 8-naphthalimide, m.p. 296—297°, and 20% fuming H_2SO_4 at 160° also give (**VII**), but conc. H_2SO_4 at 185°, 200°, or 230°, affords (**VI**) only. 1 : 2-3′ : 4′(or 5′ : 6′)-Phthaloyl-1′ : 5′-naphthoylenebenziminazole, m.p. 320—325° (shrinks from 300°), is best prepared from (**VI**), a poor yield only being derived by cyclisation of 1 : 2-4′(or 5′)-*o-carboxybenzoyl-1′* : 8′-*naphthoylenebenziminazole*, m.p. 285—287°. A. T. P.

IV.—STEROLS AND STEROID SAPOGENINS.

Cafesterol. II. H. Hauptmann and J. França (*J. Amer. Chem. Soc.*, 1943, **65**, 81—85; cf. A., 1939, II, 367).—Cafesterol (**I**) is purified as *solvate*, +MeOH (lost at 120°), m.p. 156—158°, and then has $[\alpha]_D$ −114°; its m.p. is a poor criterion of purity. Its inert O is probably present in an ether group. $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ is without effect. Its acetate with H_2–Raney Ni in EtOH at 25°/696 mm. yields an *oxcafestanediol acetate* (60%), m.p. 156°, colourless in $C(NO_2)_4$ and unaffected by *o*-$CO_2H{\cdot}C_6H_4{\cdot}CO_3H$ (**II**) or dil. acid, but hydrolysed by hot $KHCO_3$–MeOH–H_2O to *oxcafestanediol* (**III**), m.p. 188°. *Cafestanetriol*, m.p. 227°, $[\alpha]_D^{29}$ −33·7° in EtOH, and HIO_4–MeOH give CH_2O. With boiling Ac_2O–C_5H_5N, (**I**) gives *oxcafestatrienol acetate* (**IV**), m.p. 114°, $[\alpha]_D^{26}$ −78·5° in $CHCl_3$ (absorption spectrum given), which absorbs 2 O from (**II**), absorbs 4 H_2 in presence of PtO_2 in AcOH (to give a syrup, hydrolysed to an oil, which is stable to HIO_4), but absorbs 2 H_2 in presence of Raney Ni in EtOH at 27°/703·6 mm. No adduct is obtained from (**I**) and $(CH{\cdot}CO)_2O$ at 135°. (**III**) and its isomeride, (**I**), and (**IV**) have no androgenic or cortenic activity. R. S. C.

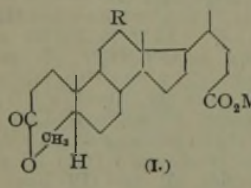
Acyl migration in steroids. V. A. Petrow, O. Rosenheim, and W. W. Starling (*J.C.S.*, 1943, 135—139; cf. A., 1937, II, 191).—A very facile acyl migration, without analogy in the steroid series, but similar to that in glycerides, occurs in the monoesters of *cis*-Δ⁵-cholestene-3 : 4-diol (**I**); intermediate formation of orthocarbonic esters is probable, and other mechanisms are discussed. Cholesteryl dibromide (**II**) and AgOAc–C_5H_5N–Et_2O followed by $CHCl_3$–AcOH give, after decomp. of its 1 : 1 AcOH compound, m.p. 142—144° (softens at 124°), with boiling 85% EtOH, 4-*acetoxy-Δ⁵-cholesten-3-ol* (**III**), m.p. 164—165°, $[\alpha]_D^{24}$ −88·8°, $[\alpha]_{5461}^{24}$ −107·8° (1 : 1 $EtCO_2H$ compound, solvent lost at 120°). Cholesteryl acetate and SeO_2–95% AcOH in C_6H_6 or dioxan also give (**III**) and ~5% of 3-acetoxy-Δ⁵-cholesten-4-ol (**IV**). (**IV**) is converted into (**III**) by AcOH in dioxan at 90°, or in boiling C_6H_6. The acetates, m.p. 165° and 191°, of Marker *et al.* (A., 1940, II, 17) are (**III**) and (**IV**), respectively, and the so-called 3-acetates of 4-hydroxy-sitosterol and -stigmasterol (Marker *et al.*, A., 1938, II, 276) are similarly the *cis*-3 : 4-diol 4-monoacetates. (**II**) and $EtCO_2Ag$–C_5H_5N–Et_2O give 4-*propionoxy-Δ⁵-cholesten-3-ol* (**V**), m.p. 134—135°, $[\alpha]_D^{18}$ −87·8° (AcOH compound, m.p. 110—112°), also obtained from cholesteryl propionate and SeO_2–C_6H_6–95% AcOH. Acetylation of (**V**) or propionylation of (**IV**) gives 3-*acetoxy-4-propionoxy-Δ⁵-cholestene*, m.p. 156—157°, $[\alpha]_D^{20}$ −96·5°. 4-*Butyroxy-Δ⁵-cholesten-3-ol*, m.p. 125—126°, $[\alpha]_D^{21}$ −75·3° (AcOH compound, m.p. 99—100°), and 3-*acetoxy-4-butyroxy-Δ⁵-cholestene*, m.p. 139—140°, $[\alpha]_D^{16}$ −90·8°, are also prepared. 4-*Benzoyloxy-Δ⁵-cholesten-3-ol*, m.p. 154—155°, $[\alpha]_D^{18}$ −29·5° [identical with compound *C* of Spring *et al.* (A., 1939, II, 477)], is acetylated to 4-benzoyloxy-3-acetoxy-Δ⁵-cholestene, new m.p. 132—134°, $[\alpha]_D^{19}$ −59·5°, also obtained by benzoylating the 3-monoacetate. Δ⁵-Androsten-3(β)-ol-17-one and Br–$CHCl_3$ afford a product, which with AgOAc–C_5H_5N–Et_2O gives 4-*acetoxy-Δ⁵-androsten-3(β)-ol-17-one*, m.p. 192—193°, $[\alpha]_D^{18}$ −60·7°, hydrolysed to cis-Δ⁵-*androstene-3 : 4-diol-17-one*, m.p. 204—205°, $[\alpha]_D^{20}$ −28·5°. Cholesteryl acetate and SeO_2 in aq. dioxan afford (**IV**), also obtained by partial conversion of (**III**) by AcOH–dioxan (1 : 1) at 90°. Cholesteryl benzoate similarly gives 3-benzoyloxy-Δ⁵-cholesten-4-ol (**VI**). (**I**), (**III**), or (**IV**) with boiling AcOH (5 min.) affords (after acetylation) 3 : 6-diacetoxy-Δ⁴-cholestene (**VII**) and thence the diol. (**IV**) and $SOCl_2$–Et_2O–C_5H_5N at room temp., or by gentle refluxing, give 4-*chloro-3-acetoxy-Δ⁵-cholestene* (**VIII**), m.p. 108—109°, $[\alpha]_D^{19}$ −70·4°, also obtained from 6-chloro-3-acetoxycholestan-5-ol and cold $SOCl_2$–C_5H_5N. (**VIII**) and KOAc–dioxan–AcOH at 100° (bath) yield the AcOH compound of (**III**); (**VIII**)–KOAc–AcOH at 90° and then at the b.p., followed by acetylation, afford (**VII**). (**VI**) and $SOCl_2$–Et_2O–C_6H_6–C_5H_5N give 4-*chloro-3-benzoyloxy-Δ⁵-cholestene*, m.p. 127—128°, $[\alpha]_D^{18}$ −81·9°, identical with the 6-chloro-3-benzoyloxy-Δ⁴-cholestene prepared from 6-chloro-3-benzoyloxycholestan-5-ol (cf. Spring *et al.*, *loc. cit.*). (**I**) is converted by boiling Et_2O–C_5H_5N (1 mol.)–$SOCl_2$ (1 mol.) into its endo-*sulphite*, m.p. 146—148° (decomp.), $[\alpha]_D^{19}$ −64·6°; (**III**) similarly affords *di*-(4-*acetoxycholesteryl*) *sulphite*, m.p. 159—160°, $[\alpha]_D^{18}$ −106·1°. [α] are in $CHCl_3$. A. T. P.

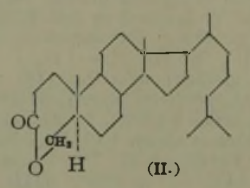
Action of *B. coli* on dehydronorcholene. A. Butenandt and H. Dannenberg (*Naturwiss.*, 1942, **30**, 585—586).—The oxidation of dehydronorcholene to 22-ketodehydronorcholene is not as previously reported (A., 1942, II, 364) due to the action of *B. coli*, but is an autoxidation, since it proceeds to the same extent in sterile Sauton medium without addition of the bacteria. J. H. B.

Attempted asymmetric syntheses employing choleic acids.—See A., 1943, II, 159.

Catalytic reduction of dehydrocholic acid in presence of Raney nickel. W. M. Hoehn and H. E. Ungnade (*J. Amer. Chem. Soc.*, 1943, **65**, 124).—Dehydrocholic acid and H_2–Raney Ni in MeOH at 105°/3800 lb. give reductodehydrocholic acid (67—85%), its Me ester (up to 20%), and Me dehydrocholate (up to 12%). R. S. C.

Bile acids and related substances. XVII. Formation of lactones from ketones and perbenzoic acid. V. Burckhardt and T. Reichstein (*Helv. Chim. Acta*, 1942, **25**, 1434—1443; cf. A., 1942, II, 411).—Me 3-keto-12(β)-acetoxycholanate is oxidised by BzO_2H in $CHCl_3$ at 18° to the *lactone* (**I**) (R = OAc), m.p. 187—190°; under similar conditions Me 12-keto-3(α)-acetoxycholanate remains unchanged. Coprostan-3-one gives the lactone, $C_{27}H_{46}O_2$, m.p. 155—157°, $[\alpha]_D^{20}$ +49·2°±2° in $COMe_2$, identical with the compound of Gardner *et al.* (A., 1914, i, 169). Me 3-ketocholanate yields the *lactone* (**I**) (R = H), m.p. 130—133°, $[\alpha]_D^{18}$ +50·0°±4° in $COMe_2$, converted


(I.)

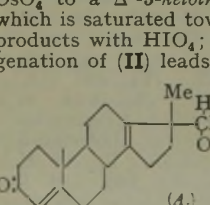

(II.)

by hydrolysis, methylation, oxidation, and renewed methylation into Me_3 lithobilianate, m.p. 108—110°. Cholestanone gives the *lactone* (**II**), m.p. 186—187°, $[\alpha]_D^{18}$ +1·2°±2° in $COMe_2$, degraded to the " dihydro-Diels' acid " (cf. Windaus, A., 1919, i, 203). *allo*-Pregnan-3(α)-ol-20-one acetate does not react whereas the 3(β)-compound gives (after hydrolysis) androstane-3(β) : 17(α)-diol in small yield. M.p. are corr. (block; limit of error ±2°). H. W.

Bile acids and related substances. XVIII. Simplified preparation of methyl Δ^{11}-cholenates by thermal fission of 12-benzoyloxy-derivatives. A. Lardon, P. Grandjean, J. Press, H. Reich, and T. Reichstein (*Helv. Chim. Acta*, 1942, **25**, 1444—1452).—Me 12(β)-hydroxycholanate is converted by BzCl and C_5H_5N at room temp. and then at 100° into the non-cryst. *benzoate*, $[\alpha]_D^{25}$ +57·3°±1° in $COMe_2$, which loses H_2O at 320°/11 mm. giving Me Δ^{11}-cholenate, needles, m.p. 61—61·5°, or leaflets, m.p. 56—58°. Similarly *Me 3-keto-12(β)-benzoyloxycholanate* (**I**), a glassy solid, $[\alpha]_D^{23}$ +54·3°±3° in $COMe_2$, affords Me 3-keto-Δ^{11}-cholenate, m.p. 121—123°. Me 12(β)-hydroxy-3(α)-acetoxycholanate gives the corresponding *benzoate*, m.p. 114—115°, $[\alpha]_D^{18}$ +71·65°±2° in $COMe_2$, hydrolysed by K_2CO_3 in aq. MeOH at room temp. to the non-cryst. 3(α)-hydroxy-12(β)-benzoyloxycholanic acid [non-cryst. Me ester (**II**)] and converted at 250°/vac. into Me 3(α)-acetoxy-Δ^{11}-cholenate, m.p. 117—118°, and, probably, Me choladienate, m.p. 75—76°. Oxidation of (**II**) by CrO_3 in AcOH gives (**I**). M.p. are corr. (block). H. W.

Steroid ketones.—See B., 1943, III, 110.

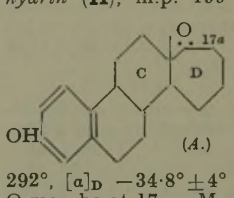
Steroids and sex hormones. LXXXII. Rearrangement of 17 : 20-oxido-Δ^4-pregnen-3-one by acetic acid. L. Ruzicka, M. W. Goldberg, and E. Hardegger (*Helv. Chim. Acta*, 1942, **25**, 1680—1689).—17 : 20-Oxido-Δ^4-pregnen-3-one (**I**) (isomeride *B*; cf. A., 1943, II, 96) is converted by AcOH at room temp. into an unsaturated CO-*alcohol* (**II**), $C_{21}H_{30}O_2$, m.p. 125·5—126·5°, $[\alpha]_D$ +30·5° in $CHCl_3$ (also +0·5$COMe_2$) [*semicarbazone*, m.p. 213—214°], which gives an intense yellow colour with $C(NO_2)_4$. (**II**) is converted by Ac_2O–C_5H_5N at room temp. into its *acetate* (**III**), m.p. 172°, $[\alpha]_D$ +58·7° in $CHCl_3$ (also +0·5H_2O), also obtained together with a *by-product*, $C_{23}H_{32}O_4$, m.p. 136°, by the action of Ac_2O–$ZnCl_2$ on (**I**). (**II**) is oxidised by *o*-$CO_2H{\cdot}C_6H_4{\cdot}CO_3H$ in $CHCl_3$ to a *compound*, $C_{21}H_{30}O_3$, m.p. 162° (softens at 159°) (acetate, m.p. 148—149°), whereas (**III**) yields a *compound*, $C_{23}H_{32}O_4$, m.p. 220—221°. (**II**) is oxidised by OsO_4 to a Δ^4-3-*ketotriol*, $C_{21}H_{32}O_4$, m.p. 227—228° (*monoacetate*), which is saturated towards $C(NO_2)_4$ and does not yield well-defined products with HIO_4; (**III**) is scarcely attacked by OsO_4. Hydrogenation of (**II**) leads to the absorption of 3 H_2 and the saturated


(A.)

[towards $C(NO_2)_4$] product is oxidised by CrO_3 to a saturated *diketone*, $C_{21}H_{32}O_2$, m.p. 80—80·5°, $[\alpha]_D$ +4° in $CHCl_3$. When treated similarly (**III**) affords an *acetoxyketone*, $C_{23}H_{34}O_3$, m.p. 116—117°, $[\alpha]_D$ +14·3° in $CHCl_3$, converted (Wolff–Kishner) into the saturated *alcohol*, $C_{26}H_{36}O$, m.p. 119°, $[\alpha]_D$ +25° in $CHCl_3$. Structure (*A*) is tentatively assigned to (**II**). M.p. are corr. (vac.). H. W.

Steroids and sex hormones. LXXX. Constitution of *D*-homoœstrone. M. W. Goldberg and S. Studer (*Helv. Chim. Acta*, 1942, **25**, 1553—1556; cf. A., 1941, II, 257).—17-Hydroxymethylene-*D*-homoœstrone 3-Me ether is oxidised by CrO_3 in AcOH at room temp. to 7-methoxy-2-methyl-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthrene-2-carboxylic-1-β-propionic acid, m.p. 251—258°, $[\alpha]_D$ +76°±4° in dioxan (Me_2 ester, m.p. 83·5—84°, $[\alpha]_D$ +73°±5° in dioxan) (cf. Bardhan, A., 1937, II, 63). The spatial arrangement of rings C and D in *D*-homoœstrone is therefore the same as that in œstrone. M.p. are corr. (vac.). H. W.

Steroids and sex hormones. LXXXI. *D*-Bishomoœstrone. M. W. Goldberg and S. Studer (*Helv. Chim. Acta*, 1942, **25**, 1556—1560; cf. A., 1941, II, 257).—*D*-Homoœstrone is converted by BzCl in 7% KOH–C_5H_5N at room temp. and then at ~60° into the *benzoate* (**I**), m.p. 161—162°, $[\alpha]_D$ +23·2°±2° in dioxan, transformed by KCN in EtOH–AcOH at room temp. into the *cyanohydrin*, m.p. 182—184° with loss of HCN, which with Ac_2O–C_5H_5N at 100° yields the corresponding *acetate*, m.p. 220—221°. *D*-Homoœstrone acetate and KCN in EtOH–AcOH at room temp. give the *cyanohydrin* (**II**), m.p. 199—200°. In the production of (**I**) and (**II**) there is no appreciable production of any epimeride. Hydrogenation (PtO_2 in AcOH) of (**II**) and treatment of the product with HNO_2 yields D-*bishomoœstrone acetate*, m.p. 149—151°, $[\alpha]_D$ −37·1°±2° in dioxan, hydrolysed by boiling KOH–MeOH to D-*bishomoœstrone* [3-*hydroxy*-$\Delta^{1:3:5}$-D-*bishomoœstratrien*-(17b)-*one*] (*A*), m.p. 290—292°, $[\alpha]_D$ −34·8°±4° in dioxan (*oxime*, m.p. 174—176°). In (*A*) O may be at 17*a*. M.p. are corr. (vac.). H. W.


(A.)

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Structure of ketonic complexes of carvone.—See A., 1943, I, 116.

Physical properties of terpenes. I. System α- and β-pinene. R. E. Fuguitt, W. D. Stallcup, and J. E. Hawkins (*J. Amer. Chem. Soc.*, 1942, **64**, 2978—2981).—*d*, *n*, and α are recorded for α- and β-pinene and their mixtures, as are v.p.–temp. relations for α- and β-pinene at 15—80 mm. and vapour–liquid composition data for mixtures at 20 mm. R. S. C.

Decomposition of pernitrosoketones. II. Pernitrosofenchone and pernitrosomenthone. A. Gandini (*Gazzetta*, 1942, **72**, 232—241).—Pernitrosofenchone (**I**) in heavy paraffin at 150—160° decomposes to a mixture of α- and β-fenchelenonitrile (also obtained by decomp. of fenchoneoxime), and a resinous product (**II**), similar to that obtained from pernitrosocamphor (**III**) (cf. A., 1943, II, 137). (**III**) contains a *substance*, $C_{19}H_{16}O_2N_2$ (**IV**) [isomeric with, but more stable than, (**I**)], in which the $\cdot N{\cdot}NO_2$ group is regarded as *cis* to the bridge-CH_2, as compared with a *trans*-structure in (**I**). At >200°, (**IV**) decomposes, as (**I**). If the decomp. of (**III**) in heavy paraffin at 150° is interrupted after evolution of gas, *camphornitroimine* (?), $C_{10}H_{16}O_2N_2$, m.p. 57—58°, is isolated. Pernitrosomenthoneoxime in heavy petroleum at 150—160° gives menthonenonitrile. The pernitroso-derivative from the oily oxime of *d*-menthone gives a product which is hydrolysed to a *substance*, $C_{10}H_{19}ON$, m.p. 128°. E. W. W.

Sesquiterpenes. LVII. Crystallised cadinol from Java oil of lemon. P. A. Plattner and R. Márkus (*Helv. Chim. Acta*, 1942, **25**, 1674—1679).—Treatment of the most volatile portions of a residual fraction of the oil with *p*-$NO_2{\cdot}C_6H_4{\cdot}COCl$ and C_5H_5N gives a *p-nitrobenzoate*, m.p. 136°, $[\alpha]_D$ −6·76° in $CHCl_3$, hydrolysed by KOH–MeOH to *cadinol* (**I**), $C_{15}H_{26}O$, m.p. 72·5°, $[\alpha]_D$ −39·8° in $CHCl_3$. (**I**) with $KHSO_4$ at 150—180° gives cadinene, b.p. 108—112°/12 mm. (dihydrochloride, m.p. 117·5°), dehydrogenated (Pd–C at 275—350°) to cadalene. (**I**) is hydrogenated (Raney Ni in EtOH at 18·5°) to *dihydrocadinol*, m.p. 124·5°, $[\alpha]_D$ −72·5° in $CHCl_3$. It is stable towards CrO_3, indicating the presence of *tert.* OH; characteristic products are not obtained by its direct oxidation or by ozonisation of its dehydrogenation product. M.p. are corr. H. W.

Triterpenes. LXXI. Attempted transformation of quinovic acid into triterpene derivatives poorer in oxygen. L. Ruzicka and A. Marxer (*Helv. Chim. Acta*, 1942, **25**, 1561—1571).—*Acetylquinovyl dichloride*, m.p. 193—194°, obtained from the acid and $SOCl_2$ in hexane, is reduced (Rosenmund) at various temp. to *acetylnorquinovadienolal* (**I**), $C_{31}H_{46}O_3$, m.p. 162—164°, with some norquinovadienolcarboxylic acid characterised as the Me ester of the acetylated acid, m.p. 175—177°, $[\alpha]_D$ −45·5° in $CHCl_3$. Reduction (Wolff–Kishner) of the *semicarbazone*, m.p. 275—276°, of (**I**) yields two isomeric *norquinovadienols*, $C_{29}H_{46}O$, m.p. 197—199°, $[\alpha]_D$ −55° in $CHCl_3$ [*acetate*, m.p. 187—188°; H_2-compound, m.p. 159—160°, $[\alpha]_D$ −66° in $CHCl_3$; gives a yellow colour with $C(NO_2)_4$], and m.p. 88—90°, $[\alpha]_D$ −31° in $CHCl_3$ (*acetate*, m.p. 152—155°, $[\alpha]_D$ −34·8° in $CHCl_3$), respectively which does not absorb H_2, together with *norquinovadienediol*, $C_{29}H_{46}O_2$, m.p. 166—169°. *Novyl chloride*, m.p. 209—212° (decomp.), is reduced (Pd–$BaSO_4$ in boiling xylene) to

nova-aldehyde, m.p. 197—201°; the *semicarbazone*, m.p. 256—258°, is converted (Wolff–Kishner) into a neutral *lactone*, $C_{30}H_{46}O_2$, m.p. 157—160°, $[\alpha]_D$ +398° in $CHCl_3$, which could not be hydrolysed satisfactorily by 3N-KOH–MeOH at 175—180° or by HBr–AcOH at 120°. *Acetylpyroquinovyl chloride*, m.p. 160—163°, is reduced (Rosenmund) to *acetylnorquinovenolal*, m.p. 170—173°, which gives a *semicarbazone*, m.p. 271—273°, transformed (Wolff–Kishner) into *norquinovenol* (**II**), m.p. 86—90°, $[\alpha]_D$ −84° in $CHCl_3$ (*acetate*, m.p. 167—169°, $[\alpha]_D$ −66° in $CHCl_3$); this is dehydrogenated by Se at 345° to 1 : 2 : 8-trimethylpicene, m.p. 308—310°. Me_2 quinovate is oxidised (CrO_3 in AcOH) to *Me_2 quinovenonedicarboxylate*, m.p. 149—150°, the *semicarbazone*, m.p. 175—180°, softens at ~150°, of which is reduced (Wolff–Kishner) to *quinovenedicarboxylic acid*, m.p. 310—314°. M.p. are corr. H. W.

Triterpenes. LXXII. Æscigenin, the aglucon of the saponin from the seeds of the horse chestnut [*Aesculus hippocastanum*, **L.**]. L. Ruzicka, W. Janett, and E. Rey (*Helv. Chim. Acta*, 1942, **25**, 1665—1673).—The finely-divided seeds are extracted successively with 2·5% NaOH and H_2O; the residue yields to 65% EtOH crude æscin, m.p. 200—210°, in 2% yield. This when hydrolysed with 5% HCl–EtOH at 100° for 72 hr. gives æscigenin (**I**), $C_{35}H_{58(56)}O_6$, m.p. 311—312°, $[\alpha]_D$ +46° in EtOH, which can be purified by crystallisation from EtOH or through the penta-acetate (**II**), m.p. 206—207°, $[\alpha]_D$ +60° in $CHCl_3$. (**I**) contains 5 OH (Zerevitinov) and according to its spectrum >CO, which cannot be detected by chemical means. (**I**) is therefore not an ester of tiglic acid. (**I**) gives a positive colour test with $C(NO_2)_4$ but attempts to hydrogenate (**II**) using PtO_2 in AcOH at room temp. or with H_2 at 175°/90 atm. or to reduce (**I**) by Na in EtOH were unsuccessful. Mild oxidation of (**II**) by CrO_3 in AcOH yields an $\alpha\beta$-unsaturated *keto-æscigenin penta-acetate*, $C_{45}H_{64}O_{12}$ (based on $C_{35}H_{56}O_6$), m.p. 222—223·5°, $[\alpha]_D$ +54° in $CHCl_3$, which does not give a colour with $C(NO_2)_4$. Hence (**I**) contains only one double linking. M.p. are corr. H. W.

Essential oil of *Cupressus macrocarpa*.—See B., 1943, III, 62.

Sapogins and sapogenins. XX. Colour reactions of triterpenoid sapogenins. C. R. Noller, R. A. Smith, G. H. Harris, and J. W. Walker (*J. Amer. Chem. Soc.*, 1942, **64**, 3047—3049; cf. A., 1941, II, 370).—Characteristic colours or series of colour changes are produced by dissolving triterpenoids in $SOCl_2$ containing traces of $SnCl_4$ (0·01%; 21 examples), $FeCl_3$ (0·01%; 5 examples), $SbCl_3$ (0·01%; 6 examples), $SbCl_5$ (0·01%; 6 examples), $POCl_3$ (10%) + H_2O (0·5%) (6 examples), $SnCl_4$ (0·01%) + $FeCl_3$ (0·005%) (6 examples), H_3PO_4, or H_2SO_4. Commercial $SOCl_2$ sometimes contains enough metal to give the colours. Pure $SOCl_2$ sometimes gives colours (7 examples). Colours are not given by pure $POCl_3$, PCl_3, PCl_5, $SiCl_4$, Cl_2, SO_2 or HCl in $SOCl_2$, or by $SnCl_4$ in C_6H_6, light petroleum, $CHCl_3$, or *cyclo*hexane. R. S. C.

VI.—HETEROCYCLIC.

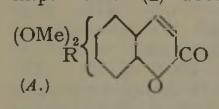
Tetrahydrofurfuryl alcohols.—See B., 1943, II, 113.

Coumaran series. R. T. Arnold and J. Moran (*J. Amer. Chem. Soc.*, 1942, **64**, 2986—2988).—2 : 4 : 1-OH·C_6H_3(OMe)·CO_2Me, m.p. 49—51°, CH_2:CH·CH_2Cl, K_2CO_3, and NaI in boiling $COMe_2$ give *Me* 4-*methoxy*-2-*allyloxybenzoate* (**I**), m.p. 49—50°, which in boiling $NPhMe_2$–N_2 gives *Me* 2-*hydroxy*-4-*methoxy*-3-*allylbenzoate* (**II**), m.p. 57—59° (reddish-violet with $FeCl_3$). With HBr–AcOH at 100° and then boiling, aq. NaOH, (**II**) gives 3-*hydroxy*-1-*methyl*-1 : 2-*dihydrobenzfuran*-4-*carboxylic*, m.p. 155—156° (red $FeCl_3$ colour; Me ester), and 3-*methoxy*-1-*methyl*-1 : 2-*dihydrobenzfuran*-6-*carboxylic acid* (**III**), m.p. 207—208°. With dry HBr–$CHCl_3$ and a trace of $FeCl_3$ at 0° and later room temp., (**II**) gives *Me* 2-*hydroxy*-4-*methoxy*-3-*β*-*bromo*-n-*propylbenzoate* (**IV**), m.p. 73—74°, and some (**III**). Aq. NaOH at room temp. and later the b.p. converts (**IV**) into (**III**). The acid derived from (**I**) in boiling $NPhMe_2$ gives CO_2 and 2 : 4 : 1-OH·C_6H_3(OMe)·CH_2·CH:CH_2, an oil (positive $FeCl_3$ test), identified by conversion into 2 : 4 : 1-$(OMe)_2C_6H_3$·CO_2H by successive methylation, isomerisation by alkali, and oxidation. Attempts at cleavage of (**III**) by HBr gave red polymerides. R. S. C.

Styrylchromones. G. B. Marini-Bettòlo (*Gazzetta*, 1942, **72**, 201—208).—2 : 4 : 1-(OH)(OMe)C_6H_3·COMe in EtOH with CHPh:CH·CHO (C_5H_5N) gives 2-*hydroxy*-4-*methoxy*-*α*-*cinnamylideneacetophenone* (**I**), m.p. 147°. From the appropriate ketones 2-hydroxy-3 : 4-dimethoxy- (**II**), -4 : 5-*dimethoxy*- (**III**), m.p. 153°, and 2 : 4-*dimethoxy*- (**IV**), m.p. 98°, and 2 : 4 : 5-*trimethoxy*-*α*-*cinnamylideneacetophenone* (**V**), m.p. 110°, are prepared similarly [using 50% NaOH for (**IV**) and (**V**)]. With SeO_2 in boiling C_5H_{11}·OH (16 hr.), (**I**) gives 7-methoxy-, (**II**) 7 : 8-dimethoxy-, and (**III**) 6 : 7-*dimethoxy*-2-*styrylchromone*, m.p. 184°. By the reaction of Algar and Flynn (A., 1934, 1226), (**I**) and its analogues give with KOH–EtOH–H_2O_2 (10 min. at 100°) 7-*methoxy*-, m.p. 221°, 7 : 8-*dimethoxy*-, m.p. 248°, and 6 : 7-*dimethoxy*-2-*styrylchromonol*, m.p. 237°, all strongly fluorescent. Since (**IV**) and (**V**) with NaOH–MeOH–H_2O_2 give *β*-2 : 4-*dimethoxy*-, m.p. 113°, and *β*-2 : 4 : 5-*trimethoxy*-*benzoyl*-*α*-*styrylethylene oxide*, m.p. 120° (cf. Weitz *et al.*, A., 1921, i, 868), it is suggested that Algar and Flynn's reaction proceeds through a similar intermediate ethylene oxide stage. E. W. W.

Benzopyrone series. VII. Stages in the synthesis of karanjin. T. R. Seshadri and V. Venkateswarlu (*Proc. Indian Acad. Sci.*, 1943, **17**, **A**, 16—19; cf. A., 1941, II, 330).—The condensation product of 2 : 6 : 1-$(OH)_2C_6H_3$·CHO with CH_2Br·CO_2Et and NaOEt was hydrolysed to 3-*hydroxy*-2-*aldehydophenoxyacetic acid*, m.p. 176—177°, which with NaOAc and Ac_2O at 150° yields 4-hydroxycoumarone (cf. Reichstein and Hirt, A., 1933, 281). F. R. G.

Constitution of natural coumarins of *Toddalia aculeata*. P. Dutta (*J. Indian Chem. Soc.*, 1942, **19**, 425—434).—Extraction of the stem bark with Et_2O gives a *substance*, $C_{16}H_{16}O_4$, m.p. 238—239°, neutral to litmus and indifferent to $FeCl_3$, in very small amount, *aculeatin* (**I**), m.p. 113° (corr.), $[\alpha]_D^{24}$ −16·8° in EtOAc, and *aculeatin hydrate* (**II**), m.p. 150° (corr.), $[\alpha]_D^{29}$ +50·9° in $CHCl_3$, also obtained from (**I**) by prolonged treatment with dil. H_2SO_4 at 100°. (**I**) contains 2 OMe and behaves as a lactone, being hydrolysed by alkali in presence of a trace of HgO to the stable *acid*, $C_{16}H_{22}O_7$, m.p. 171°. (**I**) does not condense with the usual reagents for aldehydes or ketones but an oxide ring is present since (**I**) is convertible into (**II**). (**I**) is therefore *A* (R = ·CH_2·CH<$^{CMe_2}_{O}$). (**II**) gives a *diacetate*, m.p. 127°, hydrolysed by alkali to (**II**), and a *H phthalate*, m.p. 204°, so that 1 OH is probably *tert*. When oxidised by CrO_3 (**II**) yields $COMe_2$. Oxidation (Criegee) of (**II**) leads to an *aldehyde*, $C_{13}H_{12}O_5$, m.p. 142—142·5° (corr.) (p-*nitrophenylhydrazone*, m.p. 213°), which reduces Ag_2O–NH_3; hence (**II**) is an $\alpha\beta$-glycol [*A*; R = ·CH_2·CH(OH)·CMe_2·OH]. (**I**) is converted by fused $ZnCl_2$ at 140—145° and (**II**) by dil. HCl at 140° into a *ketone*, $C_{16}H_{18}O_5$, m.p. 119—120° (corr.) (semicarbazone, m.p. 209°; p-*nitrophenylhydrazone*, m.p. 210°). The aldehyde and ketone are also obtained from toddalolactone (**III**) (A., 1938, II, 451). Chemical evidence is definitely in favour of the identity of (**II**) and (**III**). H. W.



Aluminium chloride, a new reagent for the condensation of β-ketonic esters with phenols. VI. Condensation of resacetophenone with ethyl α-alkylacetoacetates. C. V. Deliwala and N. H. Shah (*Proc. Indian Acad. Sci.*, 1943, **17**, **A**, 7—10; cf. A., 1941, II, 332).—2 : 4 : 1-$C_6H_3(OH)_2$·COMe condenses with CHMeAc·CO_2Et in presence of $AlCl_3$ in $PhNO_2$ to yield 5-*hydroxy*-6-*acetyl*-3 : 4-*dimethylcoumarin* (*Ac* derivative, m.p. 105—106°; *oxime*, m.p. ≮245°); with Me_2SO_4 this gives 2 : 6-*dimethoxy*-3-*acetyl*-*αβ*-*dimethylcinnamic acid*, m.p. 158—159°, and is converted by Kostanecki acetylation into 3′-*acetyl*-2′ : 3 : 4-*trimethylchromono*-7′ : 8′ : 6 : 5-*α*-*pyrone*. Similarly were prepared 5-*hydroxy*-6-*acetyl*-4-*methyl*-3-*ethyl*-, m.p. 158—159° (*Ac* derivative, m.p. 119—120°), and -6-*acetyl*-3-*benzyl*-4-*methylcoumarin*, m.p. 186—187° [*Ac* derivative, m.p. 147—148°; *oxime*, m.p. 250—251° (decomp.)], which is converted (Kostanecki) into 3′-*acetyl*-3-*benzyl*-2′ : 4-*dimethylchromono*-7′ : 8′ : 6 : 5-*α*-*pyrone*, m.p. 181—182°. No condensation occurs with CHRAc·CO_2Et where R is Pr^a, allyl, or Cl. F. R. G.

Pigments of the flowers of *Hibiscus sabdariffa*. Sabdaretin, new hydroxyflavone. P. S. Rao and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1942, **16**, **A**, 323—327; cf. A., 1942, II, 327).—The EtOH extract of the petals, after separation of hibiscitrin and gossypitrin, on pptn. with basic Pb acetate yields *sabdaritrin*, $C_{21}H_{20}O_{14}$,$3H_2O$, m.p. 251—253° (decomp.), hydrolysed (7% H_2SO_4) to a hydroxyflavone, *sabdaretin*, $C_{15}H_{10}O_9$,$3H_2O$, m.p. ≮360° (shrinks at 300°) [acetate, m.p. 198—200° (decomp.; sinters ~160°)], colour reactions of which are given. A. Li.

Chemical components of Indian tulip (*Thespasia populnea*) flowers. K. Neelakantam, P. S. Rao, and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1943, **17**, **A**, 26—31; cf. A., 1938, II, 394).—The three yellow pigments of the flower petals (cf. Rao and Reddy, A., 1941, III, 405) are accompanied by the colourless *populneol*, $C_{15}H_{12}O_3$, m.p. 116—118°, which is phenolic. Contrary to earlier work (*loc. cit.*), populnetin is a tetrahydroxyflavone, $C_{15}H_{10}O_6$,0·5H_2O, improved m.p. 278—280° (*Ac*$_4$ derivative, m.p. 242—244°). F. R. G.

Kanugin, crystalline component of the roots of *Pongamia glabra*. S. Rangaswami, J. V. Rao, and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1942, **16**, **A**, 319—322; cf. A., 1942, II, 431).—Light petroleum (b.p. 90—110°) extracts from the root bark a methoxyflavone, *kanugin*, $C_{16}H_9O_4(OMe)_3$, m.p. 197° (0·05% of dry bark), which gives a red colour with Mg + HCl. A. Li.

Kanugin. I. S. Rangaswami and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1943, **17**, **A**, 20—25; cf. preceding abstract).—Oxidation of kanugin (**I**) by $KMnO_4$ in $COMe_2$ yields 4 : 2 : 1-C_6H_3(OMe)(OH)·CO_2H (**II**) and a *OMe-compound*, $C_{11}H_{14}O_3$ (or $C_7H_8O_2$), m.p. 135—140°, which was hydrolysed (KOH, EtOH) to (probably) (**II**). Hydrolysis (KOH–EtOH) of (**I**) in H_2 gives a *OMe-acid*, $C_8H_8O_4$, m.p. 145°. Demethylation (HI) of (**I**) gives a flavonol, *norkanugin*, $C_{16}H_{12}O_7$, darkens 290°, the *tri*- (?) -*acetate*, m.p. 198—199°, sinters 193°, of which with Me_2SO_4 yields a Me ether, m.p. 153°. F. R. G.

Synthesis of tectorigenin dimethyl ether. R. L. Shriner and R. W. Stephenson (*J. Amer. Chem. Soc.*, 1942, **64**, 2737—2738).—*p*-OMe·C_6H_4·CH_2·CN (prep. from PhOMe by aq. CH_2O–light petroleum–$ZnCl_2$–HCl and then aq. NaCN; 29%), b.p. 154—156°/20 mm., with 4 : 5 : 1 : 3-$(OMe)_2C_6H_2(OH)_2$, $ZnCl_2$, and HCl gas in Et_2O at 0° and then boiling 10% HCl gives 2 : 6-*dihydroxy*-3 : 4 : 4′-*trimethoxydeoxybenzoin* (29%), m.p. 116·5°, which with HCO_2Et–Na at 0° gives tectorigenin Me_2 ether, m.p. 188° (diacetate, m.p. 213°).
R. S. C.

Benzoylation of 5-hydroxy-6-acylcoumarins in presence of pyridine. N. M. Shah and C. V. Deliwala (*Proc. Indian Acad. Sci.*, 1942, **16**, **A**, 387—391).—5-Hydroxy-6-acetyl-4-methylcoumarin and BzCl–C_5H_5N give, not the *O*-Bz derivative (probably formed initially), but 2′-*phenyl*-4-*methylchromono*-7′ : 8′-6 : 5-*α*-*pyrone* (**I**), m.p. 251—252°, also obtained from 5-hydroxy-4-methylcoumarino-6-styryl ketone and SeO_2–*n*-C_5H_{11}·OH at 170—180°. Unsuccessful attempts were made to remove the 3′-Bz group from 3′-benzoyl-2′-phenyl-4-methylchromono-7′ : 8′ : 6 : 5-*α*-pyrone (cf. A., 1938, II, 152). 5-Hydroxy-6-propionyl-4-methylcoumarin (**II**) (no simple Bz derivative could be obtained) and BzCl–C_5H_5N afford 3′-*benzoyl*-*methyl*-2′-*phenyl*-4-*methylchromono*-7′ : 8′ : 6 : 5-*α*-*pyrone* (**III**), m.p. 221° (attempts to remove Bz unsuccessful), and the *dibenzoyloxy*-derivative (**IV**), m.p. 159—160°, of (**II**). (**III**) is also formed by Kostanecki benzoylation (Bz_2O–NaOBz at 160—170°) of (**II**). (**IV**) and HBr–AcOH or conc. H_2SO_4 give (**II**). 5-Hydroxy-6-butyryl-4-methylcoumarin reacts in its enol form with BzCl–C_5H_5N to give the *dibenzoyloxy*-derivative, m.p. 168°, whereas Kostanecki benzoylation affords 3′-*benzoylethyl*-2′-*phenyl*-4-*methylchromono*-7′ : 8′ : 6 : 5-*α*-*pyrone*, +0·5H_2O, m.p. 220—221°. The above coumarins with Ac_2O give only the 5-OAc-derivatives. The action of C_5H_5N on resacetophenone dibenzoate does not cause migration of the acid residue, and the above transformations in presence of C_5H_5N, with flavone-ring formation, are caused by the presence of the α-pyrone ring.
A. T. P.

Synthesis of 2-keto*cyclo*hexylsuccinic acid and related substances.—See A., 1943, II, 165.

Phenoxthionins.—See B., 1943, II, 109.

Hydroxyamine fissions. I. F. Kröhnke and A. Schulze (*Ber.*, 1942, **75**, [*B*], 1154—1157).—Treatment of *β*-piperidino-*α*-phenylethanol hydrobromide (**I**) with AcOH–HBr containing a little H_2O at 150° gives nearly the calc. amount of piperidine (**II**), ~2% of CH_2Ph·CHO (**III**), but no COPhMe. With 90—95% H_3PO_4 at 100° (**I**) gives 90—98% of (**II**) and ~67% of (**III**) (as semicarbazone), the odour of which only gradually develops. Probable schemes are: OH·CHPh·CH_2·N: → H_2PO_3·O·CHPh·CH_2·N: → H_2PO_3·O·CHPh·CH_2·OH + NH: or OH·CHPh·CH_2·NC_5H_{10} (**IV**) → CHPh:CHC_5H_{10} → CHPh:CH·O·PO_3H_2 + (**II**) → CHPh:CH·OH → CH_2Ph·CHO. The last scheme is supported by the production of (**III**) by dehydration of (**IV**) by $KHSO_4$, $ZnCl_2$, or $H_2C_2O_4$. (**I**) with HBr (*d* 1·49) or conc. HCl gives 65—88% of (**II**) but only very small amounts of (**III**). *β*-Piperidino-*α*-3 : 4-methylenedioxyphenylethanol hydrobromide and 95% H_3PO_4 at 60° afford 60% of piperonal. A similar yield is obtained from the *α*-*m*-C_6H_4Cl compound in 5 hr. at 100°. The *α*-*o*-C_6H_4Cl substance is much more resistant, giving only 32% of aldehyde after 41 hr. at 100°.
H. W.

Isomerisation during dehydrogenations in the pyridine series. V. Prelog, A. Komzak, and E. Moor (*Helv. Chim. Acta*, 1942, **25**, 1654—1664).—Condensation of CH_2Ac·CO_2H with CH_2O and NH_2Me,HCl under "physiological" conditions affords *α*- (**I**), m.p. 132° (*picrate*, m.p. 172°; 2 : 4-*dinitrophenylhydrazone*, m.p. 200—200·5°; *picrate* of Ac derivative, m.p. 175°), and *β*- (**II**), m.p. 86° [*picrate*, m.p. 172°; 2 : 4-dinitrophenylhydrazone hydrochloride, m.p. 235° (decomp.); *picrate* of Ac derivative, m.p. 155—156°], 4-hydroxy-3-acetyl-1 : 4-dimethylpiperidine (cf. Mannich *et al.*, A., 1926, 522); a *base*, $C_{10}H_{17}O_2N$ [*picrate*, m.p. 217—220° (decomp.)], is obtained as by-product. (**I**) and (**II**) pass by loss of H_2O into 3-acetyl-1 : 4-dimethyl-1 : 2 : 5 : 6-tetrahydropyridine (**III**), b.p. 115—116°/14 mm. Hydrogenation (Pd–C in MeOH) of (**III**) or of its hydrochloride in acid medium gives a mixture of 3-acetyl-1 : 4-dimethylpiperidines (**IV**), one of which gives a *picrate*, m.p. 189—190°, a *hydrochloride*, m.p. 144—147°, and a 2 : 4-*dinitrophenylhydrazone*, m.p. 147°. (**III**) or (**IV**) is hydrogenated (PtO_2 in MeOH) to 1 : 4-*dimethyl*-3-*α*-*hydroxyethylpiperidine*, b.p. 125—135°/27 mm., from which a non-homogeneous picrate, m.p. 137—150°, is derived. 1 : 4-*Dimethyl*-3-*α*-*hydroxyethyl*-1 : 2 : 5 : 6-*tetrahydropyridine* (**IV**), m.p. 78—79°, is obtained by the action of $Al(OPr^{\beta})_3$ in $Pr^{\beta}OH$ on (**III**). (**III**) is dehydrogenated and isomerised by Se at 300°, by Pd–C at 300°, or by Se in boiling xylene to 2 : 3 : 4-trimethylpyridine (**VI**), b.p. 185° [*picrate*, m.p. 164°; *styphnate*, m.p. 169°; *picrolonate*, m.p. 239°; *platinichloride*, m.p. 265—266° (decomp.); *aurichloride*, m.p. 181—182°], oxidised by $KMnO_4$ to pyridine-2 : 3 : 4-tricarboxylic acid (*Me*$_3$ ester, m.p. 101—102°); Me_2Se is also formed when Se is used. $CHMeAc_2$ and $CN·CH_2·CO·NH_2$ in EtOH containing piperidine afford 5-cyano-6-hydroxy-2 : 3 : 4-trimethylpyridine, m.p. 303°, hydrolysed and decarboxylated to 6-hydroxy-2 : 3 : 4-trimethylpyridine, m.p. 252°; this gives the corresponding 6-Cl-compound, b.p. 112—115°/15 mm., m.p. 48°, converted (H_2–Raney Ni) into (**VI**). (**V**) is similarly transformed by Se into 4-methyl-3-ethylpyridine. Isomerisation requires the presence of >CO but a double linking is not essential.
H. W.

3-Methoxypyridine [**picrate, m.p. 139° (corr.)**].—See A., 1943, III, 294.

Dihydropyridones.—See B., 1943, II, 74.

Nitrogenous compounds in petroleum distillates. XXIV. Isolation and identification of a $C_{11}H_{17}N$ base from Californian petroleum. H. L. Lochte, W. W. Crouch, and E. D. Thomas (*J. Amer. Chem. Soc.*, 1942, **64**, 2753—2755; cf. A., 1942, II, 328).—The "non-aromatic" bases (A., 1933, 1305) contain dl-4 : 5-*dimethyl*-2-sec.-*butylpyridine* (**I**), b.p. 214°/752 mm. (*picrate*, m.p. 127—128°), and *bases*, $C_{12}H_{19}N$, b.p. 101°/20 mm., 214°/754 mm. (*picrate*, m.p. 174°), and $C_{13}H_{21}N$ (*picrate*, m.p. 121°). The structure of (**I**) is proved by prep. of a *CHPh*: derivative, m.p. 143°, failure to condense with Ac_2O at 210°, and oxidation by O_3–CCl_4 to *dl*-CHMeEt·CO·NH_2 + Ac_2 and by aq. $KMnO_4$ at 100° to pyridine-2 : 4 : 5-tricarboxylic acid, anhyd. and +H_2O m.p. 242—243° (decomp.), stable at 170°.
R. S. C.

Cyanine dyes of the pyridine series. III. M. Q. Doja and D. Prasad (*J. Indian Chem. Soc.*, 1942, **19**, 377—384; cf. A., 1942, II, 329).—Condensation of *p*-NEt_2·C_6H_4·CHO and 2-methylpyridine methiodide by piperidine in boiling abs. EtOH gives 2-p-*diethylaminostyrylpyridine methiodide*, m.p. 241°; the corresponding *ethiodide*, m.p. 205°, *propiodide*, m.p. 235°, and *butiodide*, m.p. 244°, are obtained similarly. In the given order the total range of photographic sensitisation of these dyes is 4250—5650, 4200—5750, 4250—5750, 4200—5800 A. and the range of uniformly intense sensitisation is 4400—5450, 4350—5500, 4400—5650, and 4350—5750 A., respectively. On the whole they are better sensitisers than the dyes obtained from *p*-NMe_2·C_6H_4·CHO (*loc. cit.*).
H. W.

Molecular resonance systems. VIII. Intermediate products of the fission of pyridine. Simple, long-chained polymethine dye. G. Schwarzenbach and R. Weber (*Helv. Chim. Acta*, 1942, **25**, 1628—1639).—Addition of a solution of CNBr and C_5H_5N in Et_2O to an ethereal suspension of $NHEt_2$,$HClO_4$ yields *α*-*diethylimmonium*-*ε*-*pyridiniumglutacondialdehyde diperchlorate* (**I**), [NEt_2:CH·CH:CH·CH:CH·NC_5H_5]$(ClO_4)_2$, also obtained from homogeneous solution in EtOH–Et_2O and purified from accompanying pyridinium perchlorate through the picrate. (**I**) readily yields $NHEt_2$ when treated with H_2O, giving *α*-*pyridiniumglutacondialdehyde perchlorate* (**II**), [CHO·[CH:CH]$_2$·NC_5H_5]ClO_4, m.p. 112—113° (decomp.). (**I**) and (**II**) are converted by alkali hydroxide through the red anion [CHO·[CH:CH]$_2$·N:CH·[CH:CH]$_2$·O]$^-$ slowly into glutacondialdehyde enolate. 2 mols. of base, probably $NHEt_2$ + NH_3, are formed from 1 mol. of (**I**) or (**II**); C_5H_5N is not produced. (**I**) and warm NH_2Ph afford the dianil, [NHPh:CH·[CH:CH]$_2$·NHPh]$^+$, whilst $NHEt_2$ gives the perchlorate, [NEt_2:CH·[CH:CH]$_2$·NEt_2]ClO_4. Treatment of (**I**) or (**II**) with cold alkali followed by acidification of the red solution leads to the *dialdehyde* (**III**), CHO·[CH:CH]$_2$·N:CH·[CH:CH]$_2$·OH; the dark yellow solution of this compound becomes nearly colourless when kept or warmed owing to re-formation of (**II**). (**I**), but not (**II**), and NaOAc give a small proportion of a violet dye, probably [NEt_2:CH·[CH:CH]$_2$·N:CH·[CH:CH]$_2$·O], whilst unstable blue-red dyes result from (**I**) or (**II**) and piperidine, $NHEt_2$, or other aliphatic amine; the colours are well observed when filter-paper impregnated with (**I**) or (**II**) is placed in the amine vapour or by working in solution in $COMe_2$. (**III**) gives a dark violet phenylhydrazone which does not crystallise. In dyes of the type (**III**) a bathochromic effect is produced when 1st, 3rd, 5th, 7th, 9th, or 11th CH is replaced by N but a hypsochromic change when the 2nd, 4th, 6th, 8th, or 10th CH is similarly replaced.
H. W.

Effects of solvents on absorption spectra of dyes.—See A., 1943, I, 114.

Derivatives of 2-aminopyridine-5-sulphonamide and of pyrid-2-one-5-sulphonamide. C. Naegeli, W. Kündig, and H. Suter (*Helv. Chim. Acta*, 1942, **25**, 1485—1498).—The m.p. curves of the substituted amides of $C_6H_4R·SO_2H$ (R = Cl, NH_2, or OH) are generally similar to those of the corresponding C_5H_5N derivatives, showing that the rings retain their general influence on the lattice structure no matter what the substituent may be. With unsubstituted or singly-substituted amides there is no evidence of intramol. salt formation. With derivatives of C_5H_5N the association relationships do not appear to be influenced by alkyl substitution. The introduction of NH_2 causes a greater increase of m.p. than does that of OH. With few exceptions the pyridonesulphonic acids and pyridinesulphonamides show a strong fluorescence under ultra-violet light when solid but not in EtOH or H_2O. The corresponding 2-chloropyridine-5-sulphonamides are converted by aq. NH_3 in presence of a little $CuSO_4$ in a sealed tube into 2-*aminopyridine*-5-*sulphon*-*methyl*-, m.p. 140—141°, -*dimethyl*-, m.p. 157—159°, -*diethyl*-, m.p. 148—149·5°, -n-*butyl*-, m.p. 114—116°, -*allyl*-, m.p. 136—137°, and -cyclo*hexyl*-*amide*, m.p. 129—131°, -*piperidide*, m.p.

160—162°, *-morpholide*, m.p. 178—180°. 2-Chloropyridine-5-sulphonyl chloride (**I**) in $COMe_2$ and glycine in 10% NaOH yield *2-chloropyridine-5-sulphonamidoacetic acid*, m.p. 193° (decomp.), converted by conc. NH_3 at 130° into the 2-NH_2-compound (**II**), m.p. 226—227° (decomp.). *2-Chloro-*, m.p. 193—195°, and *2-amino-*, m.p. 250—252° (decomp.), *-pyridine-5-sulphon-o-amidobenzoic acid* are obtained analogously. (**I**) and $NH_2{\cdot}CH_2{\cdot}CO_2Et$,HCl in $COMe_2$-aq. NaOH afford *Et 2-chloropyridine-5-sulphonamidoacetate*, m.p. 116—118°, hydrolysed by conc. NH_3 at 145° to (**II**). *2''-Aminopyridine-5''-sulphon-4-amidobenzenesulphonylsulphanildimethylamide* has m.p. 171—172°. The requisite Cl-compounds and boiling aq. NaOH give *pyrid-2-one-5-sulphon-2'-pyridylamide*, m.p. 268—269°, *2-hydroxypyridine-5-sulphonamidoacetic acid*, m.p. 263—264°, and *2-pyridone-5-sulphonanthranilide*, m.p. 263° (decomp.). *2''-Chloropyridine-5''-sulphonylsulphanilylsulphanildimethylamide*, m.p. 147—149°, from (**I**) and *p*-sulphanilylsulphanildimethylamide in C_5H_5N, is converted by boiling 10% NaOH into the corresponding *pyridone*, decomp. 188°. 2-Aminopyridine-5-sulphonic acid and *p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ in aq. NaOH–C_5H_5N give *2-p-acetamidobenzenesulphonamidopyridine-5-sulphonic acid*, m.p. 326—328°, hydrolysed by boiling 10% NaOH to the p-NH_2-compound. *2-p-Acetamidobenzenesulphonamidopyridine-5-sulphonamide* has m.p. 247° (Ac-free *compound*, m.p. 227°); the corresponding *dimethylamide* has m.p. 151—153°. H. W.

Indoles.—See B., 1943, II, 109.

Hofmann type rearrangement in liquid ammonia. H. C. White and F. W. Bergstrom (*J. Org. Chem.*, 1942, **7**, 497—507).—2-Phenylquinoline-4-carboxylamide is converted in ~40—50% yield into 4-amino-2-phenylquinoline, m.p. 163·5—164·5°, by reaction with KNH_2 in liquid NH_3. Almost quant. yields are obtained in the presence of KNO_3 or of Hg. Analogously *2-phenyl-6-methylquinoline-4-carboxylamide* gives 4-amino-2-phenyl-6-methylquinoline, m.p. 184—185°, and *2-phenylbenzoquinoline-4-carboxylamide*, m.p. 268—269°, yields *4-amino-2-phenylbenzoquinoline*, m.p. 162·5—163°. NH_2Bz, $CH_2Ph{\cdot}CO{\cdot}NH_2$, stearamide, and α-phenyl-γ-methyl-α-*n*-propylvaleramide do not thus give the corresponding amine. *o*-$C_6H_4Bz{\cdot}CO{\cdot}NH_2$ gives *o*-$NH_2{\cdot}C_6H_4{\cdot}COPh$ in 20% yield. *2-β-Naphthyl-*, m.p. 250·5—251°, 2-p-*tolyl-*, and 2-p-*anisyl-*, m.p. 245—246°, *-quinoline-4-carboxylamide* react readily with KNH_2 and KNO_3 in liquid NH_3 but without production of well-defined products. It thus appears that a reaction of the above type occurs only if the $CO{\cdot}NH_2$ group is activated by C:O or C:N at a favourable position in the mol. 2-p-*Xenylquinoline-4-carboxylic acid*, m.p. 292—293°, its *amide*, m.p. 245·5—246°, and *3-phenylbenzoquinoline-4-carboxylamide*, m.p. 239—240°, are described incidentally. Direct replacement of $CO{\cdot}NH_2$ by NH_2 is very unlikely and it is more probable that $R{\cdot}CO{\cdot}NH_2$ reacts with KNH_2 reversibly to form some of the ion, $R{\cdot}CO{\cdot}N^-$. This loses 2 electrons to KNO_3 or Hg to give the rearranged product RNCO which excess of KNH_2 transforms into $R{\cdot}NHK$ and KNCO. The over-all reactions are $R{\cdot}CO{\cdot}NH_2 + 3KNH_2 + KNO_3 \rightarrow R{\cdot}NHK + KNCO + 2NH_3 + KOH + KNO_2$ or $R{\cdot}CO{\cdot}NH_2 + 4KNH_2 + x\text{Hg} \rightarrow R{\cdot}NHK + KNCO + K_2Hg_x + 3NH_3$. 2-Phenylquinoline-4-carbimides or 2-phenyl-6-methylquinoline-4-carbimides react with KNH_2 to form the corresponding amine more slowly than this latter is produced in accordance with the above equations from quinoline-4-carboxylamide derivatives. Carbimides are therefore not true intermediates in the reactions or are much more readily hydrolysed by KNH_2 immediately after their formation. Phenyl- and naphthyl-carbimides react with liquid NH_3 at −33° to form monosubstituted carbamides but disubstituted carbamides are also formed in presence of KNH_2. This can be interpreted as involving the intermediate formation of a salt of a primary amine, *e.g.*, KNHPh, which adds to the carbamide to form a disubstituted carbamide. Accordingly the assumption of the formation of the carbimides (see above) receives some support. 9-Phenyl-9-fluorylamine, KNH_2, and KNO_3 yield 9-aminophenanthridine (**I**) by a method related to the Pinck–Hilbert modification of the Stieglitz rearrangement. The expected primary product, 9-phenylphenanthridine, has been converted by KNH_2 into (**I**). KNH_2, KNO_3, and $CPh_3{\cdot}NH_2$ give NH_2Bz. It is assumed that a Stieglitz type of rearrangement takes place with the formation of $CPh_2{:}NPh$, which is cleaved by KNH_2 to K benzamidine; this is hydrolysed to NH_2Bz. H. W.

5 : 5-Dimethylhydantoins containing a NRR substituent. II. H. R. Henze and D. D. Humphreys (*J. Amer. Chem. Soc.*, 1942, **64**, 2881; cf. A., 1940, II, 222).—The appropriate $NBu^{\alpha}R{\cdot}CH_2{\cdot}COMe$, KCN, and $(NH_4)_2CO_3$ in aq. EtOH at 55—60° give the following *5-methyl-5-N-alkyl-N-butylaminomethylhydantoins*: alkyl = Me (**I**), m.p. 137—138°, Et (**II**), m.p. 136—137°, Pr^{α}, m.p. 146—147°, Pr^{β}, m.p. 160—162°, Bu^{β}, m.p. 177·5—178°, *sec.*-Bu, m.p. 188—189°, CH_2Bu^{α}, m.p. 165—166°, and CH_2Bu^{β}, m.p. 181·5—182°. (**I**) and (**II**) are slightly analgesic in nearly fatal doses. The other products are not hypnotic. R. S. C.

Dihydroglyoxalines.—See B., 1943, II, 76.

Structure of glyoxaline.—See A., 1943, I, 144.

Structures of ketonic complexes of antipyrine.—See A., 1943, I, 116.

Pharmacological studies. XVI. Antipyryl ketones. H. P. Kaufmann, L. S. Huang, and H. Bückmann (*Ber.*, 1942, **75**, [*B*], 1236—1247).—Antipyric acid (**I**), antipyrine (**II**), and P_2O_5 in CO_2 at 100°/50 atm. yield *di-1-phenyl-2 : 3-dimethylpyrazol-5-on-4-yl ketone* [*diantipyryl ketone*], m.p. 246° [*hydrochloride*, m.p. 184° (decomp.); *hydriodide*, m.p. 229° (decomp.); *semicarbazone*, m.p. 263°, obtained by heating the reactants in a sealed tube at 150—170°], reduced by Zn dust and AcOH containing Et_2O at 100° to *diantipyrylmethane*, m.p. 178—179°. (**I**), $NPhMe_2$, and P_2O_5 at 120° afford p-*dimethylaminophenyl antipyryl ketone*, m.p. 217°, not identical with the *N-antipyroyl-N-methylaniline*, m.p. 147°, derived from antipyroyl chloride (**III**) and NHPhMe. p-*Ethoxyphenyl 4-antipyryl ketone*, m.p. 194°, is prepared from (**I**), PhOEt, and P_2O_5 at 140° and Ph 4-antipyryl ketone, m.p. 148°, from (**III**), C_6H_6, and $AlCl_3$. $ZnEt_2$ and (**III**) in boiling Et_2O or (**II**) and EtCOCl give *4-antipyryl Et ketone*, m.p. 146°. *4-Antipyryl 2-phenyl-4-quinolyl ketone*, m.p. 198°, is obtained from (**II**), *2-phenylquinoline-4-carboxylic acid*, and P_2O_5 at 150°, and *4-antipyryl 6-methoxy-4-quinolyl ketone*, m.p. (indef.) 130—132°, from quinic acid, (**II**), and P_2O_5 at 110—120° or from quinyl chloride hydrochloride and (**II**) at 120—130° and subsequently at 120°. (**II**), $CHEt_2{\cdot}COCl$, and $AlCl_3$ in boiling CS_2 yield *4-antipyryl $CHEt_2$ ketone*, m.p. 133°. (**II**) is converted by $CH_2Cl{\cdot}COCl$ at 100° into 4-antipyryl CH_2Cl ketone, m.p. 167°, transformed by the usual methods into *4-antipyroyl $CH_2{\cdot}NHMe$*, m.p. 242°, *$CH_2{\cdot}NEt_2$*, m.p. 177°, *$CH_2{\cdot}NH{\cdot}CH_2Ph$*, m.p. 222°, *$CH_2{\cdot}NHPh$*, m.p. 152°, *$CH_2{\cdot}NH{\cdot}C_6H_4{\cdot}OEt$*-p, m.p. 185°, *$CH_2{\cdot}CN$*, m.p. 156°, *$CH_2{\cdot}OH$*, m.p. 121°, *$CH_2{\cdot}OAc$*, m.p. 175°, *$\cdot CH_2{\cdot}CO_2{\cdot}C_6H_4{\cdot}OH$*-o, m.p. 196° (*acetate*, m.p. 141°), and *antipyroyloxymethyl*, m.p. 256°, *ketone*. (**II**) and *p*-$NO_2{\cdot}C_6H_4{\cdot}COCl$ at 130° and then at 100° yield *p*-nitrophenyl 4-antipyryl ketone (**V**), m.p. 209° (lit. m.p. 165—168°). The corresponding o-*nitrophenyl* compound has m.p. 172°. Reduction of (**V**) by $SnCl_2$ in AcOH saturated with HCl at room temp. or catalytically in EtOH containing Ni or Al_2O_3 at 160—180°/60 atm. gives *p*-aminophenyl 4-antipyryl ketone (**VI**), m.p. 260° (*Ac* derivative, m.p. 216°). o-*Aminophenyl 4-antipyryl ketone* has m.p. 144°. *p*-Aminophenyl 4-antipyryl ketone hydrochloride and KCNO give N-p-*antipyroylphenylcarbamide*, m.p. 223° (decomp.). *N'-Phenyl-N-p-antipyroylphenylcarbamide*, m.p. 210°, is derived from (**VI**) and PhNCO in C_6H_6 at 100°. H. W.

Pharmacological studies. XV. 1-Phenyl-2 : 3-dimethylpyrazol-5-one-4-carboxylic acid (antipyric acid) and its derivatives. H. P. Kaufmann and L. S. Huang [with H. Schmitz and G. Hültenschmidt] (*Ber.*, 1942, **75**, [*B*], 1214—1236).—Gradual addition of a solution of antipyrine in warm C_6H_6 to $COCl_2$ in C_6H_6 followed by warming the mixture to 50° and cautious addition of dil. NaOH to the cooled solution gives *1-phenyl-2 : 3-dimethylpyrazol-5-one-4-carboxylic* [*antipyric*] *acid* (**I**), m.p. 213° (decomp.) [*Na*, *K*, *Ca*, *Ag*, *Pb*, *Cu*, and *$Cu(NH_3)_4$* salts], the constitution of which is established by its conversion by HNO_3–H_2O (1 : 1) at 100° into 4-nitroantipyrine, m.p. 273°, in good yield. Homoantipyrine similarly affords *1-phenyl-3-methyl-2-ethylpyrazol-5-one-4-carboxylic* [*homoantipyric*] *acid*, m.p. 178°. (**I**) is transformed by boiling $SOCl_2$ into *antipyrinecarboxyl chloride* (**II**), m.p. 171—174°, converted by well-cooled, anhyd. HCN into the corresponding *cyanide*, m.p. 174°, and by MeOH–C_5H_5N at 0° into *Me antipyrinecarboxylate*, m.p. 158°. Analogously prepared are the *Et*, m.p. 152° (also from the Na salt and EtBr), *Buβ*, m.p. 111°, iso*amyl*, m.p. 99°, *Ph*, m.p. 198° [also from (**I**), P_2O_5, and PhOH at 130°], *CH_2Ph*, m.p. 126° (from the Na salt and CH_2PhCl in EtOH), *hydroxyquinolyl*, m.p. 217°, *α-$C_{10}H_7$*, m.p. 175°, and *β-$C_{10}H_7$*, m.p. 186°, esters. (**II**) and warm $Cl{\cdot}[CH_2]_2{\cdot}OH$ afford *β-chloroethyl antipyrinecarboxylate* (**III**), m.p. 144°, obtained also in C_5H_5N at room temp. and converted by usual methods into *β-cyano-*, m.p. 230° (decomp.), *β-amino-*, m.p. >260° (decomp.), *β-methylamino-*, m.p. 208°, *β-dimethylamino-*, m.p. 202° (decomp.), *β-diethylamino-*, m.p. 135°, *β-anilino-*, m.p. 242° (decomp.), *β-diphenylamino-*, m.p. 134°, *β-p-ethoxyanilino-*, m.p. 186°, and *β-p-carbethoxyanilino-*, m.p. 175°, *-ethyl antipyrinecarboxylate*. With $CO(NH_2)_2$ and $NH_2{\cdot}CO_2Et$ in C_6H_6 containing C_5H_5N (**III**) gives *β-antipyroyloxyethyl-carbamide*, m.p. 130°, and *-urethane*, m.p. 138°, respectively. (**II**) in C_5H_5N is transformed by *o*-$OH{\cdot}C_6H_4{\cdot}CO_2Me$, salol, and guaiacol respectively into o-*carbomethoxyphenyl*, m.p. 138°, o-*carbophenoxyphenyl*, m.p. 179°, and o-*anisyl*, m.p. 163—165°, *antipyrate*. *Quinine antipyrate* has m.p. 265°. (**II**) is transformed by lactophenin in C_5H_5N into O-*antipyroyl-lactyl*-p-*phenetidine*, m.p. 160°, and 4-O-*antipyroyloxyacetylantipyrine*, m.p. 256°, is derived from 4-chloroacetylantipyrine and Na antipyrate in boiling EtOH. (**II**) and conc. aq. NH_3 yield *antipyramide* [*antipyrinecarboxylamide*], m.p. 242—243°, also obtained from antipyrine (**IV**), $NH_2{\cdot}COCl$, and $AlCl_3$ in boiling CS_2. It is slowly transformed by P_2O_5 at 160—170° into *antipyronitrile*, m.p. 224°, also obtained from (**IV**), CNBr, and $AlCl_3$ in CS_2. It does not give a nitroso-reaction and only a weak reaction with $FeCl_3$; its basic character is not sharply defined. (**II**) with the appropriate base yields the corresponding *anilide*, m.p. 250°, *methylamide*, m.p. 207°, *dimethylamide*, m.p. 211°, *diethylamide*, m.p. 107°, *benzylamide*, m.p. 141°, p-*phenetidide*, m.p. 186°,

diphenylamide, m.p. 208°, *α-naphthylamide*, m.p. 210°, *β-naphthylamide*, m.p. 230°, p-*toluidide*, m.p. 208°, 2 : 4-*dimethylanilide*, m.p. 172°, m-*nitroanilide*, m.p. 245°, p-*nitroanilide*, m.p. 230°, *piperidide*, m.p. 169°, and 2-*pyridylamide*, m.p. 197°. (**II**) and *p*-NH_2·C_6H_4·NHAc in warm C_5H_5N afford N-*acetyl*-N′-*antipyroyl*-p-*phenylenediamine*, m.p. 260° (decomp.). *Antipyroylphthalimide* has m.p. 186° (decomp.). With the requisite base (**II**) affords NN′-*diantipyroylethylenediamine*, m.p. 234°, -p-*phenylenediamine*, m.p. 370° (decomp.), -*benzidine*, m.p. 304°, and -*diaminopyridine*, m.p. 298°. *Antipyroylantipyrylamide* has m.p. 246·5°. *Antipyrureide*, m.p. 251°, gives an *Ac*, m.p. 249°, and an *Et*, m.p. 252°, derivative. Adaline and (**II**) in warm C_6H_6 afford N-*antipyroyl*-N′-*bromodiethylacetylcarbamide*, m.p. 182°; the corresponding N′-*α-bromo*isovaleryl compound, m.p. 135°, is obtained from bromural. (**II**) and NH_2·CH_2·CO_2Et,HCl in warm C_5H_5N give *Et antipyramidoacetate*, m.p. 128°. o-*Antipyramidobenzoic acid*, m.p. 228° (*Et*, m.p. 194°, and *Buβ*, m.p. 203°, ester), is described. N-*Antipyroylsulphanil-amide*, m.p. 261°, and -*dimethylamide*, m.p. 188°, are obtained from (**II**) and the requisite sulphanilamide whereas N-*antipyroylsulphanildiethylamide*, m.p. 174°, is derived from (**IV**) and *p*-diethylaminosulphonylcarbanilyl chloride in C_5H_5N. Boiling Ac_2O transforms (**X**) into *antipyric acetic anhydride*, m.p. 154°. *Antipyric α-ethyl*-n-*butyric anhydride*, m.p. 218° (decomp.), *benzoic anhydride*, m.p. 185°, *benzenesulphonic anhydride*, m.p. 103°, and p-*toluenesulphonic anhydride*, m.p. 102°, are obtained from (**II**) and the requisite Na salt or from Na antipyrate and the necessary acid chloride. H. W.

Pyrimidines.—See B., 1943, II, 109.

Derivatives of *o*-3′-acenaphthoylbenzoic acid.—See A., 1943, II, 165.

Pyrazoleanthrones.—See B., 1943, II, 111.

Dipole moment and structure of *ms*-tetraphenylporphine.—See A., 1943, I, 117.

Absorption spectra and structures of cytochrome-*c* and hæmoglobin derivatives.—See A., 1943, I, 114.

Synthesis of di*iso*oxazole derivatives. II. C. Musante (*Gazzetta*, 1942, **72**, 242—250).—Et 5-styryl*iso*oxazole-3-carboxylate (**I**) in C_6H_6 with $COMe_2$ and Na gives the *Na* salt (**II**) of 3-*acetoacetyl*-5-*styryl*iso*oxazole*, m.p. 131° (*Cu* salt). With NH_2OH,HCl (**III**), (**II**) gives 3′-*methyl*-5-*styryl*-3 : 5′-*di*iso*oxazole*, m.p. 182°, which with $K_2Cr_2O_7$–H_2SO_4, or better CrO_3–AcOH, gives 3′-*methyl*-3 : 5′-*di*iso*oxazole*-5-*carboxylic acid*, m.p. 227—228° (decomp.) (*Ag* salt; *Me* ester, m.p. 164—165°). In C_6H_6, (**I**) with EtOAc and Na gives *Et* 5-*styryl*-3-iso*oxazoloylacetate*, m.p. 83—84° (*Cu* salt, decomp. from ~200°), which with 20% H_2SO_4 at the b.p. gives 3-*acetyl*-5-*styryl*-iso*oxazole*, m.p. 123° (*oxime*, m.p. 185—186°; p-*nitrophenylhydrazone*, m.p. 220—221°; *semicarbazone*, m.p. 234—235°). This in C_6H_6 with $Et_2C_2O_4$ and Na, followed by dil. H_2SO_4, gives *Et* 5-*styryl*-3-iso*oxazoloylpyruvate*, m.p. 123—124° [*Cu* salt, m.p. ~220° (decomp.)]. With (**III**), this gives a *di*iso*oxazole*. Et 3-methyl*iso*-oxazole-5-carboxylate with EtOAc and Na gives *Et* 3-*methyl*-5-iso*oxazoloylacetate*, m.p. 52—54° (*Cu* salt, decomp. ~215°), which in dil. H_2SO_4 gives 5-acetyl-3-methyl*iso*oxazole. E. W. W.

Derivatives of *o*-, *m*-, and *p*-aminobenzamides and related compounds. N. W. Hirwe and P. Y. Kulkarni (*Proc. Indian Acad. Sci.*, 1942, **16**, **A**, 294—297).—5 : 2 : 1-$C_6H_3Br\langle^{N=CMe}_{CO\cdot O}$ (**I**) and conc. aq. NH_3 at room temp. and later 0° give 5-*bromo*-2-*acetamidobenzamide*, m.p. 194°. 2 : 5 : 1-NH_2·C_6H_3Br·CO_2H, BzCl, and 10% NaOH at room temp. and later 100° give 5-*bromo*-2-*benzamidobenzoic acid*, m.p. 260°, converted by boiling Ac_2O into 6-*bromo*-4-*keto*-2-*phenyl*-1 : 3-*benzoxazine* [(**I**), with Ph for Me], m.p. 193—194°, which with conc. aq. NH_3 at room temp. and later 0° gives 5-*bromo*-2-*benzamidobenzamide*, m.p. 211—212°, and thence by warm dil. aq. NH_3 5-*bromo*-2-*phenyl*-4-*quinazolone*, m.p. >300°. NH_2·C_6H_4·CO_2Me (prep. from the acid by HCl–MeOH at <10° and then at the b.p.) gives NHAcyl·C_6H_4·CO_2Me, which with aq. NH_3 at room temp. gives NHAcyl·C_6H_4·CO·NH_2, converted at > the m.p. into substituted 4-quinazolones. Similarly, *o*-NHBz·C_6H_4·CO·NHPh at ~300°, o-*benzamidobenz*-m-*toluidide* [prep. from benzoylanthranil (**II**) by *m*-C_6H_4Me·NH_2 at 170°], m.p. 220°, at 250°, and o-*benzamidobenzhydrazide* [prep. from (**II**) by N_2H_4,H_2O], m.p. 176°, at 220° give 2 : 3-*diphenyl*-, m.p. 186°, 2-*phenyl*-3-m-*tolyl*-, m.p. 145°, and 3-*amino*-2-*phenyl*-, m.p. 184—186°, -4-*quinazolone*, respectively. m-, m.p. 223°, and p-*Benzamidobenzamide*, m.p. 284—285°, *Me* p-*acet*-, m.p. 114°, and p-*benz-amidobenzoate*, m.p. 160°, are described. R. S. C.

Piperidine and morpholine derivatives.—See B., 1943, III, 63.

Chemotherapy. VI. Sulphanilamido-heterocyclic compounds. G. W. Anderson, H. E. Faith, H. W. Marson, P. S. Winnek, and R. O. Roblin, jun. (*J. Amer. Chem. Soc.*, 1942, **64**, 2902—2905; cf. A., 1942, II, 400).—*A*, *B*, *C*, and *D* below denote activity against *E. coli* in a synthetic medium, *A* is <, *B* equal to, that of sulphanilamide, *C* and *D* equal to that of sulpha-pyridine and -thiazole, respectively. Standard methods yield 2-sulphanilamido-glyoxaline, m.p. 262° (lit. 259°) (*B*), 4-*sulphanilamido*-1 : 2 : 4-*triazole*, m.p. 237° (*A*) (N^4-*Ac* derivative, m.p. 237°), 3-*sulphanilamido*-4-*methylfurazan*, m.p. 148—150° (*C*), -5-*methyl*-1 : 2 : 4-*oxadiazole* (**I**), m.p. 211—213° (*C*), and -*pyridazine*, m.p. 189—190° (*D*), 5-*sulphanilamido*-3-*naphthyl*isoo*xazole* (**II**), m.p. 169—170° (*C*), 5-*amino*-2-*sulphanilamido*-1 : 3 : 4-*thiadiazole*, m.p. 259° (*C*), 4-*amino*-, m.p. 271—272° (*B*), and 4-*diethylamino*-2-*sulphanilamidopyrimidine*, m.p. >300° (*A*). 2-*Sulphanilamido-oxazole*, m.p. 175—176° (*D*), is prepared by way of the *p*-NO_2·C_6H_4·CO_2·NH-derivative, m.p. 175—177°, which is reduced by $FeSO_4$–aq. NH_3. 3-*Sulphanilamido*-1 : 2 : 4-*triazole*, m.p. 195—196° (*A*), and 4 : 6-*diamino*-2-*sulphanilamido*-1 : 3 : 5-*triazine*, m.p. 290—295° (*B*), are prepared by way of the *p*-NO_2·C_6H_4·SO_2·NH-derivatives, which are reduced by Fe dust in AcOH. (**I**) and (**II**) are slightly active against *Streptococci* or *Pneumococci* in mice; the other products are inactive. CH_2Cl·CHCl·OEt and $CO(NH_2)_2$ in boiling H_2O give 2-*amino-oxazole*, m.p. 96—98°. Adding Ac_2O and later NaOAc to dihydroxyguanidine hydrobromide in AcOH and treating the product with 40% NaOH gives 3-*amino*-5-*methyl*-1 : 2 : 4-*oxadiazole*, m.p. 117—119°. 3-*Aminopyridazine*, m.p. 168—170°, is prepared from the 3-Cl-compound by NH_3–EtOH at 175°, and 2-*amino*-4-*dimethylaminopyrimidine*, m.p. 86—88°, from 4-chloro-2-aminopyrimidine by $NHEt_2$ at 110—120°. M.p. are corr., usually with decomp. for the *p*-NH_2·C_6H_4·SO_2·NH-compounds. R. S. C.

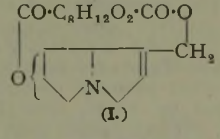
Sulphanilamide type heterocyclic compounds.—See B., 1943, III, 63.

Benzthiazoles.—See B., 1943, II, 75, 77.

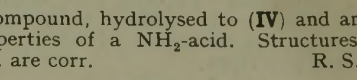
VII.—ALKALOIDS.

3 : 2′-Nicotyrine. Insecticidal properties of azo-derivatives. R. L. Frank, R. W. Holley, and D. M. Wikholm (*J. Amer. Chem. Soc.*, 1942, **64**, 2835—2838).—Nicotine and Pd–asbestos in the vapour (41% at 300—325°) or liquid phase (30—35% yield at 230—280°) give 3 : 2′-nicotyrine (**I**), b.p. 104—107°/1 mm., and fractions, b.p. 210—230°/1 mm. (~30%) and 48—70°/1 mm. By coupling, (**I**) gives *azo*-derivatives, $C_{10}H_9N_2$·N:NX, in which X = *p*-C_6H_4·SO_3Na (**II**), m.p. >300°, *p*-, m.p. 200—201°, and *m*-C_6H_4·NO_2, m.p. 156—157°, *p*-C_6H_4·CO_2H, m.p. 245—246° (decomp.), and *β*-$C_{10}H_7$, m.p. 148°, which dye wool and protect it considerably from attack by *Attagenus piceus*. $SnCl_2$–HCl reduces (**II**) to 5′-*amino*-3 : 2′-*nicotyrine*, m.p. 86—87° [unstable dihydrochloride; stable *dipicrate*, m.p. 173—174° (decomp.)], unstable in air or hot EtOH, H_2O, Et_2O, or $CHCl_3$. R. S. C.

Structure of riddelliine, the alkaloid of *Senecio riddellii*. I. R. Adams, K. E. Hamlin, jun., C. F. Jelinek, and R. F. Phillips (*J. Amer. Chem. Soc.*, 1942, **64**, 2760—2763).—Riddelliine (prep. from *S. riddellii* described; 0—0·7%) (**I**), $C_{18}H_{23}O_6N$, m.p. 197—198° (decomp.), $[\alpha]_D^{25}$ −109·5° in $CHCl_3$ (cf. Manske, A., 1939, II, 232) [*hydrochloride*, m.p. 225—226° (decomp.; vac.). $[\alpha]_D^{25}$ −80·6° in H_2O; methiodide, m.p. 260—262° (decomp. from 235°)], in boiling aq. $Ba(OH)_2$ gives retronecine (91%) and *riddellic acid* (**II**) (85%), $C_{10}H_{14}O_6$, m.p. (+H_2O) 62° and (anhyd.) 102—103°, $[\alpha]_D^{22}$ (anhyd.) −2·65° in EtOH. Hydrogenation (PtO_2; 2—3 atm.; EtOH) of (**II**) gives a mixture, but that of its *Me*$_2$ ester (prep. by CH_2N_2), b.p. 144—145°/1 mm., $[\alpha]_D^{22}$ −2·84° in EtOH, gives *Me*$_2$ *dihydroriddellate*, b.p. 146—147°/1 mm., $[\alpha]_D^{22}$ −15·3° in EtOH. H_2–Raney Ni at 2—3 atm. reduces (**I**) in aq. EtOH to *tetrahydroriddelliine* (**III**), m.p. 205°, $[\alpha]_D^{21}$ −9·5° in EtOH, hydrolysed [$Ba(OH)_2$] to retronecanol (**IV**) and (**II**), but H_2–PtO_2 in aq. EtOH at 2—3 atm.



(I.)



(II.)

gives an amorphous H_2-compound, hydrolysed to (**IV**) and an oily acid. (**III**) has the properties of a NH_2-acid. Structures are, therefore, as shown. M.p. are corr. R. S. C.

Alkaloids of fumariaceous plants. XXXV. *Corydalis platicarpa*, Makino. R. H. F. Manske (*Canad. J. Res.*, 1943, **21**, **B**, 13—16).—The plant contains protopine, *l-iso*corypalmine, *iso*corydine (identical with luteanine, A., 1939, II, 395), corybulbine, aurotensine, *l*-tetrahydropalmatine, corydaline, bicuculline, *dl*-stylopine, and a neutral *compound*, C_6H_9ON, m.p. 172°. A. Li.

Alkaloids of seeds of *Delphinium elatum*, L. J. A. Goodson (*J.C.S.*, 1943, 139—141).—The alkaloids of the seeds of *D. elatum* consist mainly of *methyl-lycaconitine* (**I**), $C_{37}H_{48}O_{10}N_2$, m.p. 128° (sinters at 119°) (not cryst.), $[\alpha]_D^{22}$ +49·1° in EtOH (purified through the *hydriodide*, m.p. 201° (decomp.), $[\alpha]_D^{22}$ +18·5° in N-KOH–EtOH), and small quantities of two bases, viz., *delpheline*, $C_{22}H_{33}O_5N$, m.p. 227° (sinters at 222°), $[\alpha]_D^{15}$ −25·8° in $CHCl_3$ [*hydrochloride*, +H_2O,

m.p. 219°, with frothing sinters at 215°), $[\alpha]_D^{22}$ −42·8° in H_2O; *nitrate*, m.p. 191—193°, $[\alpha]_D^{22}$ −41·2° in H_2O], and *delatine*, $C_{19}H_{23}O_3N$, m.p. 148° (sinters at 141°) (+H_2O), $[\alpha]_D^{25}$ +13·5° in 0·2N-HCl, or anhyd., m.p. 261—264° (*hydrochloride*, m.p. 274—277°, $[\alpha]_D^{18}$ +13·4° in H_2O). (**I**) and N-NaOH–EtOH afford *methylsuccinylanthranilic acid* [*methyl-lycoctinic acid*] (**II**), m.p. 155° (sinters at 147°), $[\alpha]_D^{24}$ −7·0° in EtOH, and *lycoctonine* (**III**), +H_2O, m.p. 143° (sinters at 138°), $[\alpha]_D^{25}$ +53·2° in EtOH, or anhyd., m.p. 126° (sinters at 119° and froths at 143°). (**II**) is hydrolysed by boiling 10% HCl to *l*-methylsuccinic acid (**IV**), m.p. 114° (sinters at 111°), and *o*-$NH_2{\cdot}C_6H_4{\cdot}CO_2H$. Hydrolysis of (**I**) with 10% HCl in a closed vessel at room temp. gives (**IV**) and *anthranoyl-lycoctinine*, m.p. 172° (sinters at 168°), $[\alpha]_D^{24}$ +32·4° in 0·2N-HCl [hydrolysed by N-NaOH–EtOH to (**III**) and *o*-$NH_2{\cdot}C_6H_4{\cdot}CO_2H$]. (**III**) is obtainable from the roots of *Aconitum lycoctonum*; thus its presence in these two genera of Ranunculaceæ is established. A. T. P.

Alkaloid of *Berberis umbellata*, Wall. III. R. Chatterjee (*J. Indian Chem. Soc.*, 1942, **19**, 385—388).—Umbellatine (**I**) is converted by oxidation with $KMnO_4$ into hemipinic acid (ethylimide, m.p. 90°) and by fusion with KOH into protocatechuic acid. The 2 OMe groups are *ortho* in the C_6H_6 nucleus of (**I**) and other groups, such as CH_2O_2 and OH, are not present in this nucleus. H. W.

Alkaloid from *Menispermum canadense*, L. R. H. F. Manske (*Canad. J. Res.*, 1943, **21**, **B**, 17—20).—The subterranean stems and roots contain 2·2% of alkaloid, consisting (? entirely) of dauricine (Kondo *et al.*, A., 1935, 637) (dimethiodide, m.p. 201°, $[\alpha]_D^{20}$ −114° in H_2O), which on exhaustive methylation (dimethiodide of the dimethine base, m.p. 211°) and oxidation ($KMnO_4$ in $COMe_2$) yields 1 : 1′-dicarboxy-4-methoxy-, while its *O*-Et ether similarly yields the 4-ethoxy-3 : 4′-diphenyl ether. A. Lɪ.

Auricularine, a new alkaloid from the roots and stems of *Hedyotis auricularia*. A. N. Ratnagiriswaran and K. Venkatachalam (*J. Indian Chem. Soc.*, 1942, **19**, 389—392).—Chemical examination of the root and stems shows the presence of fatty matter yielding stearic and linoleic acids when hydrolysed, a *phytosterol*, m.p. 141—142° (*acetate*, m.p. 128—129°), alizarin, $H_2C_2O_4$, glucose, *auricularine* (**I**), $C_{42}H_{52}ON_2{\cdot}H_2O$, m.p. 201° (decomp.), becomes brown at 192° [*oxalate*, becomes brown at 185° and chars without melting at 230°; *picrate*, m.p. 217—218° (decomp.)], a substance giving a *hydriodide*, darkens at 195° and chars without melting at 215—220°, and amorphous bases. (**I**), which differs from hedyotine (Dey *et al.*, A., 1934, 87), is present in very small proportion. H. W.

VIII.—ORGANO-METALLIC COMPOUNDS.

Relative reactivities of organo-metallic compounds. XLIX. Reactions of group IV MR_4 compounds with silver and copper salts. H. Gilman and L. A. Woods (*J. Amer. Chem. Soc.*, 1943, **65**, 435—437).—The fate of R in cleavage of MR_4 by inorg. salts depends on the nature of both reactants. Thus, $PbPh_4$ with $AgNO_3$ in EtOH gives 67·5—70·2% of Ph_2 and 74·3—76·8% of $PbPh_3{\cdot}NO_3$, but with $Cu(NO_3)_2{,}3H_2O$ in EtOH gives 86·5% of C_6H_6, a trace of Ph_2, and 66·8—76% of $PbPh_3{\cdot}NO_3$. $SnPh_4$ with $AgNO_3$ in boiling EtOH gives C_6H_6 (80·6%), and Ph_2 (5·2%). $PbMe_4$ with $AgNO_3$ at −70° gives C_2H_6 (98·3%), C_2H_4 (2·1%), *Pb Me*$_2$ *nitrate* (82·7%), and CH_4 (4·0%), and with $Cu(NO_3)_2{,}3H_2O$ gives C_2H_6 (74·6%), $PbMe_2{\cdot}NO_3$ (71·3% isolated as iodide), and CH_4 (21·1%, formed by hydrolysis of CuMe). $PbEt_4$ with $AgNO_3$ gives C_4H_{10} (52·0), C_2H_6 (27·8), C_2H_4 (15·5), and $PbEt_2Cl$ (72·7%), and with $Cu(NO_3)_2{,}3H_2O$ gives C_4H_{10} (52·5), C_2H_6 (26·3), C_2H_4 (16·7), and $PbEt_2Cl$ (75·7%). CuMe, formed *in situ* from LiMe and CuI in Et_2O at −15° (later 0°), with BzCl at −15° gives COPhMe (56·5%). $PbMe_4$ in EtOH with $Cu(NO_3)_2{,}3H_2O$ at −70° and then BzCl gives 3% of COPhMe. $SiPh_4$ and $GePh_4$ do not react with $AgNO_3$ in boiling EtOH.
R. S. C.

Bivalent and tervalent rhodium. IV. Polynuclear complexes of rhodium and tin with tertiary arsines. F. P. Dwyer and R. S. Nyholm (*J. Proc. Roy. Soc. New South Wales*, 1942, **76**, 129—132).—$(AsPh_2Me{\cdot}RhCl_2)$ with $SnCl_2$ gives *dichlorohexakisdiphenylmethylarsine-μ-dichlorotinrhodium*^{III}*-μ-dichlorodirhodium*^{II}*-μ-dichlororhodium*^{II}*-tin*, m.p. 149°, whilst $RhCl_3$ and $SnCl_2$ in NaOH with $AsPh_2Me$ yield (probably) the isomeric *dichlorohexakisdiphenylmethylarsine-μ-dichlororhodium*^{II}*-tin-μ-dichloroditin-μ-dichlorotinrhodium*, m.p. 129°. $RhCl_3$ gives different types of complex with dialkyl- and diaryl-arsines. The following were prepared: *dichlorotris*-p-*tolyldimethylarsine-μ-dichlororhodium*^{III}*-tin*, m.p. 111°, and *tetrachlorohexatrisdiphenylmethylarsine-μ-dichlororhodium*^{III}*-tin-μ-dichlorotin-rhodium*^{III}, m.p. 176—178°. These compounds are readily dissociated and the corresponding Br- and I-derivatives could not be isolated. F. R. G.

Serological properties of simple substances. I. Precipitation reactions between antibodies and substances containing two or more haptenic groups. L. Pauling, D. Pressman, D. H. Campbell, C. Ikeda, and M. Ikawa (*J. Amer. Chem. Soc.*, 1942, **64**, 2994—3003).—p-p′-*Aminobenseneazophenylarsonic acid* is prepared by condensing *p*-$NO{\cdot}C_6H_4{\cdot}AsO_3H_2$ (**I**) with *p*-$NH_2{\cdot}C_6H_4{\cdot}NHAc$ in boiling AcOH or *p*-$N_2Cl{\cdot}C_6H_4{\cdot}AsO_3H_2$ (**II**) with $NHPh{\cdot}CH_2{\cdot}SO_3H$ in 0·3N-Na_2CO_3 and hydrolysing the products by aq. alkali. *p*-$NH_2{\cdot}C_6H_4{\cdot}AsO_3H_2$ (**III**) or *p*-$C_6H_4(NH_2)_2$ and (**I**) give *azobenzene-4 : 4′-diarsonic* and p-*benzenedi-p′-azophenylarsonic acid*, respectively. Coupling (**II**) or *p*-$N_2Cl{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}AsO_3H_2$-*p* with the appropriate phenol in dil. aq. Na_2CO_3, sometimes containing 10% of C_5H_5N, gives *o-cresol-3 : 5-*, *8-amino-5-sulpho-1-naphthol-2 : 7-*, and *4 : 4′-dihydroxydiphenyl-3 : 3′-di-p-azophenylarsonic acid*, *resorcinol-* and *phloroglucinol-2 : 4 : 6-tri-p-azophenylarsonic acid*, *2 : 4 : 4′-trihydroxyazobenzene-3 : 5 : 3′ : 5′-tetra-*p-*azophenylarsonic acid*, *diphenyl-4 : 4′-di-(4″-azoresorcinol-2″ : 6″-di-p-azophenylarsonic acid)*, *o-cresol-3 : 5-di-* and *resorcinol-2 : 4 : 6-tri-p-p′-azobenzeneazophenylarsonic acid*, *diphenyl-4 : 4′-di-(4″-azoresorcinol-2″ : 6″-p-p′-azobenzeneazophenylarsonic acid)*, *4-hydroxy-*, *2 : 4-dihydroxy-*, and *4-amino-azobenzene-4′-arsonic acid*. *p′-Hydroxybenzeneazo-*p-*azobenzene-*p″*-azophenylarsonic acid* is similarly prepared in NaOAc–AcOH. *2 : 4 : 4′-Trihydroxyazobenzene* and *diphenyl-4 : 4′-di-(2″ : 4″-dihydroxyazobenzene)* are prepared from *m*-$C_6H_4(OH)_2$ by *p*-$OH{\cdot}C_6H_4{\cdot}N_2Cl$ and $(\cdot C_6H_4{\cdot}N_2Cl\text{-}p)_2$, respectively, in NaOH. *p*-$CO_2Et{\cdot}NH{\cdot}C_6H_4{\cdot}COCl$ and (**II**) give, after hydrolysis, *p-aminobenz-p′-arsonoanilide*. The appropriate acid chloride or anhydride with (**III**) in alkaline or buffered aq. solution gives *carbanilide-4 : 4′-diarsonic acid*, *oxal-*, *succin-*, *adip-*, *sebac-*, *phthal-*, *isophthal-*, and *terephthal-dianilide-4 : 4′-diarsonic acid*. For biological results see A., 1943, III, 442. R. S. C.

Preparation of bisarylphosphonic acids. G. M. Kosolapoff (*J. Amer. Chem. Soc.*, 1942, **64**, 2982—2983).—Adding MgPhBr in Et_2O to $POCl_3$ in boiling Et_2O gives, after hydrolysis, 55% of Ph_2PO_2H and some PPh_3O. *p*-$C_6H_4Cl{\cdot}MgBr$ gives 51% of *di-p-chlorophenylphosphonic acid*, m.p. 171—172·5°, and some (*p*-$C_6H_4Cl)_3PO$. Yields are slightly lower at 0°. Dil. solutions (0·2 mol. per l.) are beneficial. R. S. C.

Mercuriphenyl salts.—See B., 1943, II, 110.

Ionic nature of the Grignard reagent. W. V. Evans and R. Pearson (*J. Amer. Chem. Soc.*, 1942, **64**, 2865—2871).—Transference of $MgBu^aBr$ and MgEtBr and conductance of $MgEt_2$ and $ZnEt_2$ in Et_2O are determined. Interaction of $ZnCl_2$ and MgEtBr in Et_2O is instantaneous. From these and known facts it is concluded that halogen and alkyl ions are formed from MgRX, that the cation is small, slow, and co-ordinated with Et_2O, whereas the anion is large, mobile, and co-ordinated with MgRX, MgX_2, and MgR_2.
R. S. C.

Grignard reactions. XVI. F. C. Whitmore and C. E. Lewis. **XVII. Reactions of esters and acid chlorides with Grignard reagents.** F. C. Whitmore and W. S. Forster. **XVIII. Reactions of magnesium benzyl chloride.** F. C. Whitmore and T. K. Sloat (*J. Amer. Chem. Soc.*, 1942, **64**, 2964—2966, 2966—2968, 2968—2970; cf. A., 1942, II, 393).—XVI. Substitution on the CH_2 of $COR{\cdot}CH_2R'$ decreases the amount of enolisation occurring in presence of MgMeI, Et being more effective than Me. β-Substitution has much less effect. The following % of enolisation and addition of MgMeI, respectively, are recorded: $COMe{\cdot}CEt_3$ 94, 0; $COMe{\cdot}CMeEt_2$ 84, 0; $COMe{\cdot}CMe_2Et$, 14, 74; $COMeBu^\gamma$ 5, 86; $COMe{\cdot}CH_2Bu^\gamma$ 0, 100; $COBu^\gamma{\cdot}CEt_3$ 85, 0; $CH_2{:}CH{\cdot}CO{\cdot}CEt_3$ (**I**) 0, 58; $CEt_3{\cdot}CO_2R$ (R = Me, b.p. 164—165°/734 mm., or Et, b.p. 85—87°/30 mm.) 0, 0; $CMeEt_2{\cdot}CO_2Et$ (**II**), b.p. 73°/35 mm., 25, 45 {apparent enolisation due to that of the ketone formed; cf. $CMeEt_2{\cdot}CO_2Bu^a$ from (**II**) and $NaOBu^a$–Bu^aOH; b.p. 104—105°/38 mm.] 22, 60}; $CMe_2Et{\cdot}CO_2Et$, b.p. 140—141°/744 mm., 0, 100; $CEt_2{\cdot}CO{\cdot}[CH_2]_2{\cdot}OH$ 58, 27; $CH_3(CO{\cdot}CEt_3)_2$ (**III**) 91·2, 55·2; $CHMe(CO{\cdot}CEt_3)_2$ (**IV**) 79·2, 19·2%. The following reactions are recorded: EtOAc + MgEtBr → $CMeEt_2{\cdot}OH$ → (+HCl) $CMeEt_2Cl$ → (Mg; CO_2) $CMeEt_2{\cdot}CO_2H$, b.p. 157°/734 mm. → ($SOCl_2$) $CMeEt_2{\cdot}COCl$ → (+MgMeBr) $COMe{\cdot}CMeEt_2$, b.p. 77—79°/20 mm. (2 : 4-dinitrophenylhydrazone, m.p. 73—74°); $CEt_3{\cdot}CO{\cdot}[CH_2]_2{\cdot}OH$ + $CuSO_4$ → (**I**), b.p. 97°/36 mm., polymerises when kept; $CEt_3{\cdot}COCl$ + MgMeBr → $CEt_3{\cdot}CH_2{\cdot}OH$ (40%), b.p. 96—100°/40 mm. (α-naphthylurethane, m.p. 131—132°), + $COBu^\beta{\cdot}CEt_3$ (43%), b.p. 86—87°/12 mm. (no CO derivatives obtainable); $CMeEt_2{\cdot}COCl$ + MgMeBr → $COMe{\cdot}CMeEt_2$ (48%), b.p. 77—79°/20 mm. (2 : 4-dinitrophenylhydrazone, m.p. 73—74°); $CMe_2Et{\cdot}MgCl$ + MeCHO → carbinol → (+CrO_3–AcOH; <30°) $COMe{\cdot}CMe_2Et$, b.p. 130°/733 mm. (2 : 4-dinitrophenylhydrazone, m.p. 112°); RCOCl + NaOR′–R′OH → RCO_2R'; (**III**) with Na in Et_2O and then MeI–dioxan gives (**IV**) (41%), b.p. 164°/6 mm. (no $FeCl_3$ colour or Cu salt).

XVII. The following amounts of *sec.* and *tert.* alcohols, respectively, are formed by MgRBr: (*a*) from $Bu^\gamma COCl$, R = Et 60, 26·1, Pr^α 76, 0 [also $CH_2Bu^\gamma{\cdot}OH$ (**V**) 20], Pr^β 53, 0 [also (**V**) 23], Bu^α 71, 0 [also (**V**) 28], and Bu^β 26, 0 [also (**V**) 61]; (*b*) from $Bu^\gamma CO_2Me$, R = Et 8·6, 76·5, Pr^α 48, 40, Pr^β 0, 44·8, Bu^α 40, 50, Bu^β 25·7, 29·4, (*c*) from $CH_2Bu^\gamma{\cdot}COCl$, R = Et 0, 57·6, Pr^α 24·4, 57, Pr^β 26·7, 0 (32·7% of ketone), Bu^α 20·5, 9·9, Bu^β 48·9, 13·8 (20·1% of ketone), (*d*) from $CH_2Bu^\beta{\cdot}CO_2Me$, R = Et 0, 68·5 (5% of ketone), Pr^α 20·4, 61·8 (7% of ketone), Pr^β 16·1, 55·3, Bu^α 0, 71·4 (trace of ketone), Bu^β 9·2, 34·2% (32% of ketone). Non-formation of primary alcohols shows that aldehydes are not intermediates in the reactions. The following are recorded: $CMe_2Et{\cdot}COCl$, b.p. 129·8°/727 mm.;

βεε-trimethyl-n-*γ-hexyl α-naphthylurethane*, m.p. 88—90°; *βδδ-trimethyl*-n-*γ-hexyl α-naphthyl*-, m.p. 76·5—77·5°, and phenyl-urethane, m.p. 58—59°; *ββζ-trimethyl*-n-*δ-heptyl α-naphthylurethane*, m.p. 99—101°.

XVIII. Adding CH_2Ph·MgCl to AcCl at 0° gives 18% of *o*-C_6H_4Me·COMe, but the reverse addition gives only 3% thereof; at 25° 16·5% is obtained. Only the normal products are obtained by adding CH_2Ph·MgCl to MeCN, NH_2Ac, CO_2, O_2, EtOAc, CH_2PhCl, or H_2O (cf. lit.). R. S. C.

IX.—PROTEINS.

Iodinated proteins and their action. I. Abelin (*Helv. Chim. Acta*, 1942, **25**, 1421—1432).—Iodination of proteins does not occur homogeneously but leads to mono- and di-iodotyrosine, iodohistidine, iodotryptophan, and products containing thyroxine (**I**) which yield the latter in pure form after energetic hydrolysis. Although many iodinated proteins resemble the thyroid protein in containing (**I**) there is a pronounced physiological difference. In contrast to thyroglobulin the intact iodinated proteins are without sp. influence on the glycogen metabolism of the liver or the creatine changes of the heart and striated muscle; they have no action on the activity of heart, lungs, or nervous system. Certain synthetic iodinated proteins cause increased caloric output but in a degree much inferior to that of the thyroproteins. Outside the animal body only (**I**) can be obtained by chemical means. The prep. of synthetically iodinated proteins with full thyroid activity has not yet been achieved. H. W.

Effect of salts on the formation of protein complexes during heat-denaturation. A. Kleczkowski (*Biochem. J.*, 1943, **37**, 30—36).—The formation of complexes between different proteins undergoing heat-denaturation together occurs in the absence of salts only in mixtures containing H_2O-sol. serum-globulin. The efficiency of salts in promoting the formation of complexes is determined by the valency of the anion on the acid side and of the cation on the alkaline side of the isoelectric point of the protein, ions of higher valency being more effective than those of lower valency. H. G. R.

Fixation of formaldehyde by scleroproteins. C. T. Baudouy (*Compt. rend.*, 1942, **214**, 692—695).—Only those proteins which contain tryptophan and histidine units combine irreversibly with CH_2O. Collagens which do not contain these acids liberate CH_2O quantitatively from the complex by distillation or the action of H_2SO_4. Globin (from horse blood) under the same conditions liberates only 30% of the combined CH_2O. P. G. M.

Tryptophan content of various proteins. H. S. Milone and E. L. Everitt (*Proc. Soc. Exp. Biol. Med.*, 1942, **51**, 82—83).—Tryptophan of a no. of proteins was determined by a short procedure (A., 1939, II, 44) and found to agree with the results already obtained by Jones *et. al.* by their longer method (A., 1925, i, 98). V. J. W.

Partial acid hydrolysis of cow-hide gelatin. A. H. Gordon, A. J. P. Martin, and R. L. M. Synge (*Biochem. J.*, 1943, **37**, 92—102).—Cow-hide gelatin is hydrolysed by 10N-HCl at 37°. Electrodialysis at pH 6 effects a separation into basic and neutral fractions of NH_2-acids. Analysis of the former suggests that residues of basic NH_2-acids are linked to residues of higher $(NH_2)_1$-acids in gelatin. The neutral fraction is acetylated and fractionally chromatographed on SiO_2 gel; a 4-day hydrolysate yields a glycine–leucine dipeptide, and a 19-day hydrolysate proline–alanine dipeptide, proline–glycine dipeptide, and proline–alanine–glycine tripeptide, in addition to $(NH_2)_1$-acids including *l*-valine. The diketopiperazines isolated by some earlier workers are probably artefacts resulting from the corresponding dipeptides. Evidence is presented to show that acids with longer fatty side-chains, *e.g.*, phenylalanine, leucine, etc., are not linked to one another. P. G. M.

Amino-acid content of gramicidin. A. H. Gordon, A. J. P. Martin, and R. L. M. Synge (*Biochem. J.*, 1943, **37**, 86—92).—Gramicidin (from tyrothricin) is hydrolysed with HCl in aq. AcOH with exclusion of air (cf. Hotchkiss, A., 1942, II, 42). The following NH_2-acids have been demonstrated (N as % of total): leucine 20·2, tryptophan 4·0—4·5, valine 1·6·6, alanine 10·1, glycine 5·3—6·6. These vals. are in close agreement with the calc. vals. for a min. mol. containing 30 atoms of N as demanded by a mol. with 24 residues, *i.e.*, 6 leucine, 6 tryptophan, 5 valine, 3 alanine, 2 glycine, and 2 of an unknown hydroxyamino-acid. Gramicidin does not contain serine. P. G. M.

Partition chromatography applied to protein constituents. A. H. Gordon, A. J. P. Martin, and R. L. M. Synge (*Biochem. J.*, 1943, **37**, 79—86).—The theory of partition chromatography in relation to the separation of NH_2-acids and peptides is discussed. The prep. of the SiO_2 gel and the micro-determination of phenylalanine, leucine + *iso*leucine, valine, methionine, proline, alanine, and tyrosine as their Ac derivatives is described, and the method is applied to hydrolysates of wool and cow-hide gelatin. The val. for phenylalanine-N (as % of total N) in wool hydrolysates is only 0·8%, < half the vals. obtained by earlier workers. P. G. M.

Separation of basic amino-acids from protein hydrolysates.—See A., 1943, III, 363.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Bitter principles of neem oil. (A) S. Rangaswami. (B) S. Siddiqui (*Current Sci.*, 1942, **11**, 367—368, 368).—(A) Polemical. A comparison is drawn between nimbin (**I**), and nimbinin (**II**) (Siddiqui, A., 1943, II, 19), and the substances $(C_5H_7O_2)_n$ and $(C_4H_7O_2)_n$ isolated from the EtOH extract of neem oil by Murti *et al.* (A., 1942, II, 123).

(B) EtOH extraction of neem oil is too mild and the substances obtained are not the same as (**I**) and (**II**). F. R. G.

Quassin. IV. Minor constituent of Jamaican quassia wood. E. P. Clark (*J. Amer. Chem. Soc.*, 1942, **64**, 2883—2884; cf. A., 1938, II, 288).—Mother-liquors (A., 1937, II, 297) from this wood yield 0·015% of a mixture, m.p. 166—167°, partly separated by adsorption into neoquassin and a non-cryst. material. R. S. C.

Action of organic acids on cornstalk lignin. E. Fisher (*Iowa State Coll. J. Sci.*, 1943, **17**, 241—250).—The amount and OMe content of the lignin extracted by aq. org. acids of different concns. is reported. The results show that hydrolysis plays an important part, and that during the extraction with lactic acid fractionation takes place. Aq. HCO_2H containing HCl appears to cause condensation–polymerisation reactions. Anhyd. HCO_2H, AcOH, and $EtCO_2H$ form esters with the lignins they extract. The action of acids on isolated lignin is not the same as on that in the plant. Lactic acid adds CO_2H groups to both natural and isolated lignin; a mechanism for this process is suggested. A. Li.

Toxic principles of poison ivy.—See A., 1943, III, 447.

XI.—ANALYSIS.

Absorption tube tares in carbon and hydrogen micro-determinations. W. M. MacNevin and J. E. Varner (*Ind. Eng. Chem.* [*Anal.*], 1943, **15**, 224—225).—The precautions to be observed when using a Pregl-type tube as a control or as a tare in micro-weighings are described. J. D. R.

Micro-determination of hydroxyl content of organic compounds, acetic anhydride–pyridine mixture as reagent. J. W. Petersen, K. W. Hedberg, and B. E. Christensen (*Ind. Eng. Chem.* [*Anal.*], 1943, **15**, 225—226).—Free OH is determined by esterification with Ac_2O–C_5H_5N and titrimetric determination of the excess of Ac_2O. J. D. R.

Cerate and periodate oxidimetry. Perchlorato-cerate and periodate ions as oxidants in the determination of organic compounds. G. F. Smith and F. R. Duke (*Ind. Eng. Chem.* [*Anal.*], 1943, **15**, 120—122).—The mechanism of the oxidation of aliphatic org. compounds by HIO_4 using Malaprade's procedure (A., 1928, 867) is discussed. The principles governing the oxidation of aliphatic org. compounds by $Ce(ClO_4)_6''$ in presence of 4M-$HClO_4$ are discussed. Experimental procedure follows that previously given (A., 1941, II, 386) for glycerol. Results of analysis of a series of org. compounds are given. The $Ce(ClO_4)_6''$ method is of wider application than the HIO_4 method; speed of reaction and the no. of oxidation equivs. are also greater. L. S. T.

Indirect analysis of organic mixtures.—See A., 1943, III, 447.

Histochemical reactions for lipin aldehyde and ketones.—See A., 1943, III, 368.

α-Naphthol colour test for dihydroxyacetone and hydroxymaleic acid.—See A., 1943, III, 448.

Nature of Waser's specific colour reaction for α-amino-acids.—See A., 1943, II, 153.

Adsorption analysis of amino-acids and peptides.—See A., 1943, I, 151.

Fluorometric determination of tocopherol. M. Kofler (*Helv. Chim. Acta*, 1942, **25**, 1469—1474).—The substance is dissolved in abs. EtOH and oxidised with conc. HNO_3. The resulting solution is shaken with H_2O and light petroleum. The residue from the last solvent is condensed with *o*-$C_6H_4(NH_2)_2$ in AcOH and the fluorescence of the resulting phenazine is compared with that produced analogously from a known wt. of tocopherol (**I**). The method determines essentially free (**I**); if tocopheryl esters are present the oxidation should be preceded by hydrolysis. H. W.

INDEX OF AUTHORS' NAMES, A., II.

JUNE, 1943.

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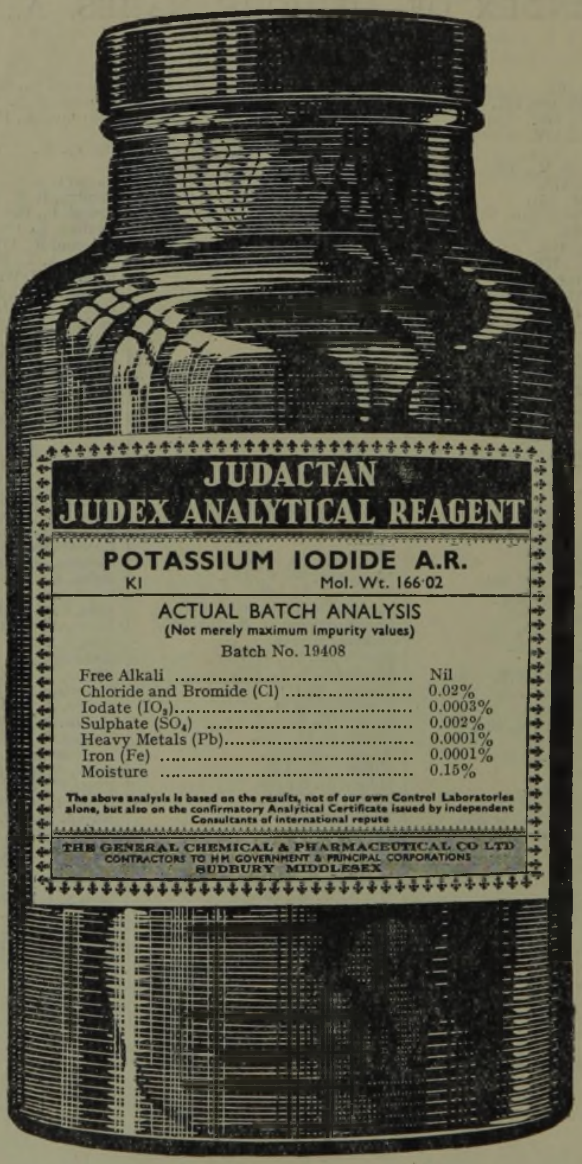

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