BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

JULY, 1939.

Conception of mesomerism in organic chemistry. B. EISTERT (Angew. Chem., 1939, **52**, 353—361).—Mesomerism, the displacement of π electrons in systems with multiple linkings from the defined extreme positions into an intermediate arrangement which cannot be symbolised in the usual manner, is a phenomenon necessitated by much experiment and explained fundamentally. The electron theory enables this intermediate state to be circumscribed by giving the limits within which the π electron cloud remains "suspended." For mesomerism, the method of writing limiting formulæ has the advantage that it gives definite information concerning the electron balance; usually these formulæ are also the reaction formulæ of mesomeric compounds. The following are the constitutional essentials so that two or more isomeric formulæ have mesomeric and not tautomeric relationships. There must be the same steric sequence of all actually united atoms (*i.e.*, they must not stand in ionic relationship) and only the distribution of the electrons must be different; all atoms concerned with electron displacements must be able to lie in a plane. The energy of a mesomeric system is less than that calc. for each of the limiting formulæ. The passage to a mesomeric "energy cavity" and the consequent gain in energy is frequently the driving force for reactions in systems with multiple linkings. The quantum theoretical foundation for mesomerism and for its representation by limiting formulæ is given by regarding the total function of the π electron cloud approx. as "resonance" between the functions proper to the limiting formulæ. H. W.

Kinetics of cracking of normal paraffin hydrocarbons under pressure.—See A., 1939, I, 375.

Vapour-phase nitration of *iso*pentane [β-methylbutane]. L. W. SEIGLE and H. B. HASS (Ind. Eng. Chem., 1939, **31**, 648—650; cf A., 1938, II, 79).—$CHMe_2Et$ when nitrated at 380° or 420° gives $COMe_2$, $MeNO_2$ (6 : 2), $EtNO_2$ (6 : 6), $Pr^{\beta}NO_2$ (6 : 11), $Bu^{\beta}NO_2$ + $CHMeEt{\cdot}NO_2$ (12 : 10), $CHMeEt{\cdot}CH_2{\cdot}NO_2$ (11 : 28), $CMe_2Et{\cdot}NO_2$ (19 : 14), $CH_2Bu^{\beta}{\cdot}NO_2$ (13 : 13), and $CHMePr^{\beta}{\cdot}NO_2$ (27 : 16%). A. T. P.

Isomerisation of *n*-octane. A. P. MESCHTSCHERIAKOV and E. P. KAPLAN (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 1055—1060).—*n*-Octane with HCl and $AlCl_3$ or HBr and $AlBr_3$ at room temp. undergoes 15—40% isomerisation, the octane no. being increased by 16 after 140 hr. The product after 1 hr. at 408—418° under pressure in presence of MoS_3 has an octane no. 8 > that of *n*-octane; in the change from *n*-octane to methylheptane, or from this to dimethylhexane, there is an increase of 30—40. A. LI.

βζ-Dimethylheptane: its synthesis and comparison with an *iso*nonane from petroleum. J. D. WHITE, F. W. ROSE, jun., G. CALINGAERT, and H. SOROOS (J. Res. Nat. Bur. Stand., 1939, **22**, 315—319).—βζ-Dimethylheptan-δ-ol hydrogenated (Calingaert and Soroos, A., 1936, 107) gives βζ-dimethylheptane of 99·6% purity, the properties of which, extrapolated to 100% (b.p. 135·21±0·02°, f.p. −102·95± 0·10°, etc.), agree with the vals. for an *iso*nonane from petroleum (B., 1937, 314). F. R. G.

Cracking of hexadecane under pressure. A. D. PETROV and M. A. TSCHELTZOVA (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 1033—1037).—Cracking of $C_{16}H_{34}$ at 440—460° under pressure is accompanied by considerable isomerisation of the products. In presence of H_3PO_4, the isomerisation and the yield of gas, unsaturated hydrocarbons, and liquid boiling above 200° are increased. A. LI.

Polymerisation of ethylene, propene, and Δ^{α}-butene in still discharges. D. N. ANDREEV (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 1039—1053).—With the gas flowing at 18—20 l. per hr., the chief products are unsaturated aliphatic hydrocarbons, with considerable quantities of the dimeride of the original hydrocarbon. Of the product from C_3H_6 65%, from C_4H_8 46%, and from C_2H_4 29%, boils below 160°. A. LI.

Exchange reaction between ethylene and deuterium on a nickel catalyst.—See A., 1939, I, 377.

Infra-red analysis applied to the exchange reaction between ethylene and deuteroethylene.—See A., 1939, I, 377.

Isomerisation phenomena accompanying the reduction of diolefinic and aromatic hydrocarbons by means of calcium–ammonia. B. A. KAZANSKI and N. F. GLUSCHNEV (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 1065—1072).—With Ca–NH_3 at 0°, $(\cdot CMe{:}CH_2)_2$, *cyclo*pentadiene, $CHPh{:}CH_2$, $CHPh{:}CHMe$, $CH_2{:}CMe{\cdot}[CH_2]_2{\cdot}CMe{:}CH_2$, and $CH_2Ph{\cdot}CH{:}CH_2$ are reduced respectively to $CMe_2{:}CMe_2$, *cyclo*pentene, 1-ethyl- and 1-*n*-propyl-Δ^1-*cyclo*hexene (I), $(:CH{\cdot}CMe_2)_2$, and (I). Non-conjugated systems undergo isomerisation to conjugated systems before reduction. A. LI.

Preparation of true acetylene hydrocarbons. D. BODROUX (Compt. rend., 1939, **208**, 1022—1024).—The Na_1 derivative of NH_2Ph with αα- or αβ-dihalogeno-derivatives of saturated hydrocarbons in

Et_2O at room temp. affords a product decomposed by H_2O to the unsaturated hydrocarbon. $(CH_2Cl)_2$, $(CH_2Br)_2$, or $CHMeCl_2$ affords CH:CH; $CHMeBr{\cdot}CH_2Br$ gives CMe:CH (cf. Bourguel, A., 1925, i, 770); heptylidene dichloride gives Δ^a-heptinine; $CHPhBr{\cdot}CH_2Br$ gives CPh:CH. $CHPh{:}CHBr$ with $NaNH_2$ in Et_2O containing a small amount of NH_2Ph gives CPh:CH in good yield. J. L. D.

Action of lithium on an optically active aliphatic chloride. D. S. Tarbell and M. Weiss (J. Amer. Chem. Soc., 1939, **61**, 1203—1205).—*Li α-methyl-n-heptyl* (I) is best (56%) obtained from n-$C_6H_{13}{\cdot}CHMeCl$ (II) and Li (excess) in Et_2O at 0°; treating the solution with CO_2 gives *dl*-n-$C_6H_{13}{\cdot}CHMe{\cdot}CO_2H$, but the unaltered (I) is slightly racemised. Racemisation probably occurs during reaction of (I) with Li rather than during carbonation. Racemisation of unaltered CHPhMeCl by Na may be due to the exchange reaction: *dl*-NaCHPhMe + *d*-CHPhMeCl → *dl*-NaCHPhMe + *dl*-CHPhMeCl. R. S. C.

Halogenation of optically active *tert.* carbinols. P. G. Stevens and N. L. McNiven (J. Amer. Chem. Soc., 1939, **61**, 1295—1296).—With HCl in pentane at 25°, $Bu^{\beta}{\cdot}[CH_2]_2{\cdot}CMeEt{\cdot}OH$, b.p. 89·0°/15 mm., $[\alpha]_D^{23}$ −0·45°, gives a *tert.* chloride, b.p. 71·0°/9 mm., $[\alpha]_D^{23}$ −0·28°, but at −78° gives the enantiomeric chloride (impure), b.p. 69—70°/8 mm., $[\alpha]_D^{23}$ +0·17°. Reaction may thus take either of two courses (cf. Levene *et al.*, A., 1939, II, 155). R. S. C.

Retardation of chemical reactions. IX. Stabilisation of perchloroethylene [tetrachloroethylene] for medicinal purposes. K. C. Bailey (J.C.S., 1939, 767—769; cf. B., 1938, 977).—Decomp. of C_2Cl_4, catalysed by light, is inhibited by thymol (1 : 500,000), not quite so well by Et_2O, EtOH, $CS(NH_2)_2$, $Na_2S_2O_3$, or o-$C_6H_4Me{\cdot}NH_2$, and by various other substances. An excess of solid $Na_2S_2O_3$ or $CS(NH_2)_2$ is more efficient than a saturated solution, probably owing to replacement of the inhibitor in solution as it is destroyed. R. S. C.

Action of Raney nickel on alcohols. Probability of a union of the catalyst with the hydrogen receptors. R. Paul (Compt. rend., 1939, **208**, 1319—1321).—Raney Ni with boiling primary and *sec.* alcohols forms aldehydes or ketones with evolution of H_2; part of the alcohol is reduced. Furfuryl and cinnamyl alcohol afford methylfuran and propenylbenzene, respectively, with the appropriate aldehydes, which react further (temp. >90°) to form furan and $CHPh{:}CH_2$, respectively, and CO_2. The ketones derived from *sec.* alcohols do not react with Raney Ni at 180° (cf. Palfray and Sabetay, A., 1939, II, 115). If the alcohol is slowly distilled with Raney Ni a much better yield of ketone results, probably because the catalyst–ketone union is continually broken down during the distillation. Thus $CHMeEt{\cdot}OH$, $CHEtPr{\cdot}OH$, β- and γ-hydroxyoctane, and $Pr^{\beta}OH$ yield 90%, 80%, 95%, 95%, and 30%, respectively, of the corresponding ketones. If an ethylenic or acetylenic compound is added to an easily oxidisable alcohol and Raney Ni, dehydrogenation is much reduced or prevented. J. L. D.

Butane-βγ-diol and its esters. L. Denivelle (Compt. rend., 1939, **208**, 1024—1025).—Butane-βγ-diol (I), m.p. 26°, b.p. 178°/742 mm., with H_3PO_4, H_2SO_4, P_2O_5, or anhyd. $ZnCl_2$ gives COMeEt. Equimol. amounts of (I) and $SOCl_2$ in C_6H_6 containing C_5H_5N (2 mols.) afford a neutral *sulphoxide*, b.p. 70—71°/12 mm., which when passed over $CaCO_3$ at 275° gives a mixture of βγ-oxidobutane (II) and COMeEt. With kaolin at 575°, $CH_2{:}CH{\cdot}CH{:}CH_2$ (III) (8—10%; small amounts at 450°) is formed. The diacetate of (I) with kaolin at 350—575° affords (III); with $CaCO_3$ at 225°, (II) and COMeEt are formed. J. L. D.

***iso*Propylideneglyceraldehyde. IV. Preparation of *d*(+)-*iso*propylideneglycerol. V. Synthesis of optically active glycerides from *d*(+)-*iso*propylideneglycerol. VI. Synthesis of the biological *l*(−)-α-glycerophosphoric acid.** E. Baer and H. O. L. Fischer (J. Biol. Chem., 1939, **128**, 463—473, 475—489, 491—500; cf. A., 1936, 708).—IV. d(+)-iso*Propylideneglycerol* (I), b.p. 78·5—79°/11 mm., $[\alpha]_D^{20\cdot5}$ +12·6°, +10·8° in C_6H_6, −1·70° in H_2O, +11·09° in C_5H_5N, +10·7° in MeOH, is obtained by catalytic reduction (Ni) of *iso*propylidene-*d*-glyceraldehyde (improved prep. from *d*-mannitol). (I) with BzCl–quinoline gives the *Bz* derivative, b.p. 159—160·5°/10·5 mm., $[\alpha]_D^{18}$ +12·31°, and with MeI–Ag_2O gives the *Me* derivative, b.p. 43—44°/10·5 mm., $[\alpha]_D^{20}$ +20·14°, +12·88° in C_5H_5N.

V. Acylation of (I) in C_5H_5N or quinoline gives the following derivatives: *Ac*, b.p. 85—86°/10—11 mm., $[\alpha]_D^{20}$ +3·24°; *lauryl* (II), b.p. 130—131°/0·002 mm., $[\alpha]_D^{20}$ +3·42°, +1·2° in C_5H_5N; *palmityl* (III), m.p. 33—35°, α_D^{50} +4·38°, $[\alpha]_D$ +2·5° in C_5H_5N; *stearyl* (IV), m.p. 43·5°, α_D^{50} +3·0°, $[\alpha]_D$ +1·9° in C_5H_5N. All have zero rotation in C_6H_6. Acid hydrolysis of (II), (III), and (IV) gives respectively: *α-lauryl-* (V), m.p. 53—54°, $[\alpha]_D$ −3·76° in C_5H_5N, *α-palmityl-* (VI), m.p. 71—72°, $[\alpha]_D$ −4·37° in C_5H_5N, and *α-stearyl-glycerol* (VII), m.p. 76—77°, $[\alpha]_D$ −3·58° in C_5H_5N. *Glycerol* α-p-*toluenesulphonate* (VIII), m.p. 63—64°, $[\alpha]_D$ −7·3° in C_5H_5N, and α-p-*nitrobenzoate* (IX), m.p. 88—89°, $[\alpha]_D$ −17·1° in EtOH, are also described. These α-monoglycerides belong to the *l*-glyceraldehyde series. On keeping (1 year) (V), (VI), and (VII) show a fall in rotation due to migration of the acyl groups, (VIII) and (IX) being unchanged. Acylation of (V), (VI), (VII), and (IX) in C_5H_5N or quinoline gives respectively: *glycerol α-laurate βγ-distearate* (X), m.p. 48·5°, α_D 0° in C_5H_5N, *α-palmitate βγ-dilaurate* (XI), m.p. 44°, α_D 0° in C_5H_5N, *α-stearate βγ-dipalmitate* (XII), m.p. 62·5°, α_D 0° in C_5H_5N or $CHCl_3$, *βγ-dibenzoate α-p-nitrobenzoate* (XIII), m.p. 87—88°, $[\alpha]_D$ −19·9° in $C_2H_2Cl_4$. Although (X), (XI), and (XII) have zero rotation, they are not considered to be racemic, because (V), (VI), and (VII) are not racemised in C_5H_5N and (XIII) is optically active. It is considered that natural triglycerides with zero rotation are not necessarily racemic.

VI. *l*(−)-α-Glycerophosphoric acid (XIV) (*Et₂ ether* of *Et₂ ester*, b.p. 100—100·5°/0·13 mm., $[\alpha]_D^{19}$ −5·31°, −5·76° in EtOH) is synthesised from (I) by the method of Fischer and Pfähler (A., 1920, i, 807) and is identical with the glycerophosphoric acid in phos-

phatides (Kasser *et al.*, A., 1926, 384) and that formed as an intermediate in alcoholic fermentation and glycolysis (Meyerhof *et al*, A., 1933, 1080). (XIV) belongs to the *l*-glyceraldehyde series and therefore cannot arise biologically from the natural *d*-glyceraldehyde-3-phosphoric acid, but must be formed by asymmetrical fermentative reduction from dihydroxyacetonephosphoric acid. S. H. H.

Thermal decomposition of diethyl ether.—See A., 1939, I, 375.

Mechanism of hydrolysis of carboxylic esters and of esterification of carboxylic acids. Acid hydrolysis of an ester with heavy oxygen as isotopic indicator. S. C. Datta, J. N. E. Day, and C. K. Ingold (J.C.S., 1939, 838—840).—During hydrolysis of Me H succinate by HCl in H_2O containing $H_2{}^{18}O$, the ^{18}O enters the acid, thus confirming the accepted mechanism. The fundamental mechanism of hydrolysis of esters in acid, neutral, and alkaline solutions, and the evidence in favour thereof, are reported. R. S. C.

Ancillary mechanisms in the hydrolysis and esterification of carboxylic esters. E. D. Hughes, C. K. Ingold, and S. Masterman (J.C.S., 1939, 840—842).—Esterification of n-C_6H_{13}·CHMe·OH by AcOH in H_2O occurs without racemisation, but in dil. H_2SO_4 there is slight racemisation. The reaction mechanisms are discussed. R. S. C.

Compressed catalysts [for preparation of ethyl acetate from ethyl alcohol].—See A., 1939, I, 377.

Polymerisation of vinyl acetate.—See A., 1939, I, 377.

Action of sodium on fatty acid chlorides of higher mol. wt. A. W. Ralston and W. M. Selby (J. Amer. Chem. Soc., 1939, **61**, 1019—1020).—n-$C_{11}H_{23}$·COCl, n-$C_{13}H_{27}$·COCl, n-$C_{15}H_{31}$·COCl, and n-$C_{17}H_{35}$·COCl with Na in hot Et_2O give *μν-dilauroyloxy-Δ$^{\mu}$-tetracosene*, m.p. 42—43°, *ξο-dimyristoyloxy-Δ$^{\xi}$-octacosene*, m.p. 54—55°, *πρ-dipalmitoyloxy-Δ$^{\pi}$-dotriacontene*, m.p. 61—62°, and *στ-distearoyloxy-Δ$^{\sigma}$-hexatriacontene*, m.p. 67—68°. Structures are proved by hydrolysis to RCOCl and CH_2R·COR. The reaction mechanism is: $2RCOCl + 2Na \rightarrow (RCO)_2 \rightarrow (+2Na)$ $(\dot{C}R{\cdot}ONa)_2 \rightarrow (+ROCl)$ $(RCO_2{\cdot}\dot{C}R)_2$. R. S. C.

Chemical examination of sugar-cane wax. N. L. Vidyarthi and M. Narasingarao (J. Indian Chem. Soc., 1939, **16**, 135—143).—Sugar-cane wax, extracted by C_6H_6 from the dried press mud of a sulphitation factory, contains 43·7% of acid and 53·6% of unsaponifiable matter. The acids, separated by fractionation of the Et esters, are resin (4·5%), hexoic (0·6%), palmitic (27·7%), stearic (22·4%), oleic (41·5%), and arachidic acid (3·3%). The unsaponifiable matter, separated by treatment with o-$C_6H_4(CO)_2O$, contains n-triacontanol (80%), brassica-, stigma-, and sito-sterol (10%), and n-pentatriacontane (5%). The wax contains no dibasic or OH-acids. J. D. R.

Methods of separating oleic acid from saturated acids and from linoleic acid. Preparation of oleic acid. P. J. Hartsuch (J. Amer. Chem. Soc., 1939, **61**, 1142—1144).—Crude oleic acid from olive- or tea-seed oil is best freed from much saturated acid by dissolution in $COMe_2$ at −18° to −20°; the material in the filtrate is freed from much linoleic acid by crystallisation from $COMe_2$ at −60°. The 96% pure product is then fractionally distilled, giving oleic acid containing 1% of linoleic and 1·2% of saturated acids. R. S. C.

Esters of *iso*oleic acids. A. A. Tscherno-jarova (J. Gen. Chem. Russ., 1939, **9**, 178—181).—*Me*, b.p. 196—197°/8 mm., *Pr$^{\alpha}$*, b.p. 199—200°/5 mm., *Pr$^{\beta}$*, b.p. 192—194°/5—6 mm., *Bu$^{\alpha}$*, b.p. 202—204°/6—7 mm., iso*amyl*, b.p. 216—217°/5—6 mm., and sec.-*octyl petroselate*, b.p. 236—239°/5—7 mm., *Pr$^{\alpha}$*, b.p. 198°/10 mm., *Bu$^{\alpha}$*, b.p. 216—218°/8 mm., iso*amyl*, b.p. 247—250°/15—16 mm., and sec.-*octyl* iso*oleate*, b.p. 240—241°/6—7 mm., *Me*, b.p. 214°/7 mm., *Pr$^{\alpha}$*, b.p. 228°/9 mm., *Bu$^{\alpha}$*, b.p. 229°/10 mm., iso*amyl*, b.p. 241°/9 mm., and sec.-*octyl* ι-*chlorostearate*, b.p. 254°/9 mm., and *Me*, b.p. 193—195°/8 mm., *Pr$^{\alpha}$*, b.p. 205—208°/10 mm., *Bu$^{\alpha}$*, b.p. 219°/10 mm., and iso*amyl* iso*petroselate*, b.p. 220—222°/8 mm., have been prepared, and the n, d, and I val. of the esters determined. The position of the double linking does not significantly affect the physical properties of the esters. R. T.

Elaidinisation of linoleic acid. J. P. Kass and G. O. Burr (J. Amer. Chem. Soc., 1939, **61**, 1062—1066).—When warmed for a short time with $NaNO_2$ in 1 : 1 aq. HNO_3 or 1 : 3 H_2SO_4–H_2O, or when heated with a little Se in N_2 at 200—210°, linoleic acid gives *linolelaidic acid* (I), m.p. 28—29° (*Pb* salt; *dibromide*, m.p. 78°, insol. in light petroleum), and a mixed liquid β-acid (sol. dibromide). (I) is spectroscopically inactive, is oxidised (after esterification) by $KMnO_4$ in $COMe_2$ to hexoic acid and alkyl azelate, or, as acid, by $KMnO_4$ in aq. NaOH at 0° to γ-, m.p. 122°, and δ-sativic acid, m.p. 146° [names previously reversed (Nicolet *et al.*, A., 1922, i, 320)]. The β-acid gives ε-, m.p. 126°, and ζ-*sativic acid*, m.p. 158°, and an acid, m.p. 131—135°, which may be η-sativic acid or a mixture. It is concluded that no unchanged linoleic acid remains after treatment and that isomerisation occurs first at the θ- and then at the λ-ethylenic linking. R. S. C.

Structure of petroselic acid. A .A. Tscherno-jarova (J. Gen. Chem. Russ., 1939, **9**, 149—152).—Ozonolysis of Me petroselate yields lauric and adipic acid; petroselic acid is therefore Δ$^{\zeta}$-heptadecenoic acid. R. T.

Synthesis of αα′-diketoadipic acid. Its biological importance. F. Wille (Annalen, 1939, **538**, 237—260).—Me_2 *cyclo*butene-1 : 2-dicarboxylate and H_2O_2 in Et_2O give *Me_2 αα′-diketoadipate* (60%) (I), double m.p. 98—100° and 164—165° [*bis*-2 : 4-*dinitrophenylhydrazone*, m.p. 242—243° (decomp.); bisphenylhydrazone, m.p. 143—145° (lit. 130—131°)]. At 120—140° (I) gives the dienol form, *Me_2 αα′-dihydroxymuconate* (II), m.p. 169—170° (reddish-brown $FeCl_3$ colour). Hydrolysis of (I) by $Ba(OH)_2$ gives *αα′-diketoadipic* (III), decomp. 234° (loss of CO_2 at 110°) [with CH_2N_2 gives (I); *bis*-2 : 4-*dinitrophenylhydrazone*, m.p. 245° (decomp.)], and *αα′-dihydroxymuconic acid* (IV), m.p. 226—227° (decomp.)

[in equilibrium with (III) in H_2O]. CH_2N_2 converts (IV) into *Me*$_2$ *αα'-dimethoxymuconate*, m.p. 116°, which is similarly obtained from (II), whereas (I) gives only oils. With aq. NH_2Ph (III) yields 1-*phenylpyrrole*-2 : 5-*dicarboxylic acid*, m.p. 256—259° (*Me*$_2$ ester, m.p. 110°), and with H_2O_2 yields CO_2 and $(\cdot CH_2 \cdot CO_2H)_2$. Only the dienol is a reducing agent (dichloroindophenol, methylene-blue; with I in $NaHCO_3$ gives CHI_3). (III) is determined by its O_2 absorption (10% excess) in aq. NaOH at 38°. Rat kidney, rat liver, and pigeon breast muscle destroy (III) anaërobically, but the rates bear no relation to those for $AcCO_2H$. Yeast also destroys (III) in O_2 or N_2, but produces <1 mol. of CO_2 and some acid (traces only of HCO_2H); the reaction is thus not due to co-carboxylase. Fermentation of $AcCO_2H$ thus does not proceed by way of (III).

R. S. C.

Structure of the aldobionic acid from flaxseed mucilage. R. S. Tipson, C. C. Christman, and P. A. Levene (J. Biol. Chem., 1939, **128**, 609—620).—The aldobionic acid (I) (improved prep.) from flaxseed mucilage on complete methylation ($NaOH$–Me_2SO_4, CH_2N_2, and Ag_2O–MeI) yields a *Me* ester of a *pentamethyl-methylaldobionide*, $C_{19}H_{34}O_{11}$, b.p. 165—169°/0·1—0·2 mm., m.p. 93—94° (indef.), $[\alpha]_D^{24}$ +129·8° in H_2O, hydrolysed by HCl to βγδ-trimethylgalacturonic acid and 3 : 4-dimethyl-*l*-rhamnose (II), which on oxidation with HNO_3 followed by esterification and treatment with NH_2Me yields *hydroxydimethoxyglutardi*(*methylamide*); (I) is therefore 2-(*d*-galacturonopyranosido)-*l*-rhamnose. An improved prep. of (II) from *l*-rhamnose is described.

J. D. R.

Constitution of arabic acid. I. Isolation of 3-*d*-galactosido-*l*-arabinose. F. Smith (J.C.S., 1939, 744—753).—Arabic acid (I) (prep. from gum arabic by cold, dil. HCl), $[\alpha]_D^{20}$ −28° in H_2O, is hydrolysed by hot 0·01N-H_2SO_4 or hot H_2O (p_H 2·2; final $[\alpha]_D$ +42° to +42·5° in H_2O) to ~1 mol. each of a degraded arabic acid, *l*-arabinose, *l*-rhamnose, and 3-*d*-galactopyranosido-*l*-arabinose (II). The sugars are separated by methylation (Me_2SO_4–NaOH, followed by Ag_2O–MeI) and subsequent distillation into trimethylmonoglucosides (*A*) and *heptamethyl*-3-d-*galactopyranosido*-1-*arabopyranose* (III), m.p. 82°, b.p. 180° (bath)/0·7 mm. Hydrolysis (3·5% H_2SO_4) and oxidation (Br; 30°) of (*A*) gives lactones, separated by conversion into 2 : 3 : 4-trimethyl-*l*-arabon-phenylhydrazide and -amide and 2 : 3 : 4-*l*-rhamnonphenylhydrazide, thus proving the nature of the monosaccharides. Since (III) has $[\alpha]_D^{18}$ +162° in H_2O, the biose linking may be of the α-type. The structure of (I) is proved as follows. 7% H_2SO_4 hydrolyses (III) to inseparable glucosides (*B*), which with MeI–Ag_2O give 2 : 3 : 4 : 6-tetramethyl-β-methylgalactopyranoside (IV) and 2 : 3 : 4-trimethylmethyl-*l*-arabopyranoside (V), identified by conversion (Br, followed by NH_3–MeOH) into the amides. Since (V) is obtained also from (*B*), the reducing group of the galactose provides the biose link. The nature of (*B*) is also proved by prep. of 2 : 3 : 4 : 6-tetramethylgalactose-anilide (VI) by NH_2Ph–MeOH and of 2 : 4-dimethyl-*l*-arabolactone, $[\alpha]_D^{18}$ +85° → +27° in H_2O in 14·5 hr. (therefore a δ-lactone) (with NH_3–MeOH gives 2 : 4-*dimethyl*-l-*arabonamide*, m.p. 158°, which gives a negative Weerman reaction and thus has OMe at $C_{(2)}$). The $C_{(1)}$ of the galactose is thus joined to the $C_{(3)}$ of the arabinose. The dimethylarabinose remaining after removal of the (VI) is converted by HNO_3 (*d* 1·2) at 50° into β-*hydroxy*-αα'-*dimethoxy*-l-*araboglutaric acid* [*Me*$_2$ ester, b.p. 115° (bath)/0·02 mm., $[\alpha]_D^{23}$ +41·3° in MeOH; *diamide*, m.p. 285° (decomp.), $[\alpha]_D^{17}$ +62·1° in H_2O]. Autolysis of (I) and subsequent treatment with MeI–Ag_2O yields 2 : 3 : 5-trimethyl-*l*-arabo- and -methyl-*l*-rhamno-furanoside and *heptamethyl*-3-d-*galactopyranosido*-l-*arabofuranose* (VII), b.p. 170—180° (bath)/0·01 mm., $[\alpha]_D$ +102° in H_2O. Hydrolysis of (VII) by H_2SO_4 gives (IV) and 2 : 5-*dimethyl*-l-*arabinose* (VIII), $[\alpha]_D^{16}$ +46·6° in H_2O; the latter product is oxidised to 2 : 5-dimethyl-γ-*l*-arabonolactone, m.p. 60°, $[\alpha]_D^{15}$ −59·7° → <−44·8° in H_2O (free acid, $[\alpha]_D^{18}$ +25·8° → −16·0° in H_2O in 120 hr.), which gives 2 : 5-*dimethyl*-l-*arabonamide*, m.p. 131°, $[\alpha]_D^{18}$ +38° in H_2O (negative Weerman test), or (by MeI–Ag_2O) 2 : 3 : 5-trimethyl-γ-*l*-arabonolactone and thence the derived amide. 2 : 3-Dimethyl-*l*-arabinose differs from (VIII), which has thus the structure cited. Since (I) is so readily hydrolysed, it probably contains (II) in the arabofuranose form. 3-β-*d*-Galactosido-*d*-arabinose (prep. from lactose; isolated as benzylphenylhydrazone and regenerated therefrom by PhCHO) with Me_2SO_4–NaOH–H_2O–$COMe_2$ gives a *Me*$_6$, m.p. 136°, $[\alpha]_D^{18}$ −12·1° in MeOH, and *Me*$_7$ *ether*, hydrolysed by 4% H_2SO_4 to an inseparable mixture of 2 : 3 : 4 : 6-tetramethylgalactose and 2 : 4-dimethyl-*d*-arabinose. The latter product gives 2 : 4-*dimethyl*-d-*arabinoseanilide*, m.p. 142—143°, (by Br) 2 : 4-*dimethyl*-d-*arabonolactone*, $[\alpha]_D^{22}$ −85° → −33·0° in H_2O in 18 hr. (derived *amide*, m.p. 158°, $[\alpha]_D^{17}$ −58·8° in H_2O), and (by HNO_3) β-*hydroxy*-αα'-*dimethoxy*-d-*araboglutaric acid* [*Me*$_2$ ester, b.p. 135° (bath)/0·12 mm., $[\alpha]_D^{18}$ −32° in MeOH; *diamide*, m.p. 286° (decomp.), $[\alpha]_D^{17}$ −62·8° in H_2O], enantiomorphic with, and thus confirming the structures of, the products derived from (I).

R. S. C.

Mode of union of the galacturonic residues in pectic acid. P. A. Levene, G. M. Meyer, and M. Kuna (Science, 1939, **89**, 370).—Exhaustive methylation of pectic acid gives $C_{56}H_{90}O_{37}$ (OMe 45·40%) (I) corresponding with a structure composed of ~6 units. Hydrolysis of (I) gives $C_{50}H_{78}O_{37}$ (OMe 34·30%). The methylated polygalactoside, $C_{56}H_{102}O_{31}$ (OMe 47·33%), has been prepared by heating the exhaustively methylated material with Cu chromite catalyst in H_2 at 175°/3500 lb. per sq. in. for 6 hr. The rate of hydrolysis of the fully methylated pectic acid indicates a furanose structure for the galacturonic residues, the union of which is thus through $C_{(5)}$.

L. S. T.

Reaction of iron with thioglycollic acid.—See A., 1939, I, 387.

Mechanism of the formation of the dichloride of sulphoacetic acid. Multimolecular chloroanhydrides of sulphoacetic acid. R. Vieille-fosse (Compt. rend., 1939, **208**, 1505—1507).—$SO_3H \cdot CH_2 \cdot CO_2H$ when boiled with excess of $SOCl_2$ affords little $SO_2Cl \cdot CH_2 \cdot COCl$ but when the excess of $SOCl_2$ is removed by heating in vac., a prolonged

liberation of gas occurs with the formation of a multimol. product (I) (Cl determination and acid liberated in contact with H_2O) which is unstable and usually consists of a mixture of compounds derived from 2 or 3 units of $SO_3H{\cdot}CH_2{\cdot}COCl$. $SO_2Cl{\cdot}CH_2{\cdot}CO_2H$ is only slowly decomposed on prolonged heating. J. L. D.

Action of periodic acid on acetone and diethyl ketone. P. Fleury and R. Boisson (Compt. rend., 1939, **208**, 1509—1512).—0·1N-$COMe_2$ when treated with 0·05—0·2N-HIO_4 at 37° utilises one O per mol. of $COMe_2$ in 5 days. At 100° a max. of 3 O per mol. is used to give AcOH and CH_2O. MeOH may be an initial reaction product (cf. A., 1937, II, 273) which is oxidised by HIO_4 in presence of $COMe_2$. Similarly treated, $COEt_2$ gives $EtCO_2H$ and EtOH. The ketones probably exist as the $:C(OH)_2$ derivatives before scission of the C chain. J. L. D.

Mechanism of contact hydrogenation of carbonyl groups in presence of metallic catalysts.—See A., 1939, I, 377.

Keto-ethers derived from α-chloroethyl *sec.*-butyl ether. R. J. Speer with H. R. Henze (J. Amer. Chem. Soc., 1939, **61**, 1226—1227).—Paracetaldehyde, *sec.*-BuOH, and HCl give 83% of *CHMeCl* sec.-*Bu ether*, b.p. 109° (decomp.)/741 mm., 38—39° (slight decomp.)/20 mm., converted by AgCN in C_6H_6 into *CHMeCN* sec.-*Bu ether*, b.p. 162°/744 mm. This and the appropriate Grignard reagent give *Me*, b.p. 162—163°/750 mm. (*semicarbazone*, m.p. 117—118°), and *Et*, b.p. 174°/747 mm., α-sec.-*butoxyethyl ketone* (*semicarbazone*, m.p. 126—127°), α-sec.-*butoxyethyl* Pr^{α}, b.p. 189°/750 mm. (*semicarbazone*, m.p. 116°), Pr^{β}, b.p. 186°/751 mm. (no semicarbazone), Bu^{α}, b.p. 212°/750 mm. (*semicarbazone*, m.p. 106—107°), Bu^{β}, b.p. 202°/747 mm. (*semicarbazone*, m.p. 100°), sec.-*Bu*, b.p. 206°/751 mm. (no semicarbazone), n-*amyl*, b.p. 226°/745 mm. (*semicarbazone*, m.p. 78°), and iso*amyl*, b.p. 221°/747 mm. (*semicarbazone*, m.p. 104°), *ketone*. The ketones do not condense with isatin. M.p. are corr. R. S. C.

Synthesis of aldehydo-sugars. C. D. Hurd and E. M. Filachione (J. Amer. Chem. Soc., 1939, **61**, 1156—1159).—Compounds, $RCO_2{\cdot}CHR'{\cdot}CH{:}CH_2$, are converted by O_3 into $RCO_2{\cdot}CHR'{\cdot}CHO$, if the ozonide is decomposed by 20% aq. $AcCO_2H$, the $AcCO_2H$ removing the H_2O_2 and largely preventing formation of the acid. Thus, $CH_2{:}CH{\cdot}CH_2{\cdot}OBz$, b.p. 122—123°/24 mm., gives 56% of benzoyloxyacetaldehyde (2 : 4-*dinitro*-, m.p. 186—187°, and p-*nitro-phenylhydrazone*, m.p. 155—156°), but only 25% of aldehyde and 47% of $OBz{\cdot}CH_2{\cdot}CO_2H$ if H_2O alone is used. $CH_2{:}CH{\cdot}CH_2{\cdot}OAc$ gives $OH{\cdot}CH_2{\cdot}CHO$, $OH{\cdot}CH_2{\cdot}CO_2H$, and AcOH, hydrolysis also occurring. *Erythrol dibenzoate*, b.p. 199—200°/6 mm., gives *dibenzoyl*-dl-*glycerose* (70%), m.p. 55—56° (2 : 4-*dinitrophenylhydrazone*, m.p. 151—152°), and 20% of *dibenzoyl*-dl-*glyceric acid*, m.p. 88—89°. *Mannitol triformate* (prep. by 80% HCO_2H at 140°), m.p. 108—111°, $[\alpha]_D^{24}$ +10·4° in $COMe_2$, and O_3 give, among other products, impure (?) 2-vinyl-, b.p. 104—107°, and (?) 2-α-*hydroxy*-β-*formoxyethyl*-2 : 5-*dihydrofuran*, b.p. 135—142°/17 mm., $[\alpha]_D^{24}$ −32·9° in $CHCl_3$. Triacetylglucal is hydrolysed during the reaction, giving AcOH, di- and triacetylarabinose. R. S. C.

Preparation of *d*-erythrulose. K. Iwadare (Bull. Chem. Soc. Japan, 1939, **14**, 131—134).—Prep. of *iso*propylidene-*d*-mannitol and thence by $Pb(OAc)_4$ of *iso*propylidene-*d*-glyceraldehyde (I) is described. With KOH–$KMnO_4$ (I) gives *K* iso*propylidene*-d-*glycerate*, $[\alpha]_D^{15}$ +23·7° in H_2O, the acid *chloride*, b.p. 61°/15 mm., $[\alpha]_D^{15}$ +14·9° in Et_2O, from which is converted into the *amide*, m.p. 72—73°, $[\alpha]_D^{18}$ +39·1° in H_2O, or by CH_2N_2–Et_2O, followed by hot 1% H_2SO_4, into d-*erythrulose*, b.p. 68°/0·01 mm., $[\alpha]_D^{15}$ −11°±3° in (?) H_2O. The structure of the sugar is shown by its yielding *d*-threosazone, m.p. 168°. R. S. C.

2 : 3-Dimethyl-*l*-arabinose and its derivatives. F. Smith (J.C.S., 1939, 753—755).—Methyl-*l*-arabofuranoside gives the 5-*CPh*$_3$ *ether*, $[\alpha]_D^{20}$ −17° in $CHCl_3$, converted by MeI–Ag_2O into 5-*triphenylmethyl*-2 : 3-*dimethylmethyl*-l-*arabofuranoside*, $[\alpha]_D^{20}$ −12·3° in $CHCl_3$, which with HCl–$CHCl_3$, followed by HCl–MeOH, gives 2 : 3-*dimethylmethyl*-l-*arabinoside*, b.p. 86° (bath)/0·04 mm. 3% H_2SO_4 then gives 2 : 3-dimethyl-*l*-arabinose, $[\alpha]_D^{18}$ +86·4° → +107° in 2·5 hr. in H_2O (*anilide*, m.p. 139°), which yields 3-*methyl*-l-*arabinose-phenylosazone*, m.p. 163°, and (by Br) 2 : 3-*dimethyl*-γ-l-*arabonolactone*, b.p. 120° (bath)/0·03 mm., $[\alpha]_D^{18}$ −36° → −27° in 11 days in H_2O (gives the amide, m.p. 162°, $[\alpha]_D^{21}$ +17·4° in H_2O; negative Weerman test; free acid, $[\alpha]_D^{18}$ +8·2° → −25·4° in aq. H_2SO_4 in 74 hr.), converted by HNO_3 (*d* 1·42) into α-*hydroxy*-βα′-*dimethoxy*-l-*araboglutaric acid* [*Me*$_2$ ester, b.p. 140° (bath)/0·02 mm., $[\alpha]_D^{20}$ +6° in H_2O; *diamide*, m.p. 195°, $[\alpha]_D^{21}$ +26·8° in H_2O]. R. S. C.

Synthesis of 2 : 4 : 6-trimethylglucose. J. W. H. Oldham and M. A. Oldham (J. Amer. Chem. Soc., 1939, **61**, 1112—1113).—Treating di*iso*propylideneglucose 3-*p*-toluenesulphonate successively with HCl–H_2O–MeCN, Ac_2O–C_5H_5N, HCl–AcOH, and MeOH–Ag_2CO_3 gives β-methyl-2 : 4 : 6-trimethylglucoside 3-*p*-toluenesulphonate, but the α-form cannot be obtained. 4 : 6-*Benzylidene*-β-*methylglucoside* 3-*p*-*toluenesulphonate* (prepared by PhCHO and $ZnCl_2$), m.p. 174—176° (decomp.), $[\alpha]_D$ −93·3° in $CHCl_3$, could not be methylated. Di*iso*propylideneglucose 3-*p*-toluenesulphonate and 2% HCl–MeOH give a product, methylated to α-*methyl*-2 : 4 : 6-*trimethylglucoside* 3-p-*toluenesulphonate*, m.p. 123—124°, $[\alpha]_D$ +53·6° in $CHCl_3$. β-Methyl-2-methylglucoside, PhCHO, and $ZnCl_2$ give 4 : 6-*benzylidene*-2-*methyl*-β-*methylglucoside*, m.p. 170—171°, $[\alpha]_D$ −69·2° in $CHCl_3$, methylated to 4 : 6-benzylidene-2 : 3-dimethyl-β-methylglucoside and converted by *p*-$C_6H_4Me{\cdot}SO_2Cl$ into 4 : 6-*benzylidene*-2-*methyl*-β-*methylglucoside* p-*toluenesulphonate*, m.p. 135—136°. Hydrolysis then removes :CHPh and methylation gives 2 : 4 : 6-trimethyl-β-methylglucoside 3-*p*-toluenesulphonate, m.p. 103—104°, $[\alpha]_D$ +1·9° in $CHCl_3$, also obtained from 2 : 4 : 6-trimethyl-β-methylglucoside. The structure of 2 : 4 : 6-trimethylglucose is thus proved. R. S. C.

Carbohydrates. XXI. Ethylthioglucosides and 5 : 6-*iso*propylideneglucose. P. Brigl, K. Gronemeier, and A. Schulz (Ber., 1939, **72**, [*B*], 1052—1059).—Glucose Et_2 mercaptal (I) is converted

by glucose in 22% HCl at room temp. followed by acetylation into *α-ethylthioglucopyranoside tetra-acetate*, m.p. 97·5°, $[\alpha]_D$ +189·6° in $C_2H_2Cl_4$, +207° in EtOH, hydrolysed by $Ba(OH)_2$ to *α-ethylthioglucopyranoside* (II), m.p. 117°, [α] +269° in H_2O, which is non-reducing and evolves EtSH when heated with conc. HCl. (I) is converted by $COMe_2$ containing $CuSO_4$ with 21% of H_2O into 5 : 6-iso*propylideneglucose Et₂ mercaptal*, m.p. 74—75°, [α] −6·6° in EtOH (*triacetate*, m.p. 84·5°), converted by $HgCl_2$ in not too strongly acid solution into 5 : 6-iso*propylidene-ethylthioglucofuranoside*, m.p. 103°, [α] +114·5° in EtOH; this compound is also obtained from the α-form of Schneider and Sepp (A., 1916, I, 792), which must therefore be *α-ethylthioglucofuranoside*, leaving the pyranoside structure available for (II). Gradual addition of (II) in aq. $COMe_2$ to a mixture of $BaCO_3$ and $HgCl_2$ in H_2O at 50° gives 5 : 6-iso*propylideneglucose*, m.p. 120°, $[\alpha]_D^{17}$ +10·5° in H_2O, which reduces Fehling's solution strongly and gives a colour with fuchsin–H_2SO_3. It is converted by $COMe_2$ and anhyd. $CuSO_4$ into di*iso*propylideneglucose, m.p. 110°.

H. W.

Behaviour of sulphoxides towards sulphite. F. Micheel and H. Schmitz (Ber., 1939, **72**, [*B*], 992—994).—Thio-ethers are stable towards SO_3'' and α-ethyl-*d*-thioglucoside (I), m.p. 156°, $[\alpha]_D^{18}$ +120·0° in H_2O, is not attacked thereby; the production of minute amounts of mercaptan after prolonged action is ascribed to simple hydrolysis in the somewhat acidic medium (p_H ~4·5). Oxidation of (I) with 30% H_2O_2 in H_2O at 0° affords *α-ethyl-d-glucosidosulphoxide* (II), m.p. 120°, $[\alpha]_D^{18}$ +45·7° in H_2O, the persistence of the sugar chain in which is established by the production of a *tetra-acetate*, m.p. 139°, $[\alpha]_D^{18}$ +21·4° in EtOH. *dl*-Methionine is transformed by AcO_2H into the sulphoxide which, like (II), is reduced by $Na_2S_2O_5$ to the corresponding sulphide, fission of the C·S linking not being observed. *l*-Cystine disulphoxide reacts with $Na_2S_2O_5$ without formation of the SH group.

H. W.

β-*d*-2-Deoxygalactose. H. S. Isbell and W. W. Pigman (J. Res. Nat. Bur. Stand., 1939, **22**, 397—402).—Galactal in 5% aq. H_2SO_4 after keeping overnight at 0°, followed by agitation (50 hr.; 60°) with gradual addition of excess of $BaCO_3$, and final concn. affords β-d-2-*deoxygalactose*, m.p. 120—121°, $[\alpha]_D^{20}$ +41° → +37° in 5 min. → +60·5° (final) in H_2O buffered with 0·001N-K H phthalate. The observed mutarotation indicates that equilibrium is established between an α-pyranose modification and a labile substance.

F. N. W.

Action of baker's yeast on *d*-talose.—See A., 1939, III, 724.

***aldehydo*-Derivatives of *D*-αα-galaoctose (*D*-gala-*L*-galaoctose).** R. W. Hann, W. D. Maclay, and C. S. Hudson (J. Amer. Chem. Soc., 1939, **61**, 1270—1271).—D-*Gala*-L-*galaoctose Et mercaptal* (prep. in conc., aq. HCl), m.p. 214°, $[\alpha]_D^{20}$ −3·2° in dry C_5H_5N, gives a *hepta-acetate*, m.p. 106°, $[\alpha]_D^{20}$ +29·9° in $CHCl_3$, converted by $HgCl_2$–$CdCO_3$ in $COMe_2$ into aldehydo-D-*gala*-L-*galaoctose hepta-acetate* (I), m.p. 164—165°, $[\alpha]_D^{20}$ +71·3° in $CHCl_3$ (*semicarbazone*, m.p. 203—204°, $[\alpha]_D^{20}$ −27·0° in $CHCl_3$). This yields the *oxime hepta-acetate*, m.p. 179—179·5°, $[\alpha]_D^{20}$ +20·2° in $CHCl_3$, and thence by C_5H_5N–Ac_2O the *oxime octa-acetate*, m.p. 187—188°, $[\alpha]_D^{20}$ +14·9° in $CHCl_3$. Boiling with Ac_2O–NaOAc or heating alone at 190° then gives D-*gala*-L-*galaoctononitrile hepta-acetate*, m.p. 185°, $[\alpha]_D^{20}$ +8·5° in $CHCl_3$. With 2% of H_2SO_4 in 1 : 1 Ac_2O–AcOH (I) gives the *nona-acetate*, m.p. 149—150°, $[\alpha]_D^{20}$ +26·1° in $CHCl_3$. *D*-Galactose Et_2 mercaptal, m.p. 142—143°, has $[\alpha]_D^{20}$ −3·5° in C_5H_5N, +6·0° in EtOH, and −4·8° in H_2O. [α] of these compounds show no parallelism with those of the *L*-galactose series. These and previous results show that the relations existing among cyclic sugars do not hold for open-chain derivatives. M.p. are corr.

R. S. C.

Relations between rotatory power and structure in the sugar group. XXXI. Configuration of *D*-αα-manno-octose (*D*-manno-*L*-manno-octose). R. M. Hann, W. D. Maclay, A. E. Knauf, and C. S. Hudson (J. Amer. Chem. Soc., 1939, **61**, 1268—1269; cf. A., 1930, 1023).—Identification of Fischer's *D*-αα-manno-octose as *D*-manno-*L*-manno-octose is confirmed. The derived lactone with liquid NH_3 gives D-*manno*-L-*manno-octonamide*, m.p. 218—219° (rapid heating), $[\alpha]_D^{20}$ +9·8° in H_2O [*octa*-, m.p. 172—173° (corr.), $[\alpha]_D^{20}$ +15° in $CHCl_3$, and *hepta-acetate*, m.p. 99—100° (corr.), $[\alpha]_D^{20}$ −15·9° in $CHCl_3$], and with Na–Hg, followed by H_2–Raney Ni at 98°/133 atm., gives *D*-manno-*L*-manno-octitol, m.p. 262—263° (corr.) [*octa-acetate*, m.p. 166—167° (corr.), $[\alpha]_D^{20}$ 0 in $CHCl_3$].

R. S. C.

Caramelisation of sucrose with sulphuric acid. J. Milbauer (Chem. Listy, 1939, **33**, 132—133).—The process of caramelisation of aq. sucrose in 6M-H_2SO_4 is followed with the aid of a photo-electric cell. Addition of $HgSO_4$ does not accelerate the process.

R. T.

Sucrose octa-acetate. K. Šandera (Chem. Listy, 1939, **33**, 139—141).—Sucrose octa-acetate is prepared on a laboratory scale from Ac_2O and sucrose in C_5H_5N at 100—115°.

R. T.

Carpotroside, a new glycoside or heteroside from sapucainha (*Carpotrache brasiliensis*, Endl). R. D. de G. Paula (Rev. Soc. Brasil. Quím., 1938, **7**, 129—140).—The cake from sapucainha seeds after extraction of the oil contains 0·4% of H_2O-sol. *carpotroside* (formerly called carpotrochin), $(C_6H_{10}NO_3)_n$, blackens about 260°, $[\alpha]_D^{25}$ −7·106°. Acid hydrolysis gives PhCHO, an unidentified sugar, an aldehyde, and an indole derivative. No recognisable products were obtained by enzymic hydrolysis.

F. R. G.

Saponin of *Sarcostemma australe*, R. Br. J. W. Cornforth and J. C. Earl (J.C.S., 1939, 737—742).—This saponin (I) (Earl *et al.*, A., 1937, III, 245) is sol. in org. solvents and is purified by partition. It is mainly a mixture of sarcostin benzoate cinnamate *d*-glucosides. With 0·75% HCl–MeOH at 100° it gives an aglucone (II) and α-methylglucoside, and with boiling HCl–aq. EtOH gives (II) and *d*-glucose (isolated as phenylosazone; 1 mol. obtained by dil. H_2SO_4). With hot KOH–EtOH (II) gives 1 mol. each of BzOH, CHPh:CH·CO_2H, and *sarcostin* (III), $C_{21}H_{34}O_6$, $+H_2O$ (lost at 100°/vac. over P_2O_5), m.p. 266—267° after sintering or 170° (rapid heating;

resolidifies) [*triacetate* (prep. by Ac_2O–C_5H_5N), a resin, regenerates (III) when hydrolysed]. With KOH–EtOH, followed by Ac_2O–C_5H_5N, (I) gives *sarcostin glucoside hexa-acetate*, a resin. Adsorption (Al_2O_3) shows (II) to consist almost entirely of *sarcostin benzoate cinnamate*. Hydrolysis of (I) indicates the presence of monoacylated derivatives, but these are probably not originally present and the results follow from the instability in acid. (I), (II), and (III) give the Liebermann–Burchard test; (I) and (II) give the Legal test weakly. R. S. C.

The α-*d*-mannoside of sodium *l*-glycerate in the genus *Polysiphonia* of the Floridaceæ. H. Colin and J. Augier (Compt. rend., 1939, **208**, 1450—1453).—EtOH extracts *Na* α-d-*mannoside*-l-*glycerate*, decomp. at 270° after darkening at ~245°, $[\alpha]_D$ +108°, which with hot 2% H_2SO_4 gives mannose (60% yield); with sufficient cold H_2SO_4 it affords hydrated α-d-*mannoside*-l-*glyceric acid*, m.p. 88—89°, $[\alpha]_D^{15}$ of anhyd. material +105°, easily hydrolysed by excess of acid to mannose and *l*-glyceric acid. *P. fructiculosa* also contains the glucoside. J. L. D

Water-soluble glucosan from barley roots. W. Z. Hassid (J. Amer. Chem. Soc., 1939, **61**, 1223—1225).—Extraction of barley roots with 95% EtOH gives 0·4% of a H_2O-sol. *glucosan*, $[\alpha]_D$ +201° in H_2O (*Ac*$_3$ derivative, $[\alpha]_D$ +112° in $CHCl_3$), hydrolysed to glucose only and giving a *Me*$_3$ *ether*, $[\alpha]_D$ +204° in $CHCl_3$, which with (*a*) HCl–AcOH at 100° gives 2 : 3 : 6-trimethylglucose and (*b*) HCl–MeOH gives 2 : 3 : 4-trimethyl-β-methylglucoside. The glucose units are thus probably united by 1—6 linkings. R. S. C.

Pine bark. I. E. Lehmann and F. Eisenhuth (Ber., 1939, **72**, [*B*], 1003—1011).—The bark is extracted with org. solvents, mainly EtOH, to remove fats and waxes. Separation of skeleton substance (I) from phlobaphen pigment (II) is incomplete with Na_2CO_3 but nearly quant. with alkali hydroxide. The alkaline solution gives the pigment in degraded form when acidified (54—55% of the extracted bark). (I), thus obtained, is a coffee-brown material from which the remnants of (II) can be removed by the very protracted action of AcOH–H_2O_2, which also causes some degradation of (I). Treatment with SO_3'' causes the production of Na salts of sulphonic acids sol. in H_2O; a small proportion of (II) remains which can be removed by H_2SO_3, leaving (I) as a pale grey mass (~20—22% of the crude bark) in which cellulose fibres and woody fragments are noticeable. After treatment of (I) with Et_2O, (I) results containing 8% of ash which is almost entirely loose sand and can be reduced to 2% by use of CCl_4. Analyses shows this to be a polysaccharide $[(C_6H_{12}O_6)_2,(C_6H_{10}O_5)_3]_x$ or $[(C_6H_{12}O_6)_3 - 3H_2O]_x$. To remove the remainder of the sand from (I) the product is repeatedly evaporated with 40% HF, whereby the incidental hydrolysis occurs so slowly that it is obvious that (I) is of unusual structure and a means is also afforded of obtaining (I) very pure. Its analytical composition remains unaffected. The product of the hydrolysis by HF reduces Fehling's solution, possibly owing to glucose formed from admixed cellulose. When treated with C_5H_5N and Ac_2O it gives a *pentasaccharide acetate*, m.p. 143°, which has no reducing power so that the saccharide is presumably of the trehalose type. Treatment of (I) under mild conditions with HCl, HBr, H_2SO_3, or H_2SO_4 is without effect whereas under more drastic circumstances carbonisation takes place. With 75% H_2SO_4 galactose (III) is produced. Pentosans and cellulose are shown to be merely attendants of the precursor of (III) since (I) obtained after treatment with CCl_4 (see above) is sol. in Schweitzer's solution which on acidification gives (I) with the composition $C_6H_{12}O_6$ and the properties of a polysaccharide of very high mol. wt.; this with 75% H_2SO_4 again gives (III), which is therefore a component of (I). Tentative formulæ are proposed for (I) and the pentasaccharide. H. W.

Mucopolysaccharide from synovial fluid.—See A., 1939, III, 597.

Starch. M. Samec (Chem.-Ztg., 1939, **63**, 353—357).—A review.

Isolation of a crystalline substance from starches oxidised by periodate. D. H. Grangaard, J. H. Michell, and C. B. Purves (J. Amer. Chem. Soc., 1939, **61**, 1290—1291).—Treatment of maize, wheat, potato, or arrowroot starch with $Na_3H_2IO_6$–AcOH and then with 10% HCl–MeOH (dry) gives 0·7—0·9% of a *substance*, $C_{13}H_{16}O_8(OMe)_4$, m.p. 150—150·5° (corr.), $[\alpha]_D^{26}$ −7·1° in dioxan. R. S. C.

Fractionation of cellulose. H. Tydén (Svensk Kem. Tidskr., 1939, **51**, 100—101).—Fractionation of cellulose (from Cu''–NH_4^+ solution) from ZnO–NaOH (>2N. to prevent pptn. of ZnO during fractionation) with 10% aq. Na_2SO_4 takes 12 hr. and yields the longer chain mols. first. M. H. M. A.

Molecular size of methylated cellulose. M. L. Wolfram, J. C. Sowden, and E. N. Lassettre (J. Amer. Chem. Soc., 1939, **61**, 1072—1076).—The Me_3 ether of commercial $COMe_2$-sol. cellulose acetate is hydrolysed by HCl (*d* 1·2) in presence of EtSH at 0°. Determination of S in the product shows the degree of polymerisation to be 150 after 3·5 and 50 after 17 hr. and, by mathematical and graphical analysis, to be 400±70 for the original Me_3 ether. η for the acetate shows it to contain 350±35 glucose units. Changes in $[\alpha]$ for the ether in HCl at 24° are recorded; the final val. is that of trimethyl-*d*-glucose. R. S. C.

Action of aqueous ammonia on halogeno-derivatives. Preparation of aliphatic diamines. G. Darzens (Compt. rend., 1939, **208**, 1503—1504).—$CHMeCl{\cdot}CH_2Cl$ (1 mol.) with a large excess of 34% aq. NH_3 at 75—80°/8 days gives *αβ-diaminopropane* (92%), b.p. 120°/760 mm., and a little $CMe{:}CH$. Reaction in abs. EtOH occurs only at 120° and a complex mixture of bases is formed. With anhyd. NH_3 a mixture results. $Bu^{\gamma}Br$ or $Bu^{\gamma}Cl$ with aq. NH_3 at 65° affords $CMe_2{:}CH_2$ (100%). $CH_2Ph{\cdot}CH_2Br$ gives $(CHPh{:}CH_2)_n$. CH_2PhCl gives $CH_2Ph{\cdot}NH_2$, $NH(CH_2Ph)_2$, and $N(CH_2Ph)_3$; amyl bromide gives similar products. J. L. D.

Aliphatic polyamines. VIII. J. van Alphen (Rec. trav. chim., 1939, **58**, 544—549; cf. A., 1938, II, 175).—ακ-Dibromodecane and $(CH_2{\cdot}NH_2)_2,H_2O$ in

EtOH, then KOH, afford *ακ-di(aminoethylamino)decane* (I), m.p. 37° (*tetrapicrate*, m.p. 194°), with some *hexamine* derivative, $(NH_2{\cdot}[CH_2]_2{\cdot}NH{\cdot}[CH_2]_{10}{\cdot}NH{\cdot}CH_2{\cdot})_2$, m.p. 36° (*hexaphenylthiocarbamyl* derivative, m.p. ~106°, indicates straight chain), and higher condensation products (m.p. 46°). (I) and PhNCO in Et_2O give *ακ-di-(phenylcarbamidoethyl-phenylcarbamyl)aminodecane*, m.p. 207°; PhNCS affords the *thiocarbamyl* analogue, m.p. 185°. (I) and CS_2 in EtOH give an *adduct*, decomp. 80—105°, of (I) + $2CS_2$, decomp. at 140° to *ακ-di-(2′-thio-1′ : 3′ : 4′ : 5′-tetrahydroiminazolo)decane*, $\left(\begin{matrix}CH_2{\cdot}CH_2\\NH{-}CS\end{matrix}>N{\cdot}\right)_2[CH_2]_{10}$, m.p. 166°. (I) and PhCHO give a condensation product, which with Na–EtOH gives (method : A., 1936, 1493) ακ-di(benzylaminoethylamino)decane [*tetrahydrochloride* (II), m.p. 265° (decomp.)], converted by PhCHO in Et_2O into *ακ-di-(2′-phenyl-3′-benzyl-1′ : 2′ : 4′ : 5′-tetrahydroiminazolo)decane*, m.p. 139°, decomposed by dil. HCl to PhCHO and (II). A. T. P.

Synthesis of glucosamine. W. O. Cutler and S. Peat (J.C.S., 1939, 782—783).—The structure of glucosamine is confirmed by prep. of 2-aminotrimethyl-β-methylglucopyranoside (isolated as Ac derivative, m.p. 195°, $[\alpha]_D^{17}$ −29·4° in H_2O) in poor yield from 3 : 4 : 6-trimethyl-β-methylglucoside 2-*p*-toluenesulphonate and dry NH_3–MeOH at 175° (cf. A., 1939, II, 144). R. S. C.

New acetylated derivatives of amino-sugars. G. J. Robertson and W. H. Myers (Nature, 1939, **143**, 640—641).—Acetylation of the material obtained by the action of NH_3 on 2 : 3-anhydro-4 : 6-benzylidene-α-methylalloside gives a 60% yield of 2-acetamido-3-acetyl-4 : 6-benzylidene-α-methylaltroside, m.p. 181—182°, $[\alpha]_D^{17}$ +51·3° in $CHCl_3$, and 1% of 3-acetamido-2-acetyl-4 : 6-benzylidene-α-methylglucoside, m.p. 266°, $[\alpha]_D^{17}$ +45·6° in $CHCl_3$ (cf. A., 1938, II, 348). Similar treatment of 2 : 3-anhydro-4 : 6-benzylidene-α-methylmannoside gives 60% of *3-acetamido-2-acetyl-4 : 6-benzylidene-α-methylaltroside* (I), m.p. 201°, $[\alpha]_D^{12}$ +14·6° in $CHCl_3$, and ~1% of *2-acetamido-3-acetyl-4 : 6-benzylidene-α-methylglucoside*, m.p. 235°, $[\alpha]_D^{15}$ +45·5° in $CHCl_3$. Galactose has been converted into a 2 : 3-anhydro-4 : 6-benzylidene-α-methylhexoside which has either the gulose or the talose configuration. Acetylation following the action of NH_3 on this substance gives two isomeric 4 : 6-benzylideneamino-α-methylhexoside diacetates, m.p. 188°, $[\alpha]_D^{12}$ +43·4° in $CHCl_3$ and m.p. 260°, $[\alpha]_D^{12}$ +70·3° in $CHCl_3$. The same treatment of the α-methylhexoside chlorohydrin, m.p. 160°, reported previously (*ibid.*, 218) yields (60%) 3-acetamido-α-methylglucoside triacetate (II), m.p. 179°, $[\alpha]_D^{12}$ +105·9° in $CHCl_3$ (cf. *ibid.*, 348), and a trace of an unidentified isomeride, m.p. 130°, $[\alpha]_D^{16}$ +95·7° in $CHCl_3$, whilst the other chlorohydrin, m.p. 138° (*ibid.*, 218) yields 50% of (II) and 20% of an isomeride, $[\alpha]_D^{15}$ +50·4° in $CHCl_3$, not yet identified. 2 : 3-Anhydro-4 : 6-benzylidene-α-methylmannoside gives a syrupy mixture of α-methylhexoside chlorohydrins which when treated with NH_3 followed by acetylation yields 15% of (II) and 65% of an isomeride (III), m.p. 177°, $[\alpha]_D^{12}$ +34·7° in $CHCl_3$. Removal of :CHPh from (I) and acetylation of the product gives *3-acetamido-α-methylaltroside* 2 : 4 : 6-*triacetate*, identical with (III). L. S. T.

Hofmann degradation of glutamine residues in gliadin. R. L. M. Synge (Biochem. J., 1939, **33**, 671—678).—Treatment of *N*-acetylglutamine with alkaline NaOBr yields *l*-αγ-diaminobutyric acid (I) (50%), which may also be successively isolated from a protein digest as the phosphotungstate and *diflavianate*, m.p. 239° (decomp.). Three *oxalates* have been obtained : (I),$0{\cdot}5H_2C_2O_4$,$1{\cdot}5H_2O$, m.p. 211° (decomp.), (I),$H_2C_2O_4$, m.p. 206° (decomp.), and (I),$1{\cdot}5H_2C_2O_4$, m.p. 177° (decomp.). P. G. M.

Deamination of glycine in the presence of tyrosinase and *p*-cresol.—See A., 1939, III, 624.

Preparation of natural amino-acids from racemates by means of *d*-amino-acid oxidase. R. Duschinsky and J. Jeannerat (Compt. rend., 1939, **208**, 1359—1361).—*dl*-Alanine in aq. LiOH at p_H 8·3—8·5 at 38° with *d*-amino-acid oxidase (cf. Krebs, A., 1935, 1014) in an atm. of O_2 gives *l*(+)-alanine (83·5%) $[\alpha]_D^{20}$ +14·1° in HCl, $AcCO_2H$, and NH_3. *dl*-Methionine similarly gives *l*(−)-methionine (68%), $[\alpha]_D^{20}$ −8° in H_2O, α-keto-γ-methylthiolbutyric acid (2 : 4-*dinitrophenylhydrazone*, m.p. 128°), and NH_3. The natural isomerides of valine and *iso*leucine are prepared similarly. J. L. D.

Methionine. II. *dl*-Methionine sulphoxide. G. Toennies and J. J. Kolb (J. Biol. Chem., 1939, **128**, 399—405).—*dl*-Methionine sulphoxide (improved prep.) forms a *picrate*, gives no salt with $HgCl_2$, is quantitatively reduced by NaI in $HClO_4$, and oxidises cysteine to cystine. J. D. R.

Substituted ammonium sulphamates. M. J. Butler and L. F. Audrieth (J. Amer. Chem. Soc., 1939, **61**, 914—915).—See A., 1939, I, 333. *Sulphamates*, $NH_2{\cdot}SO_3H$,*B*, are described, derived from the following bases *B* : NH_2Me, m.p. 91—92°; $NHMe_2$, m.p. 86—87°; NMe_3, m.p. 147·5—149°; NH_2Et, m.p. 65—70°; NH_2Pr^{α}, m.p. 67—69°; NH_2Pr^{β}, m.p. 74—75°; NH_2Bu^{α}, m.p. 107—108°; NH_2Bu^{γ}, m.p. 138—139°; *n*-$C_5H_{11}{\cdot}NH_2$, m.p. 128—129°; $NH_2{\cdot}[CH_2]_2{\cdot}Pr^{\beta}$, m.p. 185°; *n*-$C_6H_{13}{\cdot}NH_2$, m.p. 109—111°; $NH_2{\cdot}CH_2{\cdot}CHEt_2$, m.p. 89—90°; $(CH_2{\cdot}NH_2)_2$, m.p. 156—158°; $NH_2{\cdot}CHMe{\cdot}CH_2{\cdot}NH_2$, m.p. 155—156°; *cyclo*hexylamine, m.p. 157—158°; di*cyclo*hexylamine, m.p. 160—162°; $NH_2{\cdot}[CH_2]_2{\cdot}Ph$, m.p. 183—184°; $NH_2{\cdot}[CH_2]_3{\cdot}Ph$, m.p. 104—105°.

Condensation of cyanoacetamide with formaldehyde. III. Secondary amines as catalysts. T. Enkvist [with G. Andersson] (J. pr. Chem., 1939, [ii], **158**, 116—126; cf. A., 1937, II, 329, 403).—Determination of the initial rate of decrease of $[CH_2O]$ when equimol. amounts of CH_2O and $CH{\cdot}CH_2{\cdot}CO{\cdot}NH_2$ are mixed in PO_4'''-buffered aq. solution at const. p_H shows that approx. the same acceleration is induced by the *sec.* amines piperidine (I), $NHEt_2$, di*iso*amylamine, and $NH(C_2H_4{\cdot}OH)_2$ (as hydrochlorides). Piperazine per equiv. is somewhat less active, whilst hippuric acid and guanidinoacetic acid have no appreciable effect. In presence of piperidine hydrochloride (II) at differing p_H the magnitude of the increase in the initial rate is approx. ∝ the concn. of

(II), increases in more strongly acid solution approx. $\propto [OH']^2$, and in the less acidic region does not increase so markedly with [OH']. Kinetic evidence is therefore adduced that the reaction proceeds through the formation from (I) and CH_2O of an intermediate, the structure of which is discussed. Piperidinomethanol and $CN{\cdot}CH_2{\cdot}CO{\cdot}NH_2$ yield *cyano-dipiperidinomethylacetamide*, $(C_5H_{10}N{\cdot}CH_2)_2C(CN){\cdot}CO{\cdot}NH_2$, m.p. 112° (slight decomp.) in a bath preheated to 100°. H. W.

Acetylated aldonamides. V. Deulofeu and E. R. de Labriola (J. Amer. Chem. Soc., 1939, **61**, 1110—1111).—*l*-Arabonamide, m.p. 123°, $[\alpha]_D^{24}$ −25·3° in $CHCl_3$, *d*-xylonamide, m.p. 112°, $[\alpha]_D^{20}$ +8·1° in $CHCl_3$, and *l*-rhamnonamide tetra-acetates, m.p. 115°, $[\alpha]_D^{20}$ −48·8° in $CHCl_3$ (obtained in poor yield from the nitrile by HBr–AcOH), *d*-mannonamide penta-acetate, m.p. 112—113°, $[\alpha]_D^{20}$ +39·1° in $CHCl_3$ (not obtained from the nitrile), and *d*-galactonamide penta-acetate, m.p. 166°, $[\alpha]_D^{25}$ +26·4° in $CHCl_3$, are best obtained from the aldonamides by Ac_2O–C_5H_5N. Passage from a nitrile acetate to an amide acetate causes a diminution in [α], except in the *l*-rhamnonic series. R. S. C.

Connexion between taste and constitution of carboxylic acid hydrazides and their derivatives. J. J. Blanksma and H. A. Bakels (Rec. trav. chim., 1939, **58**, 497—513; cf. A., 1938, II, 86).—Condensation of malono- (I) and succino-dihydrazide, m.p. 166° (both have a sweet taste), with aldehydes and ketones affords *malono-* and *succino-di-alkyl(aryl)idene-hydrazides* of the following [m.p. of derivative of (I) given first]: MeCHO, m.p. 188°, 250°; EtCHO, m.p. 175°, 238°; $Pr^{\alpha}CHO$, m.p. 169°, 241°; $Pr^{\beta}CHO$, m.p. 173°, 203°; $Bu^{\alpha}CHO$, m.p. 166°, 221°; $Me{\cdot}[CH_2]_5{\cdot}CHO$, m.p. 157°, —; PhCHO, m.p. 236°, 252°; $CH_2Ph{\cdot}CHO$, m.p. 170°, 228°; 2-, m.p. 285°, 255°, and 4-hydroxy-, m.p. 202°, 240°; 2-, m.p. 249°, 286°, 3-, m.p. 228°, 315°, and 4-nitro-, m.p. 256°, 292°; 2-, m.p. 229°, 269°, 3-, m.p. 210°, 254°, and 4-chloro-, m.p. 257°, 288°; and 4-methoxy-benzaldehyde, m.p. 222°, 235° (known). 4-hydroxy-3-methoxybenzaldehyde, m.p. 219°, —; piperonal, m.p. 221°, 268°; vanillin, m.p. —, 209°; furfuraldehyde, m.p. 243°, 267°, and its 5-Me, m.p. 207°, 235°, and 5-$CH_2{\cdot}OH$, m.p. 187°, 199°, derivatives; $COMe_2$, m.p. 185°, 200°; COMeEt, m.p. 142°, 165°; $COEt_2$, m.p. 130°, 160°; COMePr, —, 144°; $COPr^{\alpha}_2$, 109°, 173°; COPhMe, m.p. 220°, 274°; $COPh_2$ and (I) do not react. The derivatives from $COMe_2$ have a bitter taste; the latter and H_2O-solubility diminish with increase in size of alkyl groups. Citric acid trihydrazide (very sweet taste) affords H_2O-insol. *trihydrazides* from: PhCHO, m.p. 213°; 2-, m.p. 206°, 3-, m.p. 185°, and 4-nitro-, m.p. 274°; 2-, m.p. 211°, and 4-hydroxy-, m.p. 280°; and 4-methoxy-benzaldehyde, m.p. 200°; piperonal, m.p. 195°; furfuraldehyde, m.p. 179°, and its 5-Me, m.p. 178°, and -$CH_2{\cdot}OH$, m.p. 166°, derivative; COPhMe, m.p. 182°. *o*-Phthalhydrazide, m.p. >320° (tasteless) [*Ac* derivative, m.p. 174°; *N*-Me, m.p. 239° (*Ac* derivative, m.p. 140°), and *NN'*-Me_2 derivative, m.p. 175°], affords a bitter hydrazine salt. iso-, m.p. 227°, and *Tere-phthaldihydrazide*, m.p. >320°, afford *di-hydrazones* with $COMe_2$, m.p. 255° and 310° (faintly bitter), PhCHO, m.p. 254° and 336° (tasteless), and COPhMe, m.p. 251° and —, respectively. 2-Hydroxymethyl- (II) and 5-nitro-2-hydroxymethyl-benzohydrazide (both bitter) afford *derivatives* from the following: $COMe_2$, m.p. 147° (bitter) and new m.p. 185° (tasteless); PhCHO, new m.p. 152° and 196°. These are new: from 2-, m.p. 186°, 207°, 3-, m.p. 186°, 189°, and 4-nitro-, m.p. 213°, 217°; 2-, m.p. 182°, 207°, 3-, m.p. 153°, 198°, and 4-chloro-benzaldehyde, m.p. 175°, 202°; furfuraldehyde, m.p. 168°, 181°; 5-methyl-, m.p. 183°, 161°, and 5-hydroxymethyl-furfuraldehyde (tasteless), m.p. 157° (Ac derivative is bitter), 166°; piperonal, m.p. 183°, 203°. (II) and MeCHO, COPhMe, or $COPr^{\alpha}_2$ give (?) $(CHPh{:}N{\cdot})_2$. 5-Amino-2-hydroxymethylbenzohydrazide, m.p. 147°, and its condensation product with $COMe_2$, are bitter. Meconine (bitter) and N_2H_4,H_2O in EtOH give 5 : 6-dimethoxy-2-hydroxymethylbenzohydrazide (bitter) (tasteless product with $COMe_2$). 3-Nitro-5 : 6-dimethoxyphthalide and N_2H_4 afford 3-nitro-5-methoxy-6-hydrazinophthalide, m.p. 220° (tasteless derivatives with $COMe_2$ and PhCHO); 3-aminomeconin, however, and N_2H_4 give 3-amino-5 : 6-dimethoxy-2-hydroxymethylbenzohydrazide, m.p. 157° (tasteless). $NHBz{\cdot}NH_2$, $NHBz{\cdot}N{:}CMe_2$, and $NHBz{\cdot}N{:}CHPh$, are tasteless. More than one $CO{\cdot}NH{\cdot}NH_2$ group, suitably situated, affords a sweet taste. A. T. P.

Reaction of phosphoric acid with trioxymethylene. P. Pratesi (Annali Chim. Appl., 1939, **29**, 123—127).—The substance reported as Ca formaldehyde phosphate (A., 1937, III, 483) is shown to be $OMe{\cdot}CaPO_3$ (corresponding Hg^{I} salt); further attempts to prepare the former failed. The mechanism of the reaction between H_3PO_4 and trioxymethylene is discussed. F. O. H.

Hydrides of boron. XII. *s*-Dimethyldiborane and the methyl derivatives of borine trimethylammine. H. I. Schlesinger, N. W. Flodin, and A. B. Burg (J. Amer. Chem. Soc., 1939, **61**, 1078—1083; cf. A., 1939, II, 205).—B_2H_5Me (prep. from BMe_3 and a large excess of B_2H_6 at 80°) and Me_2O at −80° give BH_3,Me_2O and *s-dimethyldiborane*, b.p. 4·9° (calc. from the v.p.), m.p. −124·9°, the reaction depending on fission and re-formation of B·B linkings and on the depression of the stability of BH_3,X complexes by substitution of Me in the BH_3. The decreasing stability due to Me is shown by (*a*) the ease of substitution of BR_3,NMe_3 (R = H or Me) by Cl by means of HCl, (*b*) the series: *trimethylborine trimethylammine*, BMe_3,NMe_3, 70% dissociated at 80°; *dimethylborine trimethylammine*, b.p. 171·4° (calc. from the v.p.), m.p. −18·0°, stable at 68°; *methylborine trimethylammine*, b.p. 176·4° (calc. from the v.p.), m.p. 0·8°, stable at 100°, and (*c*) the reactions: at >68°, $2BHMe_2,NMe_3 \rightarrow BH_2Me,NMe_3 + BMe_3,NMe_3$; and at 200° (not at 100°), $3BH_2Me,NMe_3 \rightarrow 2BH_3,NMe_3 + BMe_3,NMe_3$. With H_2O (excess) at room temp. $(BH_2Me)_2$ gives $BMe(OH)_2$ and 4 H_2. With NH_3 at −100° to −80° $(BH_2Me)_2$ gives an *ammoniate*, $(BH_2Me)_2,2NH_3$, which at 200° gives 40% of tri-*B*-methyltriborine triammine, 20% of mono- plus di-*B*-methyltriborine triammine, 4% of triborine triammine, and 2% of $BMe_2{\cdot}NH_2$. With NMe_3, $(BH_2Me)_2$ gives pure BH_2Me,NMe_3. $(BH_2Me)_2$

is stable for a few min. at room temp., but then rearranges to $BHMe_2{\cdot}BH_3$, which later decomposes partly to nearly equiv. amounts of B_2H_5Me and $B_2H_3Me_3$; $(BH_2Me)_2$ is absent from the final equilibrium mixture. R. S. C.

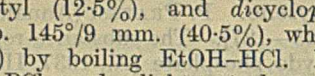
Derivatives of monosilane. I. Reactions of chlorosilane with aliphatic amines. H. J. Emeléus and N. Miller (J.C.S., 1939, 819—823).—Mainly a detailed account of results already reported (A., 1939, II, 53). $NMe(SiH_3)_2$ with NaOH gives NH_2Me, Na_2SiO_3, and H_2, and with HCl yields NH_2Me and SiH_3Cl. $NEt(SiH_3)_2$ reacts similarly with HCl. $SiH_3{\cdot}NMe_3Cl$ dissociates into NMe_3 and $SiHCl_3$, the reaction being irreversible owing to decomp. of $SiHCl_3$ into SiH_4 and SiH_2Cl_2. V.p. of $NMe(SiH_3)_2$ and $NEt(SiH_3)_2$ are recorded. Stability of $NMe_x(SiH_3)_{4-x}Cl$ increases as x increases. R. S. C.

Transformation of formals into halogen compounds. N. Turkiewicz (Ber., 1939, **72**, [*B*], 1060—1063).—The modest yields of carbinols (and hence of halides) obtained by the process, $MgRCl + CH_2O \rightarrow CH_2R{\cdot}O{\cdot}MgCl \rightarrow CH_2R{\cdot}OH$, are caused by the production of formals which, however, can readily be converted into carbinols, thus raising the overall yield to 91% of carbinol or 84·5% of chloride. Thus Mg *cyclo*pentyl chloride and $(CH_2O)_3$ or CH_2O give *cyclo*pentylcarbinol (I), b.p. 161—163° (40%), di*cyclo*pentyl (12·5%), and di*cyclopentylmethyl formal*, b.p. 145°/9 mm. (40·5%), which is converted into (I) by boiling EtOH–HCl. Rapid addition of (I) to PCl_5 under light petroleum gives *cyclo*pentylmethyl chloride. Similarly, octadecyl chloride affords a mixture of *n*-octadecane and octadecene, *n*-nonadecanol, m.p. 61·5°, and *dinonadecyl formal*, b.p. 280°/0·3 mm., m.p. 60°. *Nonadecyl chloride* has b.p. 164—167°/0·3 mm. Analogously dodecyl chloride afforded olefines, tridecanol, b.p. 152°/14 mm., m.p. 30·5°, tetracosane, and ditridecyl formal, which is converted by an excess of PBr_5 in hot C_6H_6 into *tridecyl bromide*, b.p. 162°/16 mm. H. W.

Relative reactivities of magnesium methyl chloride and magnesium dimethyl. G. F. Wright (J. Amer. Chem. Soc., 1939, **61**, 1152—1156).—$MgMe_2$ in dioxan reacts much more readily with the OH than with the CO of $COPh{\cdot}CHPh{\cdot}OH$ (I); a complex, $\begin{matrix}CHPh{\cdot}O\\CHPh{\cdot}O\end{matrix}\!\!>\!Mg$, is probably formed. By interaction with (I), COPhMe, $CH_2Ph{\cdot}COPh$, and $COPh{\cdot}CHPh_2$, it is shown that $MgMe_2$ is less reactive towards enolisable CO than is MgMeHal.

Carbonation of organo-magnesium compounds and the accompanying secondary reactions in the aliphatic series. M. Tuot (Compt. rend., 1939, **208**, 1026—1028).—Carbonation of Mg derivatives of Pr$^\alpha$Br, Pr$^\beta$Br, Bu$^\alpha$Br, and Bu$^\beta$Br at −15° to −20° affords the corresponding acids (90—100%). A large excess of MgRBr and prolonged heating at 40° gives, with Pr$^\alpha$Br and Bu$^\alpha$Br, <10% of the corresponding acid, the ketone obtained by interaction of 2MgRBr with CO_2, and a *tert.* alcohol due to the further action of MgRBr on the ketone (cf. A., 1938, II, 257), also primary and *sec.* alcohols and an unsaturated hydrocarbon. Pr$^\beta$Br and Bu$^\beta$Br give similar products, but no *tert.* alcohol is formed. The reaction mechanisms are described. The saturated hydrocarbons to be expected from the reaction mechanism proposed by Mousseron and Granger (A., 1937, II, 449) are not produced (cf. A., 1939, II, 102). J. L. D.

Organic compounds of gold. VII. Methyl and ethyl compounds. F. H. Brain and C. S. Gibson (J.C.S., 1939, 762—767; cf. A., 1936, 618).—Me and Et derivatives of Au have been prepared. Au^{III} has little, if any, tendency to become 5-covalent. Pyridinotrichlorogold and MgMeI in C_5H_5N at < 0° give 21% of *dimethyliodogold* (I), $(Me_2AuI)_2$, m.p. 78·5° (liquid explosive), the mol. wt. of which is found by cryoscopy in C_6H_6 or $CHBr_3$, although its solutions therein are unstable at room temp. With alkali in EtOH, (I) gives a Au mirror. With $(CH_2{\cdot}NH_2)_2$ in EtOH, (I) gives *ethylenediaminodimethylgold iodide*, $[Me_2Au(CH_2{\cdot}NH_2)_2]I$, m.p. 168° (decomp.), reconverted by HCl into (I), but converted by HI into *ethylenediaminotetramethyldi-iododigold* (III), $(\cdot CH_2{\cdot}NH_2 \rightarrow AuMe_2I)_2$, decomp. when heated. With $(CH_2Ph)_2S$, (I) gives *dibenzylsulphidodimethyliodogold*, $(CH_2Ph)_2S \rightarrow AuMe_2I$, m.p. 77—78° (decomp.), and with Tl acetonylacetone yields *dimethyl-*



goldacetylacetone, Me_2Au, m.p. 84°, less sensitive to light than is the Et analogue and converted by HBr–EtOH into *dimethylbromogold* (IV) [formula as (I)], m.p. 68—69° (decomp.). With Br in CCl_4 (IV) gives *methyldibromogold*, $(Me_2AuBr)_2$; cryst. $Au_2Et_4Br_2$ does not react with Et_2S, but yields normally *dibenzylsulphidodiethylbromogold*, m.p. 91°, converted by $(CH_2{\cdot}NH_2)_2$ into ethylenediaminodiethylgold. (ββ′-*Diaminodiethyl ether*)-*tetraethyldibromodigold*, $O(\cdot[CH_2]_2{\cdot}NH_2 \rightarrow AuEt_2Br)_2$, m.p. 87° (decomp.), and NN-*diethylethylenediaminotetraethyldibromodigold* (V), $NH_2{\cdot}[CH_2]_2{\cdot}NEt_2(\rightarrow AuEt_2Br)_2$, m.p. 83·5° (decomp.), are readily obtained, but the Et analogue of (III) was not formed. NN-*Diethylethylenediaminodiethylgold bromide* (VI), $[Et_2Au(NH_2{\cdot}[CH_2]_2{\cdot}NEt_2)]Br$, hygroscopic, m.p. ~ 26°, is prepared; it is sol. in H_2O and dissociates therein. However, in C_6H_6, $CHCl_3$, etc. it is a non-electrolyte, probably existing as $NEt_2{\cdot}[CH_2]_2{\cdot}NH_2 \rightarrow AuEt_2Br$, the change being reversible. It is considerably associated in C_6H_6, possibly as $NEt_2{\cdot}[CH_2]_2{\cdot}NH_2 \rightarrow AuEt_2{-}Br \rightarrow AuEt_2(\leftarrow NH_2{\cdot}[CH_2]_2{\cdot}NEt_2){-}Br \rightarrow AuEt_2$ etc.; the Au, except in the end units, would then be 5-covalent. With C_5H_5N (V) gives (VI). 2 : 2′-Dipyridyl and $Au_2Et_4Br_2$ give 2 : 2′-*dipyridyltetraethyldibromodigold*, $(\cdot C_5H_4N \rightarrow AuEt_2Br)_2$, m.p. 169°, readily converted into (VI). R. S. C.

Isomerisation of alkyl*cyclo*pentanes. H. Pines and V. N. Ipatiev (J. Amer. Chem. Soc., 1939, **61**, 1076—1077).—With $AlCl_3$ and a trace of H_2O at 50° ethyl*cyclo*pentane (I), b.p. 103·6°, gives methyl*cyclo*hexane; *n*- (II), b.p. 130·7°, and *iso*-propyl*cyclo*pentane (III), b.p. 126·8°, give 1 : 3-dimethyl*cyclo*hexane; *n*- (IV), b.p. 156·8°, *sec.*- (V), b.p. 154·6°, and *tert.*-butyl*cyclo*pentane, b.p. 145·2°, give 1 : 3 : 5-

trimethyl*cyclo*hexane. Formation of polymethyl-*cyclo*pentanes probably precedes ring-enlargement. The structure of the products is proved by dehydrogenation (7% Pt–Al_2O_3; 240°), bromination, and/or nitration. (I), (II), and (IV) are prepared by treating *cyclo*pentanone with MgAlkHal, dehydrating by passage over activated Al_2O_3 at 345°, and hydrogenating in presence of Ni at 100°/100 atm. (III) and (V) are prepared by treating *cyclo*pentadiene with $COMe_2$ or COMeEt, respectively, and NaOEt–EtOH at 40° and hydrogenating (Ni) the resulting dialkylfulvene at 125°/100 atm. R. S. C.

Synthesis of homologues of phenyl*cyclo*pentane. J. I. Denisenko and A. D. Naber (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 1025—1032).—ω-Chloro-*n*-amyl- and -hexyl-benzene with Mg and *cyclo*pentanone yield respectively 1-ω-*phenyl*-n-*amyl*-, b.p. 168—169°/3 mm., and -*hexyl*-cyclo*pentanol*, b.p. 181—182°/3 mm., dehydrated ($H_2C_2O_4$ in H_2O) to the -Δ^1-cyclo*pentenes*, b.p. 157—158°/3 mm. and 159—160°/2 mm., respectively, reduced (Pt-black) to the -cyclo*pentanes*, b.p. 304—305°/748 mm. and 315—317°/749 mm., respectively. 1-ω-Phenyl-ethyl- and -propyl-*cyclo*pentanol with anhyd. $H_2C_2O_4$ at 110—135° yield *cyclo*pentanotetrahydronapthalene and octahydrophenanthrene, respectively. The properties of $Ph{\cdot}[CH_2]_n{\cdot}C_5H_9$ ($n = 0$—6) and related compounds are tabulated. A. Li.

Multiplanar structure of the methyl*cyclo*hexane ring. D. M. Cowan, G. H. Jeffery, and A. I. Vogel (Chem. and Ind., 1939, 559; cf. A., 1938, II, 268, 354, 436).—The methyl*cyclo*hexane *B* obtained by the thermal decomp. of 2-methyl*cyclo*hexanone-semicarbazone in presence of NaOEt has b.p. 100·4°/763 mm. (vals of *d* and *n* quoted in all cases) which changes after several days. The hydrocarbon from the 4-Me compound has b.p. 100·5°/764 mm., changing to 100·4°/758 mm. after several days. The original form *B'* had b.p. 100·2—100·4°/768 mm. The prep. of form *B'* by Clemmensen reduction of 2-, 3-, and 4-methyl*cyclo*hexanones is announced. The original form *A* is now regarded as slightly impure *B'*. It is claimed that the two Sachse forms of methyl-*cyclo*hexane may have been proved capable of independent existence. H. W.

Reaction of *cyclo*pentene with sulphur dioxide solution. O. Pipik (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 1097—1104).—*cyclo*Pentene (both synthetic and that obtained from cracked petroleum) forms a sulphone with SO_2 solution. Positive and negative catalysts for the reaction have been found. A sulphone reagent is described for the determination of active groups in the mol., and of the liability of org. compounds to oxidation, and has been applied to the oxidation of petroleum products. A. Li.

Simultaneous dehydrogenation–hydrogenation of *cyclo*hexene in presence of nickel. B. B. Corson and V. N. Ipatiev (J. Amer. Chem. Soc., 1939, **61**, 1056—1057).—Ni-kieselguhr (65 : 35) catalyses change of *cyclo*hexene (3 mols.) at 125—200° into *cyclo*hexane (2 mols.) and C_6H_6 (1 mol.), but with higher temp. (up to 400°) the amount of C_6H_6 increases. Small amounts of H_2 and CH_4 are also formed, the amounts depending on the temp. and whether the steel autoclave has or has not a glass liner. R. S. C.

Addition of hydrogen to aromatic hydrocarbons by the action of ammonia complexes of lithium, strontium, and barium. III. B. A. Kazanski and N. F. Gluschnev (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 1061—1064).—C_6H_6 and PhMe are reduced by Li in NH_3, or by Sr or Ba ammoniate, to H_2- and H_4-derivatives. A. Li.

Dehydrogenation of *cyclo*octene. S. Goldwasser and H. S. Taylor (J. Amer. Chem. Soc., 1939, **61**, 1260—1263).—An apparatus for studying the catalytic behaviour of semi-micro-quantities of volatile compounds is described. In presence of Cr (prep. from Cr_2O_3 gel by H_2) at 400° *cyclo*octene gives 1 H_2 and 1 part each of *cyclo*octane and styrene. At 425—500°, however, loss of H_2 is more rapid than hydrogenation; 2·7 H_2 are liberated and the product contains 6—8% of *cyclo*octane and 92—94% of styrene. These proportions are calc. (concordantly) from the H_2 evolved, *d* and I val. of the product. Willstätter's reputed *cyclo*octatetraene (cf. A., 1912, i, 17; 1913, i, 348) was probably styrene, with which its properties accord. R. S. C.

Contact changes of phenyl*cyclo*pentane homologues. J. I. Denisenko (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 1019—1024).—With Pt–C at 300—310° in excess of H_2, *cyclo*pentylphenyl-ethane (I) and -propane (II) give mixtures containing heptyl- and octyl-benzene respectively. With Pt–C at 310—315° in an inert gas, (I) and (II) yield 4 : 5-benzoindane and phenanthrene respectively. A. Li.

α-*cyclo*Pentyl-δ-phenylbutane and its transformations. J. I. Denisenko and A. D. Naber (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 1015—1018).—δ-Chloro-*n*-butylbenzene with Mg and *cyclo*pentanone yields 1-δ-*phenyl*-n-*butyl*-cyclo*pentanol*, b.p. 155—156°/3 mm., dehydrated ($H_2C_2O_4.2H_2O$) to the -Δ^1-cyclo*pentene*, b.p. 146—147°/6 mm., which with H_2–Pt-black at room temp. yields the -cyclo*pentane* (I), b.p. 289—290°/754 mm. (I) is reduced (H_2, Pt–C at 230°) to α-cyclo*pentyl*-δ-cyclo*hexyl*-n-*butane*, b.p. 284·5—286°/745·1 mm., dehydrogenated (Pt–C at 280°) to (I). A. Li.

Hydrogenation of certain homologues of benzene under pressure. II. M. K. Djakova and A. V. Lozovoi (J. Gen. Chem. Russ., 1939, **9**, 26—32).—$Ph{\cdot}[CH_2]_2{\cdot}Br$ and $Pr^{\alpha}Br$ or α-bromo-*n*-hexane yield (Wurtz) *n*-amyl- or *n*-octyl-benzene, respectively. The following are obtained by hydrogenation of the appropriate alkylbenzene (Ni–Al_2O_3 catalyst at 160—170°/50—70 atm.): *n*-butyl-, *n*-amyl-, *iso*amyl-, 2- and 4-methyl-*n*-propyl-, and n-*octyl*-cyclo*hexane*, b.p. 117—119°/11 mm.; hydrindene similarly gives octahydroindene. R. T.

Formation of intermediate compounds in hydrocarbon syntheses by the Friedel and Crafts reaction. Preparation of *s*-trialkylbenzenes. J. F. Norris and D. Rubinstein (J. Amer. Chem. Soc., 1939, **61**, 1163—1170).—Passage of HBr into PhMe + $AlBr_3$ gives an oily *compound*, Al_2Br_6,6PhMe, decomp. in *p*-$C_6H_4Cl_2$ (mol. wt.

at the f.p.) or when kept at 10—11 mm. into PhMe and Al_2Br_6,PhMe. When aromatic hydrocarbons are alkylated (AlkHal) in presence of 1 Al_2Cl_6 or Al_2Br_6 per mol. of hydrocarbon, very high yields of *m*-derivatives are obtained; *e.g.*, with Al_2Cl_6, C_6H_6 and EtBr give 85—90% of *s*-$C_6H_3Et_3$, PhMe gives 85% of 1 : 3 : 5-$C_6H_3MeEt_2$, and crude *m*-xylene gives 50% of *s*-$C_6H_3Me_3$ (87% of the total Me_3 derivatives). Using $AlCl_3$, C_6H_6 and MeBr at 0° give mainly *ψ*-cumene, but at the b.p. mainly *s*-$C_6H_3Me_3$. At 0° PhMe and MeCl give 27·3% of *m*- and 53·5% of *o*-xylene, but at 106° 98·2% of *m*- and 1·8% of *o*-xylene. With $AlCl_3$ at 55° (10 min.) *o*-xylene gives 18·7% and *p*-xylene gives 64·3% of *m*-xylene. A cryoscopic method of analysing xylene mixtures is outlined. R. S. C.

Polymethylbenzenes. XXIV. Jacobsen reaction. VI. Trimethylethylbenzenes. L. I. Smith and M. A. Kiess (J. Amer. Chem. Soc., 1939, **61**, 989—996; cf. A., 1937, II, 372).—When 5-ethyl-*ψ*-cumene (I) or, less readily, ethylmesitylene (II) is sulphonated by 10% oleum at <40° and then heated therein at 60—70°, rearrangement occurs; hydrolysis gives largely (41·7 and 57·5%, respectively) 3-ethyl-*ψ*-cumene (III), which is unchanged by this treatment. (I) yields also *ψ*-cumene (6·7%), 4-ethyl-*m*-xylene (IV) (14·4%), prehnitene (V) (11·2%), and much tar, including a small amount of a (?) *hexa-alkylbenzene*, m.p. 173—175°. (II) yields also mesitylene (6·7%), 2-*ethyl*-m-*xylene* (VI) (15·9%), (V) (16·6%), and much tar, including a *substance* (C 89·5, H 10·4%), m.p. 185—186°. Formation of (V) indicates a novel mode of reaction. (I) shaken with 10% oleum for 5 min. gives 5-ethyl-*ψ*-cumenesulphonic acid, m.p. 72—73° (lit. 70—72°) [amide, m.p. 97—98° (lit. 86° and 153°); *anilide*, m.p. 110—111°], converted by Br–H_2O into 3 : 6-dibromo-5-ethyl-*ψ*-cumene, m.p. 60—61° (lit. 218°) [also obtained direct from (I) by Br–AcOH]. By Smith's method, (I) gives the 3 : 6-(NO_2)$_2$-derivative, m.p. 87—88°, reduced by $SnCl_2$–HCl to the 3 : 6-(NH_2)$_2$-derivative, m.p. 87—88° (*stannichloride*), which with $FeCl_3$–HCl gives *trimethylethylbenzoquinone*, m.p. 43°. Conc. H_2SO_4 converts (III) into *3-ethyl-ψ-cumenesulphonic acid*, m.p. 62—64° (*amide*, m.p. 154°; *anilide*, m.p. 118—119°). (IV), b.p. 85°/25 mm., gives a (NO_2)$_3$-, m.p. 127·5—129°, and a Br_3-derivative, m.p. 94—95° (lit. 127°), and is oxidised to 1 : 2 : 4-$C_6H_3(CO_2H)_3$. Oxidation of (VI), b.p. 80—83°/24 mm. [(NO_2)$_3$-derivative, m.p. 181°], gives 1 : 2 : 3-$C_6H_3(CO_2H)_3$. The mixture of 2- and 4-bromo-*m*-xylene, obtained directly from *m*-xylene by Br at 0°, gives a Grignard reagent, which with Et_2SO_4 in Et_2O yields (IV) and (VI), separated as (NO_2)$_3$-derivatives. By methods given above, (II) yields ethylmesitylenesulphonic acid, m.p. 78—80° (anilide, m.p. 123—124°; *amide*, m.p. 131—133°), 4 : 6-dibromo-, m.p. 59°, 4 : 6-dinitro-, m.p. 111° (lit. 123°), and 4 : 6-*diamino-ethylmesitylene*, m.p. 79—80°, and with fuming HNO_3–H_2SO_4 yields (?) 1 : 2 : 4 : 3 : 5 : 6-$C_6Me_2Et(NO_2)_3$, m.p. 123°. Clemmensen reduction of crude aceto-*p*-xylene gives ethyl-*p*-xylene [(NO_2)$_3$-derivative, m.p. 127—128° (lit. 129°)]. R. S. C.

Electrolytic reduction of nitrobenzene in liquid ammonia. H. Shiba, T. Inoue, and R. Miyasaka (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1939, **35**, 455—461).—The electrolytic reduction of $PhNO_2$ in liquid NH_3 solutions of NH_4Cl and NaCl has been investigated using an Al anode, a Ni cathode, and an asbestos diaphragm. With a 0·00001M. solution of $PhNO_2$ and 0·1M-NH_4Cl or NaCl the efficiency of reduction with NaCl was > in NH_4Cl. The nature of the reduction products was obtained by comparison of the absorption spectrum with that of the pure compounds. For this purpose the absorption spectra of $PhNO_2$, PhNO, NHPh·OH, NH_2Ph, PhNO:NPh, (:NPh)$_2$, (NHPh)$_2$ and benzidine in liquid NH_3 were determined. The following results were obtained by electrolysis in NH_4Cl in liquid NH_3 : $PhNO_2$ → PhNO; PhNO unchanged; NHPh·OH unchanged; PhNO:NPh → (NHPh)$_2$; (:NPh)$_2$ → (NHPh)$_2$. With NaCl in liquid NH_3, $PhNO_2$, PhNO, or NHPh·OH → PhN:N·ONa or NPhNa·ONa; PhNO:NPh → (:NPh)$_2$; (:NPh)$_2$ → (NHPh)$_2$. A. J. M.

Kinetics of chain polymerisation. V, VI.—See A., 1939, I, 375.

Diarylmethane derivatives. V. Derivatives of bis-(2 : 4 : 6-triethylphenyl)methane. W. T. Nauta and D. Mulder (Rec. trav. chim., 1939, **58**, 514—520; cf. A., 1939, II, 103).—*s*-$C_6H_3Et_3$ (I) (prep. from C_6H_6, C_2H_4, and $AlCl_3$ at 60—80°) and Br–$CHCl_3$ (no Fe) give 2 : 4 : 6 : 1-$C_6H_2Et_3Br$, converted (Grignard method) into 2 : 4 : 6 : 1-$C_6H_2Et_3$·CO_2H, the chloride of which with (I), $AlCl_3$, and CS_2 at 65° affords *bis-*(2 : 4 : 6-*triethylphenyl*) *ketone*, m.p. 79—80°, reduced by Na–Hg in EtOH to the *carbinol*, m.p. 27—28°, and thence converted by HCl–C_6H_6 into the *carbinyl chloride* (II), m.p. 36—37°, and some *bis-*(2 : 4 : 6-*triethylphenyl*)*methane*, m.p. 71—72°. The latter is also obtained from (I) and $(CH_2O)_3$ in AcOH–H_2SO_4 at room temp. (II) and AgOAc–Et_2O or KOH–MeOH give *bis-*(2 : 4 : 6-*triethylphenyl*)*carbinyl acetate*, b.p. 167—168°/0·75 mm., or *Me ether*, b.p. 169°/1 mm., respectively. A. T. P.

Reduction of organic halogen compounds and compounds of the tetra-arylbutane series. XII. Cathodic reduction of ββγ-trichloro-αα-di-*p*-bromophenylethane. K. Brand and D. Krücke-Amelung (Ber., 1939, **72**, [*B*], 1029—1035; cf. A., 1930, 1285).—PhBr is converted by CCl_3·CHO or CCl_3·$CH(OH)_2$ and fuming H_2SO_4 into ββγ-trichloro-αα-di-*p*-bromophenylethane (I), m.p. 144°, the structure of which is established by its transformation by boiling KOH–EtOH or, preferably, NaOBu in BuOH into ββ-dichloro-αα-di-*p*-bromophenylethylene, m.p. 123·5°, which is oxidised by CrO_3 in AcOH–H_2SO_4 to $CO(C_6H_4Br)_2$ with a very little *p*-C_6H_4Br·CO_2H. Cathodic reduction (Pb) of (I) in HCl–EtOH affords *ααδδ-tetra-p-bromophenyl-*Δ^{β}*-butinene* (II), m.p. 198·5°, but much (I) remains unattacked since (II) forms a protective coating on the electrode. The difficulty is obviated by the use of dioxan (or exluan)–MeOH–HCl. In addition there are obtained not inconsiderable amounts of ββ-*dichloro-αα-di-*p*-bromophenylethane* (III), m.p. 133—134° (converted by KOH–EtOH into β-*chloro-αα-di-*p*-bromophenylethylene*, m.p. 107—108°), and (after treatment with KOH) very

small quantities of αα*δδ-tetra*-p-*bromophenyl*-$\Delta^{\alpha\beta\gamma}$-*butatriene*, m.p. 299°. CrO_3 in AcOH smoothly oxidises (II) to CO_2 and $CO(C_6H_4Br\text{-}p)_2$. It is almost quantitatively transformed by boiling the solution in EtOH or, preferably, amyl alcohol with NaOEt into αα*δδ-tetra*-p-*bromophenyl*-$\Delta^{\alpha\gamma}$-*butadiene*, m.p. 265—266°, which, like (II), is not reduced by Zn dust in boiling AcOH. Cathodic reduction of (I) at Cu in presence of $ZnCl_2$ gives (III), ββ*γγ*-tetrachloro-αα*δδ*-tetra-*p*-bromophenylbutane, and β*γ*-dichloro-αα*δδ*-tetra-*p*-bromophenyl-Δ^{β}-butene. H. W.

Reduction of organic halogen compounds and compounds of the tetra-arylbutane series. XIII. αα*δδ*-Tetra-*p*-bromophenyl-$\Delta^{\alpha\beta\gamma}$-butatriene. K. Brand and D. Krücke-Amelung (Ber., 1939, **72**, [*B*], 1036—1047).—Examination of $CaCO_3$–Pd catalysts which have functioned irregularly in this work discloses the presence of considerable amounts of uncoloured calcite crystals in the inactive material and of brown aragonite crystals in the active compounds. Since even the brown material is not invariably useful, recourse is taken to a ZnO–Pd catalyst. Catalytic reduction of βββ-trichloro-αα-di-*p*-bromophenylethane (I) at 65° in EtOH, exluan-06, or pure C_5H_5N yields a difficultly separable mixture of ββ*γγ-tetrachloro*-αα*δδ-tetra*-p-*bromophenylbutane* (II), m.p. 299° [also $+2C_6H_6$, $+2$EtOAc, and $+1{\cdot}5$ (?) $CHCl_3$], and β*γ-dichloro*-αα*δδ-tetra*-p-*bromophenyl*-Δ^{β}-*butene* (III), m.p. 278·5—280°. It is therefore preferable to reduce (I) in exluan-06 mainly to (II), which is converted by Zn dust in exluan-05 into (III) and its diastereomeric *form* (IV), m.p. 192° after softening at 187—188°. (III) is reduced by Zn dust and AcOH to αα*δδ*-tetra-*p*-bromophenyl-Δ^{β}-butinene (V), m.p. 198·5°. (III) or (IV) is transformed by NaOEt in EtOH–amyl alcohol into αα*δδ-tetra*-p-*bromophenyl*-$\Delta^{\alpha\beta\gamma}$-*butatriene* (VI), m.p. 299° (decomp.), which on exposure to sunlight passes into a compound, m.p. 336·5° after darkening at 326°. Oxidation ($KMnO_4$ in $COMe_2$ containing $MgSO_4$) of (VI) affords $CO(C_6H_4Br\text{-}p)_2$ whilst reduction (Zn dust in AcOH) leads to (V). (VI) is slowly converted by AcOH saturated with HCl at 400° into *chloro*-αα*δδ-tetra*-p-*bromophenylbutadiene*, m.p. 161°, or under somewhat different conditions, into 6-*bromo*-3-p-*bromophenyl*-1-*di*-p-*bromophenylmethyleneindene*, m.p. 265°. H. W.

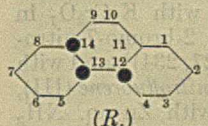
Palladous chloride as a dehydrogenating agent. G. W. Cooke and J. M. Gulland (J.C.S., 1939, 872—873).—Tetrahydronaphthalene and 2% aq. $PdCl_2$ (in least amount of HCl to give solution), refluxed for 33 hr., afford $C_{10}H_8$. Decahydronaphthalene similarly gives no $C_{10}H_8$ (odour only detected at 200° in a sealed tube). *cyclo*Hexanol affords PhOH. Tetrahydrocarbazole yields carbazole. Tetrahydro-quinoline and *-iso*quinoline, using more HCl and adjusting p_H val., give quinoline and *iso*quinoline, respectively; 2-methyltetrahydro*iso*quinoline similarly affords 2-methyl-1 : 2-dihydro*iso*quinoline. PhMe (excess) affords BzOH; *o*-cresol (p_H adjusted) gives *o*-CHO·C_6H_4·OH and *o*-CO_2H·C_6H_4·OH, the latter being obtained also from 2-methyl*cyclo*hexanol. No product is isolated from $(CH_2Ph)_2$, COMeEt (complex formation), *cyclo*hexane (very stable), stilbazole (complex salt), or cholesterol (very slow oxidation). Addition of org. solvents does not increase efficiency of reaction. A. T. P.

Separation of hydrocarbons of high mol. wt. by adsorption on silica gel. C. B. Willingham (J. Res. Nat. Bur. Stand., 1939, **22**, 321—327).—Filtration through SiO_2 gel completely removes small amounts of ε-(5 : 6 : 7 : 8-tetrahydro-β-naphthyl)docosane (I) from ε-(decahydro-β-naphthyl)docosane (II), and *n*-dotriacontane (III) from α-*p*-diphenyloctadecane (IV). A partial separation of (IV) from (I) was effected, but not of (III) from (II). The preferential adsorptions of the more aromatic constituent of the first three of these mixtures were respectively 1·8, 3·3, and 0·8 g. per 20 g. of SiO_2 gel. W. A. R.

Isomeric changes in cyclic hydrocarbons observed when trying to realise a triple linking in a ring. V. I. Nikitin (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 1265—1276).—1-Ketotetrahydronaphthalene on successive treatment with PCl_5, KOH, and Br yields 4-chloro-3 : 4-dibromo-1 : 2 : 3 : 4-tetrahydronaphthalene, which is unstable and gives 3 : 4-dibromo-1 : 2-dihydronaphthalene (I) (by loss of HCl) and 2-$C_{10}H_7Cl$ (loss of 2HBr). (I) with Na yields $C_{10}H_8$. A. Li.

Polymerisation of α-vinylnaphthalene derivatives. S. Zonis (J. Gen. Chem. Russ., 1939, **9**, 119—125).—$COMePr^{\alpha}$ and α-$C_{10}H_7$·MgBr in Et_2O yield β-1-*naphthylpentan*-β-*ol*, m.p. 65—66°, whilst with $COMePr^{\beta}$ β-1-*naphthyl*-γ-*methylbutan*-β-*ol*, b.p. 177—179°/10—11 mm., is obtained. The alcohols are dehydrated by activated clay at 140—150° to β-1-*naphthyl*-Δ^{β}-*pentene* (I), b.p. 158—160°/20 mm., and β-1-*naphthyl*-γ-*methyl*-Δ^{β}-*butene* (II), b.p. 165—166°/23 mm., respectively. When the hydrocarbons CHR:CHR′ and CRR′:CH_2 (R = α-$C_{10}H_7$, R′ = Me) were left in contact with floridin or BzO_2H for 3—8 months at room temp., dimerides were formed; under these conditions (I) and (II) do not polymerise. R. T.

Fused carbon rings. XVI. Stereoisomerism of the perhydrophenanthrenes; preliminary investigations. R. P. Linstead and A. L. Walpole (J.C.S., 1939, 842—850).—Nomenclature and structural representation of the six inactive forms of perhydrophenanthrene, 4 racemic, viz., *cis-syn-trans* (*R*), *cis-anti-cis*, *cis-anti-trans*, *trans-anti-trans*, and 2 *meso*-, viz., *cis-syn-cis* and *trans-syn-trans*, are discussed. Hexagons represent fully reduced *cyclo*hexane rings. The black dots indicate H atoms above the general plane of the mol. Di-1-hydroxy*cyclo*hexylacetylene is dehydrated (40% H_2SO_4 is preferable to $KHSO_4$) to di-Δ^1-*cyclo*hexenylacetylene, which with HCO_2H affords 9-ketododecahydrophenanthrenes, m.p. 93—94° (I) and m.p. 38—39° (b.p. 146—147°/5 mm.) (II) (cf. Marvel *et al.*, A., 1938, II, 48), purified through the respective *oximes*, m.p. 157—158° and 183—184° (prepared from NH_2OH,HCl–NaOAc–aq. EtOH); the respective semicarbazones have m.p. 232° and 227—228°. A third 9-ketododecahydrophenanthrene, m.p. 88°



(*R*.)

(III) (modified method of prep. of Rapson and Robinson, A., 1935, 1498), gives an oxime, m.p. 202°. (I) and (II) differ solely in the position of the double linking; in one it is 8 : 14 and in the other is 13 : 14. (I) or (II) react slowly with ICl in $CHCl_3$–EtOH, *i.e.*, double linkings are in αβ-positions, proved by ultra-violet absorption spectra. (III), also with an αβ-double linking, is probably a *trans*^{13}-Δ^{10}-form. No isomerisation is noted with (I) or (II) at 200° in N_2, with piperidine in N_2 at 100° or 200°, or with N-Na *tert.*-amyloxide at room temp. or 100°; (III) generally yields viscous material. (I) or (II) is hydrogenated (Pd–C in EtOH, or Adams' catalyst in AcOH) to 9-*ketoperhydrophenanthrene*, form *A*, m.p. 51° (mainly) (*oxime*, m.p. 163—164°; semicarbazone, m.p. 187°), and a form *B*, b.p. 128°/2 mm. (*oxime*, m.p. 184—185°; semicarbazone, m.p. 182—183°), which are *trans*^{13}- and *cis*^{13}-forms, respectively, and otherwise of identical configuration. *A* is unchanged at 250° in N_2 for 1 hr., or by boiling with $NaNH_2$–C_6H_6. *B* is converted into *A* at 280° in N_2. Hydrogenation of (III) affords solely a *trans*^{13}-9-*ketoperhydrophenanthrene*, form *C*, m.p. 47—48° (oxime, m.p. 227—228°), unchanged by $NaNH_2$–C_6H_6. (I) or (II) and Na–EtOH give mixtures, oxidised by CrO_3–AcOH to *A*. (III) similarly gives 9-*hydroxyperhydrophenanthrene*, m.p. 119°, oxidised to *C*. (I) or (II) is reduced (Clemmensen) to *dodecahydrophenanthrenes*, b.p. 121—122°/12 mm. or 116°/9 mm. (double linking migration is indicated as either form with amyl nitrite gives a pale blue *nitrosochloride*, m.p. 191°), and physical properties show that they differ, or at least contain considerable amounts of different isomerides. Either form and Pd–C at 330—340° give phenanthrene. *A* is reduced (Clemmensen) to a product, purified by K at 210° and then with H_2SO_4–oleum, to give a *perhydrophenanthrene*, b.p. 140—140·5°/18 mm.; *C* similarly gives an *isomeride*, m.p. 10°, which is probably homogeneous. *A* and MgMeI give a *tert.*-alcohol, dehydrated by repeated distillation at 40 mm. with a little I (followed by K at 210°) to 9-*methyldodecahydrophenanthrene*, b.p. 140°/15·5 mm., dehydrogenated (Pd–C) in the vapour phase at 330° to 9-methylphenanthrene (picrate, m.p. 148—149°).

A. T. P.

Bisdiphenylene-ethylene series. C. Courtot and J. Kroustein (Compt. rend., 1939, **208**, 1230—1233; cf. Korczyński *et al.*, A., 1927, 347).—7-Nitrofluorene with Br in $PhNO_2$ at 110—170° gives a red *compound* (I), m.p. >450° [which with $K_2Cr_2O_7$ in boiling 20% H_2SO_4 (40 hr.) gives 2-bromo-7-nitrofluorenone (II), m.p. 230° (cf. A., 1927, 234)], and with Br (2 mols.) at 150° 2 : 9-*dibromo*-7-*nitrofluorene* (III), m.p. 206° [oxidised to (II), and with Zn–aq. NH_3 gives 2-bromo-7-aminofluorene]. (III) with Br (1 mol.) in $PhNO_2$ at 160° gives (60%) 2 : 2′-*dibromo*-7 : 7′-*dinitrobisdiphenylene-ethylene* [? (I)] (cf. Bergmann *et al.*, A., 1933, 152). A suspension of (I) in $PhNO_2$ with excess of Br at 160°, affords a colourless *compound*, $C_{28}H_{12}O_4N_2Br_4$, which decomposes in hot tetralin or $PhNO_2$ or at 250° to give (I). 2 : 7-Dinitrofluorene with Br (2 mols.) in $PhNO_2$ gives 2 : 2′ : 7 : 7′-tetranitrobisdiphenylene-ethylene, m.p. >450° (cf. Hughes and Kuriyan, A., 1936, 62), oxidised to 2 : 7-dinitrofluorenone.

J. L. D.

Dehydrogenation. III. S. C. Sen-Gupta (J. Indian Chem. Soc., 1939, **16**, 89—94; cf. A., 1939, II, 148).—Hydrindene (I), $(\cdot CH_2 \cdot CO)_2O$, and $AlCl_3$ in $PhNO_2$ give γ-*keto*-γ-5-*hydrindyl*-n-*butyric acid*, m.p. 123—124°, oxidised by alkaline $KMnO_4$ to 1 : 2 : 4-$C_6H_3(CO_2H)_3$ (II) and reduced by Zn–Hg–HCl to γ-5-*hydrindyl*-n-*butyric acid*, m.p. 56°, b.p. 190—192°/6 mm., which with 85% H_2SO_4 at 100° gives 1-*keto*-6 : 7-*trimethylene*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (III), b.p. 167°/6 mm. The structure of (III) is proved by oxidation (alkaline $KMnO_4$) to 1 : 2 : 4 : 5-$C_6H_2(CO_2H)_4$ (IV). Clemmensen reduction of (I) affords 6 : 7-*trimethylene*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (V), b.p. 125—126°/6 mm. *as*-Dimethylsuccinic anhydride, (I), and $AlCl_3$ give similarly γ-*keto*-γ-5-*hydrindyl*-αα-*dimethyl*-n-*butyric acid*, m.p. 139—140° (*Me* ester, b.p. 190—191°/6 mm.) [oxidised to (II)], and thence γ-5-*hydrindyl*-αα-*dimethyl*-n-*butyric acid*, m.p. 82—83°, 1-*keto*-2 : 2-*dimethyl*-6 : 7-*trimethylene*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. 170°/10 mm. [oxidised to (IV)], and 2 : 2-*dimethyl*-6 : 7-*trimethylene*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (VI), m.p. 82°. The C_5-ring survives Se-dehydrogenation at 300—320°, for (V) gives 5 : 6-*benzhydrindene*, m.p. 94° (*picrate*, m.p. 120—121°), and (VI) gives 2-*methyl*-6 : 7-*trimethylenenaphthalene*, m.p. 104° (*picrate*, m.p. 107—108°).

R. S. C.

Catalytic oxidation and preparation of hexahydrobenzylamine. I. I. Lenarski (J. Gen. Chem. Russ., 1939, **9**, 99—103).—NH_3 and hexahydrobenzyl alcohol passed through a layer of Ni–Al catalyst at 185° give hexahydrobenzylamine (I) in 65% yield. An aq. suspension of (I) and Cu powder shaken with O_2 yields hexahydro-benzaldehyde (chief product) and -benzoic acid. The reaction is not affected by ultra-violet light.

R. T.

Mechanism of the Hofmann reaction. Retention of optical activity during the reaction with (+)hydratropamide. C. L. Arous and J. Kenyon (J.C.S., 1939, 916—920).—The Hofmann rearrangement is substantially an intramol. reaction. Hydratropaldehyde is oxidised by $KMnO_4$–$MgSO_4$ in aq. $COMe_2$ to *dl*-hydratropic acid, converted, through the strychnine salts, into the (+)-, m.p. 29°, $[\alpha]_{5893}$ +74·8° in $CHCl_3$, and (−)-acid, m.p. 29°, $[\alpha]^{17}_{5461}$ (supercooled) −61·68° (*l*, 0·5). The (+)-acid, through the chloride and NH_3 at −18°, gives (+)*hydratropamide*, m.p. 103—104°, which with Br in aq. NaOH affords (−)-α-phenylethylamine, α^{15}_{5893} −18·20°, α^{15}_{5461} −21·81° (*l*, 0·5) (Ac derivative, new m.p. 103—104°). Optical activity is almost completely retained during rearrangement. Theoretical aspects are discussed.

A. T. P.

Cathodic reduction of aromatic nitroso-compounds.—See A., 1939, I, 378.

Substituted sulphanilamides. I. N^4-Acyl derivatives. E. Miller, H. J. Rock, and M. L. Moore (J. Amer. Chem. Soc., 1939, **61**, 1198—1200).—The following are prepared by the usual methods. N^4 indicates substitution of the *p*-NH_2 of (I). Sulphanilamide* (I), m.p. 165°. N^4-Acetyl-, m.p. 215—216°, -*propionyl*-, m.p. 220—221°, -n-*butyryl*-, m.p. 230—231°, -*n*-valeryl*, m.p. 197—198°, -*n*-hexoyl*, m.p. 200—201°, -heptoyl-, m.p. 192—203°, -octoyl-,

m.p. 200°, *-n*-lauroyl-†, m.p. 205—205·5°, *-benzoyl-*†, m.p. 280°, -benzyl-, m.p. 169—174°, -iso*butyryl-*, m.p. 241·5—242·5°, *-iso*valeryl-, m.p. 216—217°, and -iso*hexoyl-*†, m.p. 193—194°, *-sulphanilamide*; 4-*benzamidobenzenesulphonanilide*†, m.p. 222—222·5°; and benzamide-3-sulphonamide†, m.p. 171—173°. Succinic and maleic anhydride and (I) in hot EtOH give N-p-*sulphamidophenyl-succinamic*, m.p. 212·5—213·5°, and *-maleinamic acid*, m.p. 208—209°, respectively; in C_5H_5N 4-*succinimidobenzenesulphonamide*, m.p. 282·3°, is formed. Substances marked * have high, those marked † no, and others intermediate therapeutic val. against β-hæmolytic streptococci in mice. R. S. C.

p-Carbamidobenzenesulphonamide.—See B., 1939, 665.

Alleged optical activity of *o*-toluidine-3 : 5-disulphonic acid. P. P. Hopf and R. J. W. Le Fèvre (J.C.S., 1939, 921).—The experiment of Sementzov (A., 1934, 763) with *o*-toluidine-3 : 5-disulphonic acid is repeated, and gives only inactive acid. The *strychnine* salt, prepared from excess of acid in $CHCl_3$, has m.p. 245° (decomp.), $[\alpha]_D^{18}$ +21·0° in $CHCl_3$. A. T. P.

Catalytic phenylation of α-naphthylamine and α-naphthylamine-8- and -5-sulphonic acids.—See B., 1939, 576.

Thionitrites. IV. History of nitrosylmercaptides or thionitrites. H. Rheinboldt and F. Tappermann [with H. Kleu] (J. pr. Chem., 1939, [ii], **153**, 65—76; cf. A., 1932, 599).—Re-examination shows that the compound isolated by Beckarts *et al.* (A., 1906, i, 650) by the addition of HCl or H_2SO_4 to SH·CH_2·CO·NHPh (I) and KNO_2 in aq. EtOH is *nitrosothiolacetanilide*, NO·S·CH_2·CO·NHPh, m.p. ~160° after becoming colourless at ~100°, also obtained from (I) and EtO·NO. $CH_2Cl·CO_2H$, NH_4CNS, and NHPhMe in EtOH afford carbamylthiolacetmethylanilide (II), new m.p. 142—143°, which when heated at ~150°, followed by extraction of the product with EtOH and treatment of the extract with $Hg(CN)_2$ in boiling MeOH, gives the *Hg* salt, m.p. 118—118·5°, of thiolacetmethylanilide, also obtained from (II) by heating with 25% NH_3 in boiling EtOH, acidifying, and adding $Hg(CN)_2$. The mercaptan is oxidised by $FeCl_3$ to *dithiodiacetdimethylanilide*, (·S·CH_2·CO·NPhMe)$_2$, m.p. 81°. Attempts to prepare nitrosothiolacetmethylanilide were unsuccessful. *Carbamylthiolacet-α-naphthylamide*, m.p. 163—164·5°, *thiolacet-α-naphthylamide*, m.p. 127—128·5° (*Hg* derivative, decomp. >200°), and *dithiodiacetdi-α-naphthylamide*, m.p. 205—206°, are described; nitrosothiolacet-α-naphthylamide could not be obtained pure. *Carbamylthioacet-β-naphthylamide*, m.p. 180—181° (decomp.), *thiolacet-β-naphthylamide* (III), m.p. 113—113·5° (*Hg* derivative decomp. 195—210°), and *dithiodiacetdi-β-naphthylamide*, m.p. 195—198° after partial decomp. at 187°, have been prepared. *Nitrosothiolacet-β-naphthylamide*, m.p. 194—198° after becoming colourless at 110—115° and brown at 155°, is obtained from (III) and EtO·NO. H. W.

Derivatives of diphenyl-*p*-phenylenediamine. J. S. Joffe and V. J. Soloveitschik (J. Gen. Chem. Russ., 1939, **9**, 144—148).—4 : 1 : 3 : 6-$NO_2·C_6H_2Cl_2·SO_3Na$, *p*-$NH_2·C_6H_4$·NHPh, and Na_2CO_3 in aq. EtOH (10 hr. at the b.p.) yield 5-*chloro*-2-*nitro*-4′-*anilinodiphenylamine*-4-*sulphonic acid* (I) (*K* salt, $+H_2O$). This is reduced (Zn in aq. Na_2CO_3) to the corresponding 2-NH_2-compound, hydrolysed by boiling 26% HCl to 5-*chloro*-2-*amino*-4′-*anilinodiphenylamine*, m.p. 148°. (I) and NH_2Ph in 1 : 1 H_2O–EtOH (20 hr. at 160—170°/20 atm.) yield 2-*nitro*-4′ : 5-*dianilinodiphenylamine*-4-*sulphonic acid*, reduced as before to the 2-NH_2-compound (attempts at desulphonation unsuccessful). R. T.

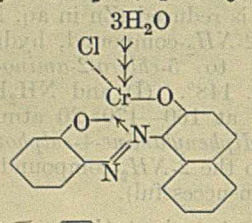
Detection of *meta*-orientation in diamino-, dinitro-, and aminonitro-compounds. A. Albert (J.C.S., 1939, 920—921; cf. A., 1938, II, 458).—*m*-Diamines are detected by the fluorescence (bright yellowish-green) of the diaminoacridines formed by reaction with $ZnCl_2$, glycerol, and $H_2C_2O_4,2H_2O$ at 160° for 10 min. A phenolic group interferes with the test. Replacement of half of the $ZnCl_2$ with $SnCl_2$ in the above test allows detection of *m*-orientation in aminonitro- or dinitro-compounds, again giving fluorescing diaminoacridines. Many examples are recorded. A. T. P.

Action of pyridine and ammonia on complex ammines of benzidine.—See A., 1939, I, 383.

Action of phenylacetic acid on azo-compounds. G. B. Crippa and R. Caracci (Gazetta, 1939, **69**, 129—136).—1-Benzeneazo-β-naphthylamine (I) and $CH_2Ph·CO_2H$ (II) at 190° give a *substance*, m.p. 243—245° (III), and *phenylacet-β-naphthylamide* (IV), m.p. 159° (identified by synthesis; the *-α-naphthylamide* has m.p. 169°). With $CH_2Ph·CO_2Et$ and a trace of conc. HCl at 220°, (I) gives (III) and (IV). 4-Benzeneazo-α-naphthylamine (V) and (II) give a *substance*, m.p. 192—195°, and an indulinic (?) *substance*, m.p. 215°. The indulinic bases obtained from (V) and NH_2Ph at 160—180° give when heated with (II) a *product*, m.p. 215°, with different properties from the above. E. W. W.

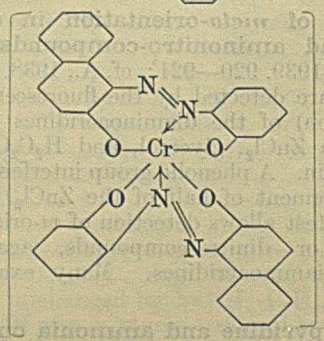
Structure of the chromium lakes of dyes. I. Lakes of *oo′*-dihydroxy- and *o*-hydroxy-*o′*-carboxy-azo-compounds, including monosulphonic acids. Behaviour of azosalicylic acids with chromic salts. H. D. K. Drew and R. E. Fairbairn (J.C.S., 1939, 823—835; cf. A., 1938, II, 180).—A single *o*-OH is insufficient to hold a Cr in stable union with an azo-N; *e.g.*, benzeneazo-β-naphthol and derivatives do not yield complexes with Cr, Fe‴, Mn″, or Zn″ (Cu, Co, and Ni give complexes). *o*-Hydroxybenzeneazo-β-naphthol (I) and $CrCl_3,4H_2O$ in boiling EtOH (97% unless otherwise stated) afford the H_2O-sol. *chromi-chloride tetrahydrate* [probably (II)] [also $+2C_5H_5N$ and (impure) $+2NH_2Ph$] (contains ionic Cl and $3H_2O$ co-ordinated with Cr), a *complex*, $(C_{16}H_{10}O_2N_2)_3Cr_2,8H_2O$ (formula given), and an *acid chromi-complex* (III) (C_5H_5N salt is sol. in H_2O), insol. in H_2O. (III) is also obtained by refluxing (I) and AcOH–$CrCl_3,4H_2O$; excess of the latter gives the *chromi-acetate* salt of (III), also obtained from (II) and AcOH. (II) and aq. $H_2C_2O_4$ give some (I). (II) and aq. NH_3 or K_2CrO_4 give the *chromi-oxide tetrahydrate* (or *chromi-hydroxide dihydrate*), $(C_{16}H_{10}O_2N_2Cr)_2O,4H_2O$ (C_5H_5N and NH_2Ph partly

replace co-ordinated H_2O). 2 : 2′-Dihydroxyazobenzene and $CrCl_3$ give a *chromi-chloride*, $C_{12}H_8O_2N_2ClCr,4H_2O$ (aq. NH_3 or K_2CrO_4 gives an



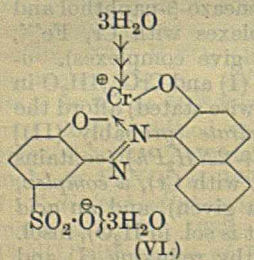
(II.)

, H_2O



H (III.)

oxide dihydrate, $C_{24}H_{16}O_5N_4Cr_2,2H_2O$, insol. in H_2O). 5′-Nitro-2′-hydroxybenzeneazo-β-naphthol (IV) affords a *chromi-chloride*, $C_{16}H_9O_4N_3ClCr,6H_2O$ (also $+5H_2O$) [*oxide* (?) *octahydrate*, insol. in H_2O], which at 140—160° loses all the H_2O and some HCl. 2′-Hydroxy-5′-sulphobenzeneazo-β-naphthol (V) and $CrCl_3$ or $Cr_2(SO_4)_3$ in boiling H_2O, or in smaller yield with $K_2Cr_2O_7$ and aq. H_2SO_4, afford the *chromi-sulphonate*, $+6H_2O$ (VI), (*NH*$_4$ salt is sol. in H_2O even after desiccation; complex *C*$_5$*H*$_5$*N* salt), and a *tribasic acid chromi-complex*, $C_{32}H_{21}O_{10}N_4S_2Cr,9H_2O$ (VII) (2 azo-residues to 1 Cr), also obtained from the Na salt of (V) and (VI) in dil. NaOH. (VI) is sol. in H_2O, and loses $6H_2O$ at 140—150° and slowly regains $0{\cdot}5H_2O$, but is then insol. in H_2O. (V) and excess of $Cr_2(SO_4)_3$ and H_2O give (VII) and a *chromi-sulphonate tetrahydrate*, probably polymerised [boiling aq. NH_3 gives NH_4 salt of (VI)], which loses $3{\cdot}5H_2O$ at 140—170° and regains $4H_2O$ in 1 month. (VI) and (IV) in aq. NaOH give a *complex*, $C_{32}H_{20}O_9N_5SCr,9H_2O$ (VIII) [similar to (VII)], and a *chromi-azosulphonic acid salt* of (VIII), $C_{48}H_{29}O_{14}N_7S_2Cr_2,14H_2O$. Formation of (VI) does not involve oxidation since (VI) and aq. $H_2C_2O_4$ afford (V). 4′-Hydroxy-*m*-tolueneazo-β-naphthol-6-sulphonic acid (with a little Na sulphonate), refluxed with $Cr_2(SO_4)_3$ in H_2O, or $CrCl_3,4H_2O$ in EtOH, gives a *chromi-sulphonate nonahydrate*, $C_{17}H_{11}O_5N_2SCr,9H_2O$ (loses $8H_2O$ at 140—150°; regains $4{\cdot}5H_2O$ and remains sol. in H_2O), and a substance (Cr, 3·6%). 2′-Hydroxy-4′-sulphonaphthalene-1′ : 4-azo-1-phenyl-3-methylpyrazol-5-one and $CrCl_3,4H_2O$ in EtOH give a *chromi-sulphonate*, $C_{20}H_{13}O_5N_4SCr,5{\cdot}5H_2O$ (loses $4{\cdot}5H_2O$ at 140—170°; regains $3H_2O$ in 10 days), sparingly sol. in H_2O. *o*-Carboxybenzeneazo-β-naphthol (IX) similarly affords



(VI.)

a *chromi-chloride*, $C_{17}H_{10}O_3N_2ClCr,2{\cdot}5H_2O$ (ionised Cl), converted by boiling H_2O (or aq. NH_3 or K_2CrO_4) into the *oxide tetrahydrate*, $C_{34}H_{20}O_7N_4Cr_2,4H_2O$. Naphthalene-1′-azosalicylic acid and $CrCl_3,4H_2O$ in H_2O (refluxed for 4 hr.) give a *complex*, $C_{51}H_{30}O_9N_6Cr_2,7H_2O$ (Cr^{III} salt of a tribasic chromi-acid) (loses $5H_2O$ at 120°; regains $2{\cdot}5H_2O$), and an (acid) *complex*, $C_{34}H_{21}O_6N_4Cr,4{\cdot}5H_2O$ (loses $4H_2O$ at 140°; regains $1H_2O$), with properties differing from those of other complexes described. (IX) and $FeCl_3,2H_2O$–EtOH (boil 5 min.) give a *complex*, $[(C_{17}H_{10}O_3N_2)_2Fe]H,2H_2O$, from which 1 mol. of (IX) is removed by alkali. *p*-Carboxybenzeneazo-β-naphthol (X) and $FeCl_3$ in C_5H_5N–EtOH (1 : 3) give a basic Fe^{III} salt, $(C_{17}H_{11}O_3N_2)Fe(OH)_2$. (IX) and $Ni(OAc)_2$–EtOH give a *complex*, $C_{17}H_{10}O_3N_2Ni,2H_2O$ (Ni probably ionised from CO_2H) ($2C_5H_5N$ compound), but $Zn(OAc)_2$ gives a simple *salt*. (I) in EtOH gives a *ferri-chloride*, $C_{16}H_{10}O_2N_2ClFe$, insol. in H_2O, converted by C_5H_5N–H_2O into the *complex*, $C_{16}H_{10}O_2N_2Fe{\cdot}OH,C_5H_5N$. The *Ni* and *Zn complexes* of (I) resemble the analogous Cu derivatives; they are co-ordinatively unsaturated, and form C_5H_5N *compounds*. (V) and aq. $FeCl_3$ give a *ferri-sulphonate*, $C_{16}H_9O_5N_2SFe,3H_2O$, insol. in H_2O, readily decomp. by dil. mineral acids. (X) and chrome alum give Cr^{III} *p-carboxybenzeneazo-β-naphthol*, $+3H_2O$. The Na salt of (X) and aq. $CuCl_2$ give the simple *Cu* salt. (X) and $CuSO_4$–aq. NH_3 give a *complex*, $\{(C_{17}H_{10}O_3N_2)_2Cu\}Cu,NH_3,6H_2O$ (loses $6H_2O$ on desiccation; regains $5H_2O$ in <2 hr. to give a *pentahydrate*). (X) and $Cu(OAc)_2$ in EtOH–C_5H_5N afford the *complex*, $\{(C_{17}H_{10}O_3N_2)_2Cu\}Cu,2C_5H_5N$, also prepared from the pentahydrate and C_5H_5N. Benzeneazosalicylic acid (XI) and $Cu(OAc)_2$–EtOH give a *complex*, $C_{13}H_8O_3N_2Cu,2H_2O$, but aq. $CuSO_4$–NH_3 affords a *complex* containing $2NH_3$. (XI) and $Ni(OAc)_2$ in EtOH give a simple *Ni* salt and a mixture of complexes. Benzeneazo-*o*-cresotic acid and $Cu(OAc)_2$–EtOH yield a complex, $C_{14}H_{10}O_3N_2Cu,2H_2O$, whilst cuprammonium sulphate gives a *diammino*-compound, whence the *compound*, $C_{14}H_{10}O_3N_2Cu,2C_5H_5N$.

A. T. P.

Decomposition reactions of aromatic diazo-compounds. VI. Reactions of benzenediazonium chloride with metals. W. A. Waters (J.C.S., 1939, 864—870; cf. A., 1938, II, 52, 405).—PhN_2Cl (I), $COMe_2$, and $CaCO_3$, with Ag, Au, Cd, Al, In, Mn, Co, Ni, Pd (no PhCl) or Bi (no PhCl), give the metal chloride, $CH_2Cl{\cdot}COMe$, C_6H_6, Ph_2, PhCl, and no organo-metallic compound. Cu and Fe yield also 60 and 20% of PhCl, respectively (catalytic effect). Mg gives $MgCl_2$, C_6H_6, and (?) PhCl, $CMe_2{:}CHAc$, and phorone. Zn (brisk at 0°) affords $ZnCl_2$ + C_6H_6. As gives $AsCl_3$, $AsCl_5$, and $CH_2Cl{\cdot}COMe$. B, Ce, Tl, C, Si, ferrosilicon, red P, Ti, Ge, Zr, Th, Cr, W, V, Ta, and Pb do not react; secondary products are sometimes formed. Mo affords also (?) $MoCl_5$. (I) does not react with As in the cold, but on heating gives $AsPh_2Cl_2$, (?) $AsPh_3Cl{\cdot}OH$, and *triphenylarsine phenoxyhydroxide*, m.p. 129°, converted by H_2S–MeOH into $AsPh_3S$ and PhOH. (I) and Sn in the cold give $SnPh_2Cl_2$; no Pb aryls are obtained (cf. Nesmejanov *et al.*, A., 1936, 66). Theoretical aspects of the reactions are discussed. (I) and $CaCO_3$ in $COMe_2$–C_6H_6, refluxed for 1 hr., or with Zn dust at room temp.,

give Ph_2. $PhN_2Cl,ZnCl_2$ (II) and $CaCO_3$ in $COMe_2$–C_6H_6–Zn dust give Ph_2. (I) or (II), $C_{10}H_8$, $COMe_2$, and Zn give 1- and 2-$C_{10}H_7Ph$ (III). β-$C_{10}H_7{\cdot}N_2Cl$, $ZnCl_2$, and Zn in $COMe_2$–C_6H_6 give (III). Thus a means is afforded of preparing unsymmetrically substituted diaryls. A. T. P.

Homologous series of *N*-acyl-*m*-aminophenols and azo-dyes obtained therefrom. H. E. Fierz-David and H. Meister (Helv. Chim. Acta, 1939, **22**, 579—585).—m-*Form-*, m.p. 116°, *-acet-*, m.p. 148°, *-propion-*, m.p. 181°, *-butyr-*, m.p. 140°, *-valer-*, m.p. 119°, -iso*valer-*, m.p. 143·5°, *-hex-*, m.p. 135·5°, *-hept-*, m.p. 147°, *-oct-*, m.p. 125°, *-non-*, m.p. 126°, *-dec-*, m.p. 124·5°, *-undec-*, m.p. 122·5°, *-laur-*, m.p. 125°, *-tridec-*, m.p. 117·5°, *-myrist-*, m.p. 116°, *-pentadec-*, m.p. 115·5°, *-palmit-*, m.p. 114·5°, *-margar-*, m.p. 114·5°, *-stear-*, m.p. 114°, *-nonadec-*, m.p. 115·5°, *-ole-*, m.p. 95·5°, and *-benz-*, m.p. 173°, *-amidophenol* are described. Four series of azo-dyes are obtained by using sulphanilic, metanilic, 6-amino-3-sulphobenzoic acid and 1 : 2 : 5-$NH_2{\cdot}C_6H_3(SO_3H)_2$ as azo components. The surface tensions of aq. solutions of these dyes determined by the " abs. tensiometer " of du Nouy give very similar graphs for each homologous series. The min. of the surface tension of 1 in 1000 solutions lies in all cases at a chain-length of 10 or 11 C. The acyl derivatives show a min. here. H. W.

Derivatives of *o*- and *p*-*cyclo*hexylphenols. D. Bodroux and R. Thomassin (Compt. rend., 1939, **208**, 1314—1316).—Equimol. amounts of the K derivatives (I) of *o*- or *p-cyclo*hexylphenol (cf. A., 1929, 1050) with $(CH_2Cl)_2$ or $(CH_2Br)_2$ in boiling EtOH afford the corresponding β-chloro- or β-bromoethyl ethers. The following are prepared : o-β-*chloro-*, b.p. 172—174°/10 mm., and *-*β*-bromo-ethoxyphenyl*-cyclo*hexane* (II), b.p. 183—185°/10 mm.; p-β-*chloro-*, m.p. 56°, and *-*β*-bromo-ethoxyphenyl*cyclo*hexane* (III), m.p. 64°. (II) and (III) (the Cl-compounds give low yields) with hot EtOH–KI afford, nearly quantitatively, o-, b.p. 189—191°/10 mm., and p-β-*iodoethoxyphenyl*cyclo*hexane*, m.p. 76°, respectively. (I) (2 mols.) with $(CH_2Br)_2$ (1 mol.) in hot EtOH affords (23%) αβ-*di*-o-, m.p. 90°, and αβ-*di*-p-cyclo*hexylphenoxyethane*, m.p. 151°, which with hot dil. EtOH–KOH/6 hr. are decomposed (30—40%) to the original phenols. (II) and (III) with Na in boiling Et_2O afford (80—86%) αδ-*di*-o-, m.p. 165°, and αδ-*di*-p-cyclo*hexylphenoxybutane*, m.p. 130°, respectively. (I) with CH_2PhCl or *p-cyclo*hexylbenzyl chloride in boiling EtOH affords (>80%) o-, b.p. 208—209°/10 mm., and p-cyclo*hexylphenyl benzyl*, m.p. 86°, or the p-cyclo*hexylbenzyl ethers*, b.p. 282—285°/13 mm., and m.p. 177·5°, respectively, which are stable to hot dil. KOH. J. L. D.

Condensation of aldehydes and ketones with aromatic compounds in presence of aluminium chloride. I. Condensation of aliphatic ketones with phenols. I. P. Tzukervanik and Z. N. Nazarova (J. Gen. Chem. Russ., 1939, **9**, 33—35).—$COMe_2$, $COEt_2$, and $COMePr^{\alpha}$ with PhOH in presence of $AlCl_3$ at 100° yield respectively *p-iso*propyl-, *p*-α-ethylpropyl-, and p-α-*methylbutyl-phenol*, b.p. 245—250°/730 mm. (*benzoate*, b.p. 340—350°/730 mm.; *acetate*, b.p. 254—255°; *Me ether*, b.p. 232—238°). R. T.

Derivatives of *p-tert.*-octylphenol.—See B., 1939, 581.

Reactions of Δ^{γ}-hexene. II. Condensations with aromatic hydrocarbons and phenols. L. Spiegler and J. M. Tinker (J. Amer. Chem. Soc., 1939, **61**, 1002—1004; cf. A., 1939, II, 238).—Condensation of 1, 2, or 3 mols. of $(CHEt{:})_2$ with aromatic hydrocarbons or phenols is effected by H_2SO_4, $HClO_4$, or $AlCl_3$ under the usual conditions, by anhyd. HF at 5—10°, $H_3BO_2F_2$ at the b.p., or $ZnCl_2$ at 130—180°. The expected products are obtained, but are oils and thus are probably partly isomerised. The following approx. pure compounds are described. p-*Di-*α*-ethyl-*n*-butylbenzene*, b.p. 104—106°/0·3 mm. p-*Chloro-*α*-ethyl-*n*-butylbenzene*, b.p. 135—140°/30 mm. p-α-*Ethyl-*n*-butyltoluene*, b.p. 162—165°/135 mm. γ-m-*Xylyl-*, b.p. 101—102°/3 mm., *γ-naphthyl-*, b.p. 148—151°/1 mm., *γ-acenaphthyl-*, b.p. 170—174°/4 mm., and *γ-chloroacenaphthyl-hexane*, b.p. 206—220°/2 mm. *Chlorodi-*α*-ethyl-*n*-butylacenaphthene*, b.p. 223—241°/2 mm. *Di-*α*-ethyl-*n*-butylanthracene*, b.p. 240—256°/3 mm. α-*Ethyl-*, b.p. 110°/3 mm., *di-*α*-ethyl-*, b.p. 159—175°/2 mm., and *tri-*α*-ethyl-*n*-butyl-phenol*, b.p. 170—195°/7 mm. 6-*Chloro-*x-α*-ethyl-*n*-butyl-*o-, b.p. 145—153°/5 mm., and -m-*cresol*, b.p. 155—160°/5 mm. α-*Ethyl-*n*-butyl-*, b.p. 124—130°/6 mm., and *di-*α*-ethyl-*n*-butyl-cresylic acid*, b.p. 165—195°/12 mm. α-*Ethyl-*n*-butyl-resorcinol*, b.p. 134°/1 mm., *-pyrocatechol*, b.p. 142—144°/1 mm., *-quinol*, b.p. 142—151°/2 mm., -α-, b.p. 160—168°/2 mm., and -β-*naphthol*, b.p. 180—218°/3 mm. *Di-*α*-ethyl-*n*-butylquinol*, b.p. 182—190°/3 mm. γ-Phenylhexane, Cl_2, and I or $FeCl_3$ give Cl_3-, b.p. 164—168°/15 mm., Cl_4-, b.p. 157—162°/5 mm., and Cl_5-derivatives, b.p. 195—197°/15 mm. R. S. C.

Hydrofluoric acid as condensing agent. II. Nuclear alkylations in presence of hydrofluoric acid. W. S. Calcott, J. M. Tinker, and V. Weinmayr (J. Amer. Chem. Soc., 1939, **61**, 1010—1015; cf. A., 1939, II, 254).—Technical anhyd. or, sometimes, 46% aq. HF causes condensation, usually at 5—10° or 20°, of (*a*) isocyclic hydrocarbons, phenols or their ethers, nitrophenols or their ethers, carboxylic or sulphonic acids, primary, *sec.*, or *tert.* aminophenols or their ethers with (*b*) olefines or compounds expected to react as such (*e.g.*, alcohols, ethers, esters, or halides). $C_{<3}$-components react more readily than do C_2-compounds. Migration or isomerisation does not occur. Ethers are unaffected under the reaction conditions and are thus not intermediates; *N*-alkyl derivatives are also not intermediates. $(CH_2Ph)_2O$ reacts normally, but $CH_2Ph{\cdot}OH$ polymerises to 1 : 2 : 3 : 4 : 5 : 6-hexaphenyl*cyclo*hexane. Di*iso*butylene gives only Bu^{γ} compounds. The dialkylated aminophenols are very unstable, losing NH_3 at room temp., and giving tetra-alkyldiphenylamines when heated. Similarly, only one Pr^{β} could be introduced into quinol, further reaction giving 2 : 4 : 6-*tri*iso*propylphenol*, b.p. 125°/7 mm. The following are described. α-*Chloro*tert.*-butyl-*, b.p. 111°/90 mm., and *di-*α*-chloro-*tert.*-butyl-benzene*, b.p. 140°/4 mm. αβ-*Diphenylpropane*, b.p. 109°/2 mm. $C_{10}H_4Pr^{\beta}_4$, m.p. 128° (*Cl*$_4$-derivative, b.p. 170°/0·1 mm.). *Naphthylstearic acid*, an oil, from $C_{10}H$ and oleic

acid. *iso*Propyltetrahydronaphthalenes, b.p. 136—270°/4·6 mm. *Di*iso*propyl*-, b.p. 202—206°/0·2 mm., *di*-x-*ethylbutyl*-, b.p. 240—256°/3 mm., and *penta*-x-*ethylbutyl-anthracene*, m.p. 89·2—101°. 1-*Nitro*-x-iso*propyl*-, b.p. 145—155°/2 mm., and -*di*iso*propyl-naphthalene*, b.p. 155—168°/? 2 mm. (NH_2-compound, b.p. 150—158°/0·5 mm.). 2-*Nitro*-4-iso*propyl-anisole*, b.p. 138·5—139·5°/3 mm. 2-*Nitro*-4-cyclo*hexyltoluene*, b.p. 198—208°/2 mm. Mixed iso*propyl*-m-, b.p. 102·5°/4 mm., m.p. 43°, *benzyl*-o-, b.p. 160°/5 mm., and *dibenzyl*-o-*cresol*, b.p. 235°/5 mm. iso*Propylquinol*, m.p. 147—148°. *Di*-α-*ethyl*-n-*butyldiphenyl ether*, b.p. 200—230°/5 mm. *Di*iso*propyl*-β-*naphthol*, b.p. 196°/2 mm. 2-*Hydroxy*-x-iso*propyl*-, m.p. ~50, and -*poly*iso*propyl*-3-*naphthoic acid*, m.p. 70—75°. *Poly*iso*propylnaphthalene*-2-*sulphonic acid*, m.p. ~40°. *m-iso*Propylbenzoic acid, m.p. ~20° (*chloride*, b.p. 125—130°/23 mm.). 4-*Amino*-xx-*di*iso*propylphenol*, b.p. 120°/2 mm. (*sulphate*, m.p. 206—208°). 4 : 4′-*Dihydroxytetra*iso*propyldiphenylamine*, b.p. 228°/4 mm. 4-*Dimethylamino*-x-iso*propylphenol*, m.p. 99—104°, b.p. 137°/3 mm., and -*di*iso*propylphenol*, b.p. 148°/3 mm. *Di*iso*propyl*-p-*anisidine*, b.p. 128°/3·6 mm. 4 : 4′-*Dimethoxytetra*-iso*propyldiphenylamine*, b.p. 230—234°/3 mm. (*hydrochloride*). cyclo*Hexyl*-p-*anisidine tetrahydrofluoride*, m.p. 185—195°, and *hydrochloride*, m.p. 225—230°. 3-*Ethoxy*-x-iso*propyl*-NN-*diethylaniline*, b.p. 110°/0·15 mm. 2-*Methoxy*-xxx-*tri*iso*propyl*-α-*naphthylamine*, b.p. 169°/0·14 mm. R. S. C.

Preparation of 3 : 6-di- and 3 : 4 : 6-tri-bromopyrocatechol. J. Frejka and B. Šefránek (Coll. Czech. Chem. Comm., 1939, **11**, 165—170; cf. A., 1936, 602).—*iso*Propylidenepyrocatechol (prep. by $COMe_2$ and P_2O_5 at 60°) gives the 3 : 6-Br_2-derivative, m.p. 92°, hydrolysed by conc. H_2SO_4 at 60° to 3 : 6-*dibromopyrocatechol*, m.p. 122° (*Ac*$_2$ derivative, m.p. 109°), which with Br–$CHCl_3$ affords the 3 : 4 : 6-*Br*$_3$-derivative, m.p. 135—136° (*Ac*$_2$ derivative, m.p. 115°), and was previously (Sloof, A., 1936, 838) considered to be the 4 : 5-Br_2-compound. R. S. C.

Synthetic œstrogenic compounds related to stilbene and diphenylethane. I. E. C. Dodds, L. Golberg, W. Lawson, and (Sir) R. Robinson (Proc. Roy. Soc., 1939, **B**, **127**, 140—166; cf. Kerschbaum *et al.*, A., 1939, II, 259).—A more detailed account of work previously reviewed (A., 1938, III, 299, 807, 908). δ-*Phenyl*-γ-*anisylhexan*-γ-*ol*, b.p. 140—143°/0·3 mm. (from *p*-OMe·C_6H_4·CO·CHPhEt and MgEtBr), is dehydrated (PBr_3–$CHCl_3$) to p-*methoxy*-αβ-*diethylstilbene*, b.p. 140—144°/0·25 mm., demethylated by EtOH–KOH at 190°/20 hr. to p-*hydroxy*-αβ-*diethylstilbene*, b.p. 135—140°/0·15 mm. Anisil and MgEtBr give γδ-*dianisylhexane*-γδ-*diol*, m.p. 193—194° [also obtained with m.p. 192—195° from *p*-OMe·C_6H_4·COEt and Mg–Hg at 100° (bath)/7 days; reduced (red P, conc. HI) to a *compound*, $C_{18}H_{22}O_2$,H_2O, m.p. 64·5—65°], together with α-*anisoyl*-α-*anisylpropyl alcohol*, m.p. 105—107°, and (probably) αβ-*dianisylbutane*-αβ-*diol*, b.p. 215—220°/0·25 mm. α-*Ethyldeoxyanisoin*, b.p. 192—195°/0·65 mm. (from deoxyanisoin and EtI in EtOH–NaOEt), and MgEtBr give γδ-*dianisylhexan*-γ-*ol*, m.p. 115—117°, b.p. 194—196°/0·8 mm. (p-*nitrobenzoate*, m.p. 120—122°), dehydrated (PBr_3–$CHCl_3$ at 0°–room temp.; $KHSO_4$ at 195—200°; boiling Ac_2O–AcCl) to 4 : 4′-*dimethoxy*-αβ-*diethylstilbene*, forms, m.p. 123—124° (I) and b.p. 175—178°/0·74 mm. (*cis*) (II) [gradually converted into (I) by sunlight]. Demethylation of (I) by $AlCl_3$ or $AlBr_3$ was not successful but EtOH–KOH at 200—210°/24 hr. yields (trans-)4 : 4′-*dihydroxy*-αβ-*diethylstilbene* [*diethylstilbœstrol*] (III), m.p. 171° (*diacetate*, m.p. 123—124°; *dipropionate*, m.p. 104°; *di*-n-, m.p. 88°, and -iso-*butyrate*, m.p. 86—87°; *di*-n-*valerate*, m.p. 89°; *dipalmitate*, m.p. 77—78°; *dibenzoate*, m.p. 210—211°; *di*-α-, m.p. 206—207°, and -β-*naphthoate*, m.p. 252—253°; *bisphenylacetate*, m.p. 100°); (II) similarly affords (III) and its cis-*isomeride* [*ψ-diethylstilbœstrol*] (IV), m.p. 140—142° (*diacetate*, m.p. 116—117°; *dibenzoate*, m.p. 193—197°). Reduction [AcOH–HI (*d* 1·94)] of (I) gives a *product*, $C_{18}H_{22}O_2$, b.p. 189—190°/0·8 mm., which is undoubtedly a mixture. Reduction (H_2, PtO_2, EtOH) of (IV) affords an alkali-insol. saturated *substance*, b.p. 184—187°/21 mm., and a saturated *compound*, $C_{18}H_{22}O_2$, m.p. 181—182°. Reduction (H_2, Pd–C, $COMe_2$) of (III) yields a γδ-*di*-p-*hydroxyphenylhexane* (V), m.p. 128° (*Me*$_2$ *ether*, m.p. 56—57°), whilst (IV) similarly gives a γδ-p-*hydroxyphenylhexane* (VI), m.p. 185°, together with some (III) (isomeric change) and hence (V); (I) and (II) both yield the Me_2 ether, m.p. 145—146°, of (VI). Similar reduction of (IX) (below) also gives (VI). The *dibenzoate*, m.p. 138—140°, of 4 : 4′-*dihydroxy*-α-*ethyldeoxybenzoin* (VII), b.p. 210—215°/0·6 mm. (*acetate*, m.p. 91—92°) (from α-ethyldeoxyanisoin and AcOH–HI), with MgEtBr affords a product which heated to 150°/~0·3 mm. yields (III). The *dibenzyl ether*, m.p. 78—80°, of (VII) and MgEtBr give γδ-*di*-p-*benzyloxyphenylhexan*-γ-*ol*, forms, m.p. 142—144° and 212—214°, converted by PBr_3–$CHCl_3$ into crude (III). αβ-*Dianisylbutan*-β-*ol*, b.p. 178—181°/0·6 mm., m.p. 61—62° (from deoxyanisoin and MgEtBr), is dehydrated [as for (I)] to 4 : 4′-*dimethoxy*-α-*ethylstilbene*, b.p. 165—166°/0·75 mm., m.p. 85°, demethylated (EtOH–KOH) to 4 : 4′-*dihydroxy*-α-*ethylstilbene*, b.p. 208—211°/0·3 mm., m.p. 128—129° (*dibenzoate*, m.p. 100—102°). ββ-*Dianisylbutan*-β-*ol*, m.p. 87—89° [from α-*methyldeoxyanisoin* (VIII), b.p. 176—177°/0·1 mm., m.p. 53—57°, and MgMeI], similarly gives 4 : 4′-*dimethoxy*-, m.p. 127—129°, and thence 4 : 4′-*dihydroxy*-αβ-*dimethylstilbene* [*dimethylstilbœstrol*], m.p. 194—196° (accompanied by some of its *Me*$_1$ *ether*, m.p. 115—116°). 4 : 4′-*Dimethoxy*-α-*methyl*-β-*ethylstilbene*, b.p. 159—161°/0·14 mm. [from (VIII) and MgEtI], is demethylated (EtOH–KOH at 200—210°) to the 4 : 4′-(*OH*)$_2$-derivative [*methylethylstilbœstrol*], m.p. 179—180° (*dibenzoate*, m.p. 217—219°). α-n-*Propyldeoxyanisoin*, b.p. 195—196°/0·14 mm., and MgEtBr give γδ-*dianisylheptan*-γ-*ol*, b.p. 176—177°/0·3 mm., whence 4 : 4′-*dimethoxy*-, b.p. 192—195°/0·4 mm. (also obtained directly from ethyldeoxyanisoin and excess of MgPr^{n}Br), and 4 : 4′-*dihydroxy*-α-*ethyl*-β-n-*propylstilbene*, b.p. 198—200°/0·14 mm. (*dibenzoate*, m.p. 208—211°). 4 : 4′-*Dimethoxy*- and 4 : 4′-*dihydroxy*-αβ-*di*-n-*propylstilbene* have b.p. 178—181°/0·8 mm. and 198—201°/0·09 mm., respectively. α-iso*Propyldeoxyanisoin*, b.p. 210—214°/0·8 mm., with MgPr^{i}Br affords γδ-*dianisyl*-βε-*dimethylhexan*-γ-*ol*, b.p. 205—207°/0·27 mm., dehydr-

ated ($KHSO_4$) to 4 : 4′-*dimethoxy-*, b.p. 181—182°/0·25 mm. (accompanied by a little 4 : 4′-dimethoxystilbene, m.p. 214°), whence 4 : 4′-*dihydroxy*-αβ-*diisopropylstilbene*, b.p. 202—204°/0·25 mm. (*dibenzoate*, m.p. 155°). 4 : 4′-Dimethoxy-, b.p. 186—188°/0·16 mm. (from α-n-*butyldeoxyanisoin*, b.p. 205—206°/0·6 mm., and $MgBu^nBr$), and 4 : 4′-*dihydroxy*-αβ-*di*-n-*butylstilbene*, b.p. 191—196°/0·2 mm. (*dibenzoate*, m.p. 192—193°), are prepared. Ethyldeoxyanisoin, Mg, and a little MeI in Et_2O followed by CH_2:$CH{\cdot}CH_2Br$ (dropwise in Et_2O) give 4 : 4′-*dimethoxy*-α-*ethyl*-β-*allylstilbene*, b.p. 197—198°/0·8 mm., which is demethylated and probably isomerised by EtOH–KOH to 4 : 4′-*dihydroxy*-α-*ethyl*-β-*propenylstilbene*, b.p. 208—211°/0·17 mm. (*dibenzoate*, m.p. 111—113°). α-*Allyldeoxyanisoin*, b.p. 196—198°/0·13 mm., Mg, I, and MeI (little) in Et_2O followed by CH_2:$CH{\cdot}CH_2Br$ afford δε-*dianisyl*-$\Delta^{\alpha\eta}$-*octadien*-ε-*ol*, b.p. 198—203°/0·23 mm., dehydrated ($KHSO_4$) to 4 : 4′-*dimethoxy*-αβ-*diallylstilbene*, b.p. 186—188°/0·09 mm., converted by EtOH–KOH into 4 : 4′-*dihydroxy*-αβ-*dipropenylstilbene*, b.p. 220—226°/0·4 mm. (*dibenzoate*, m.p. 164°). Me dianisyladipate-*a* (A., 1933, 828) and MgMeI give δε-*dianisyl*-βη-*dimethyloctane*-βη-*diol*-a, m.p. 125—126°, dehydrated ($KHSO_4$) to δε-*dianisyl*-βη-*dimethyl*-$\Delta^{\beta\zeta}$-*octadiene*, b.p. 202—203°/0·14 mm., which is reduced (H_2, PtO_2, EtOH) to the *-octane*, b.p. 210—220°/0·3 mm., and demethylated to δε-*di*-p-*hydroxyphenyl*-βη-*dimethyl*-$\Delta^{\beta\zeta}$-*octadiene*, b.p. 215—220°/0·01 mm. (*dibenzoate*, m.p. 71—72°). α-Phenyl-αβ-dianisylethyl alcohol, m.p. 111—112° (from deoxyanisoin and MgPhBr), is dehydrated (Ac_2O–AcCl) to 4 : 4′-*dimethoxy*-α-*phenylstilbene*, forms, m.p. 105—106° and 92—93°, whence (EtOH–KOH at 200°) the 4 : 4′-$(OH)_2$-derivative, m.p. 99—100°. γδ-*Di*-p-*hydroxyphenylhexane*-γδ-*diol*, m.p. 204—206° (*diacetate*, m.p. 199—200°) (from *p*-OH·C_6H_4·COEt and Al–Hg in moist Et_2O), with boiling Ac_2O–AcCl gives the *diacetate*, m.p. 119—120°, of γδ-*di*-p-*hydroxyphenyl*-$\Delta^{\beta\delta}$-*hexadiene* (IX), m.p. 227—228° (*dipropionate*, m.p. 96°). δε-*Di*-p-*hydroxyphenyloctane*-δε-*diol*, m.p. 186—187° (*diacetate*, m.p. 198—199°) (from *p*-OH·C_6H_4·COPr), similarly affords the *diacetate*, m.p. 129—130°, of δε-*di*-p-*hydroxyphenyl*-$\Delta^{\gamma\epsilon}$-*octadiene*, m.p. 127—128°. βγ-*Di*-p-*hydroxyphenyl*-$\Delta^{\alpha\gamma}$-*butadiene*, m.p. 164—165° (*diacetate*, m.p. 118—119°), is similarly obtained from (*p*-OH·C_6H_4·CMe·OH)$_2$. αδ-*Diphenyl*-βγ-*di*-p-*hydroxyphenylbutane*-βγ-*diol*, m.p. 197—198° (*diacetate*, m.p. 208—209°) (from *p*-OH·C_6H_4·CO·CH_2Ph and Al–Hg in moist Et_2O), similarly yields αδ-*diphenyl*-βγ-*di*-p-*hydroxyphenyl*-$\Delta^{\alpha\gamma}$-*butadiene*, m.p. 231—232° (*diacetate*, m.p. 202°). α-*Phenyl*-ββ-*di*-p-*hydroxyphenylethylene*, m.p. 178°, is obtained from the $(OMe)_2$-derivative and EtOH–KOH at 190°/18 hr.

m-OMe·C_6H_4·COMe (modified prep.; cf. A., 1937, II, 356) and *p*-OMe·C_6H_4·CHO in aq. EtOH–NaOH at 0° give m-*anisyl* p-*methoxystyryl ketone* [4 : 3′-*dimethoxychalkone*], m.p. 52°, which with NaCN in boiling MeOH (aq. AcOH being added so that the reaction mixture remains slightly alkaline) affords γ-*keto*-α-*cyano*-α-p-*anisyl*-γ-m-*anisylpropane*, m.p. 96—97°, hydrolysed (AcOH–conc. H_2SO_4) to β-m-*anisoyl*-α-p-*anisylpropionamide*, m.p. 136—137°, and thence (aq. EtOH–NaOH) to the *acid*, m.p. 161—162°, which is reduced (Clemmensen) to γ-m-*anisyl*-α-p-*anisylbutyric acid*, m.p. 98—99°. This with boiling $POCl_3$ yields 1-*keto*-6-*methoxy*-2-*anisyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 126—127°, converted by MgEtBr into 6-*methoxy*-2-*anisyl*-1-*ethyl*-3 : 4-*dihydronaphthalene*, m.p. 94—95°, which is demethylated and reduced by EtOH–KOH at 165°/36 hr. to 6-*hydroxy*-2-p-*hydroxyphenyl*-1-*ethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 256° (sinters at 225°) (*dibenzoate*, m.p. 213—215°). 5 : 14-*Dihydroxy*-1 : 2 : 9 : 10 : 11 : 18-*hexahydrochrysene*-a, m.p. 263—264°, is obtained from the $(OMe)_2$-derivative (A., 1933, 828) and AcOH–HI (*d* 1·9). H. B.

Synthesis of derivatives of *s*-diphenylethane related to materials occurring naturally. II. 3′-Methoxy-5-methyl-3 : 4-dihydrodibenzyl, a compound related to œstrone in structure. S. Natelson and S. P. Gottfried (J. Amer. Chem. Soc., 1939, **61**, 1001—1002; cf. A., 1936, 1248).—Conversion of *m*-$C_6H_4Br{\cdot}NO_2$ into the amine and thence (diazo-reaction) into *m*-$C_6H_4Br{\cdot}OH$ (>80% yield) and its Me ether, b.p. 105/16 mm., is described. *m*-OMe·C_6H_4·MgBr with $(CH_2)_2O$ gives β-m-*anisylethyl alcohol*, b.p. 148°/13 mm., converted by $SOCl_2$ into the *chloride*, b.p. 122°/18 mm.; the Grignard reagent thereof condenses with 3-methyl-Δ^2-*cyclo*hexenone (prep. from $CH_2Ac{\cdot}CO_2Et$, 40% aq. CH_2O, and a little piperidine in EtOH), yielding 3′-*methoxy*-5-*methyl*-3 : 4-*dihydrodibenzyl*, b.p. 184°/10 mm., which is rapidly polymerised by 80% H_2SO_4. R. S. C.

Catalytic hydrogenation of vanillin. Vanillylcreosol. A. S. Pfau (Helv. Chim. Acta, 1939, **22**, 550—554).—Hydrogenation (Pd–C in AcOH) at atm. pressure and room temp. of vanillin yields creosol and 4 : 5′-*dihydroxy*-3 : 4′-*dimethoxy*-2′-*methyldiphenylmethane*, m.p. 108·5—109°. The *Me*$_2$ *ether*, m.p. 75—76°, is oxidised by CrO_3 in warm AcOH or by SeO_2 at 200—210° to 3 : 4 : 4′ : 5′-*tetramethoxy*-2′-*methylbenzophenone* (I), m.p. 124—124·5°, converted by $NaNH_2$ in boiling C_6H_6 into veratric acid, veratrole (II), and homoveratrole. The synthesis of (I) from 6-methylveratric acid and (II) is described. H. W.

Oxidation of derivatives of vanillin with peracetic acid. J. Boëseken and J. Greup (Rec. trav. chim., 1939, **58**, 528—537; cf. A., 1936, 1510).—3 : 4-Dimethoxy-, 3-methoxy-4-ethoxy-, 4-methoxy-3-ethoxy-, 3 : 4-diethoxy-, 3-methoxy-4-butoxy-, 3-ethoxy-4-butoxy-, or 4-benzyloxy-3-methoxy- (poor yield of phenol) -benzaldehyde, with AcO_2H (prep. described) + 0·5% *p*-$C_6H_4Me{\cdot}SO_3H$ in AcOH, give the corresponding dialkoxyphenols (as acetates). 3 : 4-Dimethoxy-, new m.p. 81·5°, 3-methoxy-4-ethoxy-, new m.p. 46—48°, 4-methoxy-3-ethoxy-, new m.p. 77—78°, and 3 : 4-diethoxy-phenol, m.p. 65·5—66·5°, and 3-*methoxy*-, m.p. 24—25°, and 3-*ethoxy*-4-*butoxyphenol*, m.p. 58°, are described. Acetyl- or 2 : 4-dinitrophenyl-vanillin, however, similarly afford respectively acetylvanillic acid or a mixture (or 1 : 1 compound), m.p. 212—215°, of vanillic acid and its 2 : 4-dinitrophenyl ether. A. T. P.

Reactions of aminophenols with copper and iron. V. A. Nazarenko (J. Appl. Chem. Russ., 1939, **12**, 151—154).—*p*-Aminophenol and its derivatives give intense colorations with Cu^{II} or Fe^{III}

salts. The reactions are made more sensitive by addition of halides, in the order $Cl' > Br' > CNS' > I'$, and consist initially in oxidation of aminophenol, followed by formation of coloured complexes of the oxidation products with Fe or Cu. The most sensitive reagent for detection of Cu is 2 : 4-diaminophenol in presence of KBr (1 p.p.m. of Cu). R. T.

Aminohydroxydiarylmethanes.—See B., 1939, 580.

Migration of ester groups in the hydroxylated phenyl-β-naphthylamine series. W. Dilthey and H. Passing (J. pr. Chem., 1939, [ii], **153**, 26—34).—1-Anilino-β-naphthol (I), m.p. 158—159° (lit. 153—154°, 155—156°), with BzCl and K_2CO_3 in hot $COMe_2$ gives the N-*Bz* derivative (II), m.p. 202—203° [hydrolysed to (I) by Na–Hg], but with BzCl and KOH in aq. $COMe_2$ gives the O-*benzoate* (III), m.p. 161—162°, resolidifying with m.p. 202—203°. When heated at 205—210° or warmed with alcoholic alkali, (III) is converted into (II). With BzCl in hot C_5H_5N (I) gives the ON-Bz_2 derivative, m.p. 166—167°, hydrolysed by alkali to (II).
β-$C_{10}H_7$·NH·C_6H_4·OH-*p* (IV) and BzCl in hot C_5H_5N give the ON-Bz_2 derivative, m.p. 145—146°, hydrolysed by KOH–MeOH to the N-*Bz* derivative, m.p. 182—183°. With BzCl and K_2CO_3 in hot $COMe_2$ or with BzCl–KOH–H_2O–N_2, (IV) gives the O-*benzoate*, m.p. 165—166°, hydrolysed to (IV) by KOH–MeOH. Acetylation of (IV) gives only the N-*Ac* derivative, m.p. 231—232°. R. S. C.

Syntheses in the phenanthrene series. X. 8-Methoxy-1-methylphenanthrene. J. Lockett and W. F. Short (J.C.S., 1939, 787—790; cf. A., 1938, II, 134).—2 : 6-Dimethyl*cyclo*hexanone and Mg β-*o*-anisylethyl chloride give 1-β-*o*-*anisylethyl*-2 : 6-*dimethyl*cyclo*hexan*-1-*ol*, b.p. 185°/3·5 mm., dehydrated by $KHSO_4$ to the -Δ^1-cyclo*hexene*, b.p. 165—168°/7 mm., which with $AlCl_3$, then S, affords 8-*methoxy*-1-*methylphenanthrene*, m.p. 117·5—118° (*picrate*, m.p. 151—152°), identical with that obtained by Kon *et al.* (A., 1939, II, 326); the compound, m.p. 96—97°, stated to be this (*loc. cit.*) is wrongly named (cf. A., 1938, II, 273). 5 : 1-NH_2·$C_{10}H_6$·OH and Ac_2O (5 mols.) at room temp. give 5-*acetamido*-1-*naphthol*, m.p. 176—177°; its *Me* ether, m.p. 189—190°, and conc. HCl–EtOH give 5-*methoxy*-1-*naphthylamine*, m.p. 80—81°. The Grignard solution from 1-*iodo*-5-*methoxynaphthalene* (by diazo-reaction), m.p. 79—80°, and $(CH_2·CO)_2O$ (method: *loc. cit.*) give β-5-methoxy-1-naphthoylpropionic acid (I). Coumarin, Na, and C_5H_{11}·OH or EtOH give γ-*o*-hydroxyphenylpropyl alcohol, b.p. 176—178°/12 mm., methylated to γ-*o*-anisylpropyl alcohol (II), b.p. 145—146°/10 mm. (3 : 5-*dinitrobenzoate*, m.p. 113—114°). Methylation of coumarin (method: Reimer *et al.*, A., 1928, 288) gives Me *O*-methylcoumarinate, b.p. 150—163°/10 mm., and *o*-methoxycinnamic acid; catalytic reduction then gives Me β-*o*-anisylpropionate (III), b.p. 146—147°/10 mm., and β-*o*-anisylpropionic acid, m.p. 85·5—86°, respectively. (III) or the corresponding Et ester, with Na–EtOH, gives (II), which with $SOCl_2$ and $NPhMe_2$ or C_5H_5N affords the chloride, b.p. 120—130°/10 mm., and thence (KCN–EtOH–NaI–$CuSO_4$) the nitrile, b.p. 135—145°/12 mm., hydrolysed by KOH–MeOH to γ-*o*-*anisylbutyric acid*, m.p. 39—39·5° (IV), and a little γ-*o*-*anisylpropyl Me ether*, b.p. 120—122°/10 mm. (IV) and P_2O_5–C_6H_6, or best with $POCl_3$ in boiling $C_2H_2Cl_4$, give 1-*keto*-5-*methoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 89—89·5° (*semicarbazone*, m.p. 249—250°). The Reformatsky reaction, followed by P_2O_5, then gives Et 5-methoxy-3 : 4-dihydro-1-naphthylacetate, b.p. 160—175°/0·6 mm., reduced by Na–EtOH to β-5-methoxy-1 : 2 : 3 : 4-tetrahydro-1-naphthylethyl alcohol (V) (3 : 5-*dinitrobenzoate*, m.p. 107—108°) and a little 5-methoxy-1 : 2 : 3 : 4-tetrahydronaphthylacetic acid, m.p. 146—147°. (V) and PBr_3–$NPhMe_2$–$CHCl_3$ at < 5°, then room temp., afford the bromide (decomp. on distillation), converted by $CHK(CO_2Et)_2$ in PhMe into the malonic ester, hydrolysed to β-5-*methoxy*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthylethylmalonic acid*, m.p. 124—126°, decarboxylated at 190—210° to γ-5-*methoxy*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthylbutyric acid*, m.p. 67—68°. The latter and S (2 atoms) at 190—210° give γ-5-methoxy-1-naphthylbutyric acid (VI), m.p. 143°, also obtained by Clemmensen reduction of (I). (VI) is dehydrated (P_2O_5–C_6H_6 or $SnCl_4$) to 7-*keto*-4-*methoxy*-7 : 8-*dihydrohomophenalene*, m.p. 88—89° (semicarbazone, new m.p. 227—228°) [previously described (A., 1938, II, 134) as 1-keto-8-methoxy-1 : 2 : 3 : 4-tetrahydrophenanthrene; the latter compound, m.p. 137°, is correctly described by Kon *et al.*, A., 1936, 465], which with MgMeI, then dehydrogenation with S, gives a little of a *compound*, m.p. 105—106° (picrate, m.p. ~ 157°), which is not a methoxymethylphenanthrene. The compound described as 8-methoxy-1-methyl-3 : 4-dihydrophenanthrene (*loc. cit.*) is 4-*methoxy*-7-*methylhomophenalene*. A. T. P.

Mobility of groups in 3-chloro-4-nitro- and 5-chloro-2-nitro-diphenylsulphones. J. D. Loudon (J.C.S., 1939, 902—906; cf. A., 1938, II, 477).—The mobility of groups in the sulphones is largely but not completely controlled by the activating influence of the NO_2-substituent. 1 : 3 : 4-$C_6H_3Cl(NO_2)_2$ and PhSH–NaOH–aq.EtOH give Ph_2S_2, and 4- and 5-*chloro*-2-*nitrodiphenyl sulphide*, m.p. 127° [*sulphone* (I), m.p. 186—187°]; use of high temp. or excess of PhSH, or the latter and (I) in dioxan–EtOH, give 2 : 4-*diphenylthiolnitrobenzene* (II), m.p. 120° [H_2O_2–AcOH give the *disulphone* (III), m.p. 160°]. (I) and piperidine or NaOMe in MeOH–dioxan afford 2-*nitro*-5-*piperidinodiphenylsulphone*, m.p. 192°, or (some) 1 : 5 : 2-OMe·$C_6H_3Cl·NO_2$, respectively. (I) and NH_3–MeOH at 160° afford 2 : 5 : 1-NO_2·C_6H_3Cl·NH_2 and 2 : 4-*diphenylsulphonylaniline*, m.p. 203°, also obtained from (III) and NH_3–EtOH or $SnCl_2$–HCl–AcOH. Similarly prepared are: 5-*chloro*-2-*nitro*-4'-*methyldiphenyl sulphide*, m.p. 127° (*sulphone*, m.p. 189°); 2 : 4-*di*-p-*tolylthiolnitrobenzene*, m.p. 105° (*disulphone*, m.p. 158°), and 2-*nitro*-5-*piperidino*-4'-*methyldiphenyl sulphone*, m.p. 178°. 3-Aminodiphenylsulphone and *p*-$C_6H_4Me·SO_2Cl$–C_5H_5N give 3-p-*toluenesulphonamidodiphenylsulphone*, m.p. 152°, nitrated by boiling HNO_3 (*d* 1·4)–AcOH to 4-*nitro*-3- (IV), m.p. 220°, 2-*nitro*-5-, m.p. 152° [2-*nitro*-5-*aminodiphenylsulphone*, m.p. 235—236°, is converted (Sandmeyer) into (I)],

and 2 : 4-*dinitro*-5-p-*toluenesulphonamidodiphenylsulphone*, m.p. 173° [also by further nitration of $(NO_2)_1$-compounds; corresponding 5-NH_2-derivative, m.p. 241°]. (IV) is hydrolysed by 80% H_2SO_4 at 110° to 4-*nitro*-3-*aminodiphenylsulphone* (V), m.p. 185°, which (or its 3-nitro-4-amino-isomeride) with $SnCl_2$–HCl–EtOH gives 3 : 4-*diaminodiphenylsulphone*, m.p. 126° (whence 6-*phenylsulphonyl*-2 : 3-*diphenylquinoxaline*, m.p. 196°). 3-*Acetamidodiphenylsulphone*, m.p. 143°, and HNO_3 (*d* 1·5) at 0° give the 4-, m.p. 154°, and 2-NO_2-derivative, m.p. 187°, hydrolysed by H_2SO_4 at 110° to (V) and 2-*nitro*-3-*aminodiphenylsulphone*, m.p. 171°, respectively. 3-*Chloro*-4-*nitrodiphenylsulphone* (VI), m.p. 133° (by Sandmeyer reaction), and piperidine or NaOMe in MeOH–dioxan give 4-*nitro*-3-*piperidino*-, m.p. 116°, and 3-*chloro*-4-*methoxy-diphenylsulphone*, m.p. 111° (+ some nitromethoxy-compound), respectively. (VI) and $SnCl_2$–AcOH–HCl or NH_3–MeOH at 180° give 3-*chloro*-4-*aminodiphenylsulphone*, m.p. 197°, with (V) also in the latter reaction. (VI) and PhSH–NaOH–aq. EtOH give 4-*nitro*-3-*phenylthioldiphenylsulphone* (VII), m.p. 166—167° [convertible into (II) or (III)]. Piperidine and (III) at 100°, or NaOMe in boiling MeOH–dioxan, afford solely 1-*piperidino*-2 : 4-*diphenylsulphonylbenzene*, m.p. 156°, or 2 : 4-*diphenylsulphonylanisole*, m.p. 176°, respectively. (III) and PhSH–NaOH–aq. EtOH give (VII) and 2 : 4-*diphenylsulphonyldiphenyl sulphide*, m.p. 221°, oxidised to 1 : 2 : 4-*triphenylsulphonylbenzene*, m.p. 198°. Similarly prepared are: 1-*piperidino*-2 : 4-*di*-p-*tolylsulphonylbenzene*, m.p. 163°; 2 : 4-*di*-p-*tolylsulphonyl*-4′-*methyldiphenyl sulphide*, m.p. 220°; 1 : 2 : 4-*tri*-p-*tolylsulphonylbenzene* (IX), m.p. 185°; and 4-*nitro*-3-p-*tolylthiol*-4′-*methyldiphenylsulphone*, m.p. 124°. 1 : 3 : 4-$C_6H_3Cl(NO_2)_2$ and *p*-$C_6H_4Me{\cdot}SO_2Na$, refluxed with dioxan–$(CH_2{\cdot}OH)_2$, give (IX) and 5-chloro-2-nitro-4′-methyldiphenylsulphone. A. T. P.

Syntheses with *o*- and *p*-hydroxydiphenyls. III. 2-Hydroxydiphenyl-5-sulphonic acid and its derivatives. N. N. Voroshcov, jun., and A. T. Troschtschenko (J. Gen. Chem. Russ., 1939, **9**, 59—64).—*o*-$C_6H_4Ph{\cdot}OH$ and H_2SO_4 at room temp. or at 100° yield 2-*hydroxydiphenyl*-5-*sulphonic acid* (I) (*Ca* salt, $+4H_2O$). This heated for 5 hr. at 150° with Ac_2O, and the product treated with PCl_5 (4 hr. at 100°), yields 2-*acetoxydiphenyl*-5-*sulphonyl chloride*, m.p. 76—77°, which affords 2-*hydroxy*-, m.p. 146—147°, or 2-*acetoxy-diphenyl*-5-*sulphonanilide* (II), m.p. 141—142°, respectively with excess and the theoretical amount of NH_2Ph. (II) and Ac_2O (100 min. at 100°) yield 2-*acetoxydiphenyl*-5-*sulphonacetanilide*, m.p. 138—139°. (I) and HNO_3–H_2SO_4 give 3-*nitro*-2-*hydroxydiphenyl*-5-*sulphonic acid* (III) (*Na*, *K*, and *Ca* salts), converted by hot dil. HNO_3 into 3 : 5-dinitro-2-hydroxydiphenyl, and by HCl into 3-nitro-2-hydroxydiphenyl. 5-*Bromo*-, m.p. 113—115°, and 5-*chloro*-3-*nitro*-2-*hydroxydiphenyl*, m.p. 129—131°, are obtained by the action of Br and Cl_2 on (III) (at room temp.), or by nitration and halogenation of *o*-$C_6H_4Ph{\cdot}OH$. (III) is reduced (Sn in HCl) to 3-*amino*-2-*hydroxydiphenyl*-5-*sulphonic acid*, from which a red-violet azo-dye is obtained by diazotisation and coupling with α-$C_{10}H_7{\cdot}OH$. R. T.

Internal and external field action of substituents on methyl donors and acceptors.—See A., 1939, I, 376.

Reaction of styrene oxide with magnesium methyl iodide. C. Golumbic and D. L. Cottle (J. Amer. Chem. Soc., 1939, **61**, 996—1000).—MgMeI reacts with styrene oxide (I) and $CHPhI{\cdot}CH_2{\cdot}OH$ at room temp., but with $CH_2I{\cdot}CHPh{\cdot}OH$ only when heated; $CH_2Ph{\cdot}CHMe{\cdot}OH$ (phenylcarbamate, new m.p. 86·5—87°) is produced in all cases, and the alcohols sometimes give some $CH_2Ph{\cdot}CH_2{\cdot}OH$. With $MgMe_2$, (I) gives $CHPhMe{\cdot}CH_2{\cdot}OH$, and αβ-epoxypropane gives *sec.*-BuOH. HI converts (I) in Et_2O or H_2O into $CHPhI{\cdot}CH_2{\cdot}OH$. HgO–I converts $CHPh{:}CH_2$ in wet Et_2O into $CH_2I{\cdot}CHPh{\cdot}OH$, m.p. 34°. R. S. C.

Chloroalkylation of *p*-propylanisole. Synthesis of some derivatives. R. Quelet and J. Ducasse (Compt. rend., 1939, **208**, 1317—1319; cf. A., 1934, 290).—Saturation of *p*-$C_6H_4Pr{\cdot}OMe$, CH_2O, and $ZnCl_2$ with dry HCl at 40° affords 2-*methoxy*-5-*propylbenzyl chloride* (75%) (I), b.p. 140—145°/17 mm. (some decomp.), and a little 2 : 2′-*dimethoxy*-5 : 5′-*dipropyldiphenylmethane*, m.p. 51°. (I) with $(CH_2)_6N_4$ gives 2-*methoxy*-5-*propylbenzaldehyde* (II), b.p. 151°/16 mm. (*semicarbazone*, m.p. 239°), oxidised ($KMnO_4$) to 4-*methoxy*isophthalic *acid*, m.p. 275°. (I) with NaOAc affords (after hydrolysis) 2-*methoxy*-5-*propylbenzyl alcohol*, b.p. 163°/16 mm. (*Me*, b.p. 141°/16 mm., and *Et ether*, b.p. 147°/17 mm.; *phenylcarbamate*, m.p. 53°), which when heated with a trace of HCl gives *di*-(2-*methoxy*-5-*propylbenzyl*) *ether*, b.p. 240—245°/16 mm., m.p. 62°, decomposed by heat into (II) and 2 : 4 : 1-$C_6H_3MePr{\cdot}OMe$ (cf. A., 1936, 1504). *p*-$C_6H_4Pr{\cdot}OMe$ with $(MeCHO)_3$, dil. H_3PO_4, and dry HCl (A., 1936, 719) affords 2-α-chloroethyl-4-propylanisole (undistillable), which with C_5H_5N at 115° gives 2-*methoxy*-5-*propylstyrene*, b.p. 124—125°/16 mm., converted by O_3 into (II). J. L. D.

Action of mixed nitric and sulphuric acids on 5-bromo-3 : 6-dinitro-1 : 2 : 4-trimethylbenzene. I. J. Rinkes (Rec. trav. chim., 1939, **58**, 538—543; cf. A., 1939, II, 111, 159).—The "nitrate," new m.p. 152—153°, of Huender (*loc. cit.*) is a mixture of 4-*bromo*-3 : 6-*dinitro*-2 : 5- (I), m.p. 155·5—156°, and 5-*bromo*-3 : 6-*dinitro*-2 : 4-*dimethylbenzyl nitrate* (II), m.p. 154°. 2 : 5 : 4 : 1-$C_6H_2Me_2Br{\cdot}CH_2Cl$ (III) and $(CH_2)_6N_4$ in 60% EtOH give 2 : 5 : 4 : 1-$C_6H_2Me_2Br{\cdot}CHO$, m.p. 60—61° [semicarbazone, m.p. 243° (decomp.)]; (III) and $Pb(NO_3)_2$ give 4-*bromo*-2 : 5-*dimethylbenzyl alcohol*, m.p. 96°. (III), HNO_3 (*d* 1·5), and 10% oleum at 65° afford 4-*bromo*-3 : 6-*dinitro*-2 : 5-*dimethylbenzyl chloride*, m.p. 139°; the *iodide*, m.p. 166°, and $AgNO_3$ in dioxan give (I). 2 : 4 : 5 : 1-$C_6H_2Me_2Br{\cdot}CH_2Cl$ similarly gives 5-*bromo*-3 : 6-*dinitro*-2 : 4-*dimethylbenzyl iodide*, m.p. 153° (via the chloride, m.p. 128°), and thence (II) (cf. Smith *et al.*, A., 1937, II, 338). A. T. P.

Synthesis of growth-inhibitory polycyclic compounds. I. G. M. Badger and J. W. Cook (J.C.S., 1939, 802—806).—Attempts are made to prepare compounds which can be used to control growth of tumours. *o*-1-Naphthoylbenzoic acid and BzCl–

H_2SO_4 at 130° for 1 hr. give 1 : 2-benzanthraquinone, reduced by $SnCl_2$–HCl–AcOH to the anthranol and thence by Zn–NaOH to 1 : 2-benzanthracene. The latter and dry HCl, $(CH_2O)_x$, and AcOH at 60°, or $(CH_2Cl)_2O$–AcOH at 80°, afford 10-*chloromethyl*-1 : 2-*benzanthracene* (I), m.p. 186·5—187°, and (by former method) some 10 : 10′-*di*-(1 : 2-*benzanthranyl*)*methane*, m.p. >300°; (I) is hydrogenated (Pd-black–$COMe_2$) to 10-methyl-1 : 2-benzanthracene. (I) and KOAc–AcOH afford, through the acetate of (II), m.p. 148·5—149·5° (cf. Fieser *et al.*, A., 1938, II, 406) (hydrolysed by NaOH–EtOH), 10-*hydroxymethyl*-1 : 2-*benzanthracene* (II), m.p. 170—172° [$(CH_2{\cdot}CO)_2O$–C_5H_5N at 100° gives the *H succinate*, m.p. 185·5—186°]. (I) and KCN–EtOH give 10-*ethoxymethyl*-1 : 2-*benzanthracene*, m.p. 90—90·5°; no nitrile is formed. (I) and C_5H_5N at room temp. afford the *pyridinium chloride*, m.p. 205—208° (decomp.) (corresponding *picrate*, m.p. 199—201°), and (I) and piperidine at 100° (bath) give *N*-(1 : 2-*benzanthranyl*-10-*methyl*)-*piperidine hydrochloride*, m.p. 251—253° (decomp.) (free base, m.p. 106—107°). (I) and $CHNa(CO_2Et)_2$–C_6H_6 at room temp. overnight, then boiling for 6 hr., give *Et* (1 : 2-*benzanthranyl*-10-*methyl*)*malonate*, m.p. 120—120·5°, and a *by-product*, m.p. 224—225°. The corresponding *malonic acid*, m.p. ~200° (*Na* salt), is decarboxylated at 210—220° to β-(1 : 2-*benz*-10-*anthranyl*)*propionic acid*, m.p. 210—211°. Chloromethyl derivatives are not obtained from 9- or 10-methyl-1 : 2-benzanthracene, 3 : 4-benzpyrene, or 20-methylcholanthrene. Anthracene, dry HCl, and $(CH_2O)_x$ in AcOH at 60° give 9 : 10-*di*(*chloromethyl*)*anthracene* (III), decomp. 204—205°. 9 : 10-Dimethoxy-9 : 10-dimethyl-9 : 10-dihydroanthracene and Na in C_6H_6–Et_2O give 9 : 10-dimethylanthracene, which with $Pb(OAc)_4$–AcOH at 100° (bath) for 15 min. affords 9 : 10-*di*(*acetoxymethyl*)*anthracene*, m.p. 224—225°, also obtained from (III) and KOAc–AcOH. Thus high reactivity of Me groups is not sp. for the carcinogenic hydrocarbon. 9 : 10-Dimethyl-1 : 2-benzanthracene (IV) and Br–CS_2 at −10° give 9 : 10-*di*(*bromomethyl*)*benzanthracene*, m.p. 208—209°, converted by KOAc–AcOH into the *di*(*acetoxymethyl*) derivative, m.p. 167—168°, also obtained from (IV) and $Pb(OAc)_4$–AcOH. Hydrolysis (KOH–EtOH) yields 9 : 10-*di*(*hydroxymethyl*)-1 : 2-*benzanthracene*, m.p. 222—223° (*H_2 disuccinate*, m.p. 199·5—200·5°). A. T. P.

Reactions in sunlight. E. Oliveri-Mandalà, A. Giacalone, and E. Deleo (Gazzetta, 1939, **69**, 104—110; cf. A., 1938, II, 361).—Acenaphthene and Bz_2 in sunlight give, in addition to the product $C_{26}H_{20}O_2$ (I), m.p. 234° (*loc. cit.*), the 2 : 1 mol. *compound*, m.p. 137°, of Bz_2 and benzoin. With Ac_2O, (I) gives a *Ac_2* derivative, m.p. 195—196°, and a *substance*, m.p. 187—188°; (I) is therefore regarded as 1 : 2-*dihydroxy*-1 : 2-*diphenyl*-3 : 4-1′ : 8′-*naphthylene*-cyclo*butane*. Acenaphthenone, with or without CH_2Ph_2, and acenaphthenequinone with $C_2H_4Ph_2$ are unaltered in sunlight. $CHPh_3$ and $COPh_2$ in C_6H_6 give $CPh_3{\cdot}OH$. E. W. W.

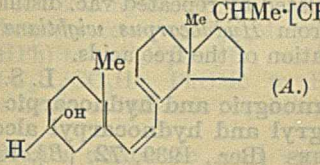
Reduction of αβ-diketones. R. B. Thompson (J. Amer. Chem. Soc., 1939, **61**, 1281—1283).—1 : 4-Reduction is shown to be the first step for αβ-diketones. Dimesityl diketone (I) absorbs only 1 H_2 when hydrogenated (PtO_2) in abs. MeOH, and forms an unusually stable enediol, *αβ-dihydroxy-αβ-dimesitylethylene*, m.p. 149—151°; this product is isolated in 70% yield by working in N_2, but in air re-forms (I). It decolorises 2 : 6-dichloroindophenol, gives a *dibenzoate* (II), m.p. 235° [with KOH–EtOH gives (I) by hydrolysis and oxidation], and is fairly stable in MeOH containing piperidine, slowly giving the benzoin. Addition of (I) to MgEtBr and then of BzCl give (cf. Fuson *et al.*, A., 1939, II, 260) a dibenzoate, m.p. 188—189°, which is stereoisomeric with (II). Hydrogenation (PtO_2) of diketones normally shows no signs of 1 : 4-addition, but hydrogenation (H_2, PtO_2, little HCl, and $ZnCl_2$) in Ac_2O gives a β-diacetate, m.p. 107—108° (lit. 110°), from benzil, and $CHPh_2{\cdot}CO{\cdot}COPh$ gives *αβ-diacetoxy-α-phenyl-β-benzhydrylethylene*, m.p. 132·5—133·5°, hydrolysed to $CHPh_2{\cdot}CO{\cdot}CHPh{\cdot}OH$ (*acetate*, m.p. 67—68°). R. S. C.

Ether-like compounds. V. Preparation of ethers of triphenylcarbinol. E. J. Salmi and E. Renkonen (Ber., 1939, **72**, [*B*], 1107—1108).—Calc. amounts of $CPh_3{\cdot}OH$ and the requisite OH-compound are subjected to azeotropic distillation in C_6H_6 containing a little *p*-$C_6H_4Me{\cdot}SO_3H$ as catalyst. When reaction is finished the acid is neutralised by solid K_2CO_3. The method has been applied with cetyl alcohol, $CH_2Ph{\cdot}OH$, $OH{\cdot}[CH_2]_2{\cdot}OMe$, $OH{\cdot}[CH_2]_2{\cdot}O{\cdot}CH_2Ph$, $OH{\cdot}CH_2{\cdot}CO_2Pr^{\beta}$, *l*-menthol, and technical borneol. *Triphenylmethyl* β-*benzyloxyethyl ether*, m.p. 73—74°, and *Pr^{β} triphenylmethoxyacetate*, m.p. 99·5—100·5°, are new. H. W.

Sensitive test for ergosterol and differentiation of ergosterol and ergosteryl esters. A. F. von Christiani and V. Anger (Ber., 1939, **72**, [*B*], 1124—1125).—The sample is dissolved in a few drops of $CHCl_3$ and the solution is treated with 90% $CCl_3{\cdot}CO_2H$ (1 c.c.) and one drop of 0·5% $Pb(OAc)_4$ solution; in the presence of ergosterol (I) a rose-violet colour is developed. Treatment of a solution of the sterol in $CHCl_3$ with 5% $Pb(OAc)_4$ followed by $CCl_3{\cdot}CO_2H$ gives a green fluorescence if (I) is present, and a violet-rose colour in presence of ergosteryl esters. A microchemical form of the test is described. H. W.

Products of irradiation of 22-dihydroergosterol. A. Windaus and B. Güntzel (Annalen, 1939, **538**, 120—127).—In general, the photochemical transformation of 22-dihydroergosterol (I) resembles that of ergosterol and 7-dehydrocholesterol. Exposure of (I) in C_6H_6 to light of long λ leads to *lumisterol$_4$* (II) (+ xH_2O), m.p. 101°, $[\alpha]_D^{20}$ +187° in $COMe_2$ (3 : 5-*dinitrobenzoate*, m.p. 141°, $[\alpha]_D^{20}$ +11·5° in $CHCl_3$), which does not give an additive product with vitamin-D_4. It is assumed to be formed in the same manner as lumisterol by steric transformation at $C_{(10)}$ and hence may be named 22-*dihydrolumisterol*. Exposure of (I) in peroxide-free Et_2O to Mg light yields tachysterol$_4$ (III), the acetate of which gives with citraconic anhydride (IV) an additive compound, m.p. 156°, $[\alpha]_D^{20}$ +79·5° in $CHCl_3$; the identity of this compound with that obtained by Lettré (A., 1934, 887) by hydrogenation of the

tachysteryl acetate–(IV) adduct proves (III) to be a 22-dihydrotachysterol (*A*). During the prep. of



(*A*.)

(II) and (III), vitamin-D_4 (Windaus *et al.*, A., 1937, III, 327) is obtained; for it and its 3 : 5-dinitrobenzoate the consts., m.p. 96—98°, $[\alpha]_D^{21}$ +85·7° in $COMe_2$, and m.p. 127—128°, $[\alpha]_D^{22}$ +93·2° in $COMe_2$, are now recorded. Very protracted exposure of (I) to Mg light leads to *suprasterol*$_4$, m.p. 132°, $[\alpha]_D^{17}$ +261° in $COMe_2$ (3 : 5-*dinitrobenzoate*, m.p. 161°, $[\alpha]_D^{17}$ +214° in $CHCl_3$), the ultra-violet absorption spectrum of which does not indicate the presence of conjugated double linkings. H. W.

Steroids. XX. New colour reaction in the steroid series and its chemistry. H. KÄGI and K. MIESCHER (Helv. Chim. Acta, 1939, **22**, 683—697).—The substance (1—2 mg.) is dissolved in glacial AcOH (1—2 c.c.) and boiled for a few sec. after addition of 1 drop of conc. H_2SO_4. After cooling, a 1% solution of Br in AcOH is added dropwise. The solution becomes intensely blue to violet. The colour is discharged by an excess of Br. Ac_2O may replace Br, whereby the colour is not developed so rapidly but is not discharged by an excess of the reagent. Under these mild conditions the change is given by substances with OH in the cisoid position at $C_{(17)}$. The following reaction is given also by substances with OH in the transoid position at $C_{(17)}$. The compound (1—2 mg.) is boiled for a short time with $POCl_3$ in quinoline; after cooling, the mixture is dissolved in AcOH (1—2 c.c.) and conc. H_2SO_4 (2—3 drops) is added followed by 1% Br–AcOH. The success of the Liebermann–Burchard reaction for sterols with a C chain at $C_{(17)}$ depends on the presence of at least one nuclear double linking or of groups from which such linking can be derived. The chemistry of the reaction is examined at the instance of the androstan-17-ols. Either of these is converted by $KHSO_4$ or $CuSO_4$ into ψ-androstene (I), $[\alpha]_D^{19}$ −25° in EtOH, which gives a marked colour change in AcOH–H_2SO_4 with Cl_2, Br, I, Ac_2O, succinic anhydride, Bz_2O_2, or CrO_3 or in AcOH–HBr or AcOH–$_3HPO_4$ with halogens but not with aliphatic anhydrides. It does not appear to be homogeneous. In AcOH containing KOAc it absorbs ~4 Br; it is hydrogenated (PtO_2 in AcOH) to ψ-androstane (II) which does not give a colour with H_2SO_4–Br but is unsaturated towards $C(NO_2)_4$. Its absorption curve differs from that of Δ^{16}-*androstene* (III), and indicates the presence of a conjugated double linking. It becomes resinified when preserved, particularly if exposed to light. Dehydrogenation (Se) of (I) or (II) gives a substance identical with or closely analogous to 3-methyl-*cyclo*pentenophenanthrene. Treatment of (I) in AcOH–HBr with 4 Br gives a brown, resinous powder which gives a blue colour in AcOH. It contains only ~11% of Br and passes when kept into a material which does not colour AcOH. Steroids with *tert.*-OH at $C_{(17)}$ do not appear to yield similar chromogens. Androstane-3*t* : 17*c*-diol 17-hexahydrobenzoate is converted by *p*-$C_6H_4Me{\cdot}SO_2Cl$ in C_5H_5N into the 3-*p*-toluenesulphonate, which passes in boiling quinoline into Δ^2-*androsten*-17*c*-*ol hexahydrobenzoate*, m.p. 117°. This is hydrogenated (PtO_2 in AcOH) to *androstan*-17*c*-*ol hexahydrobenzoate*, m.p. 138—139°, hydrolysed to *androstan*-17*c*-*ol*, m.p. 152—153°, which is converted by Tschugaev's method into (III), m.p. 44·5—45°, $[\alpha]_D^{19}$ +18·5° in EtOH, which gives only a slight colour with Br in H_2SO_4–AcOH. H. W.

Constituents of the adrenal cortex and related substances. XXV. *allo*Pregnane-3 : 17-diol derivatives of the 17(β) series. Further evidence of the adherence of substances *P* and *K* to the 17(β) series. T. REICHSTEIN and C. MEYSTRE (Helv. Chim. Acta, 1939, **22**, 728—741).—The crude product of the addition of C_2H_2 to *trans*-androsterone is acetylated and the monoacetate of the 17(α) compound is separated as far as possible by crystallisation. The mother-liquors are treated with Girard's reagent *T* and the unchanged material, after re-acetylation and eventual removal of more (I), is chromatographed (Brockmann's Al_2O_3), thus leading to Δ^{20}-allo*pregnine*-3-trans-17(β)-*diol* 3-*monoacetate* (II), m.p. 174—175°, $[\alpha]_D^{20}$ +27°±6° in $COMe_2$ (free *diol*, m.p. 228—229°). *trans*-Dehydroandrosterone is treated with C_2H_2 and the product is worked up analogously, thereby giving $\Delta^{5:20}$-*pregnenine*-3-trans-17(β)-*diol* 3-*monoacetate* (III), m.p. 186—188°, $[\alpha]_D^{19}$ −26·3°±2° in $COMe_2$ (free *diol*, m.p. 243—245°), which gives an immediate ppt. with $AgNO_3$ in MeOH. (II) and (III) are hydrogenated (PtO_2 in EtOH–AcOH) to allo*pregnane*-3-trans-17(β)-*diol* 3-*monoacetate*, m.p. 174—178°, $[\alpha]_D^{19}$ −20·05°±2° in $COMe_2$ (free *diol*, m.p. 174°, and, after re-solidification, m.p. 187°). Ozonisation of (II) in CCl_4 at −10° and treatment of the ozonide with Zn dust–AcOH followed by hydrolysis of the product gives 3-*trans*-17(β)-dihydroxyætio*allo*cholanic acid, m.p. 263—268°, identical with that derived from substance *P* [the identity is further confirmed by comparison of the Me ester (IV) (*acetate*, m.p. 184—186°, $[\alpha]_D^{20}$ +7·09°±2° in $COMe_2$) from the two sources]. A neutral by-product of the ozonisation is *trans*-androsterone acetate. (III) treated with Br in CCl_4, then ozonised, and the product decomposed and debrominated gives 3-*trans*-17(β)-dihydroxyætio-Δ^5-cholenic acid, m.p. 247—249° (decomp.) [*Me* ester (V), m.p. 238—240°, $[\alpha]_D^{19}$ −61·9°±10° in $COMe_2$], and *trans*-dehydroandrosterone acetate. The free diols of the 17(β) series are distinguished from the analogous products of the 17(α) series since they give an immediate, very sparingly sol. ppt. with digitonin in hot solution. This behaviour is shown by (IV) and (V). M.p. are corr. H. W.

Constituents of the adrenal cortex and related substances. XXIII. Partial synthesis of substance *J*. M. SUTTER, C. MEYSTRE, and T. REICHSTEIN (Helv. Chim. Acta, 1939, **22**, 618—625).—Distillation in a high vac. of *allo*pregnane-3β : 17α-diol 3-acetate with anhyd. $CuSO_4$ gives a colourless liquid (I) containing 3-β-acetoxy-Δ^{17}-pregnene but mainly isomeric compounds with a different position

of the double linking and transformation products which do not have the *allo*pregnane skeleton. Hydroxylation of (I) by OsO_4 followed by alkaline hydrolysis gives a small amount of *allo*pregnane-3 : 17 : 20-triol, isolated as the diacetate, identical with substance *J*; the configuration at $C_{(17)}$ and $C_{(20)}$ remains uncertain. The main product is another *triol* (II), m.p. 194—195° (corr.), converted by Ac_2O and C_5H_5N at room temp. into an *acetate*, m.p. 182—184° (corr.), $[\alpha]_D^{25}$ −7·65°±2° in $COMe_2$, oxidised to a neutral *product*, $C_{23}H_{36}O_4$, m.p. 102—104°. CrO_3 in AcOH oxidises (II) to a neutral compound, m.p. 148—152° (corr.); the non-formation of androstanedione shows that (II) is not a *allo*pregnane-3 : 17 : 20-triol. Two further acetates, m.p. 192° and 160° (corr.), respectively, were obtained in very small amount. H. W.

Derivatives of Δ⁵-androstene-3 : 17-diol-17-acetic acid and of Δ⁵-pregnene-3 : 17 : 21-triol. T. Reichstein, H. Müller, C. Meystre, and M. Sutter (Helv. Chim. Acta, 1939, **22**, 741—753).—*t*-Dehydroandrosterone acetate is converted by $CH_2Br{\cdot}CO_2Et$ and Zn filings activated with I in boiling C_6H_6 followed by hydrolysis of the product into Δ⁵-*androstene*-3*t* : 17-*diol*-17-*acetic acid* (I), m.p. 246—247° (corr.) [*Me* ester (II), m.p. 151—153° (corr.), or, as hydrate, m.p. 95—98° and 145—149° after re-solidification]. (I) is transformed by Ac_2O in C_5H_5N at room temp. into its 3-*monoacetate*, m.p. 206—209° (corr.), the *Me* ester (III), m.p. 66—68° and 111—113° (corr.) after re-solidification, of which is obtained with CH_2N_2 or directly in the Reformatsky reaction if $CH_2Br{\cdot}CO_2Me$ is used. Boiling Ac_2O or the protracted action of Ac_2O in C_5H_5N converts (I) into the 3 : 17-*diacetate*, m.p. 210—211° (corr.) (*Me* ester, m.p. 110—112°); the 3-*monobenzoate* of the Me ester has m.p. 180—183°. Boiling $SOCl_2$ followed by hydrolysis (KOH–MeOH) converts (III) into Δ⁵:¹⁷-*pregnadien*-3-*ol*-21-*carboxylic acid*, m.p. 217—218°, better obtained by distilling (III) with anhyd. $CuSO_4$ under 12 mm. (I) or (II) is transformed by MgPhBr into the very hygroscopic Δ⁵-21 : 21-*diphenyl*-Δ⁵-*pregnene*-3 : 17 : 21-*triol* (IV), m.p. variable (~130—132°), $CPh_2{:}CH_2$, and *t*-dehydroandrosterone. With Ac_2O in C_5H_5N at room temp. or 100° (IV) gives the 3-*monoacetate*, m.p. 228—232° (corr.), whereas acetylation at 134° appears to give 3-*acetoxy*-21 : 21-*diphenyl*-Δ⁵:¹⁶:²⁰-*pregnatriene*, m.p. 193—195° (corr.), in poor yield. MgMeBr and (II) afford 21 : 21-*dimethyl*-Δ⁵-*pregnene*-3 : 17 : 21-*triol*, m.p. 268—274° (corr.), converted by Ac_2O–C_5H_5N at room temp. or at 100° into the 3-*monoacetate*, m.p. 170—174° (corr.), whereas at 134° the main product is a 3-*acetoxy*-21 : 21-*dimethylpregnatriene*, m.p. 110—118°; at 111° the (impure) *triacetate*, m.p. 92—96°, appears to result. Reduction (Na–EtOH) of (II) gives Δ⁵-*pregnene*-3 : 17 : 21-*triol*, m.p. 243—245° (corr.) [*diacetate*, m.p. 159—160° (corr.), $[\alpha]_D^{20}$ −65·3°±1·5° in $COMe_2$], and a pregnenetriol, m.p. 180—183° (corr.) (*monoacetate*, m.p. 160—161°). H. W.

Alepric and aleprylic acids, new homologues of chaulmoogric acid. H. I. Cole and H. T. Cardoso (Science, 1939, **89**, 200; cf. B., 1938, 811).—*Alepric acid* (I), m.p. 48°, [α] +77°, the next lower homologue (by C_2H_4) to hydnocarpic acid, and *aleprylic acid*, m.p. 32°, [α] +90°, the next lower homologue (by C_2H_4) to (I), have been isolated by repeated vac. distillation of the Et esters from *Hydnocarpus wightiana* and fractional crystallisation of the free acids. L. S. T.

Esters of chaulmoogric and hydnocarpic acid and of chaulmoogryl and hydnocarpyl alcohol. III. K. Burschkies (Ber., 1939, **72**, [*B*], 1012—1016; cf. A., 1938, II, 139, 441).—Chaulmoogryl chloride and $Br{\cdot}[CH_2]_2{\cdot}OH$ in boiling Et_2O and N_2 give β-*bromoethyl chaulmoograte*, b.p. 190—192°/0·3 mm., converted by $CHPh{:}CH{\cdot}CO_2Ag$ in xylene at 130° into *ethylene glycol* β-*cinnamate* α-*chaulmoograte*, b.p. 220—240°/0·1 mm. $CHPh{:}CH{\cdot}COCl$ and $Br{\cdot}[CH_2]_2{\cdot}OH$ in boiling Et_2O afford β-*bromoethyl cinnamate*, m.p. 47—48°, transformed by Na hydnocarpate in xylene at 130° into *ethylene glycol* β-*cinnamate* α-*hydnocarpate*, b.p. 230—240°/0·1 mm., also obtained (b.p. 230—235°/0·05 mm.) from β-*hydroxyethyl hydnocarpate*, b.p. 198—200°/0·03 mm. Na oleate and $Br{\cdot}[CH_2]_2{\cdot}OH$ in xylene at 140° yield β-*hydroxyethyl oleate*, b.p. 190—200°/0·05 mm., transformed by hydnocarpyl chloride and C_5H_5N in PhMe at 130° into *ethylene glycol* β-*hydnocarpate* α-*oleate*, b.p. 270—280°/0·15 mm. Hydnocarpyl chaulmoograte, b.p. 240—260°/0·1—0·5 mm., m.p. 33—34°, is described. *Hydnocarpyl glycollate*, b.p. 180—210°/0·05 mm., m.p. 34·5°, is converted into *hydnocarpyl chaulmoogroyloxyacetate*, b.p. 260—280°/0·01 mm., m.p. 24—25°, also obtained from *hydnocarpyl chloroacetate*, b.p. 180—190°/0·1 mm. *Chaulmoogroyl cinnamoyloxyacetate*, b.p. 240—250°/0·05 mm., and *hydnocarpyl oleyloxyacetate*, b.p. 260—280°/0·03 mm., have been obtained. Many of the esters are tolerated better than the known chaulmoogric esters. H. W.

Reductions with phosphorus in presence of iodine or hydrogen iodide as catalyst. K. Miescher and J. R. Billeter (Helv. Chim. Acta, 1939, **22**, 601—610).—Reduction can frequently be effected without use of HI and in open vessels provided that sufficient P is present; either I or an iodide may be used with mineral acid as diluent. HCl is adequate for temp. ~100°. H_2SO_4 is useless since it is reduced by HI. For higher temp. H_3PO_4 is recommended, the b.p. of which can be adjusted by suitable addition of H_2O. Although the substances are frequently insol. in the medium, the reduction proceeds smoothly. The amount of I or I′ required is usually only a fraction of the calc. quantity, the min. amount being 2—15%. If it is necessary to work with solutions use is made of AcOH or of $EtCO_2H$ or other higher fatty acid if higher temp. are required. The following reductions are described: $CHPh{:}CH{\cdot}CO_2H$ to $Ph{\cdot}[CH_2]_2{\cdot}CO_2H$; COPhMe to $COPh{\cdot}CH_2{\cdot}CHPhMe$; $OH{\cdot}CHPh{\cdot}CO_2H$ to $CH_2Ph{\cdot}CO_2H$; $OH{\cdot}CPhMe{\cdot}CO_2H$ to $CHPhMe{\cdot}CO_2H$; $OH{\cdot}CPh_2{\cdot}CO_2H$ to $CHPh_2{\cdot}CO_2H$; *o*-$CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}CO_2H$ to $C_6H_4<\begin{matrix}CH(CO_2H)\\CO\end{matrix}>O$ with KI in dil. H_3PO_4 (at 130°) or dil. HCl, with I in AcOH or in H_3PO_4 at 150° if < 10% of the calc. amount of catalyst is used, or to *o*-$CO_2H{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO_2H$ with >10% of catalyst in H_3PO_4 at 150°, in

HCl at 140—145°, or in $EtCO_2H$ at 141°; $CH_2Bz{\cdot}CH_2{\cdot}CO_2H$ to $Ph{\cdot}[CH_2]_3{\cdot}CO_2H$ and 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene; *o*-$C_6H_4Bz{\cdot}CO_2H$ to dihydroanthracene; *p*-$C_6H_4Me{\cdot}SO_2R$ (R = Cl, NH_2, or NHPh) to *p*-$C_6H_4Me{\cdot}SH$; *m*-$CO_2H{\cdot}C_6H_4{\cdot}SO_2Cl$ to *m*-$SH{\cdot}C_6H_4{\cdot}CO_2H$; PhOMe to PhOH and MeI (a mol. amount of iodide is requisite). H. W.

Perkin's cinnamic acid synthesis. G. Lock and E. Bayer (Ber., 1939, **72**, [*B*], 1064—1071).—The decrease in the reactivity of aldehydes in Perkin's synthesis which is caused by Me groups can be counteracted by NO_2-groups. Cl, Br, or I in the *p*-position do not influence the rate of reaction greatly whereas F causes a marked diminution of yield. With Br- and particularly with I-derivatives there is considerable formation of resinous products. Restriction caused by Et or Ph markedly exceeds that due to Me and corresponds nearly with that observed with 2 : 4 : 6-$C_6H_2Me_3{\cdot}CHO$. OMe groups generally diminish the rate of the synthesis. The presence of substituents has also a very marked effect on the yields obtained in Knoevenagel's synthesis of cinnamic acid but the effects in this and in the Perkin reaction are not parallel. Thus *p*-$C_6H_4Et{\cdot}CH{:}CH{\cdot}CO_2H$ is obtained in very good yield by the former but with difficulty by the latter method. The following are new: 3 : 5-*dinitro*-2 : 4 : 6-*trimethylcinnamic acid*, m.p. 294° (corr.; decomp.) [*Et* ester, m.p. 121° (corr.)], converted by Br in $CHCl_3$ into αβ-*dibromo*-β-3 : 5-*dinitro*-2 : 4 : 6-*trimethylphenylpropionic acid*, decomp. ~212° after ill-defined melting; p-*ethylcinnamic acid*, m.p. 143° (*dibromide*, m.p. 130°); 2 : 6-*dibromo*-3 : 4-*dimethoxycinnamic acid*, m.p. 175·5° (corr.). *p*-$C_6H_4Et{\cdot}CHO$ could not be obtained satisfactorily from PhEt by the Gattermann–Koch method. *p*-C_6H_4ClAc is reduced (Clemmensen) to *p*-C_6H_4EtCl in 27% yield but this substance did not react satisfactorily with CuCN. PhEt, $COCl{\cdot}CO_2Et$, and $AlCl_3$ in Cl_2 yield *p*-$C_6H_4Et{\cdot}CO{\cdot}CO_2Et$, hydrolysed to $C_6H_4Et{\cdot}CO{\cdot}CO_2H$, whence $C_6H_4Et{\cdot}C(:NPh){\cdot}CO_2H$, $C_6H_4Et{\cdot}CH{:}NPh$, and *p*-$C_6H_4Et{\cdot}CHO$ in 23% yield. H. W.

Optically active stereoisomeric alicyclic acids, alcohols, and aldehydes. M. Mousseron and R. Granger (Compt. rend., 1939, **208**, 1500—1502).—The keto-form of 2-chloro-5-methyl*cyclo*hexanone with NaOMe gives only 2-hydroxy-5-methyl*cyclo*hexanone, whereas the enol form gives 60% of Me 3-methyl*cyclo*pentanecarboxylate (cf. A., 1938, II, 184), which by fractional distillation gives the cis- (?), b.p. 168°/760 mm., $[\alpha]_{579}$ −39·43°, and trans- (?), b.p. 169°/760 mm., $[\alpha]_{579}$ −5·96°, *-isomerides*, hydrolysed to cis-, b.p. 116°/15 mm., $[\alpha]_{579}$ −41·42°, and trans-3-*methyl*cyclo*pentanecarboxylic acid*, b.p. 117·5°/15 mm., $[\alpha]_{579}$ −13·96°. The esters with Na in EtOH give cis-, b.p. 85°/24 mm., $[\alpha]_{579}$ −34·71°, and trans-, b.p. 86°/24 mm., $[\alpha]_{579}$ −3·37°, -3-*methyl*cyclo*pentylcarbinol*, respectively, also separable by crystallisation of the H phthalates. Oxidation of the active carbinols gives inactive aldehydes. Active *trans*-3-methyl*cyclo*hexanol with HCl or PCl_5 affords 3-chloro-1-methyl*cyclo*hexanes (*A*), converted (Grignard) into 60 or 10—15%, respectively, of (probably) cis-, b.p. 134°/25 mm., $[\alpha]_{579}$ −1·62° (*Me* ester, b.p. 191°/760 mm., $[\alpha]_{579}$ −5·29°), and trans-3-*methyl*cyclo*hexanecarboxylic acid*, b.p. 132°/15 mm., $[\alpha]_{579}$ +1·54° (*Me* ester, b.p. 193°/760 mm., $[\alpha]_{579}$ +2·21°) (cf. A., 1938, II, 400). (*A*) with $CH(OEt)_3$ gives cis-, b.p. 176°/760 mm., $[\alpha]_{579}$ −8·97° (*semicarbazone*, m.p. 135°), and trans-3-*methyl*cyclo*hexylformaldehyde*, b.p. 178°/760 mm., $[\alpha]_{579}$ +4·16° (*semicarbazone*, m.p. 157°), separated by crystallising their semicarbazones. They are also formed by the distillation of (active) 1-methyl-3-methylene*cyclo*hexane oxide (cf. Tiffeneau *et al.*, A., 1937, II, 414), but oxidation (CrO_3) of cis-, b.p. 95°/25 mm., $[\alpha]_{579}$ −5·45°, and trans-, b.p. 96°/25 mm., $[\alpha]_{579}$ −4·43°, -3-*methyl*cyclo*hexylcarbinols* gives inactive products. J. L. D.

Alkaline dehalogenation of 1-chloro*cyclo*hexyl methyl and phenyl ketone. Transformation into 1-substituted *cyclo*hexane-1-carboxylic acids. B. Tchoubar and O. Sackur (Compt. rend., 1939, **208**, 1020—1022).—*cyclo*Hexyl Me ketone with SO_2Cl_2 affords 1-*chloro*cyclo*hexyl Me ketone* (I), b.p. 87—89°/15 mm., converted into 1-hydroxy*cyclo*hexyl Me ketone (II) (*semicarbazone*, m.p. 205°), which is dehydrated ($H_2C_2O_4$) to Δ^1-*cyclo*hexenyl Me ketone (*semicarbazone*, m.p. 220°). (I) with dry powdered KOH for 2—3 hr. gives K 1-methyl*cyclo*hexane-1-carboxylate, identified as the *amide*, m.p. 63° (also obtained from the acid from Mg 1-methyl*cyclo*hexyl chloride and CO_2). Warm NaOH and 10% Na_2CO_3 effect the same change; the latter also gives ~50% of (II). 1-*Chloro*cyclo*hexyl Ph ketone*, m.p. 59°, prepared similarly, with Na_2CO_3 in Et_2O/12 hr. affords (30—40%) 1-phenyl*cyclo*hexane-1-carboxylic acid, m.p. 123° [also obtained by oxidising the corresponding aldehyde (cf. A., 1935, 1240)], and 1-benzoyl-Δ^1-*cyclo*hexene (*semicarbazone*, m.p. 214°); only the latter is formed with boiling NaOH. The reaction is explained as a semi-benzilic acid change. J. L. D.

Microscopic investigations of polymorphous substances. II. E. Lindpainter (Mikrochem., 1939, **27**, 21—41; cf. A., 1938, II, 192).—Micro-m.p. determinations show the following nos. of modifications: PhOBz, three, m.p. 69°, 56·5°, 51—52°; benzoyl-*l*-ecgonine, four, m.p. ~202—203°, 179—181°, 130—135°, 100—105°; quinizarin, two enantiotropes, m.p. orange 195°, red 201°; chrysophanic acid, two, m.p. 195°, 190°; coumarin, three, m.p. 68·5°, 64·5°, 55°; gallic acid, two, m.p. ~258—265°, 225—230°; quinol, two, both m.p. 172·5°; morphine hydrochloride, two, m.p. ~295—300°, 280—284°; nipagin [*p*-$OH{\cdot}C_6H_4{\cdot}CO_2Me$], six, m.p. 127°, 116°, 110°, 110°, 109°, 106°; *o*-$NO_2{\cdot}C_6H_4{\cdot}CHO$, two, m.p. 42—42·5°, 39°; *m*-$NO_2{\cdot}C_6H_4{\cdot}CHO$, two, m.p. 56—57°, ~51°; *p*-$NO_2{\cdot}C_6H_4{\cdot}CHO$, two, m.p. 105°, 104—104·5°; phenanthraquinone, two, m.p. 210—211°, 207°; veronal, four, m.p. 190°, >183° but <190°, 183°, 176°; *m*-xylenol, two, m.p. 62—63°, ~55°. J. W. S.

Esterification of highly hindered acids. R. C. Fuson, J. Corse, and E. C. Horning (J. Amer. Chem. Soc., 1939, **61**, 1290).—Heating the NMe_4 salts of the acids at 200—250° gives 63—90% of Me 2 : 4 : 6-trimethyl- and *-triethyl-benzoate*, b.p. 114—115°/5 mm. R. S. C.

Methyl β-resorcylate. S. RANGASWAMI (J. Indian Chem. Soc., 1939, **16**, 160).—Me β-resorcylate when freshly prepared (from the acid with MeOH–HCl or MeOH–H_2SO_4) has m.p. 78—80°, unaltered by recrystallisation from MeOH or EtOH; this is the monohydrate. Recrystallised from $CHCl_3$ it has m.p. 85—110°; this when dried gives the anhyd. ester, m.p. 119—120° (cf. Robinson and Shah, A., 1934, 1346). J. D. R.

Structure of gossypol. XIX. Synthesis of 2 : 3-dihydroxy-4-*iso*propylbenzoic acid. R. ADAMS and M. HUNT. **XX. Synthesis of 3 : 4-dihydroxy-5-*iso*propylbenzoic acid.** R. ADAMS, M. HUNT, and B. R. BAKER. **XXI. Synthesis of 3 : 4-dimethoxy-2-*iso*propylbenzoic acid and of *apo*gossypolic acid.** R. ADAMS and B. R. BAKER (J. Amer. Chem. Soc., 1939, **61**, 1132—1133, 1134—1137, 1138—1142; cf. A., 1939, II, 77).—XIX. 3 : 1 : 2-$C_6H_3Pr^{\beta}(OMe)_2$ with $LiBu^{\alpha}$ in Et_2O–C_6H_6, followed by CO_2 in C_6H_6, gives 2 : 3-*dimethoxy*-4-iso*propylbenzoic acid*, m.p. 72—73°, sublimes at 120°/4 mm., demethylated by 48% aq. HBr to 2 : 3-*dihydroxy*-4-iso*propylbenzoic acid*, m.p. 153°.

XX. 3 : 4-*Dihydroxy*-5-iso*propylbenzoic acid* (I) is synthesised by two methods. Its identity with an acid obtained from gossic and *apo*gossypolic acid by HBr (Adams *et al.*, A., 1938, II, 453) supports the structures of the latter and that of gossypol. 2 : 1 : 3-OH·$C_6H_3Pr^{\beta}$·OMe (II) or 1 : 2 : 3-$C_6H_3Pr^{\beta}(OMe)_2$ with Ac_2O and $AlCl_3$ in CS_2 at room temp. gives 4-*hydroxy*-3-*methoxy*-5-iso*propylacetophenone* (57%), m.p. 116°, converted by NaOMe–Me_2SO_4–MeOH into the 3 : 4-(*OMe*)$_2$-*ketone*, b.p. 135—137°/2 mm., which with $KMnO_4$ and Na_2CO_3 in aq. $COMe_2$ yields 3 : 4-*dimethoxy*-5-iso*propylbenzoic acid* (III), m.p. 115°, and thence by 48% HBr (I), m.p. 215°. *o*-OH·C_6H_4·CMe:CH_2 (prep. from *o*-OH·C_6H_4·CO_2Me by MgMeI and distillation), b.p. 201—205°/750 mm., and H_2–Raney Ni at 2—3 atm. give *o*-$C_6H_4Pr^{\beta}$·OH, converted by Br–CCl_4 into 1 : 5 : 2-$C_6H_3Pr^{\beta}$Br·OH, b.p. 150—152°/20 mm. Fuming HNO_3 in AcOH then gives the 3-NO_2-derivative, m.p. 29—30° (lit. 33°), which with Me_2SO_4 and NaOEt–EtOH in PhMe gives 5-*bromo*-3-*nitro*-2-*methoxy*iso*propylbenzene*, b.p. 137—139°/3 mm., reduced (H_2–Raney Ni in EtOH) to the *NH*$_2$-compound, b.p. 134—137°/3 mm. (*hydrochloride*, m.p. 171—174°). The diazonium sulphate thereof is converted by H_2SO_4–Na_2SO_4–H_2O at 150—170° into a phenol, which yields 5-*bromo*-2 : 3-*dimethoxy*iso*propylbenzene*, b.p. 120—122°/2 mm. This is converted by a Grignard reaction into (III). Aq. KOH–I oxidises 4 : 5 : 3 : 1-OH·$C_6H_2Pr^{\beta}$(OMe)·COMe to 4-*hydroxy*-3-*methoxy*-5-iso*propylbenzoic acid* (IV), m.p. 167—169°, also obtained as follows. Br–CCl_4 and (II) give 5-*bromo*-2-*hydroxy*-3-*methoxy*iso*propylbenzene*, b.p. 113—114°/2 mm., converted by CH_2PhCl and NaOMe–MeOH into the 2-*CH*$_2$*Ph ether*, m.p. 72—73°, which with Mg, a little EtBr, and then CO_2 gives a poor yield of a product, hydrolysed by HCl–EtOH to (IV). The acid, previously (*loc. cit.*) thought to be (III), was (IV), complete methylation of (I) being very difficult. 3 : 4-$(OMe)_2C_6H_3$·CO_2Me and MgMeI in Et_2O give 3 : 4-*dimethoxyphenyldimethylcarbinol*, m.p. 78° (uncorr.), also obtained in poorer yield from 3 : 4-$(OMe)_2C_6H_3$·COMe and converted by distillation/<1 atm. into a (?) polymeride.

XXI. Synthesis of *apo*gossypolic acid (V) confirms the orientation of the terminal rings of gossypol. 2-*Acetoxy*-3-*methoxy*iso*propylbenzene* [prep. from (II) by Ac_2O], b.p. 118—120°/3 mm., and Br in CCl_4 give the 6-*Br*-derivative, b.p. 157—168°/10 mm., which by hydrolysis (KOH–EtOH) and methylation (Me_2SO_4–KOH–MeOH–H_2O) affords 6-*bromo*-2 : 3-*dimethoxy*-iso*propylbenzene*, b.p. 122—125°/3 mm. A Grignard reaction then affords 3 : 4-*dimethoxy*-2-iso*propylbenzoic acid*, m.p. 119—121°, yielding with aq. HNO_3 95% of the 6-*NO*$_2$-*acid* (VI), m.p. 157—159° [obtained (*loc. cit.*) by nitrating (V)]. The derived *Me* ester, m.p. 89—91°, sublimes at 115°/3 mm., with H_2–Raney Ni in EtOH etc. yields *Me* 4 : 5-*dimethoxy*-6-iso*propylanthranilate hydrochloride*, m.p. 181—182° (decomp.). A diazo-reaction (CuCN) then gives an oily nitrile, hydrolysed by 10% aq. NaOH to (V) [4 : 5-dimethoxy-3-*iso*propylphthalic acid], m.p. 169—170° (decomp.), which is isolated as anhydride, m.p. 92—93°. Hydrogenation (Raney Ni) of (VI) in EtOH–KOH gives the NH_2-acid, which, when sublimed, yields 4 : 5-*dimethoxy*-3-iso*propylaniline*, m.p. 74—75°, sublimes at 100°/15 mm. [Ac_2 derivative, m.p. 84—85° (cf. *loc. cit.*)]. 3 : 4-$(OMe)_2C_6H_3$·CMe:CH·CO_2Et [prep. from 3 : 4-$(OMe)_2C_6H_3$·COMe, Zn, and CH_2Br·CO_2Et], b.p. 169—170°/4 mm., is hydrolysed and then reduced (H_2–Raney Ni in aq. alkali at 2—3 atm.) to 3 : 4-$(OMe)_2C_6H_3$·CHMe·CH_2·CO_2H (60% yield), m.p. 80—82° (lit. 84—85°), which with P_2O_5 in C_6H_6 gives 5 : 6-dimethoxy-3-methylindanone (85% yield), m.p. 88—90° (uncorr.) (lit. 90—91°). $BuNO_2$ and conc. HCl in MeOH then give the 2-oximino-derivative (83% yield), m.p. 223—224° (lit. 225—226°), which with $SOCl_2$ in Et_2O gives a substance, hydrolysed by hot 10% aq. NaOH to 4 : 5-*dimethoxy*-α-*methylhomophthalic acid*, m.p. 173—175° (decomp.) [*anhydride*, m.p. 126—127°; *Me*$_2$ ester, m.p. 57—58°, sublimes at 120°/20 mm.; resists further methylation at $C_{(\alpha)}$]. Similar reactions starting from 3 : 4-$(OMe)_2C_6H_3$·COEt, Zn, and CH_2Br·CO_2Et give *Et* 3 : 4-*dimethoxy*-β-*ethylcinnamate* (78%), b.p. 165/4 mm., β-3 : 4-*dimethoxyphenyl*-n-*valeric acid*, m.p. 73°, b.p. 185—186°/4 mm., 5 : 6-*dimethoxy*-3-*ethylindanone* (80%), m.p. 92° [2-*oximino*-derivative (78%), m.p. 218° (decomp.)], 4 : 5-*dimethoxy*-, m.p. 157—158° (decomp.) (*anhydride*, m.p. 85—86°), and (by 48% HBr) 4 : 5-*dihydroxy*-α-*ethylhomophthalic* [α-2-*carboxy*-4 : 5-*dihydroxyphenyl*-n-*butyric*] *acid*, m.p. 124—125° (green $FeCl_3$ colour). M.p. are corr. except where stated. R. S. C.

Fluorenones and diphenic acids. VII. Ring cleavage of 1 : 8-, 1 : 6-, and 3 : 6-dichlorofluorenones with potassium hydroxide in diphenyl ether. E. H. HUNTRESS and (MISS) M. K. SEIKEL (J. Amer. Chem. Soc., 1939, **61**, 1066—1071; cf. A., 1939, II, 264).—Fission of chlorofluorenones by KOH in Ph_2O to acids occurs in only one direction, but, if Cl is *o*- to CO, some lactone formation occurs by replacement of the Cl by OH and rearrangement. Ring-closure of the derived chlorodiphenyl-2-carboxylic acids by

H_2SO_4 at room temp. occurs at both 2 and 6 positions. Coupling diazotised 2 : 4 : 1-NH_2·C_6H_3Cl·CO_2H gives 5 : 5′-dichlorodiphenic acid and 5 : 5′-*dichloro*-2 : 2′-*dicarboxydiphenyl ether*, m.p. variable, 310° to 336° (decomp.) [converted by H_2SO_4 into (?) a *xanthone*, m.p. 346—347° (decomp.)] (cf. Huntress *et al.*, A., 1933, 826). 3 : 3′-Dichlorodiphenyl-2-carboxylic acid, m.p. 157—158° (lit. 152·5°), is obtained by KOH from 1 : 8-dichlorofluorenone (II) in 50—60% yield and with H_2SO_4 gives 25—35% of (II) and 65—75% of 1 : 6-dichlorofluorenone (III). 5 : 3′-*Dichlorodiphenyl-2-carboxylic acid*, m.p. 154—155°, is obtained from 3 : 6-dichlorofluorenone (IV) (90—92%) and from (III) (50%; sole product), and with H_2SO_4 gives 30—40% of (III) and 60—70% of (IV). The *lactone*, m.p. 135—135·5°, of 3-chloro-2′-hydroxydiphenyl-2-carboxylic acid is obtained as by-product from (II) and KOH, and, with other products, in 3·1% yield from 1 : 6 : 2-CO_2H·C_6H_3Cl·N_2Cl and PhOH. The *lactone*, m.p. 173·5°, of 5-chloro-2′-hydroxydiphenyl-2-carboxylic acid is similarly obtained from (III) or from 1 : 4 : 2-CO_2H·C_6H_3Cl·N_2Cl and PhOH (10% yield).

R. S. C.

Alkylaminoalkyl esters of aminonaphthoic acids as local anæsthetics. F. F. Blicke and H. C. Parke (J. Amer. Chem. Soc., 1939, **61**, 1200—1203).—Prep. of 3 : 1-, 4 : 1-, 5 : 1-, and 6 : 1-NO_2·$C_{10}H_6$·CO_2H is outlined. With $SOCl_2$ at 150°, the acids give 3-, m.p. 137—139°, b.p. 205—206°/12 mm., 4-, m.p. 95—96°, b.p. 208—210°/17 mm., 5-, m.p. 132—134°, b.p. 214—217°/18 mm., and 6-*nitro*-1-*naphthoyl chloride*, m.p. 154—155°, which with dialkylamino-alcohols (1 mol.) in hot C_6H_6 give the NO_2-esters. The following are described. β-*Diethylaminoethyl*, m.p. 211—213°, β-*di*-n-*butylaminoethyl*, m.p. 169—170°, γ-*diethylamino*-n-*propyl*, m.p. 203—204°, β-, m.p. 149—150°, and γ-*di*-n-*butylamino*-n-*propyl*, m.p. 148—149°, and γ-*dimethylamino*-ββ-*dimethyl*-n-*propyl*, m.p. 114—115°, 3-*nitro*-1-*naphthoate hydrochloride* and the derived 3-*amino*-1-*naphthoate hydrochlorides*, m.p. 148—150°, 135—136°, 160—161°, 113—114°, 146—147°, and 162—163°, respectively. β-Diethylaminoethyl, m.p. 198—199° (lit. 189·8—190°), β-*di*-n-*butylaminoethyl*, m.p. 76—78°, β-, m.p. 139—140°, and γ-*diethylamino*-n-*propyl*, m.p. 161—162°, β-, m.p. 83—85°, and γ-*di*-n-*butylamino*-n-*propyl*, m.p. 117—118°, γ-*dimethylamino*-, m.p. 150—151°, and γ-diethylamino-ββ-dimethyl-*n*-propyl, m.p. 151—152°, 4-*nitro*-1-*naphthoate hydrochloride* and the derived 4-*amino*-1-*naphthoate hydrochlorides*, m.p. 214—216° (lit. 212°), 170—171°, 197—198°, 184—185°, 179—180°, 175—176°, 219—221°, and 184—186° (lit. 187—188°), respectively. β-*Diethylaminoethyl*, m.p. 198—199°, β-*di*-n-*butylaminoethyl*, m.p. 131—133°, β-, m.p. 195—196°, and γ-*diethylamino*-n-*propyl*, m.p. 193—194°, β-, m.p. 120—121°, and γ-*di*-n-*butylamino*-n-*propyl*, m.p. 118—120°, 5-*nitro*-1-*naphthoate hydrochloride* and the derived 5-*amino*-1-*naphthoate hydrochlorides*, m.p. 169—170° 178—179°, 171—172°, 175—177°, 157—159°, and 159—160°, respectively. β-*Diethylaminoethyl* 6-*nitro*-, m.p. 184—185°, and 6-*amino*-1-*naphthoate hydrochloride*, m.p. 169—170°. The NH_2-ester hydrochlorides are local anæsthetics, but some are irritant and insol. in H_2O.

R. S. C.

Synthetic experiments in the equilenin series. E. Bergmann (Chem. and Ind., 1939, 465—466).—6 : 2-OMe·$C_{10}H_6$·MgBr with Et *cyclo*pentanone-2-acetate in Et_2O yields 1-(6′-*methoxy*-2′-*naphthyl*)-Δ^1-cyclo*hexene*-2-*acetic acid*, m.p. 120—121°, and some 6 : 6′-*dimethoxy*-2 : 2′-*dinaphthyl*, m.p. 284°. Et lævulate with NaOEt in Et_2O affords a *compound*, $C_5H_6O_2$, b.p. 154°/0·9 mm., which gives no coloration with $FeCl_3$.

A. Li.

Structure and absorption [spectra] of hydroxy-derivatives of triphenylmethane dyes. Existence of two coloured isomeric forms of phenolsulphonephthaleins and phenolphthalein. P. Ramart-Lucas (Compt. rend., 1939, **208**, 1312—1314).—The phenolphthaleinsulphonic acids exist in a colourless lactone form, and two coloured forms which have absorption spectra closely resembling those of benzaurin and aurin; hence one isomeride has the fuchsone structure (cf. A., 1939, II, 260). The fuchsone (quinonoid) form of the phenolphthaleins predominates in neutral solution and the other coloured isomeride in alkali. Benzaurin and tetrabromophenolphthalein exist in both coloured isomeric forms, thus negativing the views of Meyer (A., 1899, i, 707) and Acrée (A., 1908, i, 423) which seek to explain the isomerism. The two forms have quinonoid structures probably with different valency angles.

J. L. D.

Synthesis of physiologically active lactones. I. *cyclo*Pentyl- and *cyclo*hexyl-succinic acids. Resolution of *dl-cyclo*pentylsuccinic acid. S. K. Ranganathan (J. Indian Chem. Soc., 1939, **16**, 107—113; cf. A., 1938, II, 97).—*cyclo*Pentyl bromide (prep. in 88% yield by PBr_3 at −5° to 0° and then at room temp. to 100°), b.p. 133—134°/680 mm., CO_2Et·CH_2·$CH(CO_2Et)_2$, and NaOEt give *Et*$_3$ α-cyclo*pentylethane*-αα*β-tricarboxylate*, b.p. 166°/5 mm., which with hot, conc. HCl yields α-cyclo*pentylsuccinic acid* (I), m.p. 116—117° (*anhydride*, b.p. 176°/30 mm.; *mono*-p-*toluidide*, m.p. 174°), but with alkali gives an impure acid-ester, m.p. 112°. The *Et*$_2$ ester, b.p. 120°/2 mm., of (I) with NaOEt and HCO_2Et in Et_2O gives *Et*$_2$ α-*aldehydo*-α-cyclo*pentylsuccinate*, b.p. 150—154°/3—5 mm., which does not react with PhNCO or 10% aq. KOH, is converted by hot, dil. HCl into (I), is unchanged by H_2O at 130°, and with Cu-bronze and $H_2C_2O_4$ in hot H_2O gives β-aldehydo-β-*cyclo*pentylpropionic acid (*semicarbazone*, m.p. 200°). Similarly are prepared *cyclo*hexyl bromide (88% yield), b.p. 159—160°/680 mm., *Et*$_3$ α-cyclo*hexylethane*-αα*β-tricarboxylate*, b.p. 160°/2 mm., and α-cyclo*hexylsuccinic acid*, m.p. 145° (*anhydride*, m.p. 42°, b.p. 150°/4 mm.; *mono*-p-*toluidide*, m.p. 187°). Resolution of (I) by the brucine salt yields the d- and l-*acids*, m.p. 135°, $[\alpha]_D^{26}$ +17·81°, −16·94° in $COMe_2$.

R. S. C.

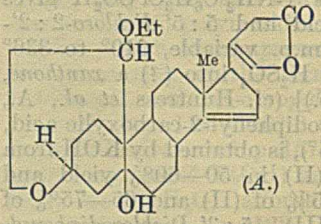
αα-Diphenylsuccinic acid. F. Salmon-Legagneur (Compt. rend., 1939, **208**, 1507—1509).—NaCPh$_2$·CN (1 mol.) with CH_2Br·CO_2Et (1·5 mols.) affords *Et* β-*cyano*-ββ-*diphenylpropionate* (I), m.p. 103—105°, converted by EtOH–KOH into β-*cyano*-ββ-*diphenylpropionic acid* (II), m.p. 183—184°, which with boiling conc. HCl gives αα-*diphenylsuccinic acid* (III),

m.p. 197—199° after softening at 170°. (III) with MeOH–HCl or EtOH–HCl gives *Me*, m.p. 141—143°, or *Et* β-*carboxy*-ββ-*diphenylpropionate* (IV), m.p. 144—146°, respectively. These with $SOCl_2$–MeOH or $SOCl_2$–EtOH give Me_2, m.p. 82—83°, or Et_2 αα-*diphenylsuccinate*, m.p. 76—77°, respectively, which are hydrolysed to β-*carbomethoxy*-, m.p. 183—184°, and β-*carbethoxy*-ββ-*diphenylpropionic acid*, m.p. 137—138°, respectively. (IV) with $SOCl_2$ followed by treatment with NH_3 affords β-*carbethoxy*-αα-*diphenylpropionamide*, m.p. 105—106°, also obtained by hydrolysis (80% H_2SO_4) of (I). Hydrolysis (80% H_2SO_4) of (II) yields β-*carboxy*-αα-*diphenylpropionamide*, m.p. 140°. (III) with AcCl or when heated gives αα-*diphenylsuccinic anhydride*, m.p. 90—91°, easily hydrolysed by aq. Na_2CO_3, and when boiled with EtOH gives (IV). The NH_4 salt of (III) when heated gives αα-*diphenylsuccinimide*, m.p. 139°. J. L. D.

Fused carbon rings. XVII. Stereoisomerism of the perhydrodiphenic acids and an examination of the Blanc rule. R. P. Linstead and A. L. Walpole (J.C.S., 1939, 850—857).—Four of the six possible inactive (four racemic and two *meso*) perhydrodiphenic acids (formulæ given) are described. 9-Ketoperhydrophenanthrene, form *A* (A., 1939, II, 307), is reduced (Ponndorf–Verley) to 9-*hydroxyperhydrophenanthrene* (I), b.p. 132°/0·5 mm. (*acetate*, b.p. 127°/1 mm.), dehydrated ($KHSO_4$) at 200° to dodecahydrophenanthrene, b.p. 127°/13 mm. Oxidation of (I) (the other above three compounds do not react) with HNO_3 (*d* 1·5 + *d* 1·42) gives a *perhydrodiphenic acid* (trans-trans), m.p. 202—203° (Ac_2O gives the *anhydride*, m.p. 135°, which evolves no CO_2 at 350°). 9-Ketoperhydrophenanthrene, form *C*, m.p. 47—48° (*loc. cit.*), and HNO_3 afford a *perhydrodiphenic acid* (cis-trans) (II), m.p. 243—244° (bath initially at 235°) (*anhydride*, m.p. 242°), which at 310—320° in N_2 evolves CO_2 and gives a perhydrofluorenone (semicarbazone, new m.p. 216—217°) (cf. Vocke, A., 1934, 189).

[With F. H. Slinger.] Phenanthraquinone refluxed with H_2O_2–AcOH gives diphenic acid, hydrogenated (Adams) in AcOH to a perhydrodiphenic acid, m.p. 273—274° (*cis-cis*) (cf. Vocke, *loc. cit.*) (*anhydride*, m.p. 143°, also +Ac_2O, m.p. 104°), which yields a perhydrofluorene (III) [semicarbazone, m.p. 200—202°, possibly a mixture], and is converted by AcOH–HCl at 200° into an isomeric *acid* (cis-trans) (IV), m.p. 219—220° (*anhydride*, m.p. 105—106°), which affords (III). Me diphenate (V) is similarly reduced to *Me perhydrodiphenate* (VI), m.p. 73°, hydrolysed by KOH–MeOH to (IV). Hydrogenation (Raney Ni) of (V) in methyl*cyclo*hexane at 150—300 atm. and 210—215° gives (VI) and an isomeride, hydrolysed to (II). The applicability of the Blanc rule to acids of the adipic series depends on the degree of substitution and on the configuration. The formation of anhydrides and ketones by the Blanc procedure is discussed. The perhydrodiphenic acid, m.p. 213°, of Vocke (*loc. cit.*) has a *trans-trans* configuration. A. T. P.

Configurational relationships in the steroid series. E. Bergmann (Chem. and Ind., 1939, 512—513).—"Anhydrostrophanthidin hemiacetal" (Jacobs and Collins, A., 1924, i, 867) has the structure *A* and since strophanthidin (I) belongs to the *trans*-decahydronaphthalene series its abs. configuration is established. Alkaline isomerisation of (I) to α-*iso*strophanthidin (II) involves a configurational change at $C_{(3)}$ and rearrangement of the lactonic group; hence α-*iso*strophanthidic and α-*iso*strophanthic acid derived from (II) cannot undergo lactol- or lactone-formation and contain OH at $C_{(3)}$ and CHO (or CO_2H) at $C_{(10)}$ in *trans* position. (I) is not pptd. by digitonin (III). This precipitability is not exclusively determined by configurational reasons but apparently also by the intactness of the original lactone ring. Probably, however, the cardiac aglucones which are not pptd. by (III) have the same configuration at $C_{(3)}$ as has (I), whilst uzarigenin (IV) possesses the epimeric arrangement at $C_{(3)}$. If this is the case the complete steric arrangement of (IV), gitoxigenin (V), and digitoxigenin (VI) is established since (V) and (VI) have been transformed into ætio*allo*cholanic and ætiocholanic acid, respectively. If digitonide formation in the cardiac aglucone series is ascribed to steric relationships it would seem sp. for the *trans* position between OH at $C_{(3)}$ and Me at $C_{(10)}$. It is difficult to draw definite conclusions with regard to cholesterol (VII) from the known configuration of the 3-OH-dicarboxylic acid of Lettré (A., 1935, 857), but since hydrolysis of the C–Cl linking which produces it from the Cl-acid is accompanied by Walden inversion whilst the way from (VII) to this 3-Cl-acid probably does not give rise to configurational changes at $C_{(3)}$, then OH at $C_{(3)}$ and Me at $C_{(10)}$ are in *trans* positions in (VII). The fact that substitution of a polar linking by a negative ion is generally (so far as no allylic system is concerned) accompanied by inversion of configuration permits the exact determination of a steric relationship. H. W.



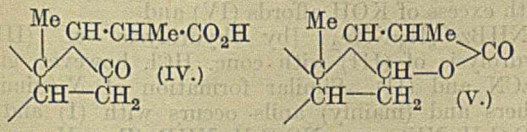
(*A*.)

Further colour reactions of sterols in their relationship to constitutive factors. G. Woker and I. Antener (Helv. Chim. Acta, 1939, **22**, 666—672).—The behaviour of digitoxigenin and gitoxigenin towards H_2SO_4 and furfuraldehyde–H_2SO_4 is described. In view of the importance of the presence of OH, the reaction with mono- and poly-hydroxybenzenes has been investigated. H. W.

Sterols. LIX. Sarsasapogenin derivatives. Deoxysarsasapogenin. LX. Oxidation products of sarsasapogenin. Structure of the C_{22} keto-acid. R. E. Marker and E. Rohrmann (J. Amer. Chem. Soc., 1939, **61**, 1284—1285, 1285—1287; cf. A., 1939, II, 276).—LIX. Deoxysarsasapogenin (I) [prep. from sarsasapogenone (II) by Zn–HCl–EtOH; 45% yield from sarsasapogenin (III)], m.p. 214—216°, gives a red ppt. with SeO_2 in C_6H_6–AcOH, is hydrogenated (PtO_2; AcOH; 70°/3 atm.) to *dihydrodeoxysarsasapogenin*, m.p. 109—110° (unaffected by SeO_2), with Zn–Hg–HCl–EtOH gives

tetrahydrodeoxysarsasapogenin, m.p. 101° [also obtained from (II)], and an *isomeride* (? polymorphous form), m.p. 118°, and with Br and a little HBr in AcOH gives a *Br*-derivative, m.p. 170° (stable to SeO_2). The *semicarbazone*, m.p. 180° (decomp.), of (II) with NaOEt–EtOH at 175—180° gives mainly (III) with 10% of (I).

LX. Sarsasapogenin acetate and CrO_3 give, among other products (cf. lit.), an *acid* (IV), $C_{22}H_{34}O_4$, m.p. 285—287° (decomp.) [*semicarbazone*, m.p. 204—207° (decomp.); *Me* ester, double m.p. 124—126° and 159°, indifferent to H_2–PtO_2], reduced by Na–EtOH or by H_2–PtO_2 in EtOH–Et_2O to a *lactone* (V), $C_{22}H_{34}O_3$, *forms* (? polymorphous or stereoisomeric),



m.p. 197—198° and 186—188° (sole product in EtOH–HCl), but giving with Zn–Hg–HCl–EtOH only the *Et* ester, m.p. 163—164°, of (IV). The above structures are probable. R. S. C.

Sterols. LXII. Position of the hydroxyl group in tigogenin and sarsasapogenin. R. E. Marker and E. Rohrmann (J. Amer. Chem. Soc., 1939, **61**, 1291—1292).—Sarsasapogeninlactone and Br give a *Br-lactone*, $C_{22}H_{31}O_3Br$, m.p. 194—195°, converted by C_5H_5N into the *keto-lactone*, $C_{22}H_{30}O_3$, m.p. 213—214°, which is reduced and epimerised by Na–EtOH to *tigogeninlactone*, m.p. 234—235° (oxidised by CrO_3 to a *keto-lactone*, $C_{22}H_{32}O_3$, m.p. 252—254°). Thus sarsasapogenin and tigogenin have OH at $C_{(3)}$ and differ only in the configuration at $C_{(5)}$. R. S. C.

Nitrones. Condensation of arylnitroso-compounds with di- and tri-nitrotoluenes. I. Tănăsescu and I. Nanu (Ber., 1939, **72**, [*B*], 1083—1092).—Nitrones are obtained by the condensation of NO-compounds with substances containing activated Me and their structures are established by the Beckmann transformation with AcCl. Reaction could not be effected between *o*-, *m*-, and *p*-$C_6H_4Me{\cdot}NO_2$ and PhNO or *p*-$NMe{\cdot}C_6H_4{\cdot}NO$. *o*-Nitrophenyl-*N*-phenylnitrone is converted by AcCl in boiling C_6H_6 or by KOH–EtOH into *o*-$NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}NHPh$ and by boiling Ac_2O–NaOAc into o-*nitrobenz-N-acetanilide*, m.p. 112—113°. *m*- and *p*-$NO_2{\cdot}C_6H_4{\cdot}CH{:}NPh{:}O$ similarly give *m*-$NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}NHPh$, m-*nitrobenz-N-acetanilide*, m.p. 86·5°, and *p*-$NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}NHPh$ and p-*nitrobenz-N-acetanilide*, m.p. 137—138°. *p*-$NO_2{\cdot}C_6H_4{\cdot}CH{:}NO{\cdot}C_6H_4{\cdot}NMe_2$-*p* reacts indefinitely with AcCl or PCl_5 but is converted by Ac_2O–NaOAc into p-*nitrobenz-N-acet*-p-*dimethylaminoanilide*, m.p. 160° (all nitrones containing $\cdot C_6H_4{\cdot}NMe_2$ appear to behave thus irregularly). 1 : 2 : 4-$C_6H_3Me(NO_2)_2$ and PhNO in presence of Na_2CO_3 or piperidine give $(NO_2)_2C_6H_3{\cdot}CH{:}NPh{:}O$, m.p. 151°, transformed by AcCl into 2 : 4-$(NO_2)_2C_6H_3{\cdot}CO{\cdot}NHPh$ and by Ac_2O into 2 : 4-*dinitrobenz-N-acetanilide*, m.p. 182°. 2 : 4-$(NO_2)_2C_6H_3{\cdot}CH{:}NO{\cdot}C_6H_4Me$-*p*, m.p. 169°, is isomerised by AcCl in $COMe_2$ to 2 : 4-*dinitrobenz*-p-*toluidide*, m.p. 215°, and converted by Ac_2O–NaOAc at 100° into 2 : 4-*dinitrobenz-N-acet*-p-*toluidide*. The condensation of 1 : 2 : 4-$C_6H_3Me(NO_2)_2$ with *p*-$NO{\cdot}C_6H_4{\cdot}NMe_2$ in C_5H_5N containing I yields 2 : 4-$(NO_2)_2C_6H_3{\cdot}CH{:}NO{\cdot}C_6H_4{\cdot}NMe_2$-*p*, m.p. 194°, whence 2 : 4-*dinitrobenz-N-acet*-p-*dimethylaminoanilide*, m.p. 206°, also obtained by acetylation of 2 : 4-*dinitrobenz*-p-*dimethylaminoanilide*, m.p. 240°. 2 : 4-$(NO_2)_2C_6H_3{\cdot}CHO$ and *p*-$NMe_2{\cdot}C_6H_4{\cdot}NH_2$ in C_6H_6 afford 2 : 4-*dinitrobenzylidene*-p-*dimethylaminoanil*, m.p. 209·5°. 1 : 2 : 4 : 6-$C_6H_2Me(NO_2)_3$ and PhNO in EtOH containing Na_2CO_3 or piperidine or in C_5H_5N containing I yield 2 : 4 : 6-*trinitrophenyl-N-phenylnitrone*, m.p. 147—148° (explosion), which gives 2 : 4 : 6-*trinitrobenzanilide*, m.p. 229—230°, and 2 : 4 : 6-*trinitrobenz-N-acetanilide*, m.p. 206—207°. H. W.

Reaction between dimethylaniline and opianic acid. V. M. Rodionov and A. M. Fedorova (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 951—959).—Opianic acid with $NPhMe_2$ in the cold yields *dimethylaminophenylmeconine* (I) (37·5%), m.p. 135—136° (*hydrochloride*), and the corresponding *Me*$_1$ *ether*, m.p. 152—154° [*Na* derivative (+ H_2O)], which gives (I) with *p*-$C_6H_4Me{\cdot}SO_3Me$ and the *Me Et ether*, m.p. 137°, with *p*-$C_6H_4Me{\cdot}SO_3Et$. With boiling $NPhMe_2$, Me opianate (> 30%) is obtained, with small quantities of 3 : 4 : 1-$C_6H_3(OMe)_2{\cdot}CHO$ and 4 : 3 : 1-$OMe{\cdot}C_6H_3(OH){\cdot}CHO$. BzOH with $NPhMe_2$, either at 1 atm. or under pressure, yields MeOBz (8%). A. Li.

Synthesis of 4-aminocyclohexyl methyl ketone. E. Ferber and H. Brückner (Ber., 1939, **72**, [*B*], 995—1002).—Reduction (colloidal Pd in HCl or 96% EtOH) of COPhMe yields PhEt. Only small amounts of difficultly isolable products result from the action of Na–Hg on *p*-$NH_2{\cdot}C_6H_4{\cdot}COMe$. Hydrogenation ($PtO_2$ in EtOH in absence of H^+) of *p*-$NHAc{\cdot}C_6H_4{\cdot}OH$ does not occur at room temp. but leads slowly at 60° to trans- (I), m.p. 164° and cis- (II), m.p. 135°, -4-*acetamido*cyclo*hexanol*. (I) is hydrolysed by 15% HCl at 120° to *trans*-4-amino*cyclo*hexanol hydrochloride, m.p. 226—227 (free base, m.p. 110—111°), whilst (II) gives the *cis*-hydrochloride, m.p. 192—194°, and base, m.p. 78—80°. In H_2O hydrogenation occurs less rapidly than in EtOH but much more rapidly in 96% EtOH containing 1% of AcOH. *p*-$NHAc{\cdot}C_6H_4{\cdot}COMe$ in EtOH–PtO_2 absorbs only 1 H_2 and gives a non-cryst. product converted by NaOAc and AcO into α-*p*-acetamidophenylethyl acetate, m.p. 109° (lit. 192°); in 96% EtOH containing 10% of AcOH there is rapid absorption of 4 H_2 with production of a non-cryst. material oxidised by CrO_3 to trans-, m.p. 147—148°, and cis-, m.p. 74—75°, -4-*acetamido*cyclo*hexyl Me ketone* (corresponding *semicarbazones*, m.p. 217° and 207°, respectively). Either ketone is hydrolysed by 20% HCl at 120° to the same p-*amino*cyclo*hexyl Me ketone hydrochloride*, m.p. 173°. Attempts to conduct the hydrolysis without isomerisation were fruitless. H. W.

Constitution of halogenated resaceto- and propio-phenones. D. Chakravarti and N. Chakravarty (J. Indian Chem. Soc., 1939, **16**, 144—150).—4 : 1 : 3-$C_6H_3Cl(OH)_2$ (I) with AcOH–$ZnCl_2$ at 145°/3 min., followed by aq. HCl, yields 5-*chloro-resacetophenone*, m.p. 171° (*semicarbazone*, m.p. 315°), reduced (Clemmensen) to 4-*chloro*-6-*ethylresorcinol*

(II), m.p. 84°, which with $CH_2Ac{\cdot}CO_2Et$ (III) and H_2SO_4 (or P_2O_5) gives 6(or 8)-*chloro*-5-*hydroxy*-4-*methyl*-8(or 6)-*ethylcoumarin*, m.p. 175° (*Ac* derivative, m.p. 100°). Similarly from (II) and $CHMeAc{\cdot}CO_2Et$ is formed 6(or 8)-*chloro*-5-*hydroxy*-3 : 4-*dimethyl*-8(or 6)-*ethylcoumarin*, m.p. 183°. 4 : 1 : 3-$C_6H_3Et(OH)_2$ (IV) in Et_2O with SO_2Cl_2 yields (II). $EtCO_2H$ with (I) and $ZnCl_2$ gives 5-*chlororespropiophenone* (V), m.p. 90°, which is reduced (Clemmensen) to 4-*chloro*-6-*propylresorcinol*, m.p. 63°, and 4-*propylresorcinol*, m.p. 77° (also formed by reduction of respropiophenone), which with (III) and H_2SO_4 gives 7-*hydroxy*-4-*methyl*-6-*propylcoumarin*, m.p. 174°. Similarly, (V) and (III) give 6(or 8)-*chloro*-5-*hydroxy*-4-*methyl*-8(or 6)-*propylcoumarin*, m.p. 185°. 4 : 1 : 3-$C_6H_3Br(OH)_2$ and $ZnCl_2$–AcOH give 5-*bromoresacetophenone*, m.p. 167° (*semicarbazone*, m.p. 255°), reduced (Clemmensen) to (IV), which with (III) in the usual way gives 7-*hydroxy*-4-*methyl*-6-*ethylcoumarin*, m.p. 210°. 4-Chloro-orcinol and $CH_2Ph{\cdot}CN$ in Et_2O with $ZnCl_2$–HCl give a *ketone*, $C_{15}H_{14}O_3$, m.p. 140°, reduced (Clemmensen) to a *substance*, m.p. 127°. Similarly, orcinol and $CH_2Ph{\cdot}CN$ afford a *ketone*, m.p. 160°, reduced to a *substance*, m.p. 72°. Clemmensen reduction of coumarin gives a *substance*, m.p. 235°. J. D. R.

Di- and poly-arylethane series. I. Di-*p*-xenylethanone [*p*-xenyl *p*-xenylmethyl ketone] and its derivatives. E. A. Schilov and F. K. Judin. **II. Synthesis of αβγδ-tetra-*p*-xenylbutane-αδ-dione and of tetra-*p*-xenylfuran.** F. K. Judin (J. Gen. Chem. Russ., 1939, **9**, 167—172, 173—175).—I. *p*-Xenoin and Zn in AcOH yield αβ-*di*-p-*xenylethanone* (I), m.p. 229—230° (*oxime*, m.p. 173·5—174°), which with Br in $CHCl_3$ affords α-*bromo*- (II), m.p. 186—187·5°, and αα-*dibromo*-αβ-*di*-p-*xenylethanone*, m.p. 181—183°. With HBr (2 hr. at 130—140°) *p*-xenoin gives (I) and $(p\text{-}C_6H_4Ph{\cdot}CO{\cdot})_2$ (III), with PBr_3 the product is (I), and with PBr_5 (III); with SO_2Cl_2 in $CHCl_3$ α-*chloro*-αβ-*di*-p-*xenylethanone* (IV), m.p. 164·5—166°, is obtained. (I) and MgPhBr or $\alpha\text{-}C_{10}H_7{\cdot}MgBr$ in Et_2O afford respectively α-*phenyl*-, m.p. 218·5°, or α-1-*naphthyl*-αβ-*di*-p-*xenylethanol*, m.p. 188°, dehydrated (HCl in C_6H_6) to α-*phenyl*-, m.p. 198·5—200°, or α-1-*naphthyl*-αβ-*di*-p-*xenylethylene*, m.p. 209—214°, respectively.

II. (I) and $Cu(NO_3)_2$ in C_5H_5N (6 hr. at the b.p.) yield αβγδ-tetra-*p*-xenylbutane-αδ-dione (V), also obtained from (II) or (IV) and Cu in PhMe. (V) and AcCl (2 hr. at 180—200°) yield *tetra*-p-*xenylfuran*, m.p. 281—282·5°. R. T.

Condensation of 2-methylnaphthalene and acetyl chloride. G. A. R. Kon and W. T. Weller (J.C.S., 1939, 792—794).—2-$C_{10}H_7Me$, AcCl, and $AlCl_3$ in $PhNO_2$ (or, less well, CS_2) at room temp. give 6- and less 8-acetyl-2-methylnaphthalene, b.p. 150—154°/1·5 mm. [*semicarbazone*, m.p. 181°; no semicarbazone, m.p. 228—230°, is isolated (cf. Dziewoński and Brand, A., 1932, 1250)], oxidised by NaOBr to 2 : 6- and 2 : 8-$C_{10}H_6Me{\cdot}CO_2H$, respectively, and reduced (Clemmensen) to 2-*methyl*-6-*ethylnaphthalene*, m.p. 44—45° [*picrate*, m.p. 109°; *styphnate*, m.p. 119°; *s*-$C_6H_3(NO_2)_3$ *derivative*, m.p. 116—117°; $C_6H_2Me(NO_2)_3$ *derivative*, m.p. 62°], and 2 : 8-$C_{10}H_6MeEt$ [*s*-$C_6H_3(NO_2)_3$ *derivative*, m.p. 127—128°; $C_6H_2Me(NO_2)_3$ *derivative*, m.p. 77—78°], respectively. 2-$C_{10}H_7Me$ and EtCOCl give (method : Haworth *et al.*, A., 1932, 1024) 6-propionyl-2-methylnaphthalene (*semicarbazone*, m.p. 224—225°) and no isomeride. A. T. P.

***N*-Oximino-ethers. IV. Formation of oximino-ethers in the Ehrlich–Sachs reaction. V. Stereoisomeric *N*-aryl ethers of oximinophenylacetonitrile.** F. Barrow and F. J. Thorneycroft (J.C.S., 1939, 769—773; 773—777).—IV. $CH_2Ph{\cdot}CN$ (I), *p*-$NO{\cdot}C_6H_4{\cdot}NMe_2$, and aq. KOH–EtOH give *p*-$NMe_2{\cdot}C_6H_4{\cdot}NH_2$ (II), *p*-$NMe_2{\cdot}C_6H_4{\cdot}N{:}CPh{\cdot}CN$ (III), and some oximinophenylacetonitrile *N*-*p*-dimethylaminophenyl ether, m.p. 90° (IV). Longer reaction with excess of KOH affords (IV) and *p*-$NHBz{\cdot}C_6H_4{\cdot}NMe_2$ [by hydrolysis of (III)]; hydrolysis of (III) with conc. HCl, however, gives BzCN and (II). Similar formation of *N*-oximino-ethers and (mainly) anils occurs with (I) and *p*-$NO{\cdot}C_6H_4{\cdot}NEt_2$ or *p*-$NO{\cdot}C_6H_4{\cdot}NHR$ (R = Me or Et) (with which ether formation is more pronounced). PhNO and (I) in aq. Na_2CO_3–EtOH afford $CN{\cdot}CPh{:}NPh$, α- and β-forms of $CN{\cdot}CPh{:}NPh{:}O$ (V) (cf. A., 1934, 770), azoxybenzene, and NHPhBz. The amide, m.p. 141°, described by Sachs and Bry (A., 1901, i, 272) is probably (V) (β-form). 2 : 4 : 1-$(NO_2)_2C_6H_3{\cdot}CHO$ and (II) in EtOH (+AcOH) give 2 : 4-*dinitrobenzylidene*-p-*dimethylaminoaniline*, green, m.p. 211°, also obtained as the main product from 1 : 2 : 4-$C_6H_3Me(NO_2)_2$ and *p*-$NO{\cdot}C_6H_4{\cdot}NMe_2$ (method : Sachs and Kempf, A., 1902, i, 377); in the latter case some 2 : 4-dinitrobenzaldoxime *N*-*p*-dimethylaminophenyl ether, red, m.p. 193°, is also formed. The mechanism advanced by Schönberg *et al.* (A., 1937, II, 248) is supported.

V. $ArNO_2$ and Zn in aq. EtOH–NH_4Cl at ~70° give the $NHAr{\cdot}OH$, and thence (aq. $FeCl_3$ at 0—5°) ArNO. $CHPhCl{\cdot}CN$ (VII) and *o*-$C_6H_4Me{\cdot}NO$ in aq. KOH–$COMe_2$ give the stereoisomeric *oximinophenylacetonitrile* α-, m.p. 158°, and β-N-*o*-*tolyl ether*, m.p. 117°. Similarly prepared are the analogous ethers : α-, m.p. 134°, and β-N-m-*tolyl*, m.p. 126°; α-, m.p. 135° (slow heating gives β-form), and β-N-p-*tolyl*, m.p. 161°; α-, m.p. 143°, and β-N-o-*chlorophenyl*, m.p. 100°; α-, m.p. 125°, and β-N-m-*chlorophenyl*, m.p. 156°; α-, m.p. 132°, and β-N-p-*chlorophenyl*, m.p. 142° (α → β by slow heating). Configurations are determined by measuring dipole moments. Structural evidence cannot be deduced by comparing m.p. or solubilities in C_6H_6. (IV) has the β-configuration. A. T. P.

Alkaline fission of naphthyl ketones. L. Olifson (J. Gen. Chem. Russ., 1939, **9**, 36—40).—Various naphthyl ketones are heated at 250—260° with KOH, when the reaction $CORR' \rightarrow C_{10}H_8 + R'CO_2H$ takes place (R = α- or β-$C_{10}H_7$, R' = Me, Ph, $C_{10}H_7$; R = $C_{10}H_6Et$, R' = Ph). When R' = Me the reaction $CORR' \rightarrow C_{10}H_7{\cdot}CO_2H + R'H$ also takes place. R. T.

Probable existence of three 2 : 6-dibenzyl*cyclo*hexanones. R. Cornubert and G. Morelle (Compt. rend., 1939, **208**, 1409—1411; cf. A., 1939, II, 164).—Benzylation of *cyclo*hexanone gives (2%) 2 : 6-dibenzyl*cyclo*hexanone (?) (I), m.p. 105° (cf.

A., 1935, 621), different from the ketones of m.p. 55° and 122° (II) (cf. A., 1934, 297). (I) cannot be converted into either of the other forms. When benzylated all three forms give 2 : 2 : 6 : 6-tetrabenzyl-*cyclo*hexanone, m.p. 174°. (I) with Pt–H_2 under pressure in Et_2O gives 2 : 6-dihexahydrobenzyl*cyclo*hexanol (an oil) [*phenylurethane*, m.p. 132—134°, different from that obtained similarly from (II)].

J. L. D.

Conversion of a C_5 into a C_6 ring by pinacolic dehydration. R. Calas (Compt. rend., 1939, **208**, 1413—1415).—Me *trans*-3-methyl*cyclo*pentanol-1-carboxylate with MgMeI gives 3-*methyl*-1-α-*hydroxy*-iso*propyl*cyclo*pentanol*, m.p. 57°, converted by aq. $H_2C_2O_4$ into 2 : 2 : 4-*trimethyl*cyclo*hexanone* (65%), b.p. 80°/23 mm. (*semicarbazone*, m.p. 212°) (also obtained by methylating 2 : 4-dimethyl*cyclo*hexanone), *cis*- (~35%) (*semicarbazone*, m.p. 154°) and a little *trans*-1-acetyl-1 : 3-dimethyl*cyclo*pentane (*semicarbazone*, m.p. 110°), and a very small amount of a diene *hydrocarbon*, b.p. 151—152°/760 mm., which polymerises readily. The ketones are first separated as oximes and then by fractional crystallisation of the semicarbazones.

J. L. D.

Preparation of cyclic ketones by ring-enlargement. E. P. Kohler, M. Tishler, H. Potter, and H. T. Thompson (J. Amer. Chem. Soc., 1939, **61**, 1057—1061).—Cyclic ketones are prepared in quantity by ring-enlargement by one CH_2 by adding NO·NMe·CO_2Et in MeOH to a lower cyclic ketone and Na_2CO_3 in MeOH at 20—25°. Some introduction of >1 CH_2 occurs. Other conditions give no better results. The yield is 63% for *cyclo*heptanone (I), 45% for *cyclo*octanone, 20% for *cyclo*-nonanone and -decanone (very slow reaction), but increases for $C_{>14}$-ketones. *cyclo*Hexanone gives also MeEtCO_3, 15% of *epoxymethylene*cyclo*hexane*, b.p. 148°, m.p. −38·3° to −40·5° (hydrolysed to the glycol, m.p. 74°), Δ^1-cyclo*hexenylcarbinol*, b.p. 92—94°/15 mm. (*phenylurethane*, m.p. 96°; hydrogenated to the known *cyclo*hexylcarbinol), and (?) *di*cyclo*hexyldioxan*, b.p. 147·5—148°/11 mm. H_2–Raney Ni at 150—165°/33—133 atm. hydrogenates (I) in EtOH quantitatively to *cyclo*heptanol, b.p. 185—186°, converted (distillation with 2-$C_{10}H_7$·SO_3H) in 80% yield into *cyclo*heptene, b.p. 114·38°, the oily, unstable dibromide of which with anhyd. $NHMe_2$, first in $CHCl_3$ at 0° to −5° and then in $CHCl_3$–C_6H_6 at 100°, gives Δ^2-*cyclo*heptenyldimethylamine (II) (57—62%), b.p. 184—187°, and 1-*bromo*cyclo*heptene*, b.p. 66·5—67·5°/13 mm., 191°/760 mm. The methobromide, m.p. 192—193° (decomp.), of (II) and aq. KOH give (distillation in N_2) 85—90% of *cyclo*heptadiene (III), b.p. 121·52°/758·3 mm., m.p. −110·42°, the dibromide from which with quinoline at 140° in N_2 yields 66% of *cyclo*heptatriene, b.p. 115·5°/760 mm., m.p. −79·49° [maleic anhydride *adduct*, m.p. 102—104°, formed in hot xylene, hydrolysed by 10% Na_2CO_3 to the dicarboxylic *acid*, m.p. 170—174° (decomp.), and hydrogenated (PtO_2) in AcOH–Ac_2O to the H_4-derivative (IV), m.p. 71—73°]. With Na_2CO_3, (IV) gives an *acid*, m.p. 146—147° (decomp.), but with conc. HCl at 180° yields a trans-*acid*, m.p. 205—210°. (III) gives similarly (cf. Koch, Diss., Kiel, 1932) the maleic anhydride *adduct*, m.p. 110—111°, and its H_2-derivative, m.p. 156—157° [derived cis-, m.p. 132—134° (decomp.), and trans-*acid*, m.p. 215—220°]. *cyclo*Heptanone yields *cyclo*octanone, b.p. 115—115·5°/60 mm., m.p. 43·8° (semicarbazone, m.p. 168—169°), with smaller amounts of epoxymethylene-*cyclo*heptane, b.p. 160—173°, and higher-boiling material. H_2–Raney Ni then gives *cyclo*octanol, b.p. 111·3—111·7°/25 mm., m.p. 25·06°, converted by 2-$C_{10}H_7$·SO_3H into *cyclo*octene, b.p. 143·8—144·5°/773 mm., the dibromide of which with $NHMe_2$ gives only a trace of amine and 70% of 1-*bromo*cyclo*octene*, b.p. 97—98°/23 mm. 1 : 2-*Dichloro*cyclo*octane*, b.p. 130·4—130·6°/25 mm., m.p. −5°, gives similarly almost entirely 1-*chloro*cyclo*octene*, b.p. 77—78°/19 mm. *cyclo*Nonanone, b.p. 103·5—104·2°/22 mm., m.p. 31—31·5° (semicarbazone, m.p. 183—185°), and a little *cyclo*decanone, b.p. 87·5—88°/8 mm., m.p. 20—22° (semicarbazone, m.p. 210—211°), are obtained from *cyclo*octanone (cf. Adamson *et al.*, A., 1939, II, 116).

R. S. C.

Inter- and intra-molecular acylations with hydrogen fluoride. L. F. Fieser and E. B. Hershberg (J. Amer. Chem. Soc., 1939, **61**, 1272—1281).—Commercial anhyd. HF at room temp. is often an advantageous reagent for intramol. ring-closure of γ-arylbutyric and β-arylpropionic acids. Experiments are detailed for γ-phenyl-, γ-3-acenaphthyl-, and γ-4-methoxy-3-diphenylyl-butyric acid (gives 1-*keto*-5-*methoxy*-8-*phenyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 120—120·5°, not obtainable by other methods), and β-phenylpropionic acid; success is recorded without details for 6 similar acids. The reaction failed for a β-aroylpropionic acid and for *o*-COPh·C_6H_4·CO_2H. 1-β-α′-Naphthylethyl*cyclo*hexanol gives a product, dehydrogenated by Se to chrysene (poor yield). Anthrone is obtained in 82% yield from *o*-CH_2Ph·C_6H_4·CO_2H, and *o*-α-$C_{10}H_7$·CH_2·C_6H_4·CO_2H gives 68—75% of pure 1 : 2-benz-10-anthrone, whence MgMeCl gives 56% of 10-methyl-1 : 2-benzanthracene, m.p. 140—141° [separated by adsorption on Al_2O_3 from a little (?) 1 : 2-benz-10-anthranol]. 3-Methoxy-1 : 2-benz-10-anthrone is similarly prepared in 58% yield. HF does not cause ketone formation from C_6H_6 and *o*-$C_6H_4(CO_2H)_2$ or BzOH, $C_{10}H_8$ and succinic anhydride (I) or crotonic acid (II), phenanthrene and CH_2Cl·CH_2·COCl or AcCl, 9 : 10-dihydrophenanthrene and AcCl, anthracene and CH_2Cl·COCl, or 1 : 2-benzanthracene and $H_2C_2O_4$. Quinol and BzOH merely give the monobenzoate. Acenaphthene (III), however, readily reacts to give ketones; with BzOH it gives 62% and with BzCl 87% of 3-benzoylacenaphthene; (I) yields mainly γ-keto-γ-3- with some γ-keto-γ-1-acenaphthylbutyric acid (IV). With AcOH, (III) gives 25% of 1-*acetoacenaphthene* (V), m.p. 104·7—105·2°, b.p. 154—155°/1 mm., and some of the 3-isomeride (VI), forms, m.p. 59—59·5° and 69·5—70° (lit. 75° only) [*picrate*, m.p. 97·5—98°; $C_6H_3(NO_2)_3$ *derivative*, m.p. 112—113°]. With I–KI in aq. dioxan (V) gives *acenaphthene*-1-*carboxylic acid*, m.p. 256—257°; (V) is also obtained from the Me ester of (IV) by heating its Br-derivative, m.p. 103° (decomp.), with alcoholic alkali. $AlCl_3$, AcCl, and (III) in $PhNO_2$ yield mainly (VI) with some (V).

With HF, (II) and (III) give 62% of 1′-*keto*-3′-*methyl*-$\Delta^{4'}$-cyclo*penteno*-4′ : 5′-2 : 3-*acenaphthene* (VII), m.p. 167—167·5°, the structure of which is proved as follows. It is indifferent to Br–$CHCl_3$ and $KMnO_4$–$COMe_2$. $CHMe{:}CH{\cdot}COCl$, (III), and $AlCl_3$ in CS_2 at 10—15° give 23% of 3-*crotonylacenaphthene*, m.p. 63—63·5° [oxidised by $KMnO_4$ in NaOH to 1 : 4 : 5-$CO_2H{\cdot}C_{10}H_5(CO)_2O$], which with HF yields 50% of (VII). Zn–Hg–HCl–PhMe–H_2O–AcOH and (VII) give 85% of 1′-*methyl*-$\Delta^{4'}$-cyclo*penteno*-4′ : 5′-2 : 3-*acenaphthene*, m.p. 38—38·5° [$C_6H_3(NO_2)_3$ *derivative*, m.p. 113—114°], giving no cryst. product when dehydrogenated by Se or Pd–C. With anhyd. $Na_2Cr_2O_7$ in AcOH at <100° and then at the b.p., (VII) gives 29% of 2-*acetonaphthalene*-1 : 4 : 5-*tricarboxylic acid* (VIII), m.p. 160° (instantaneous) or 189—191° (slow heating), the *anhydride*, m.p. 217—218° (*Me* ester, m.p. 261—262°, obtained from the acid by CH_2N_2–Et_2O), of which with basic Cu carbonate in hot quinoline yields 3-*aceto*-1 : 8-*naphthalic anhydride*, m.p. 217·5—218·5°. NaOCl oxidises (VIII) to *naphthalene*-1 : 2 : 4 : 5-*tetracarboxylic acid*, m.p. (impure) 250° (instantaneous), 262—262·5° (slow heating) (*dianhydride*, m.p. 262·5—263°; Me_2 ester *anhydride*, m.p. 219·5—220·5°, obtained from the acid by CH_2N_2–Et_2O). Hydrindene and perinaphthan also condense with BzCl or AcOH in presence of HF. M.p. are corr. R. S. C.

Syntheses of polycyclic compounds related to the sterols. VII. Cyclisation of γ-5-methoxy-1-naphthylbutyric acid. G. A. R. Kon and H. R. Soper (J.C.S., 1939, 790—792; cf. A., 1936, 465).—γ-5-Methoxy-1-naphthylbutyric acid (I) and $SnCl_4$ in PhMe at 100° (bath) give (results are variable) 1-keto-8-methoxy-1 : 2 : 3 : 4-tetrahydrophenanthrene (II), m.p. 137°, converted by MgMeI, followed by dehydrogenation by Pd–C at 300—330°, into 8-*methoxy*-1-*methylphenanthrene*, m.p. 121—121·5° [*picrate*, m.p. 153—154°; *s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 177—178°; *styphnate*, m.p. 179—180°]. 7-Keto-4-methoxy-7 : 8-dihydrohomophenalene, m.p. 88—89° (compound $C_{15}H_{14}O_2$, *loc. cit.*), is oxidised ($Na_2Cr_2O_7$–AcOH) to 4 : 1 : 8-$OMe{\cdot}C_{10}H_5(CO_2H)_2$, also obtained by oxidation of 3-*methoxyacenaphthene*, m.p. 66°, b.p. 174°/13 mm. (from 3-aminoacenaphthene by the diazo-reaction and subsequent methylation). A. T. P.

Syntheses in the sterol and sex hormone group. III. Synthesis of 7-hydroxy-3′-keto-3 : 4-dihydro[*cyclo*penteno-1′ : 2′-1 : 2-phenanthrene]. C. K. Chuang, C. M. Ma, Y. L. Tien, and Y. T. Huang (Ber., 1939, **72**, [*B*], 949—953).—Condensation of γ-6-methoxy-1-naphthylbutyryl chloride with Et_2 sodioacetylsuccinate (I) followed by hydrolysis of the product affords γ-*keto*-ζ-6-*methoxy*-1-*naphthylheptoic acid*, m.p. 80—81° (after purification through the *semicarbazone*, m.p. 166—167°). The Me ester is condensed by NaOEt in Et_2O to the non-cryst. 2-β-6′-methoxy-1′-naphthylethyl*cyclo*pentane-1 : 3-dione, converted by P_2O_5 into 3′-*keto*-7-*methoxy*-3 : 4-*dihydro*[cyclo*penteno*-1′ : 2′-1 : 2-*phenanthrene*] (*dehydronorequilenin Me ether*), m.p. 210—211° (*semicarbazone*, decomp. ~310°). This is demethylated by AcOH–HBr (*d* 1·49) at 110° to the 7-*OH*-derivative, m.p. 319° (decomp.) in bath pre-heated to 315°), and reduced (Clemmensen) and then dehydrogenated (Se at 300—320°) to 7-methoxy-[*cyclo*penteno-1′ : 2′-1 : 2-phenanthrene], m.p. 133—134°. γ-6-Methoxy-1-naphthyl-α-methylbutyryl chloride appears to react normally with (I) or with Et_2 sodio-α-acetylglutarate but hydrolysis of the product gives essentially the original acid in each case. H. W.

Ethyl bisindanedionecarboxylate. G. Wanag (Ber., 1939, **72**, [*B*], 973—976).—A dimeric product could not be obtained by the action of Et 2-chloro- with Et sodio-indane-1 : 3-dione-2-carboxylate (I). *Et₂ bisindanedionecarboxylate* (*diphthalylsuccinate*) (II), m.p. 211°, is obtained in 64% yield by the oxidation of (I) with PbO_2 (prepared according to Gattermann) in AcOH at room temp. (II) reacts readily with $NHPh{\cdot}NH_2$ but gives only amorphous materials with varying N content. With NH_2Ph in absence of solvent resins result; condensation does not occur in EtOH but in presence of AcOH there is ready formation of the *dianil*, $C_{36}H_{28}O_6N_2$, m.p. 221—222°. Protracted action of an excess of NH_2Ph leads to the production of some phthalanil, m.p. 207°; the *di*-p-*tolil* has m.p. 256°. Reaction does not take place with NHPhMe or $NPhMe_2$. (II) is very stable towards acids but the protracted action of boiling conc. HCl or cold conc. H_2SO_4 leads to some dihydroxynaphthacenequinone. (II) is very sensitive to alkali. H. W.

Heteropolarity. XXXV. Action of nitroso-dimethylaniline on phencyclone. W. Dilthey and H. Passing (J. pr. Chem., 1939, [ii], **153**, 35—53; cf. A., 1938, II, 494).—Phencyclone is regularly obtained from pure phenanthraquinone and $(CH_2Ph{\cdot}CO)_2$ by a limited amount of alkali in pure EtOH (cf. A., 1935, 1241). With *p*-$NO{\cdot}C_6H_4{\cdot}NMe_2$ in C_5H_5N and N_2 it gives CO and 9 : 10-*dibenzoylphenanthrenemono*-p-*dimethylaminoanil* (I), yellow, m.p. 217—218° (decomp.); in presence of 5% of C_5H_5N,HCl some 3 : 6-*diphenyl*-2-p-*dimethylaminophenyl*-4 : 5-*oo′-diphenylene*isooxazine (II), m.p. 351—352°, also results. Steric considerations show that the initial polycyclic adduct, being unstable, loses CO and forms (I) by ring-fission, and that (II) is a secondary product derived from (I). Structures are proved by the following reactions. HCO_2H, AcOH, or H_2S in hot C_5H_5N converts (I) into (II); AcOH (and other fatty acids) also causes some hydrolysis. NaOMe–MeOH or H_2O_2–NaOH are without action on (I), but H_2O_2 in HCO_2H gives 9 : 10-dibenzoylphenanthrene (III) and *p*-$NO_2{\cdot}C_6H_4{\cdot}NMe_2$, possibly by way of (II) which is similarly oxidised. (I) gives a yellowish-red *mono*-, m.p. 220—221° (decomp.), and yellow (?) *di-hydrochloride*, amorphous, a red *mono*-, m.p. 273° (decomp.) (addition of $HClO_4$ to C:N to give $CH{\cdot}N^+$), and yellow *di-perchlorate*, m.p. 239—241° (decomp.), a *monopicrate*, m.p. 194—196° (decomp.), and an *oxime*, m.p. 340—341° (slow heating) or double m.p. 250° and 339—340° (rapid heating); warm C_5H_5N reconverts the salts into (I). With MgPhBr in PhMe (I) gives 9-α-p-*dimethylaminoanilobenzyl*-10-α-*hydroxybenzhydrylphenanthrene*, m.p. 283—284° (decomp.) [*mono*-, m.p. 308—309° (decomp.), and *di*-

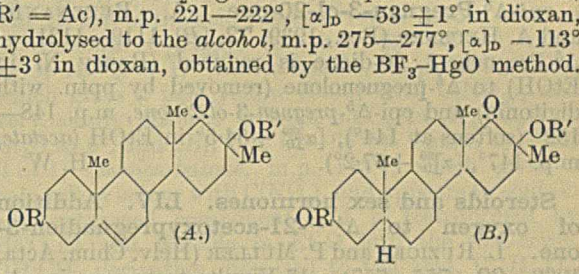
perchlorate, m.p. 297—300° (decomp.); *monopicrate*, m.p. 264—266° (decomp.)]. (II) gives a *perchlorate*, m.p. 292—293° (decomp.), and *picrate*, m.p. 211—212° (decomp.). *p*-$NH_2{\cdot}C_6H_4{\cdot}NMe_2$,HCl (not the free base) and (III) in hot C_5H_5N under N_2 give (II). R. S. C.

Œstrone and œstradiol benzyl ethers.—See B., 1939, 665.

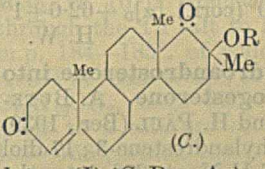
Furfuraldehyde [colour] reactions of vitamin-D_2, hormones of the adrenal cortex, the corpus luteum, and the androsterone and testosterone group and their relationships to constitutive factors. G. Woker and I. Antener (Helv. Chim. Acta, 1939, **22**, 511—519; cf. A., 1939, II, 156).—The opening of ring *B*, occurring during the activation of egosterol to vitamin-D_2, causes profound change in the H_2SO_4–furfuraldehyde reaction and to a smaller degree in the H_2SO_4 reaction whereas the complete removal of the long side-chain is of much less importance. Great change is induced by the saturation of the double linking in dehydroandrosterone but the *cis*- or *trans*-configuration of the product of the change has also considerable influence. The position of the double linkings, apart from their no., is of great significance. The presence of at least 1 OH appears essential for an intense colour reaction. H. W.

Steroids and sex hormones. LII. Constituents of the adrenal cortex and related substances. XXIV. Constitution of the ketones formed by treating 17-hydroxy-17-acetylenylandrostane derivatives with acetic acid in presence of mercury oxide and boron fluoride. L. Ruzicka, K. Gätzi, and T. Reichstein (Helv. Chim. Acta, 1939, **22**, 626—640; cf. A., 1938, II, 413).—Addition of BF_3–Et_2O to 17-acetylenylandrostane-3-*trans*-17(α)-diol 3-monoacetate in AcOH–Ac_2O containing HgO gives a *diacetate* (I), $C_{25}H_{38}O_5$, m.p. 227—229°, $[\alpha]_D^{18}$ 0·0±0·2° in $COMe_2$ (also obtained from 17-acetylenyl-3-*trans*-17(α)-diacetoxy-androstane and -androstene), and a *diacetate* (II), $C_{25}H_{38}O_5$, m.p. 222—224°, $[\alpha]_D^{18}$ −7·9°±2° in $COMe_2$. (I) appears indifferent to H_2 (PtO_2 in AcOH) or to CrO_3 in AcOH. (I) is hydrolysed by KOH–MeOH to the (*OH*)$_2$-*ketone* (III), $C_{21}H_{34}O_3$, m.p. 305—306°, or 274—275° (vac.); the corresponding *monoacetate* (IV), m.p. 244—244·5°, $[\alpha]_D^{21}$ −31·3°±2° in $COMe_2$, is hydrogenated (PtO_2 in AcOH) and then acetylated to a *monoacetate*, m.p. 251—251·5°, and a *diacetate*, $C_{25}H_{40}O_5$, m.p. 263·5—264° (which contains a *tert.*-OH); the latter substance is hydrolysed to the *triol*, m.p. 303—305°. (III) is oxidised by CrO_3 in AcOH at room temp. to the (*CO*)$_2$-*acid*, $C_{21}H_{32}O_4$, m.p. 226—228° (*Me* ester, m.p. 106—107°). Similarly (IV) gives an *acid*, $C_{23}H_{34}O_5$, m.p. 115—117° (*Me* ester, m.p. 106—106·5°, and its *semicarbazone*, m.p. 228—232°). (II) is hydrolysed to a (*OH*)$_2$-*ketone* (V), $C_{21}H_{34}O_3$, m.p. 205—206° (opaque at 110°); its *diacetate*, $C_{25}H_{38}O_5$, m.p. 161—162°, $[\alpha]_D^{21}$ −34·8°±2° in $COMe_2$, is reduced (PtO_2 in AcOH) and then acetylated (C_5H_5N–Ac_2O at room temp.) to the *triacetate*, $C_{27}H_{42}O_6$, m.p. 204—205°, which yields the *triol*, m.p. 298—300°. Oxidation of (V) gives a neutral substance, m.p. 203—205° (not identical with *allo*pregnanedione), and an acid, m.p. 283—292°. All m.p. are corr. H. W.

Steroids and sex hormones. LIII. Hydration of 17-hydroxy-17-acetylenyl derivatives of the androstane and androstene series. L. Ruzicka, M. W. Goldberg, and F. Hunziker (Helv. Chim. Acta, 1939, **22**, 707—716).—Previous results (A., 1939, II, 76) are modified. Δ^5-Acetylenylandrostene-3-*trans*-17-diol and $Hg(OAc)_2$ in EtOH or, preferably, in EtOAc at room temp. and decomp. of the product with H_2S give the *compound* A (R = H; R′ = Ac), m.p. 221—222°, $[\alpha]_D$ −53°±1° in dioxan, hydrolysed to the *alcohol*, m.p. 275—277°, $[\alpha]_D$ −113° ±3° in dioxan, obtained by the BF_3–HgO method.



Similarly, 17-acetylenylandrostanediol affords the *ketone acetate* (*B*, R = H; R′ = Ac), m.p. 202—204°, $[\alpha]_D$ ±0°±2° in dioxan, whilst under similar conditions its diacetate yields the *diacetate* (*B*, R = R′ = Ac), m.p. 227—229°, $[\alpha]_D$ −3·4°±1° in dioxan, hydrolysed to the (*OH*)$_2$-*ketone* (*B*, R = R′ = H), m.p. 274—275° when rapidly heated (when slowly heated it is converted into a modification, m.p. 305°), $[\alpha]_D$ −30°±10° in dioxan (*oxime*, m.p. 248—249°; *monoacetate*, m.p. 244—245°, $[\alpha]_D$ −31°±1° in dioxan). 17-Acetylenyltestosterone gives the *acetoxydiketone* (I) (*C*, R = Ac), m.p. 198—200°, $[\alpha]_D$ +66°±1° in dioxan, hydrolysed to the *OH-diketone* (*C*, R = H), m.p. ~280°, $[\alpha]_D$ +47°±2° in dioxan. (I) is also obtained from 17-acetylenyltestosterone acetate. All m.p. are corr. (vac.). H. W.



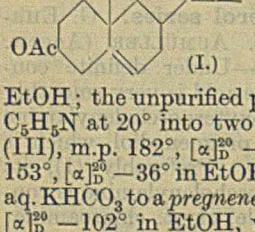
New syntheses in the sterol series. G. Ehrhart, H. Ruschig, and W. Aumüller (Angew. Chem., 1939, **52**, 363—366).—Under definite conditions 3-hydroxybisnorcholenic acid is very smoothly degraded (Curtius) to 3-hydroxyternorcholenylamine (I), converted by HNO_2 into pregnenediol, which is oxidised to progesterone (II). Preferably (I), its *O*-Ac derivative, or 3-ketoternorcholenylamine is converted by HOCl into the stable, cryst. chloroamine; this with alkali yields the ketimine, which is hydrolysed by acid to (II). This reaction with HOCl appears to be general for higher amines. Deoxycholic acid is transformed (Grignard and double degradation) into 3 : 12-dihydroxybisnorcholanic acid, acetylated and degraded (Curtius) to 3 : 12-diacetoxyternorcholanylamine; this is converted by successive treatment with HOCl and hydrolysis into 3 : 12-dihydroxypregnanone. The 3 : 12-Ac_2 derivative of this is partly hydrolysed to 3-hydroxy-12-acetoxypregnanone, which is oxidised and brominated to 4-bromo-3-keto-12-acetoxypregnanone; this is transformed by loss of HBr followed by cautious hydrolysis into 12-hydroxyprogesterone. Pregnenolone is converted by the Beckmann transformation into 3-hydroxyætiocholenylamine, oxidised to 3-keto-

ætiocholenylamine, which is transformed (HOCl etc.) into androstenedione. Acetylpregnenolone is oxidised by $Pb(OAc)_4$ to 3 : 21-diacetoxypregnenone. Progesterone is converted similarly into deoxycorticosterone acetate; by use of the corresponding Pb salt, the propionate, benzoate, palmitate, etc. are obtained. Deoxycorticosterone has m.p. 138—140° and 152—154° after resolidification; it is polymorphous. H. W.

***epi*-Δ⁵-Pregnen-3-ol-20-one.** A. Butenandt and A. Heusner (Ber., 1939, **72**, [*B*], 1119—1121).—Δ⁵-Pregnene-3 : 20-dione is reduced (Raney Ni in EtOH) to Δ⁵-pregnenolone (removed by pptn. with digitonin) and epi-Δ⁵-*pregnen*-3-*ol*-20-*one*, m.p. 148—152° (softens at 144°), $[\alpha]_D^{20}$ +54·5° in EtOH (*acetate*, m.p. 147°, $[\alpha]_D^{20}$ +57·2°). H. W.

Steroids and sex hormones. LIV. Addition of oxygen to Δ⁴:¹⁷-21-acetoxypregnadien-3-one. L. Ruzicka and P. Müller (Helv. Chim. Acta, 1939, **22**, 755—757).—17-Vinyltestosterone is obtained in excellent yield by partial hydrogenation (Pd–$CaCO_3$ in C_5H_5N) of 17-acetylenyltestosterone. *o*-$CO_2H{\cdot}C_6H_4{\cdot}CO_3H$ transforms Δ⁴:¹⁷-21-acetoxypregnadien-3-one (I) in Et_2O into Δ⁴-17 : 20-*oxido*-21-*acetoxypregnen*-3-*one*, m.p. 125° (corr.), $[\alpha]_D$ +99°±1° in dioxan. (I) is converted by OsO_4 in Et_2O followed by Na_2SO_4 in EtOH–H_2O into Δ⁴-17(β) : 20 : 21-*trihydroxypregnen*-3-*one*, m.p. 190° (corr.), $[\alpha]_D$ +62·6±1° in dioxan. H. W.

Transformation of dehydroandrosterone into 17-*iso*progesterone and progesterone. A. Butenandt, J. Schmidt-Thomé, and H. Paul (Ber., 1939, **72**, [*B*], 1112—1118).—17-Ethylandrostene-3 : 17-diol is converted by Ac_2O in C_5H_5N at 20° into the 3-*monoacetate*, m.p. 167—168°, transformed by $POCl_3$ in boiling C_5H_5N into the *substance* (I), m.p. 140°. This is converted by the successive action of OsO_4 in Et_2O and Na_2SO_3 into Δ⁵-*pregnene*-3 : 17 : 20-*triol* (II), m.p. 227°, $[\alpha]_D^{20}$ −75° in EtOH; the unpurified product is converted by Ac_2O in C_5H_5N at 20° into two stereoisomeric 3 : 20-*diacetates* (III), m.p. 182°, $[\alpha]_D^{20}$ −74° in EtOH, and m.p. 152—153°, $[\alpha]_D^{20}$ −36° in EtOH. The former is hydrolysed by aq. $KHCO_3$ to a *pregnenetriol*, m.p. 241° (slight decomp.), $[\alpha]_D^{20}$ −102° in EtOH, whereas the latter affords (II). Either triol is converted by $Pb(OAc)_4$ in AcOH to dehydroandrosterone. At 120°/~0·01 mm., (III) (m.p. 182°) and Zn dust afford 17-*iso*pregnen-3-ol-20-one acetate, m.p. 169—171°, $[\alpha]_D$ −126° in EtOH, hydrolysed (aq. $KHCO_3$) to 17-*iso*pregnen-3-ol-20-one, m.p. 170—172°, $[\alpha]_D$ −136° in EtOH. This is oxidised by $Al(OPr^{\beta})_3$ in PhMe–*cyclo*hexane to 17-*iso*progesterone, m.p. 145° after softening at 142°, $[\alpha]_D^{20}$ ±0° in EtOH, isomerised (boiling HCl–EtOH) to progesterone, m.p. 127—128°, $[\alpha]_D$ +187° in EtOH. H. W.



(I.)

Methyl 17(α)-hydroxy-3-ketoætio*allo*cholanate and methyl androstane-17(α)-ol-3-one 17-acetate. K. Gätzi (Helv. Chim. Acta, 1939, **22**, 753—754).—Oxidation (CrO_3 in AcOH) of Me 3(β) : 17(α)-dihydroxyætio*allo*cholanate gives *Me* 17(α)-hydroxy-3-ketoætio*allo*cholanate, m.p. 228—230° (corr.). Me Δ⁵-3(β) : 17(α)-dihydroxyandrostene 17-acetate is reduced (PtO_2 in AcOH) to Me 3(β) : 17(α)-dihydroxyandrostane 17-acetate, m.p. 179—181° (corr.), which is oxidised by CrO_3 in AcOH at room temp. to *Me androstan*-17(α)-*ol*-3-*one* 17-*acetate*, m.p. 119·5—120·5° (corr.). Neither ester is identical with that described by Ruzicka *et al.* (A., 1939, II, 327). H. W.

Oxidation of cholesterol and *trans*-dehydroandrosterone with osmium tetroxide. M. I. Uschakov and A. I. Liutenberg (J. Gen. Chem. Russ., 1939, **9**, 69—72; cf. A., 1937, II, 458).—Cholesterol in Et_2O and OsO_4 (42 hr. at room temp.) yield *cis*-cholestane-3 : 5 : 6-triol (3 : 6-*diacetate*, m.p. 188—189°), oxidised by CrO_3 in AcOH (23 hr. at room temp.) to *cis*-cholestan-5-ol-3 : 6-dione. Dehydroandrosterone and OsO_4 similarly give *cis*-androstane-3 : 5 : 6-triol-17-one [3 : 6-*diacetate*, m.p. 248·5—249·2° (corr.)]. Δ⁴-Androstene-3 : 6 : 17-trione is reduced (Zn in AcOH) to *androstane*-3 : 6 : 17-*trione*, m.p. 191—192°. R. T.

Photochemical transformation of αβ-unsaturated steroid ketones under the influence of ultraviolet light. A. Butenandt and A. Wolff (Ber., 1939, **72**, [*B*], 1121—1123).—The photochemical change causes alteration in the absorption spectrum and disappearance of 3-CO recognisable by the ordinary reagents; the product is not an αβ-unsaturated ketone. Cholestenone gives a product, $C_{54}H_{88}O_2$, gradual decomp. >360°, $[\alpha]_D^{23}$ +36·2° in $CHCl_3$. *Substances*, $C_{42}H_{60}O_4$, slow decomp. >340°, $[\alpha]_D^{23}$ +107° in $CHCl_3$ [*dioxime*, m.p. 390—400° after gradual decomp. at >280°, formed from CO group at $C_{(20)}$], and $C_{44}H_{64}O_6$, m.p. 350—355° after gradual decomp. >300°, are derived from progesterone and testosterone, respectively. H. W.

Halogenation in the anthraquinone series. F. H. Day (J.C.S., 1939, 816—818).—K anthraquinone-1-sulphonate and Br–HBr–H_2O at 250° for 24 hr. give 1-bromoanthraquinone. The 1 : 5- and 1 : 8-disulphonates give small yields only of (?) dibromoanthraquinones. β-SO_3H groups are not replaced at 260°. Anthraquinone-1-carboxylic acid and aq. $NaClO_3$–HCl, or Br–H_2O, at 200°, afford 1-chloro- or 1-bromo-anthraquinone, respectively. The 2-carboxylic acid does not react. 1-Nitroanthraquinone and conc. HCl at 250—280° give an impure chloroanthraquinone, m.p. 133—135°. 1-Hydroxyanthraquinone-2-sulphonic acid in cold H_2O with excess of Br in KBr (high temp. causes disruption of anthraquinone ring) gives 4-*bromo*-1-*hydroxyanthraquinone*-2-*sulphonic acid* [*K* salt is converted by aq. $Ba(OH)_2$ at 200° into a trace of purpurin, or by 80% H_2SO_4 at 170° into 4-bromo-1-hydroxyanthraquinone]. K_2 anthrarufin-2 : 6-disulphonate and Br in H_2O (cold) give a Br_4-derivative (K_2 salt). Alizarin-3-sulphonic acid and excess of Br give the 4-Br-derivative (*K* salt, +$2H_2O$). Quinizarin-3-sulphonic acid does not react similarly. 1-Aminoanthraquinone-2-sulphonic acid (from 1% aq. solution of Na salt and HBr) and Br–KBr at 100° afford 2 : 4-dibromo-1-aminoanthraquinone, m.p. 214°. 4 : 8-

Diaminoanthrarufin-2 : 6-disulphonic acid and Br–H_2O give a substance possessing dyeing properties. A. T. P.

Structure of aniline-black. III. Structure and mechanism of formation of Willstätter's imines. J. S. Joffe and V. J. Soloveitschik (J. Gen. Chem. Russ., 1939, **9**, 129—143).—In presence of 0·5 mol. of $FeCl_3$ per mol. of *p*-$NH_2{\cdot}C_6H_4{\cdot}NHPh$ (I) the sole product is *pp'p''*-$NHPh{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_4{\cdot}NH_2$ (II) (*Ac* derivative, m.p. 199—200°), whilst with excess of $FeCl_3$ the product is *pp'p''*-$NHPh{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_4{\cdot}N{:}C_6H_4{:}NH$ (III). The reactions are represented: (I) → $NPh{:}C_6H_4{:}NH$ [+(I)] → (II) → (III). (I) and 4 : 1 : 2-$NO_2{\cdot}C_6H_3Cl{\cdot}SO_3H$ (IV) (12 hr. at 160—170°, in presence of $MgCO_3$) yield 4-*nitro*-4'-*anilinodiphenylamine*-2-*sulphonic acid*, reduced (Zn in NaOH) to the corresponding 4-NH_2-compound. This is hydrolysed with 10% HCl to 4-*amino*-4'-*anilinodiphenylamine* (V), m.p. 154°, which condensed with (IV) gives 4-*anilino*-4'-(4''-*nitro*-2''-*sulphoanilino*)*diphenylamine*, hydrolysed and reduced (as above) to (II). $NHPh_2$ with *p*-$NHAc{\cdot}C_6H_4{\cdot}NO$ in 80% H_2SO_4 at −5° yields N-*acetyl*-N'-p-*anilinophenyl*-1 : 4-*benzoquinonedi-imine*, m.p. 178—180°, reduced by $NHPh{\cdot}NH_2$ to the *Ac* derivative, m.p. 168°, of (V). Similarly, $NHPh_2$ and 4-nitroso-4'-acetamidodiphenylamine yield the *Ac* derivative, m.p. 179—180°, of (III), reduced by $NHPh{\cdot}NH_2$ to that of (II). R. T.

Reaction of *p*-phenylenediamine and its derivatives with diazonium salts. III. Transformation of diazonium salts. J. S. Joffe and V. J. Soloveitschik (J. Gen. Chem. Russ., 1939, **9**, 114—118).—The following reactions take place when diazotised amines are added to *pp'p''*-$NHPh{\cdot}[C_6H_4{\cdot}NH]_2{\cdot}C_6H_4{\cdot}NH_2$ (I): (I) + $2RN_2{\cdot}OH$ → $NHPh{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_4{\cdot}N{:}C_6H_4{:}NH$ (II) + R_2 + $2H_2O$ + N_2; (II) + $2RN_2{\cdot}OH$ → $NPh{:}C_6H_4{:}N{\cdot}C_6H_4{\cdot}N{:}C_6H_4{:}NH$ (III) + R_2 + $2H_2O$ + N_2; (III) + $RN_2{\cdot}OH$ → $NPh{:}C_6H_4{:}N{\cdot}C_6H_4{\cdot}N{:}C_6H_4{:}NR$ + H_2O + N_2 (R = *o*-$CO_2H{\cdot}C_6H_4{\cdot}$, *p*-$NO_2{\cdot}C_6H_4{\cdot}$, 2 : 5-$C_6H_3Cl_2$). R. T.

Use of *dl*-menthol for the preparation of biosynthetic glucuronic acid. R. T. Williams (Nature, 1939, **143**, 641; cf. A., 1938, III, 1041).—*dl*-Menthol conjugates with glucuronic acid to the extent of 60% in the rabbit, and affords the best method of obtaining relatively large amounts of this acid, which can then be readily isolated as the NH_4 salt. This contains ~60% of *d*- and 40% of *l*-acid, and can be resolved by fractional crystallisation from H_2O. d-*Menthyl*-β-d-*glucuronide*, m.p. 110—112°, $[\alpha]_D$ +5° in alcohol, is thus obtained. L. S. T.

Ethinylborneol.—See B., 1939. 578.

Sesquiterpenes. XLIII. Constitution of the caryophyllene mixture. Degradation of dihydrocaryophyllene. L. Ruzicka, K. Huber, P. A. Plattner, S. S. Deshapande, and S. Studer (Helv. Chim. Acta, 1939, **22**, 716—727).—Technical caryophyllene (I), b.p. 118—121°/10 mm., α_D −7·4° to −8·8° (l = 1), is hydrogenated (Raney Ni in MeOH) to *dihydrocaryophyllene*, b.p. 122—123°/12 mm., α_D −14° (l = 1), which is converted by successive treatments with O_3 in AcOH and warm H_2O into a non-cryst. *Me ketocarboxylate*, $C_{16}H_{28}O_3$, b.p. 117—120°/~1 mm., α_D +47° (l = 1), and non-investigated neutral products. The corresponding acid is transformed by NaOH and Br into $CHBr_3$ and a non-cryst. dicarboxylic acid, $C_{14}H_{24}O_4$, converted by CH_2N_2 into the Me_2 ester, b.p. 106—108°/~1 mm., α_D +39° (l = 1) (corresponding *dianilide*, m.p. 188°). The Th salt of the acid passes at ~370° into a mixture of ketones, $C_{13}H_{22}O$, (*A*) b.p. 62—63°/~1 mm., α_D +44° (l = 1) (*semicarbazone*, m.p. 188—190°), which gives a pale yellow colour with $C(NO_2)_4$ and very slowly absorbs O from *o*-$CO_2H{\cdot}C_6H_4{\cdot}CO_3H$ in Et_2O at 0°, and (*B*), b.p. 62—65°/~ 1 mm., α_D −42° (l = 1) (*semicarbazone*, m.p. 145°), which gives a pale yellow colour with $C(NO_2)_4$ and appears to contain αβ-unsaturated components. *A* is transformed by HCO_2Et and NaOMe in Et_2O into the non-cryst. $OH{\cdot}CH_2$ derivative, ozonised to the acid, $C_{13}H_{22}O_4$, (Me_2 ester, b.p. ~155°/10 mm.), the Th salt of which passes into the ketone, $C_{12}H_{20}O$, isolated as the *semicarbazone*, m.p. 153·5—156·5°, which is hydrogenated to the *compound*, $C_{13}H_{25}ON_3$, m.p. 113—114°. The yields in the series are not good but the sequence establishes the great probability that at least one component of (I) has a 7-membered ring (Rydon, A., 1938, II, 107). Homocaryophyllenic acid is cyclised through the Th salt to a ketone, the semicarbazone, m.p. 184—185°, of which is hydrogenated (PtO_2 in AcOH at room temp.) to the *semicarbazido*-compound, $C_{10}H_{19}ON_3$, m.p. 172—174°. SeO_2 oxidises (I) in Ac_2O to a mixture of dihydrocaryophyllenols, b.p. 155—158°, which could not be caused to react with *o*-$C_6H_4(CO)_2O$ in C_5H_5N; it is oxidised by CrO_3 in AcOH mainly to neutral products from which a *semicarbazone*, $C_{16}H_{27}ON_3$, m.p. 243°, $[\alpha]_D$ +68·8°, is isolated. The absorption spectrum corresponds with that of an αβ-unsaturated aldehyde or ketone. H. W.

Terpenechromogenic or terpenochromic compounds. II. Spectroscopic examination of the pigments formed in the *EM* reaction with essential oils. A. Müller (J. pr. Chem., 1939, [ii], **153**, 77—90).—Examination of the common absorption bands of the terpenochromes formed from a large no. of essential oils (apart from those which show continuous absorption in the region 400—490 mμ.) permits the discrimination of two main types of terpenechromogenic components with the approx. structure of bisabolene and the azulenogen type. The former, which are rather widely distributed in essential oils, form with the *EM* reagent pigments which absorb mainly in the region 480—530 mμ. The latter show more bands in the region 530—700 mμ. which are closely similar to the visible absorption bands of the true azulenes. H. W.

Marrubiin, a diterpenoid lactone. (Miss) F. Hollis, J. H. Richards, and A. Robertson (Nature, 1939, **143**, 604; cf. A., 1908, i, 344).—Marrubiin (I), m.p. 158°, $C_{20}H_{28}O_4$, gives on hydrolysis a monobasic *acid* (II), $C_{20}H_{30}O_5$, m.p. 197° (*Me*, m.p. 85°, and *Et* ester, m.p. 88°). Hydrogenation of (I) and (II) gives the corresponding H_4-derivatives, m.p. 132°

and 187° (*Et* ester, m.p. 95°), respectively. (I) contains 1 OH, which is probably a *tert.*-OH; the fourth O is present in an oxide system. (I) is readily resinified by warm mineral acids and by hot HCO_2H, and is oxidised ($KMnO_4$) to a neutral compound, m.p. 211°, and a lactone, m.p. 161° (acid, m.p. 208°), which, with a liquid acid, is also formed by the action of O_3. Dehydrogenation (Se) yields 1 : 2 : 5-$C_{10}H_5Me_3$ (agathaline). (I) is a hydroxyditerpene lactone of the manoyl oxide type. L. S. T.

Lupeol. IV. F. Biedebach (Arch. Pharm., 1939, **277**, 163—173; cf. A., 1938, II, 288).—Oxidation (CrO_3) of lupeol acetate yields a keto-acetate (I), $C_{31}H_{50}O_3$, m.p. 265° (Heilbron *et al.*, A., 1938, II, 195, give $C_{32}H_{52}O_3$), a neutral *substance*, $C_{32}H_{52}O_3$, m.p. 259°, and a mixture of acids, the Na salts of which on methylation and further oxidation yield Me ketolupanecarboxylates, (II), m.p. 263°, and (III), m.p. 201° [2 : 4-*dinitrophenylhydrazone*, m.p. 157° (sintering at 135°)], hydrolysed to the *acids*, m.p. 266° and 281° respectively. Hydrolysis of (I) yields the keto-alcohol, $C_{29}H_{48}O_2$, oxidised (CrO_3) to a *diketone* (IV), $C_{29}H_{46}O_2$, m.p. 208°. Oxidation (CrO_3) of lupeol gives the above keto-acids, and (IV). Reduction (Clemmensen) followed by methylation of (II) and (III) affords the *Me lupanecarboxylates*, m.p. 225—228° and 194—197° respectively. Lupeol with K in C_5H_{11}·OH–PhMe, followed by CS_2 and then MeI, yields *Me lupeylxanthogenate*, m.p. 207°. Thermal decomp. of this or of lupeol benzoate yields the same lupeylene. *Lupeol acetate dibromide*, m.p. 225° (from lupeol acetate and Br in $CHCl_3$–AcOH), with $AgNO_3$ in C_5H_5N gives *bromolupeol acetate*, m.p. 205° (sintering at 197°). Bromolupeol is unaffected by boiling EtOH–KOH. A. Li.

Triterpenes. XLVI. Keto-derivatives and oxides of the α- and β-amyrin series. L. Ruzicka, G. Müller, and H. Schellenberg (Helv. Chim. Acta, 1939, **22**, 758—766).—Oxidation of β-amyrin acetate (I) by CrO_3 in AcOH affords *keto-β-amyrin acetate*, m.p. 264—265°, whilst β-amyrin benzoate similarly affords *keto-β-amyrin benzoate*, m.p. 262—263°, $[\alpha]_D$ +154·5° in $CHCl_3$, either of which is hydrolysed by alkali to *keto-β-amyrin*, m.p. 230—231°, $[\alpha]_D$ +102° in $CHCl_3$, converted by the more protracted action of alkali into a *compound*, $C_{30}H_{48}O_2$, m.p. 247—248°, $[\alpha]_D$ +81·5° in $CHCl_3$. The difference between these observations and those of Beynon *et al.* (A., 1938, II, 416) is unexplained. The compound obtained from (I) and H_2O_2, m.p. 292—293°, has in $CHCl_3$ an absorption max. at 2900 A. and the "β-amyrin oxide" obtained therefrom by alkaline hydrolysis has m.p. 207—208°, absorption max. 2800 A.; it is therefore ketodihydro-β-amyrin, identical with the compound derived from β-amyrin and BzO_2H. The absorption curves of β-amyrilene dioxide and β-hydroamyrilene oxide have max. at ~2800—2900 A. The spectra of α-amyrilene oxide, m.p. 173° and 133°, and of α-cholestene oxide are recorded. The results show that in the amyrin series oxido-groups are stable only in ring *A* whereas in ring *C* they pass into CO groups. Improved directions for the oxidation of α-amyrin to α-amyrone (II), m.p. 125—126°, are given; the semicarbazone, m.p. 204—205°, is best obtained by triturating NH_2·CO·NH·NH_2,HCl with cryst. NaOAc and MeOH, filtering, and adding the filtrate to (II) in Et_2O–MeOH at room temp. This is converted by NaOEt in EtOH at 180° into α-amyrene, m.p. 124°, $[\alpha]_D$ +95° in $CHCl_3$. All m.p. are corr. H. W.

Triterpenes. XLVII. Introduction of new double linkings in the α- and β-series. L. Ruzicka, G. Müller, and H. Schellenberg (Helv. Chim. Acta, 1939, **22**, 767—777).—Protracted heating of keto-β-amyrin with a large excess of MgMeI gives a jelly, which is acetylated to *methyldehydro-β-amyrin acetate*, $C_{33}H_{52}O_2$, m.p. 225—226°, $[\alpha]_D$ +133° in $CHCl_3$, which shows an absorption band at 2400 A. characteristic of a conjugated double linking. Under similar conditions keto-α-amyrin yields *methyldehydro-α-amyrin*, m.p. 148—152°, which gives an *acetate*, m.p. 228—230°, $[\alpha]_D$ +144° in $CHCl_3$, obtained also from keto-α-amyrin acetate and MgMeI. β-Amyrin acetate (I) is readily oxidised by SeO_2 in boiling AcOH to a *dehydro-β-amyrin acetate*, m.p. 228—229°, $[\alpha]_D$ −62° in $CHCl_3$, hydrolysed by alkali to *dehydro-β-amyrin*, m.p. 228—229°, $[\alpha]_D^{19}$ −72° in $CHCl_3$, which could not be hydrogenated (PtO_2 in dioxan) and does not add maleic anhydride; it appears to have a conjugated double linking. It is also obtained by hydrolysis of *dehydro-β-amyrin benzoate*, m.p. 249—250°, $[\alpha]_D$ −34° in $CHCl_3$. β-Amyrene under similar conditions affords *dehydro-β-amyrene*, m.p. 218—219°, $[\alpha]_D^{19}$ −73° in $CHCl_3$. The corresponding α-acetate and -benzoate are unchanged by protracted boiling with SeO_2. β-Amyrin benzoate and S at 230—240° give (after hydrolysis) a *compound*, $C_{30}H_{44}OS$, m.p. 201°, whilst (I) yields a *substance*, $C_{32}H_{46}O_2S$, m.p. 199—200°; the crude oxidation product when cryst. repeatedly from MeOH–H_2O give small amounts of an unidentified material, m.p. 251°, and a *ketone*, $C_{30}H_{44}O_3$, m.p. 281—282° (*acetate*, m.p. 231—232°, oxidised to an *acetyl-lactone*, $C_{32}H_{44}O_5$, m.p. 278—279°). Keto-α-amyrin is converted by Na and amyl alcohol into a *substance*, $C_{35}H_{60(62)}O_3$, m.p. 225—226°, $[\alpha]_D$ −50·5° in $CHCl_3$, which gives only a faint colour with $C(NO_2)_4$. Under these conditions α-amyrin is unchanged. All m.p. are corr. H. W.

Triterpenes. XLVIII. Products of the oxidation of lupeol and esters of lupeol with monoperphthalic acid and with selenium dioxide. L. Ruzicka and G. Rosenkranz (Helv. Chim. Acta, 1939, **22**, 778—788).—In agreement with Heilbron *et al.* (A., 1938, II, 195) and contrary to Dieterle *et al.* (*ibid.*, 288), lupeol absorbs only one mol. of O_2 from *o*-CO_2H·C_6H_4·CO_3H in 24 or 120 hr. giving *lupeol oxide* (I), m.p. 192—197°, $[\alpha]_D$ +8·83° in $CHCl_3$, whilst dihydrolupeol is unaffected. *Lupeol acetate oxide* (II), m.p. 226—230° after softening at 218—222°, $[\alpha]_D$ +24° in $CHCl_3$, obtained by oxidation of the acetate, is hydrolysed by alkali to a mixture of approx. equal parts of (I) and the aldehyde, *lupanalol* (III), $C_{30}H_{50}O_2$, m.p. 173—175°, $[\alpha]_D$ +8·9° in $CHCl_3$, and is converted almost quantitatively by acid into (III) (*oxime*, m.p. 221—222°; *acetate*, m.p. 223—226°, $[\alpha]_D$ +14·4° in $CHCl_3$). Oxidation of (III) by CrO_3 gives *acetylisolupanolic acid*, m.p. 290—291° (vac.), $[\alpha]_D$ +24·3° in $CHCl_3$ [*Me* ester, m.p. 280—281° (vac.),

$[\alpha]_D$ +0·4° in $CHCl_3$, hydrolysed by protracted boiling with 2N-KOH–EtOH to the OH-acid, m.p. 290—291°, $[\alpha]_D$ +8·44° in $CHCl_3$], and a neutral *substance*, $C_{31}H_{50}O_3$ or $C_{32}H_{52}O_3$, m.p. 267—268°, $[\alpha]_D$ +0·80° in $CHCl_3$. Lupeol acetate (IV) is oxidised by SeO_2 in boiling Ac_2O to *lupenediol diacetate*, m.p. 178—179°, which gives a pale yellow colour with $C(NO_2)_4$ and is hydrolysed to *lupenediol*, m.p. 227·5—228·5°. Lupeol benzoate is transformed by SeO_2 in boiling C_6H_6 into *ketolupeol benzoate*, $C_{37}H_{52}O_3$, m.p. 268·5°, which does not contain an active H, does not give a yellow colour with $C(NO_2)_4$, but gives an *oxime*, m.p. 235—237°. It is hydrolysed to *ketolupeol*, m.p. 232—233°. Under similar conditions, (IV) gives a substance, $C_{32}H_{48(50)}O_3$, m.p. 224—226°. H. W.

Triterpenes. XLIX. Oxidation of methyl acetyloleanolate and methyl acetylsumaresinonate with selenium dioxide. L. Ruzicka, A. Grob, and F. C. van der Sluys-Veer (Helv. Chim. Acta, 1939, **22**, 788—792).—Oxidation of Me acetyloleanolate with SeO_2 in boiling AcOH gives a strongly unsaturated *substance*, (?) $C_{33}H_{46}O_6$, m.p. 245—246°, $[\alpha]_D$ +146° in $CHCl_3$, and *Me acetyldehydro-oleanolate*, $C_{33}H_{50}O_4$, m.p. 227—228°, $[\alpha]_D$ +137° in $CHCl_3$, which contains two conjugated double linkings, probably in the same ring. Alkaline hydrolysis converts it into *Me dehydro-oleanolate*, m.p. 168—169°. Similarly, Me acetylsumaresinonate is oxidised to *Me dehydroacetylsumaresinonate*, m.p. 302—303°, $[\alpha]_D$ −151·6° in $CHCl_3$, the absorption spectrum of which indicates the presence of CO and two conjugated double linkings. H. W.

Triterpene group. V. Oxidation products of the β-amyrin derivative, $C_{30}H_{44}OS$. J. C. E. Simpson (J.C.S., 1939, 755—759).—Oxidation (CrO_3–AcOH) of the OH-ketone (I), $C_{30}H_{44}O_3$, obtained from the keto-acetate oxidation product (improved prep.) of the compound, $C_{30}H_{44}OS$ (improved prep., cf. Jacobs *et al.*, A., 1930, 1292), gives a *diketone*, $C_{30}H_{42}O_3$, m.p. 289—290°, $[\alpha]_D^{18}$ −94° [*monosemicarbazone*, m.p. 287—289° (decomp.)], which with HNO_3 affords a NO_2-compound, $C_{30}H_{42}O_7N_2$, m.p. 219—220° (decomp.), $[\alpha]_D^{18}$ −87°, also obtained from (I) and HNO_3. The hydroxy-keto-lactone (II), $C_{30}H_{42}O_4$ (oxidation product of $C_{30}H_{44}OS$), is oxidised (CrO_3–AcOH) to a *diketo-lactone*, $C_{30}H_{40}O_4$, m.p. 250·5—252°, $[\alpha]_D^{18}$ +66° (*monoxime*, m.p. 307—310°), which with HNO_3 yields a NO_2-compound, $C_{30}H_{42}O_7N_2$, m.p. 223·5—224·5° (decomp.), $[\alpha]_D^{18}$ +49°, also derived from (II) and HNO_3. The structural relationship between the NO_2-compounds is the same as between (I) and (II). Oxidation of (II) with CrO_3–H_2SO_4 gives (small yield) a *lactone*, $C_{28}H_{38}O_4$, m.p. 259—260°, $[\alpha]_D^{14}$ −271°, and an acid, isolated as the *Me*$_2$ ester, $C_{32}H_{44}O_7$, m.p. 216·5—217·5°, $[\alpha]_D^{18}$ −31·7°; the lactone is hydrolysed (KOH) to an acid, isolated as the *Me* ester, $C_{29}H_{42}O_5$, m.p. 210—211°. The acetate of (I) is oxidised (CrO_3–H_2SO_4) to an *acetate*, $C_{32}H_{44}O_6$, m.p. 342—344° (decomp.), $[\alpha]_D^{15}$ +63°, hydrolysed (KOH) to an *alcohol*, $C_{30}H_{42}O_5$, m.p. 337—339°, $[\alpha]_D^{13}$ +26·7°. These data are difficult to explain on the structure for β-amyrin suggested by Ruzicka *et al.* (A., 1937, II, 202). (All rotations measured in $CHCl_3$.) F. R. S.

Hydrocarbon $C_{20}H_{28}$.—See B., 1939, 582.

Volatile plant substances. X. Vetivones, the odoriferous constituents of oil of vetiver. A. S. Pfau and P. A. Plattner (Helv. Chim. Acta, 1939, **22**, 640—654; cf. A., 1939, II, 148).—The attempted isolation of the ketones from the oil by means of $SO_3H{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2$ gives a large proportion of resins. Girard's reagent *P* can be applied directly to the oil but the regeneration of the ketones is difficult. With $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$ an enriched fraction of the oil gives β-*vetivonesemicarbazone* (I), m.p. 228—229°, $[\alpha]_D^{20}$ −71° in AcOH, and α-*vetivonesemicarbazone*, m.p. 210—212° (decomp.), $[\alpha]_D^{20}$ +316° in AcOH. These are hydrolysed by *o*-$C_6H_4(CO_2H)_2$ to β- (II), b.p. 153—154°/4 mm., m.p. 44—44·5°, $[\alpha]_D^{20}$ −24·1° in EtOH, and α-, b.p. 152—153°/4 mm., $[\alpha]_D^{20}$ +225° in EtOH, *-vetivone*. (II) does not appear to combine with $NaHSO_3$. (I) is transformed by conc. aq. KOH containing $CuSO_4$ into the *hydrocarbon*, $C_{15}H_{24}$, b.p. 110—112°/2·5 mm., which does not give a cryst. hydrochloride. $Al(OPr^B)_3$ in Pr^BOH at room temp. transforms (II) into a *hydrocarbon*, $C_{15}H_{22}$, b.p. 110°/3·6 mm., and β-*vetivol*, b.p. 129—132°/0·5 mm. (II) is reduced by Na and EtOH or catalytically (Ni–95% EtOH at 70°) to β-*dihydrovetivol* (III), b.p. 144°/2·4 mm., m.p. 107° (3 : 5-*dinitrobenzoate*, dimorphous, m.p. 121° or 129·5—130°). β-Dihydrovetivone, obtained during the partial hydrogenation of (II), is characterised by a *dibenzylidene* derivative, m.p. 130·5—131·5°. Hydrogenation (PtO_2 in AcOH) of (II) or (III) leads to β-*tetrahydrovetivol*, m.p. 76—76·5°, oxidised to β-*tetrahydovetivone*, b.p. 139°/3 mm., m.p. 37·5—38° (*dibenzylidene* derivative, m.p. 101·5—102°). The mixture of dextrorotatory semicarbazones obtained during the isolation of (I) gives *iso*vetivones, reduced (Na–EtOH) to dihydro*iso*vetivols, b.p. 153°/4 mm. H. W.

Action of nitric acid on wood. Chemistry of lignin. R. S. Hilpert, W. Krüger, and G. Hechler (Ber., 1939, **72**, [*B*], 1075—1082).—The action of HNO_3 (*d* 1·51) on red beech or pine wood resembles that on cotton wool or sulphite cellulose but the nitrated wood is only partly sol. in 72% H_2SO_4, in which the nitrated cellulose (I) dissolves completely, and is almost completely denitrated by $(NH_4)_2S$, which reduces the N content of (I) to ~2% only. The solution obtained by nitrating wood when diluted with H_2O gives a yellow ppt. (II) which according to analysis is not aromatic and may consist of 5 ($C_6H_{10}O_5 - H_2O$) units into which 7 NO_2 residues have entered. The bulk of the N is present as NO_3. The ppt. gives NH_3 when warmed with alkalis and HCN when treated with acids. Methylated beech-wood is almost completely sol. in HNO_3 and is very largely pptd. from the solution by H_2O; the N content is ≪ that of the product from wood. Evaporation to dryness of the filtrate from (II) leaves a dark yellow powder (III) in which ~ half the N is present as NO_3 and the other half in another form, chiefly as NH_3 and HCN. Sucrose, when treated successively with HCl and HNO_3, gives a solution which, when evaporated to dryness, leaves a residue similar to (III). Pine lignin (15% OMe) behaves towards conc. HNO_3 very similarly to methylated

sucrose lignin, supporting the authors' view that the lignins are products of the action of conc. acids on cellulose. The reaction between wood and dil. HNO_3 can be regarded fundamentally as a hydrolysis followed by further change of the products by acid. In explanation of the formation of HCN it is shown that aromatic compounds react rapidly with dil. HNO_3 only if free OH is present. With *o*-OH·C_6H_4·CO_2H, PhOH, and vanillin the change occurs rapidly at 100° with immediate formation of HCN, whereas piperonal and methylated vanillin react much more slowly. Furfuraldehyde is first resinified and then nitrated with evolution of HCN. Further arguments are adduced against the aromatic character of lignin. H. W.

Lignin. K. Freudenberg (Angew. Chem., 1939, 52, 362—363).—Of every 100 phenylpropane groups (I) in pine lignin, ~70 belong to the guaiacyl, 25 to the piperonyl, and 5 to the syringyl type. At most 18% of the side-chains are of the type OH·CHAc and ·CO·CHMe·OH. Only a small proportion, if any, of (I) are present in unimol. form, probably as glucosides. Most are combined among themselves. Most of the reactions of lignin are best interpreted on the assumption that the side-chain is ·CH(OH)·CH(OH)·CH_2·OH, ·CHAc·OH, or ·CH(OH)·CH_2·CHO. In wood and in isolated lignin the *p*-OH groups are substituted but do not participate in glucoside formation. Pine lignin appears to contain ether linkings and all its characteristic reactions can be regarded from the single viewpoint of ether scissions. The most important observations bearing on its constitution are the isolation of veratric and *iso*hemipinic acid after methylation and oxidation, the prep. from it of vanillin by oxidation in such a manner that the scaffold is degraded while the product remains intact, and the identification of the substance 4 : 3 : 1-OHC_6H_3(OMe)·CO·CHMe·OH as product of the action of HCl–EtOH on pine wood. Since beech lignin gives notably more AcOH than pine lignin when oxidised with CrO_3 it contains more terminal Me groups. The greater instability of deciduous tree lignin (II) towards degrading agents such as HCl–EtOH is due to the syringyl component which is capable of ether formation but not of further condensation. It is therefore obvious that simpler degradation products in better yield are obtained from (II) than from pine lignin. H. W.

Lignin and methylated hydrocarbons extracted from fir-wood by dioxan. III. I. M. Orlova and N. I. Nikitin (J. Appl. Chem. Russ., 1939, **12**, 76—84).—The H_2O-insol. fraction of the lignin extracted by dioxan from the wood (at 90°) is treated according to Freudenberg (A., 1936, 995), to yield 9·4—12·2% of veratric acid. The ultra-violet absorption spectrum of the fraction in question closely resembles that of ordinary lignin and of *iso*eugenol. The H_2O-sol. fraction contains OH- 22—25 and OMe-groups 7%, and appears to consist of low mol. wt. polysaccharides, containing methylated sugars. R. T.

Study of larch lignin by the method of alkaline fusion. T. I. Rudneva and N. I. Nikitin (J. Appl. Chem. Russ., 1939, **12**, 72—75).—Treatment of larch lignin by the method of Freudenberg *et al.* (A., 1936, 995) gives 11·3% of veratric acid. Veratroylformic acid was also detected. The lignin thus contains pyrocatechol groups. R. T.

Shellac. XII. Degradations of shellolic acid. W. Nagel and W. Mertens (Ber., 1939, 72, [*B*], 985—992; cf. A., 1938, II, 24).—Treatment of shellolic acid (I) with CPh_3Cl gives only non-cryst. products. The action of Br on (I) (*loc. cit.*) is now regarded as simple substitution and lactonisation with production of the Br-lactonic acid, $C_{15}H_{17}O_5Br$ (II), which is converted by aq. K_2CO_3 at 100° into the *dicarboxylic acid*, $C_{15}H_{18}O_6$. The free OH in (II) is so resistant that the action of PBr_5 gives a bromide, which is transformed into the *amide*, $C_{15}H_{19}O_5N$, m.p. 256°, in which it is still intact (Zerevitinov). CH_2N_2 transforms (I) into a mixture of the *Me*$_1$ ester, m.p. 169—170°, and the *Me*$_2$ ester, m.p. 180° (formed by opening of the lactone ring). Attempts to obtain either exclusively were fruitless so that the production of an equilibrium is assumed. The mixture could not be caused to react with AcCl or $PhSO_2Cl$ + C_5H_5N. Zn dust and boiling dil. HCl transform (I) into *deoxyshellolic acid*, $C_{15}H_{18}O_5$ (*Me*$_2$ ester, m.p. 68°). Me_2 shellolate and MgPhBr in C_6H_6–Et_2O at 60° yield apparently a *Ph*$_4$ derivative, $C_{39}H_{40}O_4$, m.p. indef., which is stable towards $KMnO_4$ and contains only 2 OH, indicating that an ether ring has probably been formed. Oxidation of (I) with $KMnO_4$ in alkaline solution gives the *dilactone*, $C_{15}H_{18}O_6,H_2O$, m.p. 162° after loss of H_2O at 124° (*Ac* derivative, m.p. 246°); this is oxidised by $KMnO_4$ (≡4 O) in neutral solution to the monocarboxylic *acid*, $C_{14}H_{16}O_6$, m.p. 248°, which contains 2 OH (Zerevitinov) and gives a *Me* ester, m.p. 154°. In faintly acid solution (I) is oxidised by $KMnO_4$ at 20° to the *acid*, $C_{13}H_{16}O_6,2H_2O$, m.p. 153—155° after loss of H_2O at 80—90° (*Me* ester, m.p. 79—80°). H. W.

Sapogenins. III. Dehydrogenation products of methylsarsasapogenin and methylcholestanol. IV. Sapogenin of *Balanites œgyptica*, Wall. G. A. R. Kon and W. T. Weller (J.C.S., 1939, 794—800, 800—801).—III. *o-Bromobenzylmalonic acid*, m.p. 149° (decomp.), prepared from *o*-C_6H_4Br·CH_2Cl and $CHNa(CO_2Et)_2$, is decarboxylated to β-*o*-bromophenylpropionic acid, which through the chloride gives ($AlCl_3$) 4-bromohydrindone, reduced (Zn–HCl) to the hydrindene; the Grignard reagent from this compound does not react with $(CH_2)_2O$. Bromination of 7 : 1-$C_{10}H_6Me$·OMe gives 1-*bromo*-4-*methoxy*-6-*methylnaphthalene*, m.p. 72° [Br_2-compound (1 : 5 ?), m.p. 72°], which through the Grignard compound and $(CH_2)_2O$ affords β-4-*methoxy*-6-*methyl*-1-*naphthylethyl alcohol*, m.p. 73°; the bromide of the alcohol does not condense satisfactorily with 2 : 5-dimethyl*cyclo*pentanone. *cyclo*Hexenylacetyl chloride and 1-$C_{10}H_7$·MgBr yield Δ^1-cyclo*hexenyl*-1-*acetonaphthone*, reduced and cyclised (P_2O_5) to 1 : 2 : 3 : 4 : 11 : 12 : 13 : 14-octahydrochrysene [*s*-$C_6H_3(NO_2)_3$ *complex*, m.p. 147—148°]. 2-Methyl*cyclo*pentanone, CH_2Br·CO_2Me, and Mg give a OH-ester, dehydrated and hydrolysed to 2-*methyl*-$\Delta^{1(9)}$-cyclo*pentenylacetic acid*, m.p. 50°, the chloride of which can not be condensed with 1-bromo-4-methoxy-6-methylnaphthalene. 2-Methyl-6-aceto-

naphthone and furfuraldehyde yield *furfurylidene-2-methyl-6-acetonaphthone*, m.p. 121°, hydrolysed to *δη-diketo-η-(6-methyl-2-naphthyl)heptoic acid*, m.p. 181°, which with KOH affords 3-(6′-*methyl*-2′-*naphthyl*)-Δ^2-cyclo*penten*-1-*one*-2-*acetic acid*, m.p. 188°. This and Ac_2O give 3′-*keto*-4-*acetoxy*-7-*methyl*-1 : 2-cyclo*pentenophenanthrene* (I), m.p. 224° (decomp.) [*hydroxy-ketone*, m.p. 290° (decomp.)], which is hydrogenated under drastic conditions and then dehydrogenated (Pd–C) to 7-*methyl*-1 : 2-cyclo*pentenophenanthrene*, m.p. 132° [*styphnate*, m.p. 182—183°; *s*-$C_6H_3(NO_2)_3$ *complex*, m.p. 183—183·5°], identical with one of the dehydrogenation products of methylsarsasapogenin and of methylcholestanol (II). Hydrolysis and methylation (Me_2SO_4) of (I) gives 3′-*keto*-4-*methoxy*-7-*methyl*-1 : 2-cyclo*pentenophenanthrene*, m.p. 190—191°, which with MgMeI affords 4-*methoxy*-3′ : 7-*dimethyl*-1 : 2-cyclo*pentadienophenanthrene*, m.p. 130—131°. This is hydrogenated at room temp. to 4-*methoxy*-3′ : 7-*dimethyl*-, m.p. 83—84° [*s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 184—185°], and under drastic conditions to 3′ : 7-*dimethyl*-1 : 2-cyclo*pentenophenanthrene*, m.p. 139—140° [*picrate*, m.p. 128°; *styphnate*, m.p. 161°; *s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 154—155°], identical with one of the dehydrogenation compounds from (II). Dehydrogenation of 3-methylcholestene affords the two hydrocarbons and a third *hydrocarbon*, $C_{26}H_{26}$, m.p. 207—208° (*derivative* with 2 : 7-dinitroanthraquinone, m.p. 235°), which is a homologue of Diels' hydrocarbon (absorption spectrum). These results confirm the position previously assigned to the OH of sarsapogenin (cf. Farmer *et al.*, A., 1937, II, 203); they also show that in the dehydrogenation of sterol-like compounds the migration of the angular Me from $C_{(13)}$ to $C_{(17)}$ is not invariably the rule and that complete elimination of this group can sometimes occur.

IV. A sapogenin, *nitogenin*, $C_{27}H_{44}O_3$, m.p. 201°, $[\alpha]_D$ −112° in $CHCl_3$ (*Ac*, m.p. 191—192°, and *Bz* derivatives, m.p. 229°), has been isolated from the saponin occurring in the seed kernels. It is very closely related to tigogenin. F. R. S.

Saponins and sapogenins. IX. Oxidation of echinocystic acid and derivatives. W. R. White and C. R. Noller (J. Amer. Chem. Soc., 1939, **61**, 983—989; cf. A., 1938, II, 448).—Echinocystic acid (I) is shown to contain OH·C·C·CO_2H and a second OH not far removed. Its Me ester (II) is converted by $Na_2Cr_2O_7$–H_2SO_4–AcOH–H_2O at room temp. into an unsaturated [$C(NO_2)_4$] *diketo-ester* (III), $C_{28}H_{43}O_2{\cdot}CO_2Me$, dimorphic *forms*, m.p. 166—168° and 192—194°, $[\alpha]_D^{23}$ +1·6°, $[\alpha]_{5461}^{23}$ −1·6° in dioxan, distils unchanged at 2·5 mm. [*oxime*, sinters at 254°, m.p. 257·5—259·5° or 260—263°, $[\alpha]_D^{21}$ −50·0°, $[\alpha]_{5461}^{22}$ −61·8° in dioxan; *phenylhydrazone*, m.p. 179·5° (decomp.), $[\alpha]_D^{20}$ −60·4°, $[\alpha]_{5461}^{20}$ −97·7° in dioxan], which resists hydrogenation (Pt), does not condense with *o*-$C_6H_4(NH_2)_2$ or PhCHO, contains no active CH_2 or enolic OH, but shows 1 active H. No rearrangement has occurred, as (II) is converted by H_2SO_4–AcOH–H_2O merely into a *monoacetate* (IV), dimorphic, m.p. 205—208° and 170—171° (unstable), $[\alpha]_D^{22}$ +27°, $[\alpha]_{5461}^{22}$ +32·8° in dioxan, which is also obtained by hot AcOH–NaOAc. Hot KOH–EtOH hydrolyses (III) and decomposes the resulting β-CO-acid, yielding *norechinocystenedione* (V), m.p. 210—212°, $[\alpha]_D^{24}$ −92·7°, $[\alpha]_{5461}^{24}$ −115·3° in dioxan. Zn–Hg in HCl–EtOH reduces (III) to a *monoketo-ester*, $C_{31}H_{48}O_3$, m.p. 209—212°, $[\alpha]_D^{22}$ −10·3°, $[\alpha]_{5461}^{23}$ −15·0° in dioxan (no oxime or Ac derivative), from which KOH–EtOH gives *norechinocystenone*, $C_{29}H_{46}O$, m.p. 230—233°, by hydrolysis and loss of CO_2. CrO_3 in AcOH at room temp. oxidises (IV) to an *acetoxy-keto-ester*, $C_{33}H_{50}O_5$, dimorphic, m.p. 231—234° or 203—205°, $[\alpha]_D^{21}$ −9·8°, $[\alpha]_{5461}^{21}$ −17·7° in dioxan, hydrolysed by KOH–EtOH to *norechinocystenolone* (VI), $C_{29}H_{46}O_2$, dimorphic, m.p. 230—233° and 268—271°, $[\alpha]_D^{21}$ −86·7°, $[\alpha]_{5461}^{21}$ −106·0° in dioxan, which is oxidised by CrO_3–AcOH to (V). $Na_2Cr_2O_7$-oxidation of (I) involves a rearrangement, for it yields iso-*norechinocystenedione* [not (V)], m.p. 230—233°, $[\alpha]_D^{22}$ +85·6°, $[\alpha]_{5461}^{22}$ +103·2° in dioxan, the Ac_1 derivative [for prep. cf. (IV)], m.p. 204—207°, $[\alpha]_D^{24}$ −55·9°, $[\alpha]_{5461}^{24}$ −65·1° in dioxan, of which is converted by H_2SO_4–MeOH into (VI). Diacetylechinocystic acid and Br in MeOH–CCl_4 give a *Br-lactone*, $C_{34}H_{51}O_6Br$, m.p. 184—190°, $[\alpha]_D^{22}$ +8·5°, $[\alpha]_{5461}^{22}$ +12·1° in dioxan. Me diacetylechinocystate with H_2O_2–AcOH–H_2O at 70—80° gives a *substance*, $C_{35}H_{54}O_7$, m.p. 215—217·5°, $[\alpha]_D^{22}$ −74·2°, $[\alpha]_{5461}^{22}$ −87·6° in dioxan (no acetate or oxime). Regularities in [α] are noted, but not explained. R. S. C.

Vanguerin. New saponin from *Vangueria tomentosa*. K. W. Merz and H. Tschubel (Ber., 1939, **72**, [*B*], 1017—1028).—Extraction of the root bark of *V. tomentosa* with boiling H_2O removes mannitol and a large proportion of brown extractives and the residue slowly yields *vanguerin* (I), $C_{41}H_{64}O_{11}$, m.p. 275—280° (decomp.) after softening at 255—260°, $[\alpha]_D^{22}$ −10·1° in dioxan, to boiling EtOH. (I) is sol. in alkali hydroxide and is pptd. from this solution by CO_2. It gives characteristic colour reactions with Ac_2O–80% H_2SO_4 and with α-$C_{10}H_7{\cdot}OH$ and reduces Fehling's solution after being boiled with dil. HCl. It is converted by Ac_2O–NaOAc or by Ac_2O in hot or cold C_5H_5N into non-cryst. *vanguerin penta-acetate*, decomp. 184°; cryst. derivatives are not obtained from (I) and BzCl, *p*- or *m*-$NO_2{\cdot}C_6H_4{\cdot}COCl$. (I) is hydrolysed by 4·5% HCl to *vanguerigenin* (II), $C_{30}H_{46}O_3$, m.p. 266°, $[\alpha]_D^{22}$ +191·3° in $CHCl_3$ [Ac_1 derivative (+1EtOH), m.p. 295°], *l*-arabinose, and *l*-rhamnose. (II) contains CO_2H since 2 active H atoms (Zerevitinov) are present and it is converted by KOH–MeI in MeOH at 100° into *vanguerigenin Me ester*, m.p. 195° (Ac_1 derivative, m.p. 248°), which can be hydrolysed only with great difficulty. (II) gives an intense yellow colour with $C(NO_2)_4$ in CCl_4; in AcOH containing PtO_2 it absorbs ~1 H_2 giving a poorly cryst. product with ill-defined m.p. It is stable towards $KMnO_4$ but reacts with Br in CCl_4 or AcOH evolving HBr and giving small amounts of an uninvestigated *Br*-compound, m.p. 263—265°. When heated above its m.p., (II) loses CO_2 giving the non-acidic *vanguerol* (*decarboxyvanguerigenin*), $C_{29}H_{46}O$, m.p. 207°, which gives a yellow-brown colour with $C(NO_2)_4$ in $CHCl_3$, immediately decolorises alkaline $KMnO_4$, and gives a cryst. additive product with Br. Strong acids, *e.g.*, HCl, isomerise (II) to *vanguerigenin-*

lactone, $C_{30}H_{46}O_3$, m.p. 281° [*Ac* derivative, prisms, m.p. 314°, from $CHCl_3$ or Et_2O and cubes, m.p. 325°, from AcOH; does not contain active H (Zerevitinov)]. Dehydrogenation (Se) of (II) leads to 1 : 2 : 7-$C_{10}H_5Me_3$. (II) is therefore a triterpene, and the foaming power and colour reactions of (I) cause it to be regarded as a saponin the aglucon of which has the picene skeleton. In properties there is a great similarity between (I), oleanolic acid, and hederagenin. (I) is therefore regarded provisionally as dedihydro-oleanolic acid or an isomeride thereof. H. W.

Pyroabietic acids. R. Lombard (Compt. rend., 1939, **208**, 1321—1323).—Abietic acid (I) when heated with Pd–C gives (cf. Fleck and Palkin, A., 1939, II, 30) dehydroabietic acid, m.p. 173°, $[\alpha]_D^{20}$ +62° (*Me* ester, m.p. 59°, $[\alpha]_D^{20}$ +62°), identical with that obtained from (I) (1 mol.) and SeO_2 (0·5 mol.) in cold EtOH/10 days. (I) with Pd–C–H_2 at 250°/100 kg. gives a dihydroabietic acid, m.p. 176°, $[\alpha]_D^{20}$ +107°. (I) with Raney Ni–H_2 at 250°/100 kg. gives a *tetrahydroabietic acid*, m.p. 170°, $[\alpha]_D^{20}$ +47°, the *X*-ray spectrum of which differs from that of pyroabietic acid (II). When (I) is heated with Pd–C, only (II) is formed. J. L. D.

Dibromodihydroabietic acid. T. Hasselstrom and J. D. McPherson (J. Amer. Chem. Soc., 1939, **61**, 1228—1230).—Abietic acid (from rosin), m.p. 171—174°, $[\alpha]_D$ −99° in EtOH, with HBr–AcOH at 0° gives *dibromodihydroabietic acid*, m.p. 172—173° (decomp.), $[\alpha]_D$ 0° to +29·2° in EtOH, converted by hot AcOH into an *acid*, $C_{20}H_{30}O_2$, m.p. 168—171°, $[\alpha]$ −90·0° in EtOH (*di*-n-*amylamine* salt, m.p. 136—138·5°, $[\alpha]_D$ −44·5° in EtOH), and by Na–EtOH into *dihydroabietic acid*, m.p. 217·5—218·5°, $[\alpha]_D$ −23° in dry Et_2O (*di*-n-*amylamine* salt, m.p. 121·5—122°, $[\alpha]_D$ −24° in dry Et_2O; *Me* ester, m.p. 131·5—132·5°, $[\alpha]_D$ −21·5° in dry Et_2O). M.p. are corr. Refined ψ-pimaric (dihydroabietic) acid is obtained having m.p. 195·5—198°, $[\alpha]_D$ +0·33°. R. S. C.

Active principles of leguminous fish-poison plants. I. Properties of *l*-α-toxicarol isolated from *Derris malaccensis* (Kinta type). S. H. Harper (J.C.S., 1939, 812—816).—The optically active precursor of toxicarol has been obtained by direct crystallisation of an ethereal extract of *D. malaccensis*. After removal of sumatrol, the *l*-α-toxicarol (I) was identical in properties with that described by Tattersfield and Martin (B., 1937, 728). It is concluded that the optical data of Cahn *et al.* (B., 1938, 1098) are untrustworthy, and their criticism is unjustified. Racemisation of (I) in C_6H_6–MeOH by KOH ∝ the amount of MeOH added with the alkali. F. R. S.

Rottlerin. H. Brockmann and K. Maier (Naturwiss., 1939, **27**, 259—260; cf. A., 1938, II, 108, 334).—Under the action of weak alkali *iso*rottlerin (I) is transformed into an *isomeride* (II), m.p. 194°. This is converted by Me_2SO_4 into a *Me*$_5$ ether (III), $C_{30}H_{23}O_3(OMe)_5$, m.p. 136°, which is hydrogenated to a H_4-compound (IV), m.p. 98°. Dehydro*iso*-rottlerin (V) and weak alkali afford a H_2-isomeride (VI), m.p. 215° or 207°, which passes successively into (III) and (IV). (I) gives a H_4-derivative, m.p. 225°, also obtained by hydrogenation (Pd-black) of (II) or (VI), of (I) with Pd-black in the presence of a little alkali carbonate, or of (V) in presence of Pt; it is methylated to (IV). H. W.

Condensation accompanying reduction. Z. C. Glacet and J. Wiemann (Compt. rend., 1939, **208**, 1233—1234).—CH_2:CH·CHO with AcOH–Mg gives a mixture of 2-hydroxy- and 4-hydroxy-5-vinyltetrahydrofuran, b.p. 79°/12 mm. (*acetate*, b.p. 88—89°/13 mm.). The terminal double linking is indicated by the Raman spectrum. J. L. D.

Condensation accompanying reduction. Z. C. Glacet (Compt. rend., 1939, **208**, 1323—1325).—CHMe:CHO with Mg–AcOH gives 4-*hydroxy*-2-*methyl*- (I), b.p. 106—107°/13 mm. (*acetate*, b.p. 109·5—110°/12 mm., easily hydrolysed by cold H_2O), which quickly resinifies in air, and 2-*hydroxy*-4-*methyl*-5-*propenyl*-2 : 3 : 4 : 5-*tetrahydrofuran* (II), b.p. 113—115°/15 mm. (*acetate*, b.p. 115—116°/13 mm.), unstable in air. (I) and (II) with $H_2C_2O_4$ or $CuSO_4$ give 2-*methyl*-5-*propenyl*-2 : 3-*dihydrofuran*, b.p. 58—59°/40 mm., and 4-*methyl*-5-*propenyl*-4 : 5-*dihydrofuran*, b.p. 58·5—59°/13 mm., respectively, each of which reacts with 2 Br. The structures are confirmed by Raman spectrum measurements. J. L. D.

Preparation of 2- and 3-hydroxyfuran. H. H. Hodgson and R. R. Davies (J.C.S., 1939, 806—809).—Na_2 5-sulphofuroate with NaOH and a trace of $KClO_3$ at 200° gives 2-*hydroxyfuran*, m.p. 80°, decomp. 90°. Bromination of furoic acid in $CHCl_3$ affords 2-*bromo*-3-*hydroxyfuran*, m.p. 85°, dehalogenated (Na–Hg) to 3-*hydroxyfuran*, m.p. 58°, which with maleic anhydride yields 4-*hydroxy*-3 : 6-end*oxo*-Δ^4-*tetrahydrophthalic anhydride*, m.p. 132° (decomp.); the anhydride and HBr give 4-hydroxyphthalic acid. F. R. S.

Ethinylfurfuryl alcohol.—See B., 1939, 578.

Methylfurfurylpropionic acid. O. Wichterle (Coll. Czech. Chem. Comm., 1939, **11**, 171—175).—$\gamma\zeta$-Diketo-octoic acid distilled with EtOH–C_6H_6 gives its *Et* ester, b.p. 154·5—155°/9·5 mm., and some *Et* β-5-*methylfurfuryl*-2-*propionate*, b.p. 102—102·5°/9·5 mm., hydrolysed to the corresponding *acid* (I), m.p. 61—62° (*amide*, m.p. 99—100°). 5-Methylfurfuraldehyde, Ac_2O, and NaOAc give the acrylic acid, reduced by Na–Hg to (I). R. S. C.

Condensation of furan derivatives. IX. Eutectics of ketone–phenol systems, and the formation amongst them of oxonium complexes. V. V. Tschelincev and V. and G. Kuznetzov (J. Gen. Chem. Russ., 1939, **9**, 160—166).—The fusion diagrams exhibit max. corresponding with 2 : 1 *compounds* in the systems furfurylideneacetone–*p*-$C_6H_4(OH)_2$ (I), m.p. 33°, benzylideneacetone (II)–*o*-$C_6H_4(OH)_2$ (III), m.p. 51°, (II)–*m*-$C_6H_4(OH)_2$ (IV), m.p. 39°, (II)–(I), m.p. 81°, difurfurylideneacetone (V)–(IV), m.p. 63°, and (V)–(I), m.p. 82·5°, and with 1 : 1 *compounds* in the systems (V)–(III), m.p. 67—69°, dibenzylideneacetone (VI)–(III), m.p. 79°, (VI)–(IV), m.p. 97·5°, and (VI)–(I), m.p. 99°. R. T.

Reactivity of two diene systems of furylethylene. R. Paul (Compt. rend., 1939, **208**, 1028—

1030; cf. van Campen and Johnson, A., 1933, 280).—Equimol. amounts of furylethylene (I) with maleic anhydride (II) in Et_2O at room temp. afford the *anhydride* (?), m.p. 150°, of 3 : 4 : 5 : 6-tetrahydrobenzfuran-3 : 4-dicarboxylic acid, which with aq. Na_2CO_3 and then HCl gives 3 : 4 : 5 : 6-*tetrahydrobenzfuran*-3 : 4-*dicarboxylic acid*, m.p. 227—228°, which is stable to boiling H_2O, absorbs 4 H (H_2–Pt or –Raney Ni) with difficulty, and gives no CH_2O with O_3, which indicates that the extranuclear double linking in (I) is involved in the reaction. Furylethane with (II) affords the *anhydride*, m.p. 97—98°, of 1 : 4-oxido-1-ethyl-Δ^2-*cyclo*hexene-5 : 6-dicarboxylic acid, easily hydrolysed by boiling H_2O, and with H_2–Raney Ni rapidly affords the *anhydride*, m.p. 108°, of 1 : 4-oxido-1-ethyl*cyclo*hexane-5 : 6-dicarboxylic acid. J. L. D.

Preparation of *dl*-α-tocopherol from synthetic phytol. P. KARRER and B. H. RINGIER (Helv. Chim. Acta, 1939, **22**, 610—616).—Hexahydro-ψ-ionone, $CH_2Br{\cdot}CO_2Et$, and Cu–Zn in PhMe yield *Et* β-*hydroxy*-βζκ-*trimethyldodecoate*, b.p. 183°/12 mm., converted by successive treatments with HBr at 100° and Zn–Cu in 80% AcOH at 120° followed by hydrogenation (Pt) into *Et* βζκ-*trimethyldodecoate*. This is reduced (Bouveault–Blanc) to hexahydrofarnesol, converted by PBr_3 or by HBr at 130—140° into hexahydrofarnesyl bromide, which is transformed by successive treatments with $CHAcNa{\cdot}CO_2Et$ and KOH into βκζ-*trimethylpentadecan*-β-*one*, b.p. 166—173°/10 mm., in very modest yield. This is transformed by $NaNH_2$ and C_2H_2 into γηλο-tetramethyl-Δ^{α}-hexadecin-γ-ol, partly hydrogenated (Pt) to the corresponding ethylenic compound, which is transformed by PBr_3 into phytyl bromide (I). Trimethylquinol and (I) in ligroin containing $ZnCl_2$ afford synthetic *dl*-α-tocopherol. The allophanate derived therefrom has m.p. ~4° < that observed for the natural derivative; it is uncertain whether this is due to the presence of an obstinate impurity or is caused by steric difference. There is no difference in the physiological activity of the two materials. H. W.

Lower homologues of α-tocopherol. Oxidation products of compounds resembling tocopherol. P. KARRER, H. FRITZSCHE, and R. ESCHER (Helv. Chim. Acta, 1939, **22**, 661—665).—*dl*-7 : 8-Dimethyltocol is converted into the *acetate*, b.p. 150—160°/0·01—0·005 mm., and *allophanate*, m.p. 146°. Evidence is adduced in favour of the view that "γ-" is somewhat impure β-tocopherol. 2 : 3 : 5-Trimethyl-5-β-hydroxypropyl-*p*-benzoquinone (I) is reduced by Zn dust and AcOH at 100° to 2 : 3 : 5-*trimethyl*-6-β-*hydroxypropylquinol* (II), m.p. 137° (*triacetate*, m.p. 94°). Reduction of (I) to (II) is also effected with Zn dust–AcOH–HBr. H. W.

Higher homologue of α-tocopherol. P. KARRER and O. HOFFMANN (Helv. Chim. Acta, 1939, **22**, 654—657).—3 : 5-Dimethyl-2-ethylphenol is converted by HCl and $NaNO_2$ in EtOH at 0° into 4-*nitroso*-3 : 5-*dimethyl*-2-*ethylphenol*, m.p. 165° (decomp.), transformed by H_2O_2 in boiling dil. HCl into 3 : 5-*dimethyl*-2-*ethyl*-p-*benzoquinone*, reduced by Zn and AcOH at 100° to 3 : 5-*dimethyl*-2-*ethylquinol* (I), m.p. 157°. This is condensed by $ZnCl_2$ in ligroin with phytyl bromide to 5 : 7-*dimethyl*-8-*ethyltocol* (II), an oil, which reduces cold $AgNO_3$ and $AuCl_3$ and gives a cryst. *allophanate*, m.p. 170—171°. In doses of 16 mg. (II) has full vitamin-*E* activity. Allyl bromide, (I), and $ZnCl_2$ in boiling C_6H_6 afford 5-*hydroxy*-2 : 4 : 6-*trimethyl*-7-*ethylcoumaran*, m.p. 111°. The prep. of cumoquinone is described. H. W.

7-Coumaronyloxyacetic acid.—See B., 1939, 568.

Two 4-aminocoumarans. P. KARRER and H. FRITZSCHE (Helv. Chim. Acta, 1939, **22**, 657—660).—1-Methylcoumaran is coupled with diazotised 2 : 4-$(NO_2)_2C_6H_3{\cdot}NH_2$ in AcOH to 4-2 : 4′-*dinitrobenzeneazo*-1-*methylcoumaran*, reduced (Pt in AcOH–EtOH) to the cryst. 4-*amino*-1-*methylcoumaran* (*hydrochloride*), which reduces cold $AgNO_3$–EtOH. The NH_2 group can be diazotised and the salt is hydrolysed to 4-*hydroxy*-1-*methylcoumaran*, characterised as the *allophanate*, decomp. ~210° after softening. 4-2′ : 4′-*Dinitrobenzeneazo*-1 : 3 : 6-*trimethylcoumaran* is similarly reduced to 4-*amino*-1 : 3 : 6-*trimethylcoumaran*, m.p. 113°. H. W.

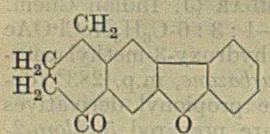
Limited applicability of Kostanecki's reaction. Influence of halogen atoms on the reaction. D. CHAKRAVARTI and B. MAJUMDAR (J. Indian Chem. Soc., 1939, **16**, 151—159).—1 : 3 : 6-$C_6H_3MeCl{\cdot}OAc$ and $AlCl_3$ yield 5-chloro-2-hydroxy-3-methylacetophenone (I), m.p. 70° [*semicarbazone*, m.p. 283° (decomp.)]. Similarly, from the propionyl derivatives of the appropriate phenols are prepared 5-*chloro*-2-*hydroxy*-3-*methyl*- (II), m.p. 61° (*semicarbazone*, m.p. 205°), 3-*chloro*-4-*hydroxy*-, m.p. 80° (*Ac* derivative, b.p. 155°/6 mm.), 3-*bromo*-4-*hydroxy*- (III), m.p. 130° and 5-*bromo*-2-*hydroxy*-*propiophenone* (IV), m.p. 78°. Heated at 170—180° for 12 hr. with NaOAc–Ac_2O, (I), 2 : 3 : 5 : 1-$OH{\cdot}C_6H_2MeCl{\cdot}COMe$ (V), (II), 2 : 3 : 5 : 1-$OH{\cdot}C_6H_2MeCl{\cdot}COEt$ (VI), 2 : 5 : 1-$OH{\cdot}C_6H_3Cl{\cdot}COEt$ (VII), and (IV) yield respectively 6-*chloro*-2 : 8-, m.p. 139°, and 8-*chloro*-2 : 6-*dimethyl*-3-*acetylchromone*, m.p. 131°, 6-chloro-2 : 3 : 8- and 8-chloro-2 : 3 : 6-trimethylchromone, 6-chloro-2 : 3- and 6-bromo-2 : 3-dimethylchromone. (II), (VI), and (VII) also yield styryl derivatives. Similarly with $EtCO_2Na$ and $(EtCO)_2O$, (I), (V), (II), (VI), (IV), and (VII) yield respectively 6-*chloro*-3 : 4 : 8-*trimethylcoumarin*, b.p. 180—200°/6 mm., m.p. 94°, 8-chloro-3 : 4 : 6-trimethylcoumarin, 6-*chloro*-3 : 8- (VIII), m.p. 85°, 8-*chloro*-3 : 6-*dimethyl*-, m.p. 74—75°, 6-*bromo*-, m.p. 87°, and 6-*chloro*-3-*methyl*-, m.p. 65—66°, -2-*ethylchromone*. The last-named is also formed by the interaction of 2 : 5 : 1-$OH{\cdot}C_6H_3Cl{\cdot}COMe$ and $EtCO_2Et$ with Na followed by heating with AcOH–HBr. Hydrolysis of (VIII) with NaOEt gives (II). With $PrCO_2Na$ and $(PrCO)_2O$, (II), (VI), (VII), and (IV) give respectively 6-*chloro*-3 : 8-, m.p. 95°, and 8-*chloro*-3 : 6-*dimethyl*, m.p. 68—71°, 6-*chloro*-, m.p. 85°, and 6-*bromo*-3-*methyl*-, m.p. 83—84°, -2-*propylchromone*. Kostanecki's reaction therefore proceeds normally except in the case of *o*-hydroxyacetophenones heated with $EtCO_2Na$ and $(EtCO)_2O$, when coumarins are formed. J. D. R.

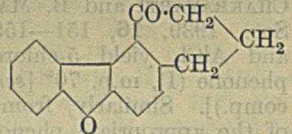
Natural coumarins. XLVI. Synthesis of seselin. E. SPÄTH and R. HILLEL (Ber., 1939, **72**, [*B*], 963—965).—Seselin, m.p. 118—119°, is obtained

by heating umbelliferone with β-methyl-Δ^{γ}-butin-β-ol at 200° vac. H. W.

Pechmann dyes. Mechanism of formation of the mono-acid by hydrolytic fission. P. Chovin (Compt. rend., 1939, **208**, 1228—1230; cf. A., 1939, II, 113).—Graded alkaline hydrolysis of the Pechmann dye (I) derived from *α-naphthoylmethyl-α'-benzoylmethylfumaric acid* (II), m.p. 272° (decomp.; block), affords 6-*naphthyl*-3-*benzoylmethyl*-1 : 2-*pyrone*-4-*carboxylic acid* (III), m.p. 246° (decomp.; block), converted by Ac_2O into (I). As partial cyclisation of (II) also affords (III), it follows that (III) is formed in each reaction from (II). Closure of both rings in (II) gives a yellow *isomeride*, m.p. 305°, of (I). J. L. D.

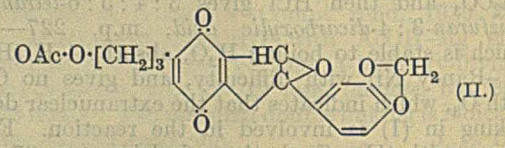
Amino-ketones derived from tetrahydrobenz[*b*]naphtho[2 : 3-*d*]furan. R. A. Robinson and E. Mosettig (J. Amer. Chem. Soc., 1939, **61**, 1148—1151).—γ-3-Dibenzfuryl-*n*-butyric acid and P_2O_5 in 85% H_3PO_4 at 170° afford 50% of 7-*keto*-7 : 8 : 9 : 10-*tetrahydrobenz*[b]*naphtho*[2 : 3-d]*furan* (I), m.p. 137—138° [*semicarbazone*, m.p. 260—265° (decomp.)], and 3—4% (more actually formed) of 1-*keto*-1 : 2 : 3 : 4-*tetrahydrobenz*[b]*naphtho*[1 : 2-d]*furan* (II),


(I.)


(II.)

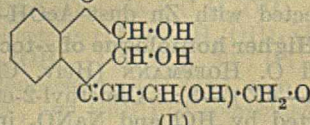
m.p. 112—113° (*oxime*, m.p. 200—203°). N_2H_4 and NaOEt–EtOH at 170° convert (I) into 7 : 8 : 9 : 10-*tetrahydrobenz*[b]*naphtho*[2 : 3-d]*furan*, m.p. 75—77° (*picrate*, m.p. 139—141°; Clemmensen reduction gives a 5—10% yield with 40—50% of a substance, m.p. ~190—210°), converted by Se into brazan, whence its structure follows. Br–Et_2O converts (I) into the 8-*Br*-derivative, m.p. 207° (decomp.), which with the appropriate *sec.* base in C_6H_6 at 100° or the b.p. yields the *hydrochlorides*, m.p. 208—212° (decomp.), 235—237° (decomp.), and 206—210° (decomp.), of the 8-*dimethylamino*- (III), 8-*piperidino*- (IV), and 8-1' : 2' : 3' : 4'-*tetrahydroisoquinolino-ketones*, respectively; some (I) is also obtained and traces of (?) 7-hydroxybrazan. The hydrochlorides are rather unstable. Attempts to reduce (III) and (IV) to *sec.* alcohols failed. The NEt_2-ketone could not be prepared. Prep. of 6-ω-bromoacetyl-1 : 2 : 3 : 4-tetrahydrodibenzfuran, the derived NH_2-ketones, 6-β-dimethylamino-, an oil, 6-β-*piperidino*-, m.p. 129—131°, and 6-1' : 2' : 3' : 4'-*tetrahydroisoquinolino*-α-*hydroxyethyl*-1 : 2 : 3 : 4-*tetrahydrodibenzfuran*, m.p. 144·5—145·5°, is described (cf. A., 1936, 733). R. S. C.

Egonol. VIII. Noregonolonidin acetate and intensely coloured compounds formed therefrom. S. Kawai, K. Sugimoto, and N. Sugiyama [with, in part, E. Yamamoto, S. Yosida, and T. Nakamura] (Ber., 1939, **72**, [*B*], 953—962).—Egonol benzoate is oxidised by 30% H_2O_2 in AcOH at 50—55° to *noregonolonidin benzoate*, m.p. 226—227°, which forms wine-red solutions; it is reduced (Pt-black in dioxan) to 4 : 7-*dihydronoregonolonidin benzoate*, colourless needles, m.p. 196·5—197·5° to a dark red melt. Finely-divided noregonolonidin acetate (I) is oxidised by 30% H_2O_2 in faintly alkaline $COMe_2$ to 2 : 3-*oxido*-2 : 3-*dihydronoregonolidin acetate* (II), which

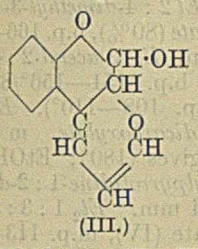

(II.)

does not give a colour with $Cu(OAc)_2$ or $FeCl_3$ in EtOH and affords a negative Legal test. NHPh·NH_2 causes only blackening, thus indicating the quinonoid nature of (II); the *oxime* decomposes at 180°. CH_2N_2 in Et_2O transforms (II) into 2 : 3-*oxido*-6-*methyl*-2 : 3-*dihydronoregonolonidin acetate*, m.p. 141·5—142°, from which OMe is absent (Zeisel). HCl in dry $CHCl_3$–Et_2O converts (II) into 3-*hydroxy*- (III), m.p. 222°, and 3-*chloro*-, m.p. 166·5°, *-noregonolonidin acetate*. Hydrogenation (PtO_2 in EtOAc) of (II) follows a complex course, giving the colourless 2-*hydroxytetrahydronoregonolonidin acetate*, m.p. 175—175·5°, and a pale yellow *substance*, m.p. 172—175·5°, solutions of which in org. media have a blue fluorescence. With Zn dust and AcOH (II) gives (III) and (I). Reducing acetylation (Zn dust and Ac_2O) of (I) yields 4 : 7-*diacetoxy*-2-3' : 4'-*methylenedioxyphenyl*-5-ω-*acetoxy*-n-*propylcoumarone*, m.p. 111°, also obtained by similar treatment of (II). The dark colour of compounds of the noregonolonidin series is ascribed to the presence of a double linking between $C_{(2)}$ and $C_{(3)}$, thus giving an uninterrupted conjugated system between the double linkings of the benzoquinone and those of the methylenedioxyphenyl nucleus. If this is absent there is only a yellow colour due to the quinonoid nucleus. The author's conception of the formation of flavylium salts (A., 1939, II, 222) differs from that of Robinson only in respect of the chalkone stage, Robinson regarding an oxonium, the author a carbonium, compound as intermediate. H. W.

Sugar–phenol condensations. Condensation of *d*-glucose with phenol. J. B. Niederl and R. K. Maurmeyer (J. Amer. Chem. Soc., 1939, **61**, 1005—1010).—PhOH, anhyd. *d*-glucose, and (*a*) HCl–AcOH (2 days) or (*b*) aq. HCl (1 month) give *substances*, (I) $C_{12}H_{14}O_5$, $+H_2O$, m.p. 115° (decomp.), $[\alpha]^{24}$ +79·2° in H_2O {with conc. HNO_3 gives picric acid (II); *tetrabenzoate*, $+H_2O$, m.p. 130°; *Na* salt; *phenylosazone*, $+H_2O$, m.p. 183°; *dibromide*, m.p. 130° (decomp.) [with conc. HNO_3 gives (II); *tetrabenzoate*, m.p. 155°; *semicarbazone*, m.p. 210°; 2 : 4-*dinitrophenylhydrazone*, m.p. 181°; $(NO_2)_3$-derivative, $+H_2O$, m.p. 107° (decomp.)]}, (III) $C_{12}H_{10}O_3$ (impure), and (IV) $C_{18}H_{14}O_3$, m.p. 238—240° (*benzoate*, m.p. 169°; *phenylurethane*, m.p. 195°). Zn–AcOH reduces (III) to an amorphous *compound*, $C_{12}H_{12}O_3$, $+H_2O$, m.p. 120° (decomp.) [*benzoate*, $+H_2O$, m.p. 145°; p-*nitrobenzoate*, m.p. 175°; *di*-


(I.)

bromide, m.p. 138° (decomp.); $(NO_2)_3$-derivative, m.p. 130° (decomp.)]. The annexed and similar structures are discussed. R. S. C.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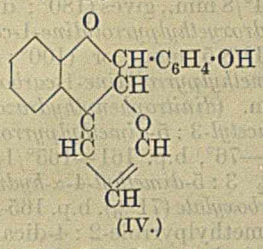

(IV.)

Action of bromine on nitrothiophen. V. S. Babasinian (J. Amer. Chem. Soc., 1938, **60**, 2906—2909).—2-Nitrothiophen (50 g.) and Br vapour at room temp. (30 days) give 2-bromo- (I), m.p. 47—48° (8·5 g.), and 2 : 3-dibromo-5-nitrothiophen (II), m.p. 75·5—76° (6 g.), 2 : 5-dibromo-3-nitrothiophen, m.p. 61° (0·8 g.; produced from 3-nitrothiophen, present as impurity), tetrabromothiophen (10 g.), and traces of other derivatives. The NO_2 in (I) is more firmly held than that in (II). R. S. C.

Valency angle. II. Angle at the sulphur atom attached to phenyl. A. Lüttringhaus [with, in part, K. Hauschild] (Ber., 1939, **72**, [*B*], 887—897).—It is shown qualitatively by comparison of yields that CH_2 and S compounds behave very similarly. The somewhat lower yields of the latter substances are due to the fact that the union $S{\cdot}C_{arom.}$ is somewhat longer than $C_{aliph.}{\cdot}C_{arom.}$; with approx. the same valency angle at CH_2 or S, this involves an increase in the O—O distance which has to be bridged. The ring system with O as central atom requires a bridge greater by about two CH_2 groups for successful intramol. ring-closure. The angle at O is therefore ⩾ that at S or CH_2. $SOCl_2$ and PhOH in $CHCl_3$ at room temp. yield $(p\text{-}OH{\cdot}C_6H_4)_2S$ (I), m.p. 150°, $p\text{-}C_6H_4Cl{\cdot}OH$, and tri-*p*-hydroxyphenylsulphonium chloride, m.p. 273° when rapidly heated [normal *sulphate*, m.p. 287° (decomp.)]. The change is probably $[(OH{\cdot}C_6H_4)_2S{\cdot}OH]Cl + PhOH \rightarrow H_2O + [(HO{\cdot}C_6H_4)_3S]Cl$ or $\rightarrow H_2O + C_6H_4Cl{\cdot}OH$ + (I), or alternatively $[(OH{\cdot}C_6H_4)_2S{\cdot}Cl]Cl + PhOH \rightarrow HCl + C_6H_4Cl{\cdot}OH$ + (I). Gradual addition of KOH–MeOH to a boiling solution of (I) and $Br{\cdot}[CH_2]_{10}{\cdot}Br$ in boiling EtOH gives p-*hydroxy*-p′-*κ-bromoundecoxydiphenyl sulphide* (II), m.p. 59—61°. p-*Hydroxy*-p′-*θ-bromo-octyloxy*-, m.p. 48·5—50°, and p-*hydroxy*-p′-*ζ-bromohexyloxy*- (III), m.p. 50—53°, *-diphenyl sulphide* are similarly obtained. (II), dissolved in amyl alcohol, is added very slowly to a boiling suspension of K_2CO_3 in the same solvent; the residue, after removal of the solvent, is extracted with boiling C_6H_6–petroleum and the solution is extracted with Claisen's alkali, thus giving 4 : 4′-*dihydroxydiphenyl sulphide decamethylene ether*, $S<^{C_6H_4{\cdot}O}_{C_6H_4{\cdot}O}>[CH_2]_{10}$, m.p. 66·5°, which is indifferent towards MgMeI in abs. amyl ether, is incompletely hydrolysed by boiling 48% HBr–Ac_2O with production of $Br{\cdot}[CH_2]_{10}{\cdot}Br$, and is smoothly transformed by $AlBr_3$ in boiling C_6H_6 into (I). It is oxidised by $o\text{-}CO_2H{\cdot}C_6H_4{\cdot}CO_3H$ to the corresponding *sulphone*, m.p. 144·5°. 4 : 4′-*Dihydroxydiphenyl sulphide octamethylene ether*, m.p. 53°, is prepared similarly in 15·8% yield; the *sulphone* has m.p. 174·5°. Under the same conditions (III) affords *dimeric* 4 : 4′-*dihydroxydiphenyl sulphide hexamethylene ether*, m.p. 148°. H. W.

Valency angle. IV. Determination of linking angles by chemical methods. A. Lüttringhaus and R. Kohlhaas (Ber., 1939, **72**, [*B*], 907—913).—It is shown that the angle at X in compounds $X<^{C_6H_4{\cdot}O}_{C_6H_4{\cdot}O}>[CH_2]_n$ (X = CH_2, O or S) can be determined from measurement of the yields obtained by ring-closure of $OH{\cdot}C_6H_4X{\cdot}C_6H_4{\cdot}O{\cdot}[CH_2]_n{\cdot}Br$ if the angle is determined in a single case by an independent method. The angle at S in $(p\text{-}OH{\cdot}C_6H_4)_2S$ is 112·4° ±1·5° as determined röntgenographically. For CH_2 and O in the above cyclic compounds the vals. are 110°±3° and 129°±4°, respectively. H. W.

Dyes derived from acenaphthenequinone. VII. 2-(5-Chloro)thionaphthenacenaphthyleneindigos. S. H. Guha (J. Indian Chem. Soc., 1939, **16**, 127—130).—5-Chloro-3-hydroxythionaphthen (I) with acenaphthenequinone in AcOH–HCl yields 2-(5-*chloro*)-*thionaphthenacenaphthyleneindigo* (II). Similarly from (I) and 3-chloro-, 3-bromo-, or 1-methoxy-acenaphthene and phenanthraquinone are obtained, respectively, 2-(5-*chloro*)*thionaphthen*-8′-(3′-*chloro*)- (III), -(3′-*bromo*)- (IV), and -(1′-*methoxy*)-*acenaphthyleneindigo* (V) and 2-(5-*chloro*)*thionaphthen*-9′-*phenanthreneindigo*. (II) dyes wool and cotton dark red, (III) and (IV) dye wool brownish-red and cotton dark red, and (V) dyes wool light red. J. D. R.

Onium compounds. XXI. Pyrrolidinium analogues of choline and betaine. R. R. Renshaw and W. E. Cass (J. Amer. Chem. Soc., 1939, **61**, 1195—1198; cf. A., 1939, II, 226).—Na in EtOH, first boiling and then at 130°, reduces Et hygrate, b.p. 74—76°/12 mm., 2-acetyl- and 2-*n*-propionyl-pyrrole to 1-*methyl*-2-*hydroxymethyl*- (I), b.p. 67—68°/12 mm. [*aurichloride*, m.p. 203—207° (decomp.); *picrate*, m.p. 173—174° (decomp.)], 2-α-hydroxyethyl-, b.p. 97—102°/21 mm., 188—196°/760 mm. (*picrate*, m.p. 122—130°), and 2-α-hydroxy-*n*-propyl-, m.p. 48—50°, b.p. 96—102°/18 mm. (*picrate*, m.p. 124—130°), *-pyrrolidine*, respectively. (I) gives a *methiodide*, m.p. 283—284° (decomp.; uncorr.) (*acetate*, m.p. 127—128°), an *acetate hydrochloride*, hygroscopic, m.p. 73—74°, *acetate hydrobromide*, hygroscopic, m.p. 74—75°, and *benzoate hydrochloride*, m.p. 162—163°. MeI–$Ba(OH)_2$ in hot MeOH converts the other alcohols into 1 : 1-*dimethyl*-2-α-*hydroxyethyl*-, m.p. 111—123° and 127—138° (*acetate*, m.p. 129—140°), and 1 : 1-*dimethyl*-2-α-*hydroxy*-n-*propyl-pyrrolidinium iodide*, m.p. 106—113° (*acetate*, m.p. 166—170°). H_2–PtO_2 in 20—50% aq. EtOH containing a slight excess of HCl or H_2–Raney Ni in EtOH at 150—160°/130—150 atm. reduces 2-methylcarbamyl-1-methylpyrrole to hygr-*N*-methylamide (70—90% yield) (*hydrochloride*, m.p. 146·5—148°; *methiodide*, m.p. 130—132·5°), hydrolysed by HCl at 125° to hygric acid, the Me ester (hygroscopic *hydrobromide*, m.p. 108—109·5°; *methiodide*, m.p. 103·5—104°) of which is obtained by HCl–MeOH in 60—65% yield and

with NH_3–MeOH at 70—80° gives 90% of *hygramide*, m.p. 135·5—137° [*auri*-, m.p. 173—174° after sintering, *platini*-, m.p. 196—197° (decomp.), and *hydrochloride*, m.p. 192—193°; *picrate*, m.p. 132·5—133·5°; *methiodide*, m.p. 133—135°]. *Et hygrate hydrobromide*, hygroscopic, m.p. 83·5—85°, and *methiodide*, m.p. 88—89°, are also prepared. M.p. are corr.

R. S. C.

Reactions of hydrogen with pyrrole derivatives. II. J. L. Rainey and H. Adkins (J. Amer. Chem. Soc., 1939, **61**, 1104—1110; cf. A., 1936, 861).—1-CO_2Et greatly increases the ease of hydrogenation of pyrroles to pyrrolidines; 1-Bz may do so, but is often removed as $CH_2Ph{\cdot}OH$. This effect is due to electronic shifts. Hydrogenation of 2- or 3-CO_2Et-derivatives usually (one exception) occurs at the CO_2Et before the ring and yields Me derivatives, but occasionally the intermediate primary alcohols can be isolated. Reactions given below without description are hydrogenations in presence of Raney Ni, the solvent and temp. being stated in parentheses. 1-Carbethoxypyrrole (prep. by $ClCO_2$Et from K pyrrole in PhMe), b.p. 175—180°/740 mm., gives (70°; dioxan) 1-carbethoxypyrrolidine (93%). 1-Benzoylpyrrole (prep. from K pyrrole and BzCl in PhMe), b.p. 169—170°/8 mm., gives (70°; dioxan) 1-benzoylpyrrolidine (93%), b.p. 169—170°/8 mm. *Et* 3 : 5-*dimethyl*-2 : 4-*diethylpyrrole*-1-*carboxylate* (this and other 1-derivatives similarly prepared from the 1-K derivative), b.p. 123—126°/7 mm., gives (180°; dioxan) *Et* 3 : 5-*dimethyl*-2 : 4-*diethylpyrrolidine*-1-*carboxylate* (87%), b.p. 119—121°/7 mm. *Et*$_3$ 3 : 5-*dimethylpyrrole*-1 : 2 : 4-*tricarboxylate*, b.p. 158—160°/1·2 mm., gives (180°; dioxan) the derived *pyrrolidine* ester (I) (95%), b.p. 151°/1·2 mm. *Et*$_2$ 3 : 5-*dimethyl*- (II), b.p. 156—158°/11·5 mm., and -3 : 5-*dimethyl*-4-*ethyl*-*pyrrole*-1 : 2-*dicarboxylate*, b.p. 126—129°/1 mm., give (120°; 170°; dioxan; 90% yield) *Et*$_2$ 3 : 5-*dimethyl*-, b.p. 146—147°/11 mm., and 3 : 5-*dimethyl*-4-*ethyl*-*pyrrolidine*-1 : 2-*dicarboxylate*, b.p. 164—166°/11 mm. When heated with conc. HCl at 150° and then esterified, (I) gives (II). *Et*$_2$ 2 : 4-*dimethylpyrrole*-1 : 3-*dicarboxylate*, m.p. 35—38°, b.p. 159—162°/9 mm., gives (200°; dioxan) the *pyrrolidine* ester (60%), b.p. 146—147°/7 mm. *Et*$_2$ 1-*benzoyl*-3 : 5-*dimethylpyrrole*-2 : 4-*dicarboxylate*, m.p. 74—75°, b.p. 191—195°/1 mm., gives (125° or 150°; dioxan) $CH_2Ph{\cdot}OH$ (60%) and 2 : 4-dicarbethoxy-3 : 5-dimethylpyrrole (III) (85%). *Et* 1-*benzoyl*-2 : 4-*dimethylpyrrole*-3-*carboxylate*, m.p. 65—66°, b.p. 144—148°/1 mm., gives (150°; dioxan) $CH_2Ph{\cdot}OH$ (60%) and 3-carbethoxy-2 : 4-dimethylpyrrole (85%), m.p. 75—76°, b.p. 152°/7 mm., also obtained by hydrolysing (III) by NaOH–EtOH and heating the product in glycerol at 145—155°/7 mm. The products obtained (270°; methyl*cyclo*hexane) from *Et*$_2$ 1-*trimethylacetyl*-3 : 5-*dimethylpyrrole*-2 : 4-*dicarboxylate* (prep. from the 1-K derivative by Bu$^{\gamma}$COCl in PhMe), m.p. 56—58°, b.p. 148—149°/1 mm., were not identified. *Et* 2-*acetylpyrrole*-1-*carboxylate*, b.p. 119—121°/7 mm., gives (140°; dioxan) *Et* 2-α-*hydroxyethylpyrrolidine*-1-*carboxylate* (94%), b.p. 135—137°/7 mm., or (80°; dioxan) 15% thereof with 77% of *Et* 2-*acetylpyrrolidine*-1-*carboxylate*, b.p. 125—127°/7 mm. (*dinitrophenylhydrazone*, m.p. 102—104°). *Et* 3-*acetyl*-2 : 4-*dimethylpyrrole*-1-*carboxylate*, b.p. 162—164°/8 mm., gives (180°; dioxan) *Et* 2 : 4-*dimethyl*-3-α-*hydroxyethylpyrrolidine*-1-*carboxylate* (80%), b.p. 166—171°/8·5 mm., or (100°; dioxan) *Et* 3-*acetyl*-2 : 4-*dimethylpyrrolidine*-1-*carboxylate*, b.p. 151—156°/8·5 mm. (*dinitrophenylhydrazone*, m.p. 108—110°). *Et*$_2$ 4-*acetyl*-3 : 5-*dimethylpyrrole*-1 : 2-*dicarboxylate*, m.p. 74—76°, b.p. 161—165°/1 mm., gives (180°; EtOH) *Et*$_2$ 3 : 5-*dimethyl*-4-α-*hydroxyethylpyrrolidine*-1 : 2-*dicarboxylate* (71%), b.p. 165—170°/1 mm. *Et*$_2$ 1 : 3 : 5-trimethylpyrrole-2 : 4-dicarboxylate (IV), m.p. 113—114°, b.p. 142—144°/1 mm., gives (*a*) (Ni; 250°; methyl*cyclo*hexane) 1 : 2 : 3 : 4 : 5-*pentamethylpyrrolidine* (V) (29%), b.p. 146—149°/742 mm. [*picrate*, m.p. 192—193° (decomp.)], and 57% of unchanged (IV), (*b*) (Cu chromite; 250°; EtOH) 80% of (V), or (*c*) (Cu chromite; 220°; EtOH) 23% of (V), 27% of (IV), and 36% of *Et* 1 : 2 : 3 : 5-*tetramethylpyrrole*-4-*carboxylate*, m.p. 72—73°, b.p. 121—125°/? mm. *Et*$_2$ 3 : 5-*dimethyl*-1-*ethylpyrrole*-2 : 4-*dicarboxylate* (prep. from the 1-Na derivative by Et_2SO_4), m.p. 39—39·5°, b.p. 145—148°/1 mm., gives (250°; methyl*cyclo*hexane) 19% of 2 : 3 : 4 : 5-tetramethyl-1-ethylpyrrolidine, 55% of ester being recovered. Et 2 : 4-dimethylpyrrole-3-carboxylate gives (220°; EtOH) *Et* 2 : 4-*dimethyl*-1-*ethylpyrrolidine*-3-*carboxylate* (VI) (50%), b.p. 86—89°/7 mm. (*picrate*, m.p. 110—112°; *hydrochloride*, m.p. 96—99°), 2 : 3 : 4-*trimethyl*-1-*ethylpyrrolidine* (VII) (10%), b.p. 147—150°/740 mm. (*picrate*, m.p. 105—108°), and mixed pyrrolidones (12%, formed by ring-fission and re-closure), but with less catalyst in dioxan at 220° 15% of carbethoxypyrrolidines are formed; introduction of the 1-Et is due to the solvent EtOH. *Et* 2 : 4-*dimethyl*-1-*ethylpyrrole*-3-*carboxylate* (prep. from the 3 : 5-dicarboxylate), b.p. 138—141°/7 mm., gives (220°; EtOH) 78% of (VI) and 3% of (VII). Et 3 : 5-dimethylpyrrole-2-carboxylate (prep. from the 2 : 4-dicarboxylate by hydrolysing with H_2SO_4 at 50° and decarboxylating the product in glycerol), m.p. 124—125°, gives (220°; EtOH) 2 : 3 : 5-*trimethyl*-1-*ethylpyrrolidine*, b.p. 139—142°/740 mm. (*picrate*, m.p. 135—138°), 60% of the ester being unchanged. 2-Carbethoxypyrrole gives (220°; EtOH) 2-methyl-1-ethylpyrrolidine (35%) and 2-hydroxymethyl-1-ethylpyrrolidine (14%), b.p. 75—81°/11 mm. With H_2–Cu chromite in EtOH at 190° (VI) gives 2 : 4-*dimethyl*-3-*hydroxymethyl*-1-*ethylpyrrolidine* (83%), b.p. 100—102°/8 mm. (*hydrochloride*, m.p. 90—95°), and 3% of (VII). *Et*$_2$ 3 : 5-*dimethylpyrrolidine*-2 : 4-*dicarboxylate*, b.p. 140—142°/7 mm., and 4-*carbethoxy*-3 : 5-*dimethyl*-1-*ethylpyrrole*-2-*carboxylic acid*, m.p. 137°, are described.

R. S. C.

Catalytic transformations of heterocyclic compounds. XI. Mechanism of simultaneous catalytic dehydrogenation of furan and furanidin (tetrahydrofuran) with *sec.* and *tert.* amines. J. K. Juriev [with O. A. Kantscheeva] (J. Gen. Chem. Russ., 1939, **9**, 153—159).—Tetrahydrofuran (I)–amine mixtures passed over Al_2O_3 at 400° yield *N*-ethylpyrrolidine (II) (with NH_2Et 56, with $NHEt_2$ 29, and with NEt_3 9% yield). The reactions are: (I) + $NHEt_2$ → $OH{\cdot}[CH_2]_4{\cdot}NEt_2$ (+H_2O) → $OH{\cdot}[CH_2]_4{\cdot}NHEt$ → (II) + H_2O. Under the same

conditions (I) alone yields a variety of products, of which $CHMe{:}CH_2$ is identified. R. T.

Hydrogenations and dehydrogenations in the pyridine series. Model experiments for the mode of transportation of hydrogen by co-dehydrase. O. Mumm and J. Diederichsen (Annalen, 1939, **538**, 195—236).—1 : 2-Dihydropyridines, the structure of which is proved by the prep. of some of them by hydrogenation of 2-methylene derivatives, are yellow, show no or yellowish-green fluorescence in ultra-violet light, are strongly basic and strongly reduce $AgNO_3$ and methylene-blue, and rapidly absorb 2 H but no more. 1 : 4-Dihydropyridines, including those prepared by the Hantzsch synthesis, are colourless, have blue fluorescence in ultra-violet light, are not or only slightly basic and reducing, and are difficultly reducible but then direct to the H_6-stage. The products formed by reduction by activated Al are 1 : 2 : 1′ : 2′-tetrahydro-2 : 2′-dipyridyls, the more stable isomerides being 1 : 2 : 1′ : 2′-tetrahydro-4 : 4′-dipyridyls. Dihydronicotinamide is probably the 1 : 6-H_2-derivative. Electronic interpretations of the reactions are offered. Reduction of the pyridinium methosulphate with $Na_2S_2O_4$ in aq. $NaHCO_3$ gives *Et*$_2$ 1 : 2 : 6-*trimethyl*-1 : 4-*dihydropyridine*-3 : 5-*dicarboxylate* (I), m.p. 88°; reduction by Na–Hg and AcOH in H_2O–Et_2O gives similarly *Et*$_2$ 4-*phenyl*-1 : 2 : 6-*trimethyl*-1 : 4-*dihydropyridine*-3 : 5-*dicarboxylate* (II), m.p. 131°. Et_2 4-phenyl-1 : 2 : 6-trimethyl-1 : 2-dihydropyridine-3 : 5-dicarboxylate (III) and maleic anhydride give the *adduct*, $C_{24}H_{27}O_7N$, m.p. 153°, but (II) does not react. Hydrogenation (PtO_2) of (II) and (III) in AcOH affords the piperidine *derivative* (*picrate*, m.p. 164°), and Se at 215° yields Et_2 4-phenyl-2 : 6-dimethylpyridine-3 : 5-dicarboxylate with loss of the 1-Me. *Et*$_2$ 1 : 2 : 6-*trimethyl*-1 : 4-*dihydropyridine*-3 : 4-*dicarboxylate*, m.p. 54°, is obtained from the methosulphate by $Na_2S_2O_4$. Et_2 2 : 6-trimethyl-1 : 4-dihydropyridine-3 : 4-dicarboxylate (IV) is isomerised at 22° to the 1 : 2-H_2-ester, gives a 1-*Ac* derivative, m.p. 119°, and is hydrogenated to the piperidine *derivative*, b.p. 160—163°/15 mm. (*hydrochloride*, m.p. 198°; *platinichloride*, m.p. 225—226°) (the H_4-derivative could not be isolated after partial hydrogenation), which is hydrolysed by 5N-HCl to 2 : 6-*dimethylpiperidine*-3 : 4-*dicarboxylic acid*, m.p. 234°. N_2O_3 reacts as if (IV) had a 3-CH_2, giving a bimol. *product*, $C_{26}H_{37}O_9N_3$, m.p. 162° (decomp.); *p*-$NO_2{\cdot}C_6H_4{\cdot}CHO$ reacts similarly, but disproportionation also occurs and *Et*$_2$ 3-*p*-*nitrobenzylidene*-2 : 6-*dimethylpiperidine*-3 : 4-*dicarboxylate*, m.p. 196° (decomp.), is isolated. The position of the H in Et 1 : 2-dimethyl-6-methylene-1 : 6-dihydropyridine-3-carboxylate is proved by its reaction with PhNCS without ring closure to give 1 : 6-*dimethyl*-2-β-*anilino*-β-*thionethylidene*-1 : 2-*dihydropyridine*-5-*carboxylate*, m.p. 70°. The 1 : 2-H_2-analogue of (I) reacts with maleic anhydride, but the product is unstable, decomp. into succinic anhydride, and, presumably, the pyridine ester. *Et*$_4$ 1 : 2 : 6 : 1′ : 2′ : 6′-*hexamethyl*-1 : 2 : 1′ : 2′-*tetrahydro*-2 : 2′-*dipyridyl*-3 : 5 : 3′ : 5′-*tetracarboxylate* (V) (prep. from the pyridine methosulphate by Na–Hg and AcOH in H_2O), m.p. 168°, is converted by heating at 180° or by dry hot HCl–MeOH, but not by KOH–EtOH, into *Et*$_4$ 1 : 2 : 6 : 1′ : 2′ : 6′-*hexamethyl*-1 : 2 : 1′ : 2′-*tetrahydro*-4 : 4′-*dipyridyl*-3 : 5 : 3′ : 5′-*tetracarboxylate* (VI), m.p. 193°. Oxidising agents (I, Br, etc.) convert (V) and (VI) into the unimol. pyridine derivatives. When heated, (V) and (VI) dissociate and lose H_2 or disproportionate. H_2–PtO_2 converts the 2 : 6 : 2′ : 6′-Me_4 analogue of (VI) into Et_2 2 : 6-dimethylpiperidine-3 : 5-dicarboxylate (picrate, m.p. 155°), hydrolysed to the corresponding acid (*hydrochloride*, m.p. 151°). H_2–PtO_2 reduces (V) or (VI) to *Et*$_2$ 1 : 2 : 6-*trimethylpiperidine*-3 : 5-*dicarboxylate*, an oil (*picrate*, m.p. 155°), hydrolysed to an *acid*, m.p. ~265° (decomp.) (*mercurichloride*, sinters at 160°, decomp. 167°), but an isomeric ester (*picrate*, m.p. 129°; hydrolysed to the same acid), is obtained from Et_2 2 : 6-dimethylpyridine-3 : 5-dicarboxylate methosulphate. The 2 : 6 : 2′ : 6′-Me_4 analogue of (V) and HCl–MeOH give a mixture of the C_5H_5N ester and *Et*$_2$ 2 : 6-*dimethyl*-2 : 3-*dihydropyridine*-3 : 5-*dicarboxylate*, m.p. 101°. HCl–EtOH and (V) give the 2-CH_2 ester and *Et*$_2$ 2 : 4 : 6-*trimethyl*-2 : 3-*dihydropyridine*-3 : 5-*dicarboxylate*, m.p. 69°. R. S. C.

ω-Trichloro- and ω-dichloro-α-picoline. P. Dyson and D. L. Hammick (J.C.S., 1939, 781—782).—Chlorination of α-picoline in AcOH containing excess of KOAc gives ω-*trichloro*-α-*picoline* (I), b.p. 112—115°/15 mm., which is reduced ($SnCl_2$–HCl–$COMe_2$) to the ω-Cl_2-compound (II), b.p. 90—92°/15—16 mm. Hydrolysis (H_2SO_4) of (I) yields picolinic acid and of (II) affords pyridine-2-aldehyde (2 : 4-*dinitrophenylhydrazone*, m.p. 213°). F. R. S.

[**Nitration of methyl homologues of pyridine.**] E. Plażek (Ber., 1939, **72**, [*B*], 1126; cf. A., 1939, II, 226).—Nitrocollidine has been described previously by van Rijn (A., 1926, 525). H. W.

4-Thiopyridone and derived substances. H. King and L. L. Ware (J.C.S., 1939, 873—877).—4-Pyridone and P_2S_5 give 4-*thiopyridone* (I), m.p. 186° [*picrate*, m.p. 222° (decomp.)], which is methylated (MeI) to 4-*methylthiopyridine*, m.p. 44—45° (*hydriodide*, m.p. 170°; *picrate*, m.p. 245°; *methiodide*, m.p. 177°), oxidised ($KMnO_4$) to 4-*methylsulphonylpyridine*, m.p. 81°. $CH_2Cl{\cdot}CO_2H$ and (I) afford *pyridine*-4-*thioacetic acid*, m.p. 270° (efferv.) (*Na* salt), whilst NaOH–H_2O_2 and (I) form *Na pyridine*-4-*sulphonate* (II) (+2H_2O). PCl_5 and (II) do not give the desired pyridine-4-sulphonyl chloride but, depending on the method of working up, either 1-4′-pyridylpyridine-4-imine, m.p. ~160° [*hydrochloride* (+3·5H_2O), m.p. 100°, anhyd., m.p. 280°; *dinitrate*, m.p. 226° (decomp.); *mononitrate*, m.p. 255° (decomp.); *dipicrate* (+H_2O), m.p. 216°, anhyd., m.p. 227° (decomp.); *diaurichloride*, m.p. 280°], and some *NH*$_4$ *pyridine*-4-*sulphonate*, m.p. 257° (efferv.), or 1 : 4′-pyridyl-4-pyridone [picrate (+H_2O), m.p. 202°; *aurichloride* (+2H_2O), m.p. ~226°] (also isolated, 4-*pyridone picrate*, m.p. 240°, and 4-*chloropyridine picrate*, m.p. 146°). Cl_2 and (I) afford 4-chloropyridine and *di*-4-*pyridyl sulphide*, m.p. 71° (*dipicrate*, m.p. 229°), and Br and (I) yield *di*-4-*pyridyl disulphide*,

m.p. 74—75° (*dipicrate*, m.p. 231°; *zincichloride* (+0·5H_2O), m.p. >300°). F. R. S.

Structure of vitamin-B_6. I. E. T. Stiller, J. C. Keresztesy, and J. R. Stevens. II. S. A. Harris, E. T. Stiller, and K. Folkers (J. Amer. Chem. Soc., 1939, **61**, 1237—1242, 1242—1244).—I. Vitamin-B_6 is shown to be probably 3-hydroxy-2-methyl-4 : 5-di(hydroxymethyl)pyridine (I). -B_6, $C_8H_{11}O_3N$, m.p. 159—160°, sublimes at 140—145°/10^{-4} mm., α 0, contains 3 active H, 1 *C*-Me, no OAlk or NAlk, gives a red $FeCl_3$ colour [cf. 3-hydroxypyridine (II)], is stable to acid and alkali, and is indifferent to HNO_2. It has *pK* (base) $6·2 \times 10^{-10}$, compared with 6·0 and $1·7 \times 10^{-10}$ for (II) and 2-pyridone, respectively. At p_H 10·2 it has absorption max. at 2550 and 3260 A., changing gradually to a single max. at 2920 A. at p_H 4; three derivatives of (II) show exactly similar absorption, but 2- and 4-pyridone behave differently. With CH_2N_2 in MeOH -B_6 gives a Me ether, m.p. 101—102° (*hydrochloride*, m.p. 147—148°) (cf. Kuhn *et al.*, A., 1938, II, 373, m.p. 89·5—90°), oxidised by $Ba(MnO_4)_2$ (4·4 O) in H_2O to 3-*methoxy*-2-*methylpyridine*-4 : 5-*dicarboxylic acid* (III), +H_2O, m.p. variable, ~209—210° (decomp.), and a small amount of a *lactone* (IV), $C_9H_9O_3N$, m.p. 108·5—109·5°. $FeSO_4$ gives no colour with (III) (absence of a 2-CO_2H in the C_5H_5N ring), and gives a phthalein with *m*-$C_6H_4(OH)_2$ [vicinal CO_2H, *i.e.*, CO_2H at positions 4 and 5). The Na salt of (III) with $Ca(OH)_2$–N_2 at 360—370° gives 3-*hydroxy*-α-*picoline* (*picrate*, m.p. 147—148°), the nature of which is shown by absorption max. at 2400 and 3000 A. at p_H 10·5 (OH at $C_{(3)}$), its red $FeCl_3$ colour, its coupling with *p*-$C_6H_4Br·N_2Cl$, and its blue colour with 2 : 6-dichloroquinonechloroimide (absence of substituent *p*- to the OH).

II. The structure of -B_6 is proved by synthesis of the degradation products, (III) and (IV). $CH_2Ac·CO·CH_2·OEt$, $CN·CH_2·CO·NH_2$, and piperidine in 95% EtOH give 3-*cyano*-6-*methyl*-4-*ethoxymethyl*-2-*pyridone*, m.p. 210° (corr.), converted by conc. HCl or, better, 50% H_2SO_4 at 120° into the *lactone*, m.p. >320°, of 6-*methyl*-4-*hydroxymethyl*-2-*pyridone*-3-*carboxylic acid*. With HNO_3 (*d* 1·5) in H_2SO_4 this gives the 5-NO_2-*lactone*, m.p. 279—280° (decomp.), and thence successively (by $POCl_3$–PCl_5) the *lactone*, m.p. 176—178°, of 6-*chloro*-3-*nitro*-4-*hydroxymethyl*-α-*picoline*-5-*carboxylic acid* (V), (by H_2–PtO_2; 3 atm.; AcOH) the *lactone*, m.p. 280—282°, of 6-*chloro*-3-*amino*-4-*hydroxymethyl*-α-*picoline*-5-*carboxylic acid*, (by H_2–Pd–$BaCO_3$; abs. EtOH; 60°/3 atm.) the *lactone*, m.p. 224—226° (*picrate*, m.p. 229—230°), of 3-*amino*-4-*hydroxymethyl*-α-*picoline*-5-*carboxylic acid* [also obtained directly from (V) in EtOH–EtOAc], (by $NaNO_2$–25% H_2SO_4; boiling with more H_2SO_4) the *lactone* (VI), m.p. 272—273°, of 3-*hydroxy*-4-*hydroxymethyl*-α-*picoline*-5-*carboxylic acid*. The *Me ether* of (VI) is (IV); with $Ba(MnO_4)_2$ it gives (III). R. S. C.

Synthesis of vitamin-B_6. S. A. Harris and K. Folkers (J. Amer. Chem. Soc., 1939, **61**, 1245—1247).—3-Cyano-6-methyl-4-ethoxymethyl-2-pyridone (cf. preceding abstract), fuming HNO_3, and a little $CO(NH_2)_2$ in Ac_2O give the 5-NO_2-derivative, m.p. 164—165°, converted by PCl_5–C_6H_6 into 6-*chloro*-3-*nitro*-5-*cyano*-4-*ethoxymethyl*-α-*picoline*, m.p. 47—48°, and thence successively by H_2–Pt in EtOH at 3 atm. into 6-*chloro*-3-*amino*-5-*cyano*-4-*ethoxymethyl*-α-*picoline*, m.p. 146—148°, by H_2–PtO_2–Pd–C in AcOH at 3 atm. into 3-*amino*-5-*aminomethyl*-4-*ethoxymethyl*-α-*picoline* (*dipicrate*, m.p. 184—187°; *dihydrochloride*, m.p. 195°), by $NaNO_2$–2N-H_2SO_4 at 90° into 3-*hydroxy*-5-*hydroxymethyl*-4-*ethoxymethyl*-α-*picoline* (*hydrochloride*, m.p. 123—125°), by 48% HBr into 3-hydroxy-4 : 5-di(bromomethyl)-α-picoline hydrobromide, m.p. 223—224° (decomp. at 219°) (cf. Kuhn *et al.*, A., 1938, II, 373), and by hot H_2O, followed by AgCl, into 3-hydroxy-4 : 5-di(hydroxymethyl)-α-picoline (vitamin-B_6) hydrochloride. R. S. C.

Pyrrolizidine (1-aza*dicyclo*-[0·3·3]-octane). V. Prelog and S. Heimbach (Ber., 1939, **72**, [*B*], 1101—1103).—$OEt·[CH_2]_3·Br$ and $CHNa(CO_2Et)_2$ in boiling abs. EtOH afford Et_2 γ-ethoxypropylmalonate, b.p. 145°/9 mm., converted by NaOEt and $OEt·[CH_2]_3·Br$ into Et_2 αη-*diethoxyheptane*-δδ-*dicarboxylate*, b.p. 185°/8 mm., which is hydrolysed and decarboxylated to αη-*diethoxyheptane*-δ-*carboxylic acid*, b.p. 169°/0·08 mm. This is transformed by NaN_3 and conc. H_2SO_4 in presence of $CHCl_3$ at 50° into δ-*amino*-αη-*diethoxyheptane*, b.p. 132°/11 mm., which with 68% HBr at 100° yields αη-*dibromo*-δ-*aminoheptane hydrobromide*, m.p. 127—128°. Gradual addition of 0·1N-NaOH to this salt in H_2O at 50° followed by removal of any non-*tert.* base with $PhSO_2Cl$ and NaOH leads to *pyrrolizidine* (1-*aza*dicyclo-[0·3·3]-*octane*), b.p. 148° (*picrate*, m.p. 257°; *picrolonate*, m.p. 227°; *platinichloride*, m.p. 205°). H. W.

New synthesis of norlupinane (1-aza*dicyclo*-[0·4·4]-decane). V. Prelog and K. Božičević (Ber., 1939, **72**, [*B*], 1103—1106).—$PhSO_3·[CH_2]_2·OEt$ and $CHNa(CO_2Et)_2$ yield Et_2 β-*ethoxyethylmalonate*, b.p. 152—156°/16 mm., hydrolysed and decarboxylated to $OEt·[CH_2]_3·CO_2H$, the Et ester of which is reduced by Na and EtOH to $OEt·[CH_2]_4·OH$. This is transformed by PBr_3 and C_5H_5N into δ-*ethoxybutyl bromide* (I), b.p. 69°/15 mm., which condenses with $CHNa(CO_2Et)_2$ to Et_2 δ-*ethoxybutylmalonate* (II), b.p. 158°/15 mm., hydrolysed and decarboxylated to ε-*ethoxyhexoic acid*, b.p. 147—148°/15 mm. (I) and (II) in presence of boiling NaOEt–EtOH give Et_2 αι-*diethoxynonane*-εε-*dicarboxylate*, b.p. 202—203°/14 mm., hydrolysed and decarboxylated to αι-*diethoxynonane*-ε-*carboxylic acid*, b.p. 169—170°/0·16 mm. The acid is converted by NaN_3 and conc. H_2SO_4 in presence of $CHCl_3$ at 50—55° into ε-*amino*-αι-*diethoxynonane*, b.p. 162°/15 mm., which is transformed by 69% HBr at 100° into αι-*dibromo*-ε-*aminononane hydrobromide* (corresponding *picrate*, m.p. 118—119°). The salt is transformed by 0·1N-NaOH exclusively into norlupinane *A*, b.p. 69—70°/11 mm., further identified as the picrate, m.p. 196°, picrolonate, m.p. 249°, aurichloride, m.p. 167—168°, and platinichloride, m.p. 333° (decomp.). H. W.

Reaction of chloronitrobenzenes with unilaterally positivised ethylenes. R. Wizinger and M. L. Coenen (J. pr. Chem., 1939, [ii], **153**, 127—159).—It is shown that an ethylene through strong positivisation of $C_{(\alpha)}$ can develop a very marked proton affinity at $C_{(\beta)}$ and hence like the typical

proton acceptors OMe, OH, NH_3 can react with chlorinated nitrobenzenes. Thus 1-methyl-2-methylenedihydroquinoline and picryl chloride (I) in boiling C_6H_6 afford 1-methylquinaldinium chloride and 1-*methyl*-2-2′ : 4′ : 6-*trinitrophenylmethylenequinoline*, decomp. 193°, the yield of which cannot exceed 50% unless a more powerful reagent (*e.g.*, NaOAc in EtOH) is added to combine with the liberated acid. The following are obtained analogously: 5-*methoxy*-1 : 3 : 3-*trimethyl*-2-*trinitrophenylmethyleneindoline*, m.p. 188—190° (decomp.); 1 : 3 : 3-*trimethyl*-2-*trinitrophenylmethyleneindoline*, decomp. 175—177°; 4 : 6-*diphenyl*-2-*trinitrophenylmethylenepyran*, decomp. 212—215°; *trinitrophenylmethylenedinaphthoxanthen*, m.p. 265° (decomp.); αα-*tetraethyldiaminodiphenyl*-β-*trinitrophenylethylene*, m.p. 145—146° (slight decomp.); αα-*tetramethyldiaminodiphenyl*-β-*trinitrophenylethylene*, decomp. 200—202°. The ethylene hydrochlorides are usually methylcarbenium salts. With more feebly positivised ethylenes which do not add HCl under the experimental conditions free HCl is evolved and the change is 1 mol. of ethylene + 1 mol. of (I) → 1 mol. of picrylethylene + HCl. This is the case with 4 : 6-diphenyl-2-methylenepyran and methylenedinaphthoxanthen. Intermediate products of the type $[CRR'\cdot CH_2\cdot C_6H_2(NO_2)_3]^+Cl'$ can be stable only in the presence of a large excess of acid; their formation in solution is readily observed owing to the change in colour. Dimethylaminodiphenylethylene and all more feebly positivised ethylenes, $(OMe\cdot C_6H_4)_2C{:}CH_2$, $OMe\cdot C_6H_4\cdot CPh{:}CH_2$ and $CPh_2{:}CH_2$, do not react with (I) under the chosen experimental conditions. The limit of smooth substitution is with $(NMe_2\cdot C_6H_4)_2C{:}CH_2$. Me at $C_{(\beta)}$ diminishes the reactivity with (I); $(NMe_2\cdot C_6H_4)_2C{:}CHMe$ does not react and $C_6H_4<^{CMe_2}_{NMe}>C{:}CMe_2$ does not yield a primary adduct with (I). 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$ is less reactive than (I) but in boiling C_6H_6 at greater concn. unites with very strongly positivised ethylenes to the following: 1-methyl-2-2′ : 4′-dinitrophenylmethylene-1′ : 2-dihydroquinoline, decomp. 210—212°; 5-*methoxy*-2-*dinitrophenylmethylene*-1 : 3 : 3-*trimethylindoline*, m.p. 148°; 2-dinitrophenylmethylene-1 : 3 : 3-trimethylindoline, m.p. 139—140°. 4 : 6-Diphenyl-2-methylenepyran and 10-methyl-5-methylenedihydroacridine give characteristic colours but not pure products; reaction is not observed with $(NMe_2\cdot C_6H_4)_2C{:}CH_2$ and only a colour with $(NEt_2\cdot C_6H_4)_2C{:}CH_2$. Reactions with *o*- or *p*-$C_6H_4Cl\cdot NO_2$ have not been observed. 1 : 2 : 4-$C_{10}H_5Cl(NO_2)_2$ yields 5-*methoxy*-1 : 3 : 3-*trimethyl*-2-2′ : 4-*dinitro*-1′-*naphthylmethyleneindoline*, m.p. 174°, 1 : 3 : 3-*trimethyl*-2-2′ : 4′-*dinitro*-1′-*naphthylmethyleneindoline*, decomp. ~220°; αα-*tetraethyldiaminodiphenyl*-β-2 : 4-*dinitro*-1-*naphthylethylene*, m.p. 211°, and αα-*tetramethyldiaminodiphenyl*-β-2 : 4-*dinitro*-1-*naphthylethylene*, decomp. 238—240°.

1 : 3 : 4 : 6-$C_6H_2Cl_2(NO_2)_2$ affords 5-*methoxy*-1 : 3 : 3-*trimethyl*-2-3′-*chloro*-4′ : 6′-*dinitrophenylmethyleneindoline*, m.p. 129—130°, 1 : 3 : 3-*trimethyl*-2-3′-*chloro*-4′ : 6′-*dinitrophenylmethyleneindoline*, m.p. 187—188°, and αα-*tetraethyldiaminodiphenyl*-β-3′-*chloro*-4′ : 6′-*dinitrophenylethylene*, m.p. 153—154°. 1 : 2 : 3 : 4 : 6-$C_6HCl_3(NO_2)_2$ gives 5-*methoxy*-1 : 3 : 3-*trimethyl*-2-2′ : 3′-*dichloro*-4′ : 6′-*dinitrophenylmethyleneindoline*, m.p. 150—151°, 1 : 3 : 3-*trimethyl*-2-2′ : 3′-*dichloro*-4′ : 6′-*dinitrophenylmethyleneindoline*, m.p. 133—134°, αα-*tetraethyldiaminodiphenyl*-β-2′ : 3′-*dichloro*-4′ : 6′-*dinitrophenylethylene*, m.p. 179°, and αα-*tetramethyldiaminodiphenyl*-β-2′ : 3′-*dichloro*-4′ : 6′-*dinitrophenylethylene*, m.p. 185° (decomp.). From 1 : 3 : 5 : 2 : 4 : 6-$C_6Cl_3(NO_2)_3$ are derived 1 : 3 : 3-*trimethyl*-2-3′ : 5′-*dichloro*-2′ : 4′ : 6′-*trinitrophenylmethyleneindoline*, m.p. 168°, and αα-*tetraethyldiaminodiphenyl*-β-3′ : 5′-*dichloro*-2′ : 4′ : 6′-*trinitrophenylethylene*, m.p. 191—192°. Only one Cl of the di- and tri-chloronitrobenzenes can be replaced by a C_2H_4 residue. The reactivity of 1 : 2 : 4-$C_{10}H_5Cl(NO_2)_2$ is intermediate between those of $C_6H_3Cl(NO_2)_2$ and $C_6H_2Cl(NO_2)_3$. $C_6H_2Cl_2(NO_2)_2$ and $C_6HCl_3(NO_2)_2$ are more reactive than $C_6H_3Cl(NO_2)_2$, reactivity increasing with the no. of Cl. As judged (approx.) by the rate at which the additive compound with HCl separates from the C_6H_6 solution, the sequences of decreasing activity are $C_6H_2Cl(NO_2)_3$, 1 : 2 : 4-$C_{10}H_5Cl(NO_2)_2$, 1 : 2 : 3 : 4 : 6-$C_6HCl_3(NO_2)_2$, 1 : 3 : 4 : 6-$C_6H_2Cl_2(NO_2)_2$, 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$, and 5-methoxytrimethylmethyleneindoline, trimethylmethyleneindoline, and $(NEt_2\cdot C_6H_4)_2C{:}CH_2$. In every case the reactivity of one-sidedly positivised ethylenes towards aromatic chloronitro-compounds is parallel to the proton affinity of the $C_{(\beta)}$. As with many compounds with electrical contrast between co-ordinatively unsaturated atoms, the colours of solutions of the new compounds depend very greatly on the nature of the solvent. H. W.

Compounds of zinc salts with quinoline.—See A., 1939, I, 380.

Additive power of metallic compounds of 8-hydroxyquinoline for hydrogen chloride. E. THILO and B. DEMANT (Ber., 1939, **72**, [*B*], 1048—1052).—Metallic derivatives of 8-hydroxyquinoline (I) add HCl in such a manner that the no. of mols. of acid is equal to the no. of mols. of (I) contained in the complex increased by the valency of the metallic atom. The following *compounds* are described: $[Mg(C_9H_8ON)_2]Cl_4$; $[Ca(C_9H_8ON)]Cl_4$, also $+2H_2O$; $[Sr(C_9H_8ON)_2]Cl_4$ $+2H_2O$ and $+1H_2O$; $[Ba(C_9H_8ON)_4]Cl_6$; $[Zn(C_9H_8ON)_2]Cl_4$; $[Cd(C_9H_8ON)_2]Cl_4$ (also $+1H_2O$); $[Hg(C_9H_8ON)_2]Cl_4$; $[Pb(C_9H_8ON)_2]Cl_4$, also *mono*- and *di*-*hydrate*; $[Co(C_9H_8ON)_2]Cl_4$ also *tri*- and *mono*-*hydrate*; $[Ni(C_9H_8ON)_2]Cl_4,2H_2O$; $[Cu(C_9H_8ON)_2]Cl_4$; $[Fe(C_9H_8ON)_3]Cl_6$; $[Al(C_9H_8ON)_3]Cl_6$. H. W.

Nitrogen compounds from petroleum distillates. XII. Fractional sulphiting of bases and fractional degassing of their hydrogen sulphites. XIII. Isolation of four quinoline homologues and two aromatic bases of probable trinuclear cyclic structure. W. N. AXE and J. R. BAILEY (J. Amer. Chem. Soc., 1938, **60**, 3025—3028, 3028—3032; cf. A., 1938, II, 245).—XII. Fractional formation and thermal decomp. of the H sulphites of bases from kerosene are described. Bases, otherwise inseparable, are thus separated. Unless "degassing," *i.e.*, the decomp. of the salts by heating in vac., is effected in N_2 or CO_2 etc., some oxidation to sulphates occurs.

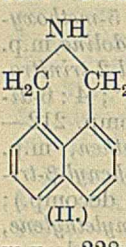
XIII. The fractionation described above depends on the ionisation consts. of the bases. The fraction,

b.p. about 295°, of bases from kerosene yields by the more usual methods *bases*, (I) $C_{13}H_{15}N$ and (II) $C_{14}H_{17}N$. The sulphite procedure yields 2 : 3-*dimethyl*-8-n-*propylquinoline* (III), m.p. 14·5—15·5°, b.p. 299·5° [different from (II); *nitrate*, m.p. 169° (decomp.); *picrate*, m.p. 198—199°; *H sulphate*, m.p. 212—212·5°; *hydrochloride*, m.p. 161—162°; $ZnCl_2$ double *salt*, m.p. 193—194°], oxidised by $K_2Cr_2O_7$–H_2SO_4 to 2 : 3-*dimethylquinoline*-8-*carboxylic acid*, m.p. 201—202° (with soda-lime yields 2 : 3-dimethylquinoline), and synthesised by the reactions: $CH_2Ph{\cdot}MgCl + Me_2SO_4 \rightarrow PhPr^a \rightarrow$ (40°) 1 : 2 : 4-$C_6H_3Pr^a(NO_2)_2 \rightarrow [+(NH_4)_2S]$ 2 : 1 : 4-$NO_2{\cdot}C_6H_3Pr^a{\cdot}NH_2 \rightarrow o$-$C_6H_4Pr^a{\cdot}NO_2 \rightarrow (H_2$–Ni) o-$C_6H_4Pr^a{\cdot}NH_2$ (IV); (IV) + CHMe:CMe·CHO (+hot, conc. HCl) → (III). The undecomposed residue contains [as *H sulphate*, m.p. 298° (decomp.)] 2 : 3 : 4 : 8-*tetramethylquinoline*, m.p. 77—78° [different from (I); *picrate*, m.p. 240° (decomp.); *hydrochloride*, m.p. 252—253° (decomp.); *nitrate*, m.p. 184·5° (decomp.); *zincichloride*, m.p. 266—267°; *phthalone*, m.p. 264°], oxidised to 2 : 3 : 4-*trimethylquinoline*-8-*carboxylic acid*, m.p. 233·5—234° (with soda-lime at ⩾360° gives 2 : 3 : 4-trimethylquinoline), and synthesised from o-$C_6H_4Me{\cdot}NH_2$, $CHMeAc_2$, and conc. HCl. The bases, b.p. 340°, from transformer oil yield, by way of the picrates and H sulphates, a *base*, $C_{15}H_{13}N$, m.p. 83·5—84° [*picrate*, m.p. 228·5—229·5°; *H sulphate*, m.p. 265—267° (decomp.)], and then by the sulphite procedure a *base*, $C_{16}H_{15}N$, m.p. 86—87° (*picrate*, m.p. 338—339°; *nitrate*); these bases are probably acridines or naphthoquinolines. R. S. C.

Nitrogen compounds in petroleum distillates. XIV. Isolation of 2 : 4-dimethyl-8-ethylquinoline from the kerosene distillate of California petroleum. W. N. Axe (J. Amer. Chem. Soc., 1939, 61, 1017—1019).—2 : 4-*Dimethyl*-8-*ethyl*- (I) and -8-n-*propyl*-*quinoline* are isolated from California petroleum. Common quinoline bases isolated from petroleum are alkylated in positions 2, 3, and 8, those alkylated in positions 2, 4, and 8 being rare. (I), b.p. 288°/747 mm. (*picrate*, m.p. 165—166°; *zincichloride*, m.p. 261—262°), and $K_2Cr_2O_7$–H_2SO_4–H_2O give 2 : 4-dimethylquinoline-8-carboxylic acid, m.p. 241—242° (decomp.), also obtained from 2 : 4 : 8-trimethylquinoline. o-$C_6H_4Et{\cdot}NH_2$ (modified purification) and CH_2Ac_2 at 100° yield (I). R. S. C.

Mechanisation of decarboxylation. II. Production of cyanide-like ions from α-picolinic, quinaldinic, and *iso*quinaldinic acids. M. R. F. Ashworth, R. P. Daffern, and D. L. Hammick (J.C.S., 1939, 809—812).—When the above acids are decarboxylated in the presence of aldehydes and ketones, carbinols containing the pyridyl, quinolyl, and *iso*quinolyl radicals are obtained. This reaction is sp. for these acids and it is suggested that the reason for this is that the anion radicals produced when the acids lose CO_2 contain $[\dot{N}{=}\dot{C}]^-$, which when added to CO would be analogous to cyanohydrin formation. Chelation between the acidic and basic centres is suggested to explain the readiness with which α-imino-carboxylic acids lose CO_2 and the action of carboxylase. The following are described: *diphenyl*-2-*quinolyl*-, m.p. 189°, phenyl-2-pyridyl- (*phenylurethane*, m.p. 143·5°), phenyl-2-pyridylmethyl- (*picrate*, m.p. 176°; *phenylurethane*, m.p. 151°), diphenyl-2-pyridyl-, and p-*methoxyphenyl*-2-*pyridylcarbinol*, m.p. 131·5° (*phenylurethane*, m.p. 145°). F. R. S.

Electro-reduction of naphthalimide. E. Späth, F. Kuffner, and F. Kittel (Ber., 1939, 72, [*B*], 1109—1112; cf. A., 1929, 194).—Electrolytic reduction of naphthalimide (I) at a Pb cathode gives 1 : 2 : 3 : 6-*tetrahydronaphthalino*-1′ : 9′ : 8′-3 : 4 : 5-*pyridine* (II), m.p. 102—103° (vac.) (p-*nitrobenzoyl* derivative, m.p. 171·5°), oxidised by $KMnO_4$ in acid solution to (I). This is converted by Pd sponge at 200° into 4 : 5-*trimethyleneiso*quinoline, m.p. 47·5—48° (*picrate*, m.p. 228—230°), which does not react with p-$NO_2{\cdot}C_6H_4{\cdot}COCl$ and gives a *methiodide*, m.p. 204—205° (vac.), oxidised by alkaline $K_3Fe(CN)_6$ to 2-*methyl*isoquinolone, m.p. 105—106°; it gives a characteristic additive product, m.p. 134—135° (vac.), with $HICl_2$. H. W.



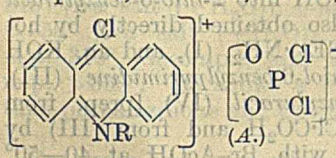
(II.)

Bromination of some 4-quinolones. H. P. W. Huggill and S. G. P. Plant (J.C.S., 1939, 784—787).—1 : 2 : 3 : 4-Tetrahydroacridone (I) and Br (1 mol.) give 7-bromotetrahydroacridone, also obtained from 5-bromoanthranilic acid and *cyclo*hexanone, and converted ($POCl_3$–PCl_5) into 5-*chloro*-7-*bromotetrahydroacridine*, m.p. 99°; the bromination also yields other products containing reactive Br, from which a *compound*, m.p. 152°, can be prepared by the action of $POCl_3$–PCl_5. Further bromination of (I) affords 7 : 9-*dibromotetrahydroacridone*, m.p. 287° (also obtained from 3 : 5-dibromoanthranilic acid), which with $POCl_3$–PCl_5 gives 5-*chloro*-7 : 9-*dibromotetrahydroacridine*, m.p. 170—173°. 7 : 9-Dimethyltetrahydroacridone, converted ($POCl_3$–PCl_5) into 5-*chloro*-7 : 9-*dimethyltetrahydroacridine*, m.p. 94°, is brominated to a *Br*-derivative, m.p. 196° (decomp.), which gives a pyridinium salt, and suggests that the Br is attached to the reduced ring. 2 : 6 : 8-Trimethyl-4-quinolone yields a *Br*-derivative, m.p. 272—274°, unchanged by C_5H_5N, and forming 4-*chloro*-?-*bromo*-2 : 6 : 8-*trimethylquinoline*, m.p. 107°. 1 : 3 : 4-$C_6H_3Me_2{\cdot}NH_2$ and $CH_2Ac{\cdot}CO_2Et$, followed by MeI, give 2 : 3 : 6 : 8-*tetramethyl*-4-*quinolone*, m.p. 300°, converted into 4-*chloro*-2 : 3 : 6 : 8-*tetramethylquinoline*, m.p. 89°. Anthranilic acid with 1-keto-1 : 2 : 3 : 4-tetrahydrocarbazole, and *cyclo*hexane-1 : 2-dione and -1 : 4-dione affords respectively 5-*keto*-5 : 6 : 7 : 10-*tetrahydroacrindoline*, m.p. >360°, N-2′-*keto*cyclo*hexylideneanthranilic acid*, m.p. 172°, and the *di*-*o*-*carboxyanil* of *cyclo*hexane-1 : 4-dione, m.p. 261° (decomp.). F. R. S.

Acridine. XXI. Quaternary 10-methoxyacridinium bases. K. Lehmstedt and F. Dostal (Ber., 1939, 72, [*B*], 1071—1074).—10-Methoxyacridone is converted by LiPh in C_6H_6 followed by H_2O into 5-*hydroxy*-10-*methoxy*-5-*phenyl*-5 : 10-*dihydroacridine* (I), decomp. 141—142°, which passes at ~250° into CH_2O and 5-phenylacridine. (I) is converted by crystallisation from MeOH into 5 : 10-*dimethoxy*-5-*phenyl*-5 : 10-*dihydroacridine*, decomp. 150—151°.

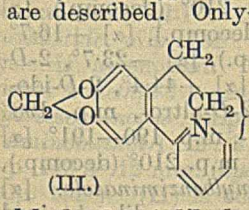
When the solution of (I) in HCl is treated with NH_3 5-*amino*-10-*methoxy*-5-*phenyl*-5 : 10-*dihydroacridine*, decomp. 116—117·5°, is pptd.; this is transformed by boiling EtOH into 10-*methoxy*-5-*ethoxy*-5-*phenyl*-5 : 10-*dihydroacridine*, m.p. 180·5—181·5° (decomp.), also obtained from (I) and boiling EtOH. Prolonged boiling of (I) with 2N-HCl followed by pptn. with KOH gives 5-*phenylacridine* 10-*oxide*, decomp. 228—230°, and 5-amino-5-hydroxy-10-methoxy-5 : 10-dihydroacridine, decomp. 115—117°. H. W.

Action of phosphoryl chloride and oxalyl chloride on acridones. K. Gleu, S. Nitzsche, and A. Schubert (Ber., 1939, **72**, [*B*], 1093—1099).—*N*-Arylanthranilic acids are transformed by $POCl_3$ into acridones, converted by further action of the reagent into 5-chloroacridines. The formation of the last-named is preceded by that of additive *compounds* (1 : 1) of acridone and $POCl_3$ (the parent compound, its 2-Me, 10-Me, and 10-Ph derivatives are described). The structure *A* is assigned to these compounds since they have salt-like character, being readily sol. in cold H_2O but insol. in org. media; those without substituent at (10) are quantitatively hydrolysed to the 5-chloroacridines whilst those with such substituent are essentially similar in behaviour but can yield only 10-substituted acridones. Analogy is traced between $H(PO_2Cl_2)$ and $HClO_4$. The supposed acridone dichlorides obtained by the action of $POCl_3 + PCl_5$ on 10-substituted acridones are compounds of structure (*A*). For the prep. of the dichlorides PCl_5 is unsuitable since $POCl_3$ is a product of the change. Acridones are transformed by oxalyl chloride (free from HCl) in hot xylene into acridone dichlorides (10-Me and 10-Ph *compounds* described); evidence of the formation of an intermediate, additive compound is not obtained, probably owing to the instability of the anion $[O_2C{\cdot}COCl]^-$ which immediately decomposes into $CO + CO_2 + Cl^-$. H. W.



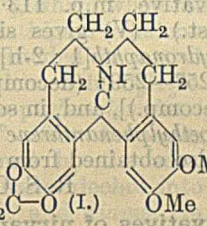
(*A*.)

Synthesis of hetero-rings containing nitrogen. XV. Oxidation of β-phenylethyl-pyridinium and -quinolium salts. S. Sugasawa and N. Sugimoto (Ber., 1939, **72**, [*B*], 977—979).—1-β-Phenylethylpyridinium bromide is oxidised to 1-β-*phenylethylpyrid*-2-*one*, m.p. 87°. Oxidation of 1-β-3′ : 4′-dimethoxyphenylethylpyridinium bromide could not be effected with $K_3Fe(CN)_6$ in presence of aq. NH_3, Na_2CO_3, Na_3PO_4, or NaOAc, with Ag_2O or $KMnO_4$, or in presence of C_6H_6. 1-β-3′ : 4′-*Methylenedioxyphenylethylpyrid*-2-*one* (I), m.p. 148°, 1-β-4′-*methoxyphenylethylquinol*-2-*one*, m.p. 110·5°, and 1-β-3′ : 4′-*methylenedioxyphenylethylquinol*-2-*one* (II), m.p. 138°, are described. Only brown products insol. in C_6H_6 are given by 6 : 7-dimethoxy-1-β-3 : 4′-dimethoxyphenylethylquinolinium bromide. Successive treatments of (I) with $POCl_3$ in xylene at 135—140° and HI lead to 4′ : 5′-*methylenedioxy*-9 : 10-*dehydro*-3 : 4-*dihydro*-1′ : 2′-1 : 2-*benzoquinolizinium iodide* [(III), X = I], m.p. 191°, hydrogenated (Adams) to a non-cryst. *base*, $C_{14}H_{17}O_2N$ [*hydriodide*, m.p. 198°; *hydrochloride*, m.p. 213°; *methiodide*, m.p. 164° (slight decomp.)]. Similarly, (II) is transformed into 4′ : 5′-*methylenedioxy*-9 : 10-*dehydro*-3 : 4-*dihydro*-1′ : 2′-1 : 2-1″ : 2″-5 : 6-*dibenzoquinolizinium iodide*, m.p. 254° (decomp.). The corresponding hydrogenated base and its derivatives are not cryst.; the very hygroscopic *hydrochloride* has m.p. ~227°. H. W.



(III.)

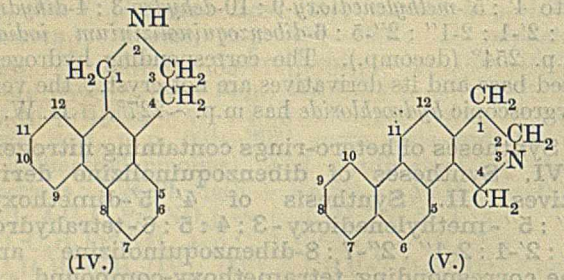
Syntheses of hetero-rings containing nitrogen. XVI. Syntheses of dibenzoquinolizine derivatives. II. Synthesis of 4′ : 5′-dimethoxy-4″ : 5″-methylenedioxy-3 : 4 : 5 : 6-tetrahydro-1′ : 2′-1 : 2-1″ : 2″-7 : 8-tetrahydroisoquinolizine and the corresponding tetramethoxy-compound. S. Sugasawa and K. Kakemi (Ber., 1939, **72**, [*B*], 980—984).—Oxidation of 6 : 7-dimethoxy-3 : 4-dihydro*iso*quinoline methiodide with aq. $K_3Fe(CN)_6$ gives 6 : 7-dimethoxy-2-methyl-3 : 4-dihydro*iso*quinol-1-one, m.p. 125—126°. 6 : 7-Dimethoxy-3 : 4-dihydro*iso*quinoline and β-3 : 4-methylenedioxyphenylethyl bromide give 6 : 7-*dimethoxy*-2-β-3′ : 4′-*methylenedioxyphenylethyl*-3 : 4-*dihydro*isoquinolinium *bromide*, m.p. 187—188°, converted by oxidation with $K_3Fe(CN)_6$ in alkaline solution in presence of C_6H_6, followed by treatment with $POCl_3$ at 100° and then with NaI, into 4′ : 5′-*dimethoxy*-4″ : 5″-*methylenedioxy*-9 : 10-*dehydro*-3 : 4 : 5 : 6-*tetrahydro*-1′ : 2′-1 : 2-1″ : 2″-7 : 8-*dibenzoquinolizinium iodide* (I), m.p. 188—189°; the corresponding *chloride*, m.p. 150°, is reduced to 4 : 5′-*dimethoxy*-4″ : 5″-*methylenedioxy*-3 : 4 : 5 : 6-*tetrahydro*-1′ : 2′-1 : 2-1″ : 2″-7 : 8-*dibenzoquinolizine* (+0·5EtOH), m.p. 101—102° [*hydrochloride* (+EtOH), m.p. 219—220°; *hydriodide*, m.p. 209° (decomp.); *methiodide*, m.p. 199—200°; *picrate*, decomp. 176—177°]; the free base is dehydrogenated by I to (I). Similarly, 6 : 7-*dimethoxy*-2-β-3′ : 4′-*dimethoxyphenylethyl*-3 : 4-*dihydro*isoquinolinium bromide, m.p. 192°, is converted into 4′ : 5′ : 4″ : 5′-*tetramethoxy*-9 : 10-*dehydro*-3 : 4 : 5 : 6-*tetrahydro*-1′ : 2′-1 : 2-1″ : 2″-7 : 8-*dibenzoquinolizinium iodide* (+0·5H_2O), m.p. 195°, and thence into 4′ : 5′ : 4″ : 5″-*tetramethoxy*-3 : 4 : 5 : 6-*tetrahydro*-1′ : 2′-1 : 2-1″ : 2″-7 : 8-*dibenzoquinolizine*, m.p. 116° [*hydrochloride* (+0·5EtOH), m.p. 236—237°; *hydriodide*, m.p. 207°]. H. W.



(I.)

Phenanthrene series. XXII. Derivatives of dibenz*iso*quinoline and naphth*iso*quinoline. E. Mosettig and (Miss) E. L. May (J. Amer. Chem. Soc., 1938, **60**, 2962—2966; cf. A., 1938, II, 510).—The appropriate phenanthraldehyde, $MeNO_2$, and KOH–EtOH give 9- (I), m.p. 173—173·5° (corr.), 3- (II), m.p. 180—180·5° (corr.), and 2-β-*nitrovinylphenanthrene*, m.p. 134·5—137° (corr.), reduced electrolytically to 9-, m.p. 307—309° (decomp.) (*CHO*-derivative, m.p. 111—112°), 3- (III), m.p. 254—256° [*CHO*-derivative, m.p. 122—124° (corr.)], and 2-β-*aminoethylphenanthrene*, m.p. 317—318° (*picrate*, m.p. 225—226°). 40% aq. CH_2O converts the amines into 1 : 2 : 3 : 4-*tetrahydrodibenz*[f : h]*isoquinoline* (IV), m.p. 223—225° [*hydrochloride*, m.p. 304—306° (de-

comp.)], and (?) 1 : 2 : 3 : 4-*tetrahydronaphtha*[1 : 2-h]iso*quinoline* (V) [*hydrochloride*, m.p. 313—315° (decomp.)], but (III) was unchanged by CH_2O. With NaOMe–MeOH (I) and (II) give 9-, m.p. 134—134·5°



(IV.) (V.)

(corr.), and 3-β-*nitro*-α-*methoxyethylphenanthrene*, m.p. 102—104°, hydrogenated (PtO_2) in EtOH to 9-, m.p. 252—253° (decomp.) [*picrate*, m.p. 215—217° (decomp.); *CHO*-, m.p. 138—140° (corr.), and *Bz* derivative, m.p. 147·5—148·5° (corr.)], and 3-β-*amino*-α-*ethoxyethylphenanthrene* [*hydrochloride*, m.p. 232—233° (decomp.)], which resisted cyclisation by all methods, as also do all the CHO-derivatives. With MeI–KOH in $COMe_2$ (IV) gives the *methiodide*, m.p. 268—270°, of its 2-Me derivative, and thence at 200—220°/high vac. the 2-*Me* derivative, m.p. 113·5—114° (corr.) (*hydrochloride*, cryst.). (V) gives similarly 3-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphth*[1 : 2-h]iso*quinoline* [*hydrochloride*, m.p. 257—259° (decomp.); *methiodide*, m.p. 244·5—246° (decomp.)], and, in some experiments, 2-β-*dimethylaminoethylphenanthrene hydrochloride*, m.p. 247—249°, also obtained from the $NH_2{\cdot}[CH_2]_2$ compound. R. S. C.

Synthesis of coloured derivatives of nirvanol. J. J. Spurlock with H. R. Henze (J. Amer. Chem. Soc., 1938, **60**, 3005—3007).—5-Phenyl-5-ethylhydantoin is nitrated and then hydrogenated, but the isomerides produced resist separation. *m*-$NO_2{\cdot}C_6H_4{\cdot}COEt$, m.p. 99—100°, KCN, and $(NH_4)_2CO_3$ in EtOH give 5-m-*nitrophenyl*-5-*ethylhydantoin*, m.p. 219—220°, reduced (H_2–PtO_2) in $COMe_2$ to the NH_2-compound, $+H_2O$, double m.p. 82—83° and 165—166°, which is diazotised and coupled with β-$C_{10}H_7{\cdot}OH$, β-$C_{10}H_7{\cdot}NH_2$, $NPhMe_2$, and G salt, yielding *dyes*, m.p. 276—277° (decomp.), 247—248°, 233—235°, and a *Ba* salt, $+8H_2O$, respectively. M.p. are corr. R. S. C.

5-Alkyl-5-crotylbarbituric acids. W. J. Doran and H. A. Shonle (J. Amer. Chem. Soc., 1938, **60**, 2880—2882).—The following are prepared: 5-*ethyl*- (? cis–trans-*isomerides*), m.p. 108—110° and 120—121°, -n-*propyl*-, m.p. 160—161°, -*iso*propyl-, m.p. 144—145° (lit., 137—138°), -n-, m.p. 142—143°, -sec.-, m.p. 130—131°, and -*iso*-butyl-, m.p. 126—127° (lit., 115°), -α-*methyl*-n-*butyl*-, m.p. (anhyd.) 110—113° and ($+H_2O$) 88—90°, and -iso*amyl*-, m.p. 147—148°, -5-*crotylbarbituric acid*, which have a very short anæsthetic effect. 5-*Ethyl*-5-α-*methylallylbarbituric acid*, m.p. 146·5—148°, has a slightly longer effect. 5-n-*Butyl*-5-*crotylthiolbarbituric acid*, m.p. 238—239°, is only convulsant. R. S. C.

Phenyl alkyl nitrogen substitution. Reactivity in the barbituric acid series. D. Nightingale and R. G. Taylor (J. Amer. Chem. Soc., 1939, **61**, 1015—1017).—5 : 5-*Dibromo*-1-*phenyl*-3-*methyl*- (I) and -3-n-*butyl*-*barbituric acid* (II) resemble the 1 : 3-Ph_2 derivatives in not reacting with amines, $CS(NH_2)_2$, or KSCN. $CH_2(CO_2H)_2$ with N-*phenyl*-N′-n-*butylcarbamide* (prep. from PhNCO and NH_2Bu^a in dry Et_2O), m.p. 135°, $NHPh{\cdot}CO{\cdot}NHMe$, or *o*-$C_6H_4Me{\cdot}NH{\cdot}CO{\cdot}NH_2$ in Ac_2O gives (II), m.p. 96—98° (5-*anilinomethylene*, m.p. 146—148°, and 5 : 5-Br_2-derivative, m.p. 108—110°), (I) (5-*anilinomethylene*, m.p. 170°, and 5 : 5-Br_2-derivative, m.p. 161°), and 1-o-*tolylbarbituric acid*, m.p. 181°. 5 : 5-*Dibromo*-1 : 3-*di*-o-*tolylbarbituric acid* melts at 190—191°. R. S. C.

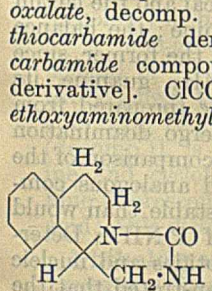
Pyrimidines. CLIX. Synthesis of 6- and 5-benzyluracils. T. B. Johnson and J. C. Ambelang (J. Amer. Chem. Soc., 1938, **60**, 2941—2944; cf. A., 1938, II, 379).—$CH_2Ph{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$ (I) and $CS(NH_2)_2$ with a little HCl give (?) the ureide, converted by hot KOH–EtOH into 2-*thio*-6-*benzyluracil* (II), m.p. 222—223°, also obtained directly by hot NaOEt–EtOH. $NH{:}C(SEt){\cdot}NH_2$, (I), and aq. KOH give 4-*hydroxy*-2-*ethylthiol*-6-*benzylpyrimidine* (III), m.p. 128—129°. 6-*Benzyluracil* (IV) [prep. from (II) by 10% aq. $CH_2Cl{\cdot}CO_2H$ and from (III) by HCl], m.p. 261—262°, with Br–AcOH at 40—50° gives the 5-*Br*-derivative (V), m.p. 230—232° (gives BzOH by $KMnO_4$), and with Cl_2–MeOH gives 5 : 5-*dichloro*-2 : 4-*diketo*-6-*methoxy*-6-*benzylhexahydropyrimidine*, m.p. 157—159° (decomp.) (160—162°), unchanged by C_5H_5N, but converted by HBr–AcOH into 5-*chloro*-6-*benzyluracil*, m.p. 266—267°, which is also obtained in poor yield from (IV) and Cl_2 in 10% AcOH. Attempts to cyclise (V) by $AlCl_3$ failed. $Ph{\cdot}[CH_2]_2{\cdot}CO_2Et$ (prep. by H_2–Raney Ni) and HCO_2Et with Na in Et_2O give the HCO-derivative, the Na salt of which with $CS(NH_2)_2$ in EtOH gives 2-*thio*-5-*benzyluracil*, m.p. 210—211°. With 10% $CH_2Cl{\cdot}CO_2H$ this yields 5-*benzyluracil* (VI), m.p. 294—295°, converted by Cl_2–MeOH into 5-*chloro*-2 : 4-*diketo*-6-*methoxy*-5-*benzylhexahydropyrimidine*, double m.p. 217—218° and 232—234° [converted by HBr–AcOH into (VI)]. R. S. C.

Preparation of *L*-tartaric acid from racemic tartaric acid through resolution by a substituted benziminazole base. W. T. Haskins and C. S. Hudson (J. Amer. Chem. Soc., 1939, **61**, 1266—1268).—Aldonic acids or their lactones with *o*-$C_6H_4(NH_2)_2$ and 1—2 mols. of HCl in hot H_2O give (usually) 52—75% yields of 2-substituted benziminazoles. Thus are obtained 2-*D*-gluco-*D*-gulo- (I), m.p. 215° (decomp.), [α] +14·3°, 2-*D*-gluco-*D*-ido-, m.p. 192° (decomp.), [α] −27·6°, 2-*D*-manno-*D*-gala-, m.p. 241° (decomp.), [α] +49·5°, and 2-*D*-gala-*L*-manno-, m.p. 218° (decomp.), [α] +18·5°, -*hexahydroxyhexylbenziminazole*, 2-*D*-gluco-, m.p. 210° (decomp.), [α] +8·9°, 2-*D*-gulo-, m.p. 201° (decomp.), [α] +16·7°, 2-*D*-manno-, m.p. 224° (decomp.), [α] −23·7°, 2-*D*-galacto-, m.p. 246° (decomp.), [α] +44·4°, 2-*D*-ido-, m.p. 154—156°, [α] −19·2°, 2-*D*-altro-, m.p. 198° (decomp.), [α] −48·1°, 2-*D*-talo-, m.p. 190—191°, [α] −23·0°, and *L*-mannomethylo-, m.p. 210° (decomp.), [α] +29·1°, -*pentahydroxy*-n-*amylbenziminazole*. [α] are $[\alpha]_D^{20}$ in 0·1N-HCl. *L*-(−)- is very readily obtained

from *dl*-tartaric acid by means of its *salt*, $+2H_2O$ (lost at 78°/vac.), m.p. 118—125°, $[\alpha]_D$ −0·5° in H_2O. M.p. are corr. R. S. C.

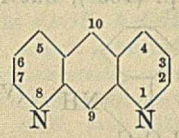
Chemiluminescent organic compounds. VII. Substituted phthalaz-1 : 4-diones. Effect of substituents on the luminescent power. H. D. K. Drew and R. F. Garwood (J.C.S., 1939, 836—837).—Observations on new diones tend to confirm the conclusion previously reached (cf. Drew *et al.*, A., 1937, II, 118). In the halogenated diones, the lighter is the halogen the more its presence enhances the luminescent power. 3-*Bromophthalimide*, m.p. 260°, prepared from the corresponding NH_2-compound, with N_2H_4 gives 5-*bromophthalaz*-1 : 4-*dione*, m.p. 322°. 6-*Bromo*-, m.p. 343°, and 6-*iodo-phthalaz*-1 : 4-*dione*, m.p. 345°, are similarly prepared. The following are prepared from N_2H_4 and the appropriate anhydride: 5-*methylphthalaz*- (I), m.p. 340°, ββ-*naphthalaz*-, m.p. 345° [*Na* salt $(+H_2O)$], 6-*nitro*-ββ-*naphthalaz*-, m.p. >350° [*Na* salt $(+H_2O)$], 6-*amino*-ββ-*naphthalaz*-, m.p. 320° (decomp.), and αβ-*naphthalaz*-1 : 4-*dione*, m.p. >360°. (I) shows a lower luminescent power than phthalazdione and this effect is anomalous. F. R. S.

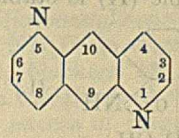
Catalytic hydrogenation of 1-cyano-2-benzoyl-1 : 2-dihydro*iso*quinoline (Reissert's substance from *iso*quinoline). H. Rupe and W. Frey (Helv. Chim. Acta, 1939, **22**, 673—683).—Addition of BzCl to a suspension of *iso*quinoline in 10% aq. KCN gives 1-cyano-2-benzoyl-1 : 2-dihydro*iso*quinoline, m.p. 128° (Reissert's substance from *iso*quinoline), reduced (Ni–EtOAc) by H_2 at 90°/70 atm. to 1-*benzamidomethyl*-1 : 2 : 3 : 4-*tetrahydroisoquinoline* (I), m.p. 125° (*NO*-derivative, m.p. 127°, reduced by Zn dust in AcOH–EtOH to the *hydrazino*-compound, m.p. 141°, in poor yield; *Bz*, m.p. 144°, and *Ac*, m.p. 201°, derivatives). This is slowly hydrolysed by boiling 20% HCl to 1-*aminomethyl*-1 : 2 : 3 : 4-*tetrahydroisoquinoline* (II), b.p. 153°/12 mm. [*hydrochloride* $(+2H_2O)$, decomp. 281°; *perchlorate*, m.p. 117°; *picrate*, m.p. 186°; *citrate* $(+2H_2O)$, m.p. 166°; *oxalate*, decomp. 198°; *tartrate*, m.p. 125°; *phenylthiocarbamide* derivative, $C_{24}H_{24}N_4S_2$, m.p. 188°; *carbamide* compound, $C_{11}H_{15}ON_3$, m.p. 173°; Ac_2 derivative]. $ClCO_2Et$ and (II) in Et_2O afford 1-*carbethoxyaminomethyl*-1 : 2 : 3 : 4-*tetrahydroisoquinoline*, b.p. 166°/12 mm., and the *iminazolone* (III), m.p. 148°, also obtained readily by use of $COCl_2$; in the presence of C_5H_5N at room temp. the product is *Et* 1-*carbethoxyamino*-1 : 2 : 3 : 4-*tetrahydroisoquinoline*-2-*carboxylate*, b.p. 180°/12 mm., m.p. 103°. (I) is transformed by MeI in MeOH at 100° into (?) 2-*methyl*-1-*benzamidomethyl*-1 : 2 : 3 : 4-*tetrahydroisoquinoline methiodide*, m.p. 152°, which loses MeI when hydrolysis is attempted. With boiling MeI–MeOH (I) yields 2-*methyl*-1-*benzamidomethyl*-1 : 2 : 3 : 4-*tetrahydroisoquinoline*, m.p. 122°, hydrolysed to 2-*methyl*-1-*aminomethyl*-1 : 2 : 3 : 4-*tetrahydroisoquinoline* (IV), b.p. 143·5°/12 mm. (*hydrochloride*, m.p. 256°; *picrate*, m.p. 192°). (II) is converted by MeI and KOH in boiling MeOH into 2-*methyl*-1-*dimethylaminomethyl*-1 : 2 : 3 : 4-*tetrahydroisoquinoline methiodide*, m.p. 199°, (IV), and 2-*methyl*-1-*dimethylaminomethyl*-1 : 2 : 3 : 4-*tetrahydroisoquinoline*, b.p. 135°/12 mm. (*picrate*, m.p. 202°). Similar results are obtained when methylation is effected under pressure. H. W.



(III.)

Heterocyclic compounds containing nitrogen. XLII. Linear and angular benzodipyridines. VI. 1 : 5-Anthrazoline and 4 : 5-phenanthroline. P. Ruggli and E. Preiswerk (Helv. Chim. Acta, 1939, **22**, 478—495; cf. A., 1939, II, 231).—The

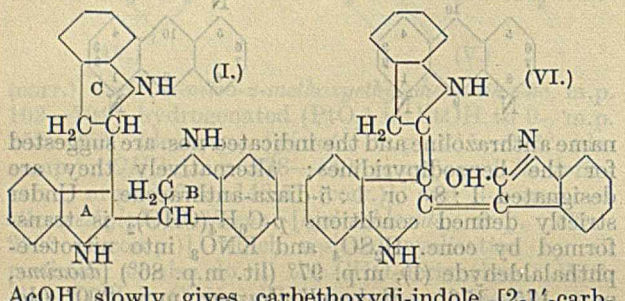




name anthrazoline and the indicated nos. are suggested for the benzodipyridines; alternatively they are designated 1 : 8- or 1 : 5-diaza-anthracene. Under strictly defined conditions *p*-$C_6H_4(CHO)_2$ is transformed by conc. H_2SO_4 and KNO_3 into nitroterephthalaldehyde (I), m.p. 97° (lit. m.p. 86°) [*dioxime*, m.p. 175—176°; *diphenylhydrazone*, m.p. 200° (decomp.) after softening at 185°; *dianil*, m.p. 133—134°], which when reduced chemically or catalytically gives higher condensation products which could not be divided or acetylated. $CH_2(CO_2H)_2$ and (I) are condensed in C_5H_5N at 40—50° and then at 90° to *nitro*-p-*phenylenediacrylic acid* (II), decomp. 300—305° after becoming discoloured at ~290°, transformed by the successive action of PCl_5 and the requisite alcohol into the *Me*$_2$, m.p. 166°, *Et*$_2$, m.p. 125°, and *diamyl*, m.p. 93—94°, ester. Hydrogenation (Raney Ni in EtOH–MeOH–EtOAc–H_2O) of (II) at room temp. affords *amino*-p-*phenylenediacrylic acid*, softens at 360° (decomp.) after becoming discoloured at 280° [Ac_2 derivative, softens at ~310—315° (decomp.) after darkening at ~310—315°; *Me*$_2$ ester, m.p. 159°, and its *Ac* derivative, m.p. 168°; *Et*$_2$ ester, m.p. 178°]. This is converted by boiling conc. HCl into 2-*keto*-1 : 2-*dihydroquinoline*-7-*acrylic acid* (III), which becomes brown at 330—335° (*Et* ester, m.p. 209—210°), converted by the successive action of PCl_5 and MeOH into *Me* 2-*methoxyquinoline*-7-*acrylate*, m.p. 193—195°. Hydrogenation (Raney Ni in MeOH–EtOH–EtOAc–H_2O) of (III) 75° leads to 2-*keto*-1 : 2 : 3 : 4-*tetrahydroquinoline*-7-*propionic acid* (IV), m.p. 240° (*Me*, m.p. 142—143°, and *Et*, m.p. 123—124°, ester). Conc. H_2SO_4, KNO_3, and (III) at room temp. afford 6-*nitro*-2-*keto*-1 : 2-*dihydroquinoline*-7-*acrylic acid*, slow decomp. 310°. Nitration of (IV) gives 6-*nitro*-2-*keto*-1 : 2 : 3 : 4-*tetrahydroquinoline*-7-*propionic acid* (V), m.p. 260° (*Et* ester, m.p. 137—138°), or, if treatment is prolonged, 6 : 8-*dinitro*-2-*keto*-1 : 2 : 3 : 4-*tetrahydroquinoline*-7-*propionic acid* (VI), m.p. 234—235° (decomp.) (*Me* ester, m.p. 166°). Hydrogenation (Raney Ni in EtOAc–EtOH–MeOH–H_2O) of (V) at room temp. leads to 2 : 6-*diketo-octahydro*-1 : 5-*anthrazoline* (VII), darkens at ~360°. (VI) is similarly reduced and then acetylated to *acetamidodiketo-octahydrophenanthroline*, decomp. >310° (*hydrochloride* of the corresponding amine, m.p. >360°). (VII) is transformed by $POCl_3$–PCl_5 into 2 : 3 : 6 : 7-*tetrachloro*-1 : 5-*anthrazol*-

ine, m.p. ~300° (decomp.) after softening at ~260°, which is converted by HI–AcOH–red P at 150—173° into 1 : 5-*anthrazoline monohydrate*, m.p. 240—242° after softening at 228° (*picrate*, indef. m.p.). A method of preparing Raney Ni in the laboratory is described. H. W.

Constitution of tri-indole. O. Schmitz-Dumont and J. ter Horst [and, in part, H. Müller] (Annalen, 1939, **538**, 261—282).—"Tri-indole" is probably 2-3′-*indolinyl*-3-2″-*indolinylindole* (I). Carbethoxytri-indole (II) is stable at >m.p. (163°), but in hot



AcOH slowly gives carbethoxydi-indole [2-1′-carbethoxy-3′-indolinylindole] and indole, confirming the presence of the di-indole skeleton in (I). Inability of 3-methylindole to give more than a dimeride indicates union of ring *C* to position 3 of ring *A*. Presence of 3 active H in (I) is confirmed by prep. of 1 : 1′-*dinitroso*-1″-*carbethoxy*- (III), m.p. 142° (decomp.), and -1″-*benzoyl-tri-indole*, m.p. 159—160° (decomp.), although (I) gives only a $(NO)_2$-derivative; the structure of the NO-derivatives is proved by conversion of dinitrosoacetyl-tri-indole into acetyltri-indole, and attachment of the acyl to N of ring B is proved by fission of (II). With MeI and anhyd. K_2CO_3 in $COMe_2$, (I) gives 2-1′ : 2′- or 2-1′ : 3′-*dimethyl*-3′-*indolinyl*-3-2″-*indolinylindole* (IV), m.p. 165—166° [2 active H; *picrate*, m.p. 181°; *maleate*, m.p. 168—170°; $(NO)_2$-derivative, m.p. 113—114°], which, when distilled, partly decomposes to give indole. With BrCN (IV) gives N-*cyano*-2′- or -3′-*methyltri-indole*, m.p. 230°; in hot AcOH it gives indole; with Zn–HCl–AcOH it gives a (?) *dimethyltetrahydrodi-indole*, m.p. 178·5°. With *iso*-$C_5H_{11}I$ and K_2CO_3 in $COMe_2$ (I) gives a N-iso*amyl* derivative, m.p. 153·5° (2 active H), which yields a *methyl*iso*amyl* derivative, m.p. 141—141·5° [2 active H; $(NO)_2$-derivative, m.p. 245° (decomp.)]. With KOH–EtOH at room temp. (III) gives *carbethoxydehydrotri-indole* [3-2′-*indolyl*-2-1′-*carbethoxy*-2′-*indolinylindole*] (V), m.p. 201° (decomp.), and an orange-red substance (? VI), $C_{24}H_{17}ON_3$, m.p. 373—374° (corr.; decomp. from 369°). (VI) is also obtained from (V) by KOH–EtOH or by thermal decomp., is reduced with difficulty (Na in boiling C_5H_{11}·OH only) to an autoxidisable leuco-compound, with PhNCO gives an orange-yellow *compound*, decomp. (?) 350° or 310°, or a red *compound*, decomp. 356—361° (both are $C_{31}H_{22}O_3N_4$), with Ac_2O–NaOAc gives a Ac_3 derivative, m.p. 298—300° (decomp.), with $NaNO_2$–AcOH–C_5H_5N gives a *substance*, $C_{24}H_{19}O_2N_3$, m.p. 320—322° (decomp.) after sintering, and with $NaNO_2$–AcOH gives a *substance*, $C_{24}H_{18}O_4N_4$, m.p. 302—305° (decomp.) (*Ac* derivative). Tri-7-methylindole behaves abnormally; it gives no benzoate or maleate, and its Me_2 derivative, m.p. 197—198°, does not react with BrCN; it gives a Ac_2, m.p. 205°, and Ac_1 derivative (VII), m.p. 264°; with $ClCO_2Et$ and K_2CO_3 it gives a CO_2Et-derivative, m.p. 124—125°. *Dinitrosoacetyltri-7-methylindole*, m.p. 171° (decomp.; sinters at 168°), in hot EtOH gives (VII). R. S. C.

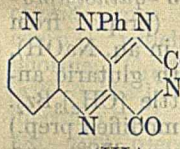
Dinuclear condensation products from alloxan and 3-amino-2-anilinopyridine. H. Rudy and O. Majer (Ber., 1939, **72**, [*B*], 940—945).—3-Amino-2-anilinopyridine (I) and alloxan in hot 30% AcOH give *alloxan*-2-*anilino*-3-*pyridyl*-5-*imide* (I), m.p. 255° (block; decomp.), which can be cryst. by cautious use of AcOH–H_2O, HCO_2H–H_2O, or C_5H_5N but is isomerised by protracted use of these reagents (best by acids) to 2-*keto*-1-*phenyl*-1 : 2-*dihydro*-8-*azaquinoxaline*-3-*carboxureide* (III), m.p. 252° (decomp.; bath pre-heated to 220°), which does not fluoresce in ultra-violet light and is not affected by CH_2N_2 in MeOH–Et_2O or $COMe_2$–Et_2O. (III) is relatively stable towards mineral acids but is readily degraded by dil. alkali through the moderately stable 1-*phenyl*-1 : 2-*dihydro*-8-*azaquinoxal*-2-*one*, m.p. 245° to (I). 9-Phenyl-8-azaflavin could not be obtained from (II) or (III) by boiling with anhyd. AcOH–H_3BO_3, HCO_2H–H_3BO_3, or $ZnCl_2$ or with AcOH–H_2SO_4 containing H_3BO_3; melting with $H_2C_2O_4$ is ineffective. Xanthhydrol does not ppt. (II) or (III). H. W.

Constitution of yeast-ribonucleic acid. II. Guanine-uridylic acid. R. Falconer, J. M. Gulland, G. I. Hobday, and (Miss) E. M. Jackson (J.C.S., 1939, 907—915).—Samples of yeast-ribonucleic acid supplied by certain firms yield on aq. hydrolysis guanine-uridylic acid (I) (purified through its Pb salt), whereas those supplied by others do not (cf. Bredereck *et al.*, A., 1936, 868; Tipson *et al.*, A., 1939, II, 128). This implies the existence of two types of nucleic acid, possibly interconvertible, and throws doubt on the conclusion of Bredereck that (I) is a secondary product of the procedure used in its prep. (I) may contain a P·NH linking or an ester linking between the phosphoryl radical and the lactim form of the CO·NH linking of guanine; the balance of evidence seems to be in favour of the former, since in Van Slyke determinations of NH_2, guanine, its derivatives, *phenylphosphorylguanine* (prepared from guanine and $PPhCl_2$), and (I) undergo deamination at 0° and 20°. On the other hand, comparison of the stabilities towards alkali of (I) and analogous compound shows that (I) is much less stable than would be expected from the presence of P·NH. Determinations of NH_2 in various nucleotides and nucleic acids are recorded. It is also demonstrated that the group in ribonucleic acids shown by Gulland *et al.* (A., 1938, III, 1051) to be resistant to enzymic fission is not that which unites the components of (I), and enzyme experiments with phenylphospho-amide and -anilide and monophenylphosphorylbenzamidine (*Na* salt) are recorded. F. R. S.

Azo-derivatives of chemotherapeutic compounds of the sulphonamide type with diuretic compounds of the purine group. F. P. Mazza and C. Migliardi (R. C. Atti Accad. Lincei, 1939, [vi], **29**, 80—83).—*p*-NH_2·C_6H_4·SO_2·NH_2 (I) diazotised

and poured into theophylline in 10% $NaHCO_3$ gives *8-benzeneazotheophylline-4′-sulphonamide* (II), m.p. 121° (decomp.), reduced by $Na_2S_2O_4$ to aminotheophylline. *8-Benzeneazotheobromine-4′-sulphonamide*, m.p. 93° (decomp.), and *8-benzeneazotheophylline-4′-sulphonanilide-4″-sulphondimethylamide*, m.p 146° (corr.), are prepared similarly. All three compounds are protective to mice against β-hæmolytic streptococci. Unlike (I), (II), injected intravenously, is absorbed into the lymph, where in 30 min. it reaches the same concn. as in the blood (0·02%), and remains after 1 hr., when it is no longer in the circulatory system. E. W. W.

9-Phenyl- and 9-*cyclo*hexyl-azaflavin. H. Rudy and O. Majer (Ber., 1939, **72**, [*B*], 933—939).—Alloxan (I) condenses with 3-amino-2-anilinopyridine (II) in boiling glacial AcOH containing H_3BO_3 ($ZnCl_2$ is not necessary) to *9-phenyl-8-azaflavin* (III),



(III.)

complete decomp. 335—340° (bath preheated to 310°). It is unusually unstable since it is rapidly decomposed in hot AcOH in absence of light and does not survive dry heating at 100°. It is more sensitive than most flavins towards alkali hydroxide, readily giving (II). In boiling AcOH (I) and *3-amino*-2-*cyclohexylaminopyridine* (III) afford *9-cyclohexyl-8-azaflavin* (V), complete decomp. 320—325° when placed in a bath preheated to 310° and then rapidly heated. It is relatively stable towards acids and oxidising agents but is degraded by alkalis. It is decomposed in visible light in the absence of air without yielding a substance with blue fluorescence; this is formed in presence of air and hence is a consequence of photolysis and oxidation. Exposure in a SiO_2 vessel to the unfiltered light of a Hg arc causes a blue-green fluorescence, one of the products acting as oxidising agent. Chromatographic treatment of the products obtained by use of a 200-w. lamp in presence of air shows the presence of ~5 components. The most weakly adsorbed substance, $(C_9H_7O_2N_3)_n$, m.p. 350—355° (decomp.) in bath preheated to 310°, is characterised by a blue-green fluorescence visible in daylight in neutral or AcOH solution; before the quartz lamp this changes to bright yellow on addition of NaOH. (IV), b.p. 190°/12 mm., m.p. 119° [*picrate*, m.p. 210° (decomp.)], is obtained from 2-chloro-3-aminopyridine and *cyclo*hexylamine at 200—210°. It gives a blue fluorescence when dissolved in AcOH or mineral acid; this disappears on addition of alkali. H. W.

Phthalocyanines and allied compounds. R. P. Linstead (Ber., 1939, **72**, [*A*], 93—103).—A lecture.

Heterocyclic compounds containing nitrogen. XLIII. Di- and tri-acetylbenzene and *p*-phenylenediglyoxal. P. Ruggli and E. Gassenmeier Helv. Chim. Acta, 1939, **22**, 496—511).—*m*-$C_6H_4(COCl)_2$ in C_6H_6 is converted by EtOH-free $CHAcNa{\cdot}CO_2Et$ into Et_2 *isophthalyldiacetoacetate*, b.p. 150—158°/15 mm., m.p. 99°, converted by NH_3–EtOH at 60° into Et_2 *isophthalyldiacetate*, hydrolysed and decarboxylated by boiling 15% H_2SO_4 to *m*-$C_6H_4Ac_2$, m.p. 31—32° (*dibenzylidene*, m.p. 142°, *dianisylidene*, m.p. 135°, *disalicylidene*, blackens >150°, and *divanillylidene*, blackens >200°, derivatives). *p*-$C_6H_4Ac_2$ (I) is converted by Cl_2 in AcOH at room temp. (without irradiation) into p-*di(chloroacetyl)benzene*, m.p. 153°. In boiling $CHCl_3$ under the influence of light (I) is converted by Cl_2 according to the duration of the experiment into p-*chloroacetyldichloroacetyl-*, m.p. 147°, p-*di(dichloroacetyl)-*, m.p. 143°, p-*dichloroacetyltrichloroacetyl-*, m.p. 136°, and *di(trichloroacetyl)-* (*A*), m.p. 120—121°, *-benzene*. Br and (I) in AcOH afford p-*di(bromoacetyl)benzene* (II), m.p. 173°; in various media further halogen atoms could not be introduced even with an excess of Br. KI and (II) in EtOH–AcOH yield p-*di(iodoacetyl)benzene*, m.p. 135°, which is transformed by NH_2Ph in warm EtOH into p-*di(anilinoacetyl)benzene*, blackens at >200°. (I), NaOEt, and amyl nitrite in EtOH afford *oximino-*, m.p. 142°, and with a larger excess of reagents, *dioximino-*, decomp. 165°, *-p-diacetylbenzene*, which give resins when hydrolysed. SeO_2 in boiling Ac_2O transforms (I) into p-*phenylenediglyoxal dihydrate* (III), m.p. 110—111° (decomp.), less advantageously obtained from KOAc and (*A*) in boiling EtOH; the *diphenylhydrazone*, decomp. 210°, *disemicarbazone*, m.p. 246° (decomp.), *dianil*, m.p. 155°, and *diquinoxaline* derivative, $C_{22}H_{14}N_4$, m.p. 262°, are described. Catalytic hydrogenation (Raney Ni in EtOH–H_2O at 50°) of (III) gives *p*-dihydroxyacetylbenzene, of which the (impure) *benzoate*, m.p. 85°, and *semicarbazone*, m.p. 226°, are described. Addition of HNO_3 (*d* 1·52) to (I) in Ac_2O at +5° yields *2-nitro*-p-*diacetylbenzene* (IV), m.p. 46°, whereas conc. H_2SO_4 and HNO_3 (*d* 1·52) transform (I) into *2 : 6-dinitro*-p-*diacetylbenzene*, m.p. 160—163°. Oxidation of (IV) with SeO_2 in boiling dioxan affords oily or resinous 2-nitrophenylene-1 : 4-diglyoxal, characterised by a pulverulent *disemicarbazone*, m.p. 251° (decomp.), and *diphenylhydrazone*, decomp. ~100°. It is reduced (Raney Ni in dioxan and 95% EtOH at 50°) to non-cryst. 2-aminophenylene-1 : 4-diglyoxal, which gives a *trisemicarbazone*, decomp. ~280°, and a *triphenylhydrazone* and is converted by Ac_2O at 50—60° into non-cryst. (?) 6-glyoxalylindolone, characterised by a powdery monosemicarbazone and monophenylhydrazone. Isatin, (I), and 30% NaOH in EtOH at 100° afford p-*phenylenedicinchonic acid*, m.p. 315° (decomp.) [Na_2 and $(NH_4)_2$, m.p. ~337° (decomp.), darkens at 270°, salts]. 1 : 3 : 5-$C_6H_3Ac_3$ gives a *triphenylhydrazone*, m.p. 183—185°, and *trisemicarbazone*, decomp. 340°. It is converted by Br in AcOH into 1 : 3 : 5-*tribromoacetylbenzene*, m.p. 111°; higher bromination could not be effected. SeO_2 in hot dioxan oxidises 1 : 3 : 5-$C_6H_3Ac_3$ to 1 : 3 : 5-*triglyoxalylbenzene* (+$9H_2O$), m.p. 117—118° (*trianil*, decomp. ~340°; *triphenylhydrazone*, blackens ~90°; *trisemicarbazone*, decomp. 300—303°; *tri-quinoxaline* derivative, m.p. 302—303°). H. W.

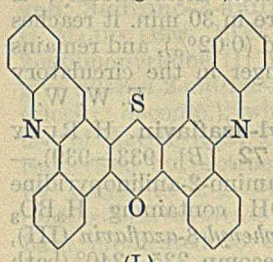
Thiazolinephenols [hydroxyphenylthiazolines]. 5-Methyl- and 5 : 5-dimethyl-thiazolinephenols, by-products, and derivatives. W. F. Hart and J. B. Niederl (J. Amer. Chem. Soc., 1939, **61**, 1145—1148).—Repeated saturation of a mixture of a phenol and $CH_2{:}CH{\cdot}CH_2{\cdot}NCS$ (I) or $CH_2{:}CMe{\cdot}CH_2{\cdot}NCS$ (II) with HCl at room temp. during 1—4 weeks gives ~50% yields of 2-*p*-hydroxy-

aryl-5-methyl- or -5 : 5-dimethyl-thiazolines, respectively. Poorer yields are obtained by $AlCl_3$ or H_2SO_4. PhOH and (I) give also some β-p-*hydroxyphenyl*-n-*propylisothiocarbimide*, m.p. 150°. With H_2SO_4 (II) gives some 2-*thiol*-5 : 5-*dimethylthiazoline* (III), m.p. 162°, whether or not phenols are present. The following are new. 2-6′-*Hydroxy*-m-*tolyl*-, m.p. 134° (*hydrochloride*, m.p. 220°; *picrate*, m.p. 159°), 2-3′ : 4′-*dihydroxyphenyl*-, m.p. 136° (*hydrochloride*, m.p. 247°; *picrate*, m.p. 188°), 2-2′-*hydroxy*-1′-*naphthyl*-, m.p. 65° (*hydrochloride*, m.p. 220°; *picrate*, m.p. 169°), 2-5′-*hydroxy*-o-*tolyl*-, m.p. 131° [*benzoate hydrochloride*, m.p. 185—186°; *Me ether hydrochloride* (prep. by NaOMe–MeOH, followed by Me_2SO_4–C_6H_6 etc.), m.p. 159—160°; p-*nitro*-, m.p. 87—88° (*hydrochloride*, m.p. 205°), and p-*amino-benzoate*, m.p. 142° (*dihydrochloride*, m.p. >250°)], 2-p-*hydroxyphenyl*-, m.p. 168° [3′-NO_2-, m.p. 135° (*hydrochloride*, m.p. 215°), reduced by $SnCl_2$ to the 3′-NH_2-derivative (*dihydrochloride*, m.p. >250°)], -5-*methylthiazoline*. 2-p-*Hydroxyphenyl*-, m.p. 181—182° (*hydrochloride*, m.p. 240°; *picrate*, m.p. 190°), 2-5′-*hydroxy*-o-*tolyl*-, m.p. 134° (*hydrochloride*, m.p. 180—181°; *picrate*, m.p. 186°), and 2-2′ : 4′-*dihydroxyphenyl*-, m.p. 144—145° (*hydrochloride*, m.p. >270°; *picrate*, m.p. 195°), -5 : 5-*dimethylthiazoline*. The products have PhOH coeff. <1, but are potent anæsthetics, only slightly toxic, irritant as hydrochlorides, non-irritant as tartrates. The p-*nitro*-, m.p. 168°, and p-*amino-benzoate* (*hydrochloride*, m.p. 265°) of (III) and the derived *disulphide*, m.p. 162°, are prepared. R. S. C.

Preparation and reactions of some arylsulphonylbenz*iso*thiazolones. R. G. Bartlett, L. E. Hart, and E. W. McClelland (J.C.S., 1939, 760—762).—Condensation of the chlorination product of 2 : 2′-dithiobenzoyl chloride with arylsulphonamides gives 1-arylsulphonylbenz*iso*thiazolones; the same substances and 2-arylsulphonyloxybenz*iso*thiazoles are formed from arylsulphonyl chlorides and the unsubstituted benz*iso*thiazolone. The 1-aryl compounds undergo fission with NaOH to the corresponding disulphides and acid hydrolysis eliminates the arylsulphonyl group. The following are described: 1-p-*toluene*-, m.p. 207° (oxidised with H_2O_2 to N-p-*toluenesulphonyl*-o-*benzoicsulphinide*, m.p. 214°), 1-*benzene*-, m.p. 218°, 4-*chloro*-1-*benzene*-, m.p. 205°, 4 : 6-*dichloro*-1-*benzene*-, m.p. 162°, and 4-*chloro*-1-p-*toluene-sulphonylbenz*iso*thiazolone*, m.p. 203°; 2-*benzene*-, m.p. 68°, and 2-p-*toluene-sulphonyloxybenz*iso*thiazole*, m.p. 96°; 2 : 2′-*bis*-p-*toluene*-, m.p. 218°, 2 : 2′-*bisbenzene*-, m.p. 225—227°, and 4 : 4′-*dichloro*-2 : 2′-*bisbenzene-sulphonylcarbamyldiphenyl disulphide*, m.p. 225°; and (by heating with NH_2Ph) 2-*anilinothiobenzobenzene*-, m.p. 167°, 2-*anilinothiobenzo*-p-*toluene*-, m.p. 187°, and 5-*chloro*-2-*anilinothiobenzobenzene-sulphonamide*, m.p. 167°. F. R. S.

Isosteric and structurally similar compounds. XI. Preparation and properties of 2 : 2′-dithiazolyl. H. Erlenmeyer and E. H. Schmid (Helv. Chim. Acta, 1939, **22**, 698—700; cf. A., 1939, II, 39).—2-Bromothiazole is converted by Cu powder in *p*-cymene at 170—180° into 2 : 2′-*dithiazolyl*, m.p. 102·5°. This is a much weaker base than 2 : 2′-dipyridyl (I), with which it does not form mixed crystals. Unlike (I) it shows little tendency to form complex salts with $Fe^{\cdots}$. H. W.

Polycyclic condensed systems with heterocyclic rings. V. VI. 1 : 2 : 3 : 4 : 6 : 7-Tribenzacridine. W. Borsche and F. Sinn (Annalen, 1939, **538**, 283—292, 292—298; cf. A., 1939, II, 227).—V. 2-Phenylquinoline-3-carboxylic acid and H_2SO_4 at 100—110° give 50% of 2 : 3-benz-4-aza-9-fluorenone.



(I.)

2-Phenylquinoline-3-acetic acid and $SOCl_2$, followed by $AlCl_3$, give 3 : 4 : 6 : 7-*dibenzdiquinolino*-2′ : 3′ : 2″ : 3″-2 : 1 : 8 : 9-*phenoxthionine* (I), m.p. 367—370° (decomp.) (cf. Borsche *et al.*, A., 1937, II, 520), and attempts to prepare a benzacridine failed. β-2-*Phenyl*-3-*quinolylpropionic acid* (prep. from Bz·$[CH_2]_3$·CO_2H and *o*-NH_2·C_6H_4·CHO in aq. NaOH), m.p. 169°, could not be cyclised; with glutaric anhydride and $AlCl_3$ it gives only a little $[CH_2]_3Bz_2$. 4-Phenylcarbostyril-3-carboxylic acid (modified prep.) (*Et* ester, m.p. 199°; *benzanilide*, m.p. 278°) and H_2SO_4 give 85% of 1-*hydroxy*-2-*aza*-3 : 4-*benz*-9-*fluorenone*, m.p. ~340° (decomp. from ~310°). 4-*Phenylquinoline*-3-*carboxylic acid* (prep. from the Me ester of the 2-Cl-acid by HI–red P), m.p. 226—228° (*picrate*, m.p. 196°; *Me* ester, m.p. 116—117°), and $SOCl_2$, followed by $AlCl_3$ in $PhNO_2$, yield 2-*aza*-3 : 4-*benz*-9-*fluorenone*, m.p. 216—217° [*oxime*, m.p. 261° (decomp.); 2 : 4-*dinitrophenylhydrazone*, m.p. 290° (decomp.)], also obtained by H_2SO_4 at 105° and reduced by N_2H_4,H_2O at 200° to 2-*aza*-3 : 4-*benzfluorene*, m.p. 96°. *o*-NH_2·C_6H_4·COMe and CH_2Ac·CO_2Et at 150° give 3-*acetyl*-4-*phenylcarbostyril*, m.p. 251—252° [*oxime*, m.p. 256—258° (decomp.); 2 : 4-*dinitrophenylhydrazone*, m.p. 291—293° (decomp.)]. *o*-NH_2·C_6H_4·COPh with CH_2Bz·CO_2Et at 160°, $(CH_2$·$COMe)_2$ at 150°, or COPhMe and 5% KOH–EtOH at 100° gives 3-*benzoyl*-4-*phenyl*-, m.p. 259—260°, 4-*phenyl*-2-*acetonyl*-, m.p. 113—115°, and 2 : 4-diphenyl-carbostyril, m.p. 114° (lit. 112° and 106—107°), respectively.

VI. 2-*Phenyl*-3-*o*-*aminophenyl*-5 : 6-*benzoquinoline*-4-*carboxylic acid* (prep. by H_2–Pd–C in dil. NaOH from the NO_2-acid), m.p. 206—210° (decomp.), could not be decarboxylated, probably owing to betaine formation; above the m.p., decomp. is total. β-$C_{10}H_7$·NH_2, CH_2Ph·CO·CO_2H, and *o*-NO_2·C_6H_4·CHO in hot EtOH give variable yields of 3-*phenyl*-2-*o*-*nitrophenyl*-5 : 6-*benzquinoline*-4-*carboxylic acid* (II) (up to 59% yield), m.p. 278° (decomp.), and the isomeric *diketopyrrolidine*, m.p. 237° (decomp.). Hydrogenation of (II) gives the NH_2-*acid*, m.p. 284° (decomp.), decarboxylated, when heated, to yield 3-*phenyl*-2-*o*-*aminophenyl*-5 : 6-*benzquinoline*, m.p. 201°, the diazonium sulphate from which in hot, dil. H_2SO_4 affords 1 : 2 : 3 : 4 : 6 : 7-*tribenzacridine*, m.p. 244—246°. With $SOCl_2$, followed by $AlCl_3$ in $PhNO_2$, (II) gives 4-*o*-*nitrophenyl*-3-*azanaphtha*-1′ : 2′-1 : 2-*fluoren*-9-*one*, m.p. 228° [2 : 4-*dinitrophenylhydrazone*, m.p. 298° (decomp.)], hydrogenated (Pd–C) in C_5H_5N to the NH_2-*ketone* (III), m.p. 260—265°, and much

of the (?) azo- or azoxy-compound, m.p. 345—348°. N_2H_4,H_2O at 190—200° reduces (III) to 4-*o*-*aminophenyl*-3-*azanaphtha*-1′ : 2′-1 : 2-*fluorene*, m.p. 236°, but further ring-closure by diazotisation etc. could not be effected. α-$C_{10}H_7$·NH_2, CH_2Ph·CO·CO_2H, and *o*-NO_2·C_6H_4·CHO give only 21% of 3-*phenyl*-2-*o*-*nitrophenyl*-7 : 8-*benzquinoline*-4-*carboxylic acid*, m.p. 294° (decomp.). R. S. C.

***Erythrina* alkaloids. III. Isolation and characterisation of a new alkaloid, erythramine.** K. Folkers and F. Koniuszy (J. Amer. Chem. Soc., 1939, **61**, 1232—1235; cf. A., 1937, II, 434).—Many species of *Erythrina*, particularly *E. sandwicensis*, Deg., and *E. subumbrans* (Hassk.), Merrill, contain *erythramine* (I), $C_{18}H_{21}O_3N$, m.p. 103—104°, b.p. 125°/0·00039 mm., $[\alpha]_D^{29\cdot5}$ +227·6° in EtOH [*hydriodide*, m.p. 249° (decomp.), $[\alpha]_D^{25}$ +220° in H_2O; *hydrobromide*, m.p. 228°, $[\alpha]_D^{26}$ +203·2° in H_2O; *hydrochloride*, m.p. (+0·5H_2O) 249°, (anhyd.) 250° (decomp.)], which has no curare-like action. Hypaphorine, $C_{14}H_{18}O_2N_2$, m.p. 236—237° (decomp.), $[\alpha]_D^{27}$ +113·1° in H_2O [nitrate, m.p. 223·5—224·5° (decomp.) (lit. 215—220°, 220°); hydrochloride, m.p. 231—232° (decomp.) (lit. 227°), $[\alpha]_D^{32}$ +89·6° in H_2O], also has no curare-like action, but is converted by MeI–NaOH in MeOH into Me α-dimethylamino-β-3-indolylpropionate methiodide, m.p. 200·5—201·5° (decomp.) (lit. 197°), which has such action. R. S. C.

Anæsthetising action of convolvine and convolamine. M. S. Rabinovitsch and R. A. Konovalova (J. Gen. Chem. Russ., 1939, **9**, 41—58).—Convolvine in $CHCl_3$ and $(CH_2)_2O$ (4 hr. at 60°) yield N-β-*hydroxyethylconvolvine*, m.p. 128—129° [*hydrochloride*, m.p. 235—237°; *picrate*, m.p. 212—214°; *benzoate*, m.p. 131—133° (*hydrochloride*, m.p. >250°; *picrate*, m.p. 214—216°)]. Nortropine (I) in PhMe and NEt_2·$[CH_2]_2$·Cl (II) (at the b.p.) yield N-β-*diethylaminoethylnortropine*, m.p. 59—61° [*picrate*, m.p. 160—162°; *hydrochloride*, m.p. 200—201°; *hydrochloride* of *benzoate*, m.p. 228—229° (decomp.)]. (I) and *p*-NO_2·C_6H_4·COCl (III) in $CHCl_3$ (6 hr. at the b.p.) afford O-p-*nitrobenzoylnortropine*, m.p. 223—224°, reduced to O-p-*aminobenzoylnortropine*, m.p. 201—202° [*hydrochloride*, m.p. 222—224° (decomp.)]. Nortropidine (IV) and $(CH_2)_2O$ in $CHCl_3$ (5 hr. at 45—55°) give N-β-*hydroxyethylnortropidine*, b.p. 140—141°/17 mm. [*benzoate*, m.p. 187—188°; p-*nitrobenzoate*, m.p. 60—62° (*hydrochloride*, m.p. 209—210°; *picrate*, m.p. 225—226°); p-*aminobenzoate*, m.p. 96—96·5° (*hydrochloride*, m.p. 206—207°; *picrate*, m.p. 150—151°); p-*butylaminobenzoate*, m.p. 66—68° (*hydrochloride*, m.p. 149—151°); *phenylurethane* (*hydrochloride*, m.p. 182—183°; *phenylacetate*, m.p. 113—114°)]. (IV) and (II) in PhMe (at the b.p.) yield N-β-*diethylaminoethylnortropidine*, an oil (*picrate*, m.p. 173—175°). Tropine in PhMe and (III) (8 hr. at 120°) yield p-*nitrobenzoyltropine*, m.p. 135—136°, reduced (Fe in AcOH) to p-*aminobenzoyltropine*, m.p. 149—150° [*hydrochloride*, m.p. 250°; *monopicrate*, m.p. 230° (decomp.); *dipicrate*, m.p. 173—175°; *acetate*, m.p. 171—172°; *phenylacetate*, m.p. 143—145°], which with Ac_2O (5 hr. at 100°) gives p-*acetamidobenzoyltropine*, m.p. 151—152° (*hydrochloride*, m.p. >250°; *phenylacetate*, m.p. 141—142°). ψ-Tropine and (II) in PhMe (4 hr. at 130—140°) give p-*nitrobenzoyl*-ψ-*tropine*, m.p. 126—127°, reduced (Fe in AcOH, at 60°) to p-*aminobenzoyl*-ψ-*tropine*, m.p. 163—165° (*phenylacetate*, m.p. 116—117°; *hydrochloride*, m.p. >235°). Tropine and CH_2Ph·COCl in $CHCl_3$ (4·5 hr. at 120—125°) yield *phenylacetyltropine*, an oil (*hydrochloride*, m.p. 198—200°). Tropine and PhNCO in Et_2O (3 hr. at the b.p.) give *tropine phenylurethane*, m.p. 170—171·5° (*hydrochloride*, m.p. >270°). Tropine and p-NHBu^a·C_6H_4·COCl (V) in PhMe (8 hr. at 110°) afford p-*butylaminobenzoyltropine*, m.p. 89—90° (*hydrochloride*, m.p. >270°); with ψ-tropine (4 hr. at 140—150°) the product is p-*butylaminobenzoyl*-ψ-*tropine*, m.p. 109—111° (*hydrochloride*, m.p. >270°). Both the anæsthetising and the toxic action of convolvine are lowered by *N*-substitution, and are raised by introduction of NH_2 into the Bz radical; NHAc has a feebler, and NHBu a stronger, action than has NH_2. Derivatives with a free OH group are only slightly toxic, but have no anæsthetising action, and the same applies to derivatives not possessing an ester group. The toxicity of ψ-tropine is < that of tropine derivatives with an equal anæsthetising action. The anæsthetising action of phenylacetates is > that of hydrochlorides. R. T.

***Strychnos* alkaloids. CVI. Methylations in the series of ψ- and 9-monohydroxy-brucine, and migrations of methyl between oxygen and nitrogen.** H. Leuchs and K. Tessmar (Ber., 1939, **72**, [*B*], 965—972).—Under stated conditions ψ-brucine Me ether and MeI afford N-*methyl*sec.-ψ-*brucine methiodide* (I), decomp. 220—222° after softening [*methoperchlorate* (II), decomp. 280—285° after softening], hydrogenated (PtO_2 in H_2O) to a H_2-derivative, m.p. 252—254° (decomp.) (*perchlorate*). ψ-Brucine is transformed by boiling MeI into the *hydriodide* of a *tert.* base. ψ-Brucine and 30 parts of boiling MeI give N-*methyl*sec-ψ-*brucine hydriodide*, m.p. 222—224° (decomp.) after softening; the free *base*, m.p. 228—230° (*perchlorate*, decomp. 210—215° after softening at 195°), is hydrogenated (PtO_2 in 0·2N-HCl) to a H_2-derivative, m.p. 235—237° (vac.) (*perchlorate*, decomp. ~215° after softening), which is indifferent towards MeI or NH_2·CO·NH·NH_2 but is converted by $BaCO_3$–Me_2SO_4 followed by 2N-$HClO_4$ into (II). (I) is transformed by NaOMe–MeOH into the *tert.* ether base (III), $C_{25}H_{30}O_5N_2$, m.p. 225° (vac.), converted by dil. $HClO_4$ into (II); it gives a *methiodide*, m.p. 245—247; (decomp.), and a *methoperchlorate*, m.p. ~288° (decomp.). The methiodide is hydrogenated (PtO_2 in H_2O) to the tert. *base*, $C_{26}H_{36}O_5N_2$, m.p. 175° (vac.) (*perchlorate*), which gives a *methiodide* (IV), m.p. 275—278° (decomp.) (*perchlorate*). The hydriodide of (III) is reduced (Na–Hg in H_2O) to the hydrogenated tert. *base* (V), $C_{25}H_{32}O_5N_2$, m.p. 184—185° (vac.) [*perchlorate*, m.p. 215° (decomp.) after softening at 200°; *methiodide* (VI), m.p. 203—204° (vac.), whence the *methoperchlorate*, m.p. ~285° (much decomp.)]. (III) is reduced by Na–Hg to (IV). Hydrogenation and Emde fission of (VI) gives a non-cryst. base (*perchlorate*, $C_{26}H_{38}O_5N_2,HClO_4$, m.p. ~145° after softening at 100°). Similar treatment of the methiodide of (III) gives a basic resin, transformed by MeI into (IV). H. W.

Delphinine. II. Oxo-[keto-]delphinine. W. A. JACOBS and L. C. CRAIG (J. Biol. Chem., 1939, **128**, 431—437).—Delphinine (I) heated at 200—215° in H_2 yields *pyrodelphinine*, $C_{31}H_{41}O_7N$, m.p. 208—212°. Oxidation of (I) with $KMnO_4$ in $COMe_2$ yields α-keto-delphinine (II), $C_{33}H_{43}O_{10}N$, m.p. 218—221°, $[\alpha]_D^{20}$ −62° in AcOH, −55° in EtOH, apparently identical with X-214° of Keller (A., 1925, i, 830), and *β-keto-delphinine* (III), $C_{33}H_{43}O_{10}N$, m.p. 228—229°, $[\alpha]_D^{20}$ +31° in AcOH. Hydrogenation (H_2–PtO_2 in AcOH) of (II) gives *hexahydro-α-ketodelphinine*, m.p. 195°; when heated in H_2 at 220°, (II) yields *pyro-α-keto-delphinine*, $C_{31}H_{39}O_8N$, which when heated with HCl–MeOH yields an *isomeride*, m.p. 280—284°, and on hydrogenation (PtO_2 in AcOH) gives *hexahydro-pyro-α-ketodelphinine*, m.p. 183—185°. When heated at 100° with HCl–MeOH, (III) gives CO_2 and a *sub-stance*, $C_{32}H_{43}O_9N$, m.p. 220—222°. J. D. R.

Aconite alkaloids. II. Formula of oxonitine. W. A. JACOBS, R. C. ELDERFIELD, and L. C. CRAIG (J. Biol. Chem., 1939, **128**, 439—446).—Analyses of oxonitine (I) and its isomeride, formed by oxidation ($KMnO_4$–$COMe_2$–AcOH) of aconitine, indicate a formula of $C_{32}H_{43}O_{12}N$ as suggested by Späth *et al.* (A., 1931, 243) and not $C_{32}H_{41}O_{12}N$ as suggested by Majima and Tamura (A., 1937, II, 38). Aconitine is reduced (PtO_2–H_2 in EtOH) to *hexahydroaconitine* (*perchlor-ate*, m.p. 209—210°), which is hydrolysed by H_2O at 160° to hexahydrobenzoic acid and aconine. Re-duction of (I) in AcOH with PtO_2–H_2 gives *hexa-hydro-oxonitine* (II), m.p. 253°, and on heating in H_2 at 280—285° gives pyro-oxonitine (III), m.p. 180° (lit. 231°), which is hydrogenated in EtOH to *hexa-hydropyro-oxonitine* (IV), m.p. 160—163°. When heated with 6% HCl–MeOH at 100°/18 hr., (I) yields CO_2 and a *base*, m.p. 250°, $C_{31}H_{45}O_{10}N$ or $C_{32}H_{47}O_{10}N$, which contains 5 OMe and 1 NMe. Analyses of (II), (III), and (IV) support the formula proposed for (I). J. D. R.

Diphenylfluoroarsine. M. SARTORI and E. REC-CHI (Annali Chim. Appl., 1939, **29**, 128—130).—$AsPh_2Cl$ with AgF in C_6H_6 affords *diphenylfluoro-arsine*, m.p. 17—19°, b.p. 157·5°/8 mm., which with aq. KOH or HNO_3 yields bis(diphenylarseno)oxide and diphenylarsinic acid, respectively. F. O. H.

Arsenated phenoxybutanols. W. F. HOLCOMB and C. S. HAMILTON (J. Amer. Chem. Soc., 1939, **61**, 1236—1237).—*p*-$OH{\cdot}C_6H_4{\cdot}AsO_3H_2$ and *iso*butylene oxide in NaOH at 80° give p-β-*hydroxyisobutoxy-phenylarsinic acid*, m.p. 189—192° (*Na* salt, m.p. >325°), converted by HNO_3 (*d* 1·5) in H_2SO_4 at 0° into 3-*nitro*-4-β-*hydroxyisobutoxyphenylarsinic acid*, m.p. 210—215°, and thence by $FeCl_2$–NaOH at 20° or H_2–Raney Ni in aq. NaOH at 4 atm. into the 3-NH_2-*acid*, m.p. (anhyd.) 150—155°, (+H_2O) 65—70°. The usual methods then yield 3-*amino*-4-β-*hydroxyisobutoxyphenylarsine oxide*, +H_2O, m.p. 123—124°, 4 : 4′-*di*-β-*hydroxyisobutoxy*-, m.p. 135—140°, and 3 : 3′-*diamino*-4 : 4′-*di*-β-*hydroxyisobutoxy-arsenobenzene*, m.p. 125—130°. R. S. C.

Relative reactivities of organometallic compounds. XXVI. Interconversion of bismuth and alkali metals. H. GILMAN, H. L. YABLUNKY, and A. C. SVIGOON (J. Amer. Chem. Soc., 1939, **61**, 1170—1172; cf. A., 1939, II, 253).—$Bi(C_6H_4R)_3$ (R = *p*-Me, *p*-Cl, *p*-OEt, *o*-*OEt*, m.p. 121—122°) and 3 mols. of $LiBu^a$ give $BiBu^a_3$ and $Li{\cdot}C_6H_4R$, carboxyl-ation of the mixture yielding $C_6H_4R{\cdot}CO_2H$ (R = *p*-Me 70, *p*-Cl 90, *p*-OEt 27·4, *o*-OEt 64%). $Bi(C_{10}H_7\text{-}\alpha)_3$ reacts similarly, yielding 48·1% of α-$C_{10}H_7{\cdot}CO_2H$. $Bi(C_6H_4Me\text{-}p)_3$ and $NaBu^a$ (3 mols.) in light petroleum at 35° give $BiBu^a_3$ (46%) and *p*-$C_6H_4Me{\cdot}CO_2H$ (33%; by CO_2). Atm. oxidation of $BiBu^a_3$ is explosive; it gives small amounts of an aldehyde. R. S. C.

Formation of organochromium compounds from complex salts of chromium. F. HEIN (J. pr. Chem., 1939, [ii], **153**, 160—176).—The compounds $[Cr(OH_2)_6](NO_3)_3,3H_2O$ and $[Cr(OH_2)_6](OAc)_3$ are indifferent towards MgPhBr; the complex-bound H_2O is not attacked. $[Cr_3(OAc)_6(OH_2)_2](OAc)_3,H_2O$ is readily attacked; after reaction of the externally united H_2O an isomerisation to the non-electrolytic complex $[Cr_3(OAc)_9],2H_2O$ is assumed. $K_3[Cr(C_2O_4)_3]$, $(NH_4)_3[Cr(O_2C_6H_4)_3]$, and $Na[Cr(OEt)_4]$ are indifferent, showing that the homo-polar linking of all acidic residues is not in itself sufficient to permit the formation of organo-metallic compounds but that the complex must also be without charge. The Cr complexes with CH_2Ac_2, $CH_2Ac{\cdot}CO_2Et$, pæonol, hydroxyquinoline, *o*-$OH{\cdot}C_6H_4{\cdot}COMe$, and xanthic acid give CrPh com-pounds whereby the only differences observable are in the readiness and vigour of the reaction under other-wise comparable conditions. In contrast, the classic-ally internally complex salts $^+Cr\cdots_{/3}NH_2{\cdot}CH_2{\cdot}CO_2^-$ and $^+Cr_{/3}\cdots NH_2{\cdot}CHMe{\cdot}CO_2^-$ are passive towards Grignard's reagents; possibly these complexes have mainly the open structure, $\cdots Cr(NH_2{\cdot}CH_2{\cdot}CO_2)_3\text{---}\cdots Cr(NH_2{\cdot}CH_2{\cdot}CO_2)_3\text{---}$ $\cdots Cr(NH_2{\cdot}CH_2{\cdot}CO_2)_3\text{---}$, the lattice forces being mainly of an electrostatic character and saturation occurring between the positive Cr end of a zwitterion and the negative NH_2-acid end of another. The Cr lakes of alizarin, quinizarin, and 1-hydroxyanthra-quinone are indifferent towards MgPhBr. The Et_2O solution of $[CrCl_3,3H_2O]$ reacts smoothly with MgPhBr. H. W.

Cystine content of deaminised proteins. W. C. HESS and M. X. SULLIVAN (J. Biol. Chem., 1939, **128**, 93—99).—The cystine content (determined by the Sullivan method) of wool deaminised by HNO_2 is about 25% < that of the original protein. When determined by the method of Okuda or of Vickery and White the cystine vals. are approx. those of the original protein. Part of the cystine combined in the protein is apparently deaminised by HNO_2 and converted into a compound, presumably $[S{\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2H]_2$, giving the Okuda and Vickery and White but not the Sullivan reactions. Similar results with casein and lactalbumin are reported. W. O. K.

Mechanism of catalytic action of selenium in Kjeldahl nitrogen determination.—See A., 1939, I, 384.

Modified Beilstein test for halogens in volatile organic compounds. W. L. RUIGH (Ind. Org. Chem. [Anal.], 1939, **11**, 250).—The liquid to be tested is added dropwise to a heated 125-c.c. flask through

which passes the gas feed to a Bunsen burner the flame of which passes through a Cu gauze 4 cm. above the burner. The limit of sensitivity for $CH_2{:}CHCl$ is 30 p.p.m. F. N. W.

Unstable isotopes. I. Determination of radioactive isotopes in organic material. E. Chargraff (J. Biol. Chem., 1939, **128**, 579—585).—Radioactivities of substances spread in thin layers on Al trays or dissolved in suitable solvents were determined by a Geiger–Müller counter using the β-ray radiation of the unstable isotope $^{40}_{19}K$ of KF as standard. Applications to the determination of radioactive P in Na_2HPO_4, lecithin, etc. are described. T. F. D.

Analysis of hydrocarbon mixtures (boiling in the gasoline range), using thiolacetic acid to remove olefines. H. Hoog and E. Eichwald (Rec. trav. chim., 1939, **58**, 481—492).—$SH{\cdot}CH_2{\cdot}CO_2H$ (I) (300% of theoretical amount) and a synthetic mixture of 80% *n*-C_7H_{16} and 20% Δ^β-octene (II) react at room temp. (1 hr.) if $EtCO_2H$ is used as solvent; decrease in olefine content is observed by determination of Br val. The hydrocarbon mixture must first be freed from peroxides by aq. $FeSO_4$. Similar mixtures are examined, using the following in place of (II): Δ^β-pentene; $CMe_2{:}CHMe$; Δ^β-hexene; β- or γ-methyl-Δ^β-pentene; βγ- or γγ-dimethyl-Δ^α-butene; Δ^α-heptene; β-methyl-Δ^β-hexene; βγ- (III), βδ- (IV), and δδ-dimethyl-Δ^β-pentene (V); $CMeBu^\gamma{:}CH_2$; Δ^α-octene; $CHMe{:}CMeBr^\alpha$; $CMe_2{:}CMePr^\alpha$ (VI); $CH_2Bu^\gamma{\cdot}CMe{:}CH_2$; *cyclo*hexene (VII), and $\Delta^{\beta\delta}$-hexadiene (VIII). Normal olefines, C_5 to C_8, and those with one Me (C_5 to C_8) are readily removed, as is (VII). (III), (IV), (VI), and (VIII) are only partly removed, but almost completely with 475% of (I) for 48 hr. (V) is not removed at all, even with 500% of (I) for 70 hr. at 0° to 50°, with HCO_2H, AcOH, $Pr^\alpha CO_2H$, or $Pr^\alpha CHO$; attempted catalysis with (II), P_2O_5, $AlCl_3$, etc., or salts of (I), also failed. There is no general rule for removal of olefines. After removal, the quantities of aromatic, paraffin, and naphthene hydrocarbons in the residual hydrocarbons are determined in the usual manner. A. T. P.

Identification of aldehydes and ketones. G. B. L. Smith and T. G. Wheat (Ind. Eng. Chem. [Anal.], 1939, **11**, 200—201).—The Jamieson method (A., 1912, ii, 487) is applicable to the determination of N in semicarbazide, *p*-$C_6H_4Br{\cdot}NH{\cdot}NH_2$, and the semicarbazones of COPhMe, $COMe_2$, $COEt_2$, $COPh_2$, PhCHO, $CHPh{:}CH{\cdot}CHO$, and *cyclo*hexanone but fails with furfuraldehydesemicarbazone and thiosemicarbazide. F. N. W.

Semicarbazides. VIII. *p*-Xenylsemicarbazide as a reagent for identification of aldehydes and ketones. P. P. T. Sah and I. S. Kao (Rec. trav. chim., 1939, **58**, 459—464; cf. A., 1937, II, 129).—*p*-$C_6H_4Ph{\cdot}NH_2$ (I) and $NH_2{\cdot}CO{\cdot}NH{\cdot}NO_2$ in EtOH at 50° and then at 25°, or (I) and KCNO in aq. AcOH, give p-*xenylcarbamide*, m.p. 196°, converted by N_2H_4,H_2O in EtOH into p-*xenylsemicarbazide*, m.p. 275—277°, which reacts with CO-compounds in 95% EtOH + a trace of AcOH. p-*Xenylsemicarbazones* of the following are prepared: MeCHO, m.p. 208—209°; EtCHO, m.p. 186—188°; $Pr^\alpha CHO$, m.p. 180—181°; $Pr^\beta CHO$, m.p. 176—177°; $Bu^\alpha CHO$, m.p. 148—149°; *n*-$C_5H_{11}{\cdot}CHO$, m.p. 135—136°; *n*-$C_6H_{13}{\cdot}CHO$, m.p. 177—178°; *n*-$C_7H_{15}{\cdot}CHO$, m.p. 175—176°; *n*-$C_8H_{17}{\cdot}CHO$, m.p. 179—180°; *n*-$C_9H_{19}{\cdot}CHO$, m.p. 171—172°; PhCHO, m.p. 232—234°; *m*-$NO_2{\cdot}C_6H_4{\cdot}CHO$, m.p. 235—236° (decomp.); *o*-, m.p. 268—270°, and *p*-$OH{\cdot}C_6H_4{\cdot}CHO$, m.p. 204—205°; furfuraldehyde, m.p. 228—229°; $COMe_2$, m.p. 220—221°; COMeEt, m.p. 200—201°; $COMe{\cdot}C_6H_{13}$-*n*, m.p. 147—148°; $CHPh{:}CH{\cdot}COMe$, m.p. 231—232°; COPhMe, m.p. 224—225°; *p*-$C_6H_4Me{\cdot}COMe$, m.p. 227—228°; $COPh_2$, m.p. 187—188°; *cyclo*pentanone, m.p. 235—237°; camphor, m.p. 273—274°; $CH_2Ac{\cdot}CO_2Et$, m.p. 179—180°; lævulic acid, m.p. 203—204°; Et, m.p. 164—165°, and CH_2Ph lævulate, m.p. 151—152°. A. T. P.

Azides. XI. β-Naphthazide and β-naphthyl carbimide as reagents for identification of phenols. P. P. T. Sah (Rec. trav. chim., 1939, **58**, 453—458; cf. A., 1937, II, 360).—Anhyd. β-naphthazide (I), refluxed in dry ligroin until evolution of N_2 ceases, affords β-$C_{10}H_7{\cdot}NCO$ (II), m.p. ~57°. (I) or (II) and ArOH in boiling ligroin give β-*naphthylurethanes* of the following: PhOH, m.p. 149°; *o*-, m.p. 127—129°, *m*-, m.p. 123°, and *p*-$C_6H_4Me{\cdot}OH$, m.p. 159°; 3 : 4 : 1-, m.p. 148—149°, 2 : 5 : 1-, m.p. 143—145°, and 2 : 4 : 1-$C_6H_3Me_2{\cdot}OH$, m.p. 140°; *o*-, m.p. 136—137°, *m*-, m.p. 116—117°, and *p*-$C_6H_4Cl{\cdot}OH$, m.p. 169—170°; *o*-, m.p. 128°, *m*-, m.p. 118—119°, and *p*-$C_6H_4Br{\cdot}OH$, m.p. 175—176°; *o*-, m.p. 150—152°, *m*-, m.p. 148°, and *p*-$C_6H_4I{\cdot}OH$, m.p. 189°; 2 : 4 : 1-$C_6H_3Cl_2{\cdot}OH$, m.p. 166°; 2 : 4 : 1-$C_6H_3Br_2{\cdot}OH$, m.p. 150—151°; *s*-$C_6H_2Cl_3{\cdot}OH$, m.p. 161—162°; *s*-$C_6H_2Br_3{\cdot}OH$, m.p. 181—183°; *o*-, m.p. 120—121°, *m*-, m.p. 124°, and *p*-$NO_2{\cdot}C_6H_4{\cdot}OH$, m.p. 172—173°; *o*-, m.p. 108—109°, *m*-, m.p. 93—95°, and *p*-$OMe{\cdot}C_6H_4{\cdot}OH$, m.p. 167°; α-, m.p. 174—175°, and β-$C_{10}H_7{\cdot}OH$, m.p. 202—203°; thymol, m.p. 140—141°, and *iso*thymol, 89—91°; Me, Et, and benzyl salicylate, char and decomp. at 290°, 295—296°, and 299—300°, respectively. All m.p. are corr. A. T. P.

Standardisation of 2 : 6-dichlorophenol-indophenol for ascorbic acid titration. O. H. Keys (Ind. Eng. Chem. [Anal.], 1939, **11**, 293; cf. A., 1938, III, 217).—Priority for Dick is claimed. F. N. W.

Micro-determination of sugar with α-naphthol. K. Yamafuji and T. Yoshida (Biochem. Z., 1939, **301**, 61—64; cf. Ujsághy, A., 1938, III, 1066).—The sugar solution, after purification with basic Pb acetate, is mixed with 20% α-$C_{10}H_7{\cdot}OH$–EtOH and conc. H_2SO_4. After 3 min. the mixture is rapidly cooled and its colour compared with those of standard solutions [mixtures of $Co(NO_3)_2$ and $CoSO_4$ or of rhodamine, erythrosin, toluidine-blue, and tartrazine]. When the sugar concn. is <1 mg.-%, 0·05% aq. $FeCl_3$ having the same colour as the sugar–$C_{10}H_7{\cdot}OH$ mixture is used in conjunction with the standard solution. W. McC.

Micro-determination of glutaric acid.—See A., 1939, III, 639.

Determination of cholesterol and its esters. I. Precipitation of cholesterol–digitonin complex in water–acetone–trichloroethylene med-

ium. II. New method of extraction of "total cholesterol." Liebermann's reaction as basis for determination. Rapid determination of ratio of esters to total cholesterol. M. Paget and G. Pierrart (Bull. Soc. Chim. biol., 1939, **21**, 528—536, 537—548; cf. A., 1937, III, 291; A., 1938, III, 262).—I. A method for the determination of 0·1—2 mg. of cholesterol (I), but not of amounts >1 g. per l., is described. 1·5 c.c. of a 0·5% solution of digitonin (II) in a mixture of MeOH, EtOH, and C_2HCl_3 is added rapidly to 5 c.c. of a solution of (I) in C_2HCl_3 at 100°. Heating is continued until ~3 c.c. of solvent is left (no MeOH), and then 6 c.c. of $COMe_2$ +0·2 c.c. of H_2O is added slowly. The pptd. complex is washed twice with Et_2O. The filtrate and Et_2O washings are evaporated to dryness and the residual (I) is determined colorimetrically (Liebermann). A solution of (I) in C_2HCl_3 gives the reaction with H_2SO_4 and Ac_2O but the intensity of the colour is only ~ half that obtained when $CHCl_3$ is used as solvent. For complete pptn. of (I) the time of reaction should be as short as possible and only a slight excess of (II) used. In the determination of total (I) and cholesteryl esters by the method of Grigaut (A., 1933, 410; 1935, 1261), 6·5—29% of (I) does not dissolve and is therefore determined as esters. Also adsorption of esters on the complex occurs.

II. For determination of total (I), 2 c.c. of serum are added dropwise to a boiling mixture of 15 c.c. of $COMe_2$ and 5 c.c. of EtOH, with shaking. After addition of 8 c.c. of C_2HCl_3 and shaking for 1 min. the mixture is filtered, an aliquot of the filtrate evaporated, and the residue dissolved in $CHCl_3$ or C_2HCl_3 and determined colorimetrically. Liebermann's reaction should be performed at temp. 13—15° and readings taken after 30 min. For the determination of the ratio (r) of ester : total (I) the latter is extracted by Grigaut's method and, after removing Et_2O, the residue is analysed as above. The esters are determined colorimetrically in the filtrate and washings. The method is compared with those of Velluz (A., 1933, 1065) and Kanner (*ibid.*, 410, 1181) and the results for r agree with those obtained by the former. J. N. A.

Bromine index of cinnamic [acid] derivatives. A. Lespagnol, R. Herlemont, and G. Stern (J. Pharm. Chim., 1939, [viii], **29**, 447—459; cf. A., 1937, II, 290).—A modification of the procedure of Volmar and Samdahl (B., 1928, 236) is described, excess of Br being allowed to act for 24 hr. in diffused light at room temp. The excess of Br is removed with H_2SO_3. Good results are obtained with CHPh:CH·CO_2H, CH_2Ph and cinnamyl cinnamate. Immediate quant. removal of HBr from CHBrPh·CHBr·CO_2H occurs when $AgNO_3$ is added, CHPh:CHBr and unsaturated Br-acids being produced. W. McC.

Determination of iodine in sodium tetraiodophenolphthalein. A. Q. Butler and R. A. Burdett (Ind. Eng. Chem. [Anal.], 1939, **11**, 237—239).—The weighed sample (~0·2 g.) is dissolved in 15 c.c. of 5% aq. NaOH and digested (100°; ¾ hr.) with 25 c.c. of saturated aq. $KMnO_4$. After cooling and then adding 75 c.c. of H_2O and 10 c.c. of dil. H_2SO_4, conc. aq. $NaHSO_3$ is added until the solution is colourless, when 2 c.c. of glacial AcOH, ~1 g. of $(NH_4)_2CO_3$, and 1 c.c. of 0·5% EtOH–di-iodofluorescein are added prior to final titration with 0·1N-$AgNO_3$. The complete analysis requires 1½ hr. and affords results comparable with those obtained by the Pregl micro-combustion method. F. N. W.

Hordenine reineckate. P. Gonnard (Bull. Soc. Chim. biol., 1939, **21**, 617—619).—The *salt*, $C_{10}H_{15}ON(C_4H_6N_6SCr),5H_2O$, m.p. 176—178° (decomp.), is prepared by adding a saturated solution of Reinecke salt (I) to one of hordenine in dil. acid (p_H 4—4·5). The salt shows absorption in the infra-red, and has a large band in the yellow region with max. at 522 mμ.; absorption continues into the extreme ultra-violet after a min. at 232 mμ. For the determination of hordenine, the salt prepared as described above is collected, washed with aq. (I) and then with Et_2O, and dissolved in a few c.c. of $COMe_2$. After removal of the latter, the residue is ignited to Cr_2O_3, which is weighed. The error is ~1% and the solution must contain < 0·1 g. per 100 c.c. J. N. A.

Microchemical distinctive reactions for cocaine, novocaine, and stovaine. A. Martini and J. C. B. Graf (Mikrochem., 1939, **26**, 233—240).—Microchemical methods of detecting the three bases are reviewed. The picric acid method is unsatisfactory, as the crystals produced are very similar and in the case of novocaine may be very similar to those of picric acid. The Br–H_2O test for novocaine (A., 1933, 173) is sp., and its sensitivity is ~1 in 3000. K_2PbI_4 yields characteristic ppts. with all three bases. Treatment of the sample with 10% aq. KI and then an equal amount of 20% aq. $RhCl_3$ yields yellow and salmon crystals with cocaine and stovaine, respectively. With novocaine only an amorphous ppt. is obtained. The sensitivity of this test is ~1 in 10,000. J. W. S.

Microchemistry of yohimbine. A. Martini (Mikrochem., 1939, **26**, 227—232).—Previous methods of detecting yohimbine are neither sp. nor very sensitive. If aq. yohimbine hydrochloride is treated with a particle of KCN and heated the liquid becomes turbid after a few min. and after cooling long prisms are formed, bunched in feather shapes. The limiting concn. detectable by this method is 1 in 5000 and the min. quantity detectable 2 μg. Characteristic microcryst. ppts. are also obtained with $Na_2B_4O_7,10H_2O$, Na_2SeO_3, and Na_2TeO_3 (sensitivity 1 in 5000) and with $K_2C_2O_4,H_2O$ (sensitivity 1 in 3000). Yohimbine can be used for detection of B_4O_7'', SeO_3'', TeO_3'', and C_2O_4''. J. W. S.

Semimicro-colorimetric determination of alkaloid poisons. M. Duquenois (Ann. Falsif., 1939, **32**, 95—97).—The alkaloids (extracted from viscera etc.) are dissolved in H_2O slightly acidified with HCl and are treated with a known excess of a solution of Reinecke salt (I), the prep. of which is described. After 1 hr. the pptd. reineckates are removed by filtration through sintered glass and the concn. of (I) in the filtrate is determined colorimetrically. The error of determination is 8% with those alkaloids which are quantitatively pptd. by (I). E. C. S.