BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

OCTOBER, 1939.

Direct hydrogenations in presence of nickel. P. SABATIER (Bull. Soc. chim., 1939, [v], 6, 1261—1268).—A lecture.

New catalytic syntheses of hydrocarbons. V. N. IPATIEV (Chim. et Ind., 1939, 42, 215—222).—A lecture.

Hydrocarbon chemistry. E. K. RIDEAL (Trans. Faraday Soc., 1939, 35, 806—810).—An introduction to a discussion dealing with the application of differing interpretations of chain reactions in the thermal decomp., catalytic reactions, technical synthesis, and polymerisation of hydrocarbons. F. R. G.

Existence of methylene in hydrocarbon reactions. R. F. BARROW, T. G. PEARSON, and R. H. PURCELL (Trans. Faraday Soc., 1939, 35, 880—889).—A survey of the literature from which it is concluded that CH_2 has been isolated and exists as an intermediate in numerous reactions. From a qual. consideration of the reactions by which CH_2 may be removed, its rapid disappearance in systems containing H_2 or hydrocarbons becomes readily comprehensible. F. R. G.

Stability of hydrocarbon diradicals and their reactions. C. E. H. BAWN and J. MILSTED (Trans. Faraday Soc., 1939, 35, 889—896).—CH_2 from CH_2Br_2 and Na with H_2 yields mainly CH_4 with a little C_2H_4. $[CH_2]_nBr_2$ ($n = 3$, 4, 5, or 6) with Na in N_2 gives $[CH_2]_n$ as free radicals having a min. stability at $n = 4$. No evidence for the existence of CHMe could be obtained. F. R. G.

Pyrolysis of two-carbon and three-carbon paraffin and olefine hydrocarbons. I. Equilibrium mixtures. M. W. TRAVERS. **II. Pure ethane. III. Influence of nitric oxide on the secondary decomposition of ethane.** M. W. TRAVERS and J. A. HAWKES (Trans. Faraday Soc., 1939, 35, 860—864, 864—866, 866—868).—I. Results already recorded (A., 1937, I, 366) are discussed.

II. The thermal decomp. of C_2H_6 at 590° has been repeated with elimination of thermal lag and detailed results are recorded, but the surface influence makes consistent vals. difficult to obtain. The secondary decomp. (formation of CH_4 and aromatic condensate) does not begin until C_2H_4 and H_2 are produced by the primary reaction in accordance with earlier conclusions (*loc. cit.*). Contrary to Storch and Kassel (A., 1937, I, 466), the decomp. products contained $<0{\cdot}4\%$ of C_3H_6 and C_4H_8.

III. The secondary decomp. of C_2H_6 ($C_2H_6 + C_2H_4 \rightarrow CH_4 +$ condensation products) at 590° is not inhibited by NO. It is concluded that, contrary to Hinshelwood and Staveley (A., 1939, I, 30), free radicals are not involved in the primary decomp. of C_2H_6 ($C_2H_6 \rightleftharpoons C_2H_4 + H_2$). F. R. G.

Reaction of hydrogen atoms with propane and the mechanism of the paraffin decompositions. E. W. R. STEACIE and N. A. D. PARLEE (Trans. Faraday Soc., 1939, 35, 854—860).—$C_3H_8 + H$ at 30° gives exclusively CH_4 but at higher temp. up to 250° increasing amounts of C_2H_6 and C_2H_4. It is concluded that the reactions $H + C_2H_5 = 2CH_3$ and $H + C_3H_7 = C_2H_5 + CH_3$ occur readily at room temp. F. R. G.

Preparation of pure gases and of pentane for cryostats.—See A., 1939, I, 484.

Mechanism of catalytic dehydrogenation and cyclisation. R. C. PITKETHLY and H. STEINER (Trans. Faraday Soc., 1939, 35, 979—984).—Treatment of *n*-C_7H_{16} with a dehydrogenating catalyst at 475° leads to the formation of heptene (I) and PhMe; *cyclo*-paraffins or -olefines are not produced. The evidence points to the formation of (I) as an intermediate rather than a by-product. A mechanism is suggested. F. L. U.

Aromatisation of heptane, heptene, and hexene isomerides on chromic oxide.—See A., 1939, I, 479.

Destructive hydrogenation and destruction of hexadecane. H. I. WATERMAN and J. J. LEENDERTSE (Trans. Faraday Soc., 1939, 35, 985—992; cf. B., 1939, 347).—$C_{16}H_{34}$, heated for 1 hr. at 435° with H_2 in contact with Ni on kieselguhr or with Cr_2O_3, yields mainly *n*-paraffins of mol. wt. < that of $C_{16}H_{34}$. Formation of branched chains, cyclisation, and polymerisation also occur as the result of secondary reactions. The yield of CH_4 is large compared with that of other gaseous products. The main reaction is considered to be cracking of the $C_{16}H_{34}$ followed by rapid hydrogenation of the destruction products. F. L. U.

Isomerisation of alkenes on alumina and thoria.—See A., 1939, I, 478.

Olefine-*iso*paraffin additive reactions. S. F. BIRCH and A. E. DUNSTAN (Trans. Faraday Soc., 1939, 35, 1013—1020).—Problems connected with this reaction, experimental details of which have been described (B., 1938, 1007), are discussed, and a reaction scheme is proposed. F. L. U.

Mechanism of catalytic exchange reactions between deuterium and olefines. G. H. TWIGG (Trans. Faraday Soc., 1939, 35, 934—940).—The associative mechanism of Horiuti and Polanyi (A., 1935, 44) for the exchange between C_2H_4 and D

at a Ni catalyst is preferred to the dissociative mechanism of Farkas and Farkas (A., 1938, I, 149). Energies of activation for exchange and hydrogenation, recorded over the range 55—120° for C_2H_4, CH_2:CHMe, CHMe:CHMe, and CH_2:CMe_2 decrease considerably with increasing mol. wt. of the olefine, although the abs. rates of reaction are similar. However, the abs. vals. of the exchange/hydrogenation ratios are in the order expected from the energy vals. and it is concluded that all the reactions take place on a uniform type of catalytically active centre.

F. R. G.

Polymerisation of hydrocarbons. M. W. Perrin (Trans. Faraday Soc., 1939, **35**, 1062—1067).—A short survey of conditions of polymerisation and of the relation between properties and structure of polymerised hydrocarbons. F. L. U.

Dimerisation of petroleum hydrocarbons. W. J. Sparks, R. Rosen, and P. K. Frolich (Trans. Faraday Soc., 1939, **35**, 1040—1052).—Proposed mechanisms are discussed. Most of the products of the dimerisation of C_2H_4, CH_2:CHMe, CH_2:CMe_2, CHMe:CHMe, allene and its derivatives, C_2H_2, and CH:C·CH:CH_2 can be explained by an $\alpha\gamma$ rearrangement of a H atom. F. L. U.

Isomeric transformation of *n*-hexene into β-methyl-Δ^{β}-pentene. A. D. Petrov and V. Schukin (J. Gen. Chem. Russ., 1939, **9**, 506—508).—Δ^{α}-Hexene heated at 325—350° with H_3PO_4 on pumice yields CMe_2:CHEt. R. T.

Peroxides from open-chain olefines and from olefines of a technical cracked benzine. H. Hock and A. Neuwirth (Ber., 1939, **72**, [*B*], 1562—5568).—Prolonged exposure of warm and irradiated Δ^{α}-*n*-hexene to O_2 gives very small yields of γ-Δ^{α}-*n*-*hexenyl H peroxide* (I), b.p. 35°/0·2 mm.; the yields are increased by the addition of small amounts of *cyclo*hexene, active C, or fuller's earth and particularly by the salts of heavy metals, *e.g.*, anhyd. $FeCl_3$ or CuCl. 30% Na_2SO_3 reduces (I) to Δ^{α}-hexen-γ-ol, b.p. 28—30°/1 mm. The mixture of olefines obtained by passing β-methylpentan-α-ol over Al_2O_3 at ~250° gives a better yield of peroxides (not investigated), probably owing to the presence of branched chains. Autoxidation of olefines in a technical cracked benzine from petroleum occurs in the fractions of b.p. ~60—130° but not in those b.p. ~140°. The original material therefore contains inhibitors of peroxide formation. The product contains three well-defined *peroxides*, b.p. 43°/0·5 mm., 47—50°/0·4 mm., and 54—55°/0·4 mm., respectively, derived from the monoolefines C_6H_{10}, C_7H_{12}, and C_8H_{14}. Probably also the peroxide corresponding with C_9H_{16} is formed. The peroxides are reduced by Na_2SO_3 to the corresponding alcohols, $C_6H_{10}O$, b.p. 25—26·5°/0·5 mm., $C_7H_{12}O$, b.p. 29·5—30°/0·2 mm., $C_8H_{14}O$, b.p. 53°/0·2 mm., and $C_9H_{16}O$, b.p. 60—65°/0·2 mm. The cyclic nature of peroxides and alcohols is established by their analytical data. Determinations of the parachors indicate that the peroxides are derived from a *cyclo*pentene, *cyclo*hexene, and *cyclo*heptene ring with a Me substituent in an undecided position. H. W.

Low-molecular polymerisation of dienes and trienes. E. H. Farmer (Trans. Faraday Soc., 1939, **35**, 1034—1040).—Recent experimental work by the author and others (cf. A., 1937, II, 395; 1938, II, 79) is reviewed and discussed. F. L. U.

Butadiene polymerides: elucidation of structure by ozonolysis. R. Hill, J. R. Lewis, and J. L. Simonsen (Trans. Faraday Soc., 1939, **35**, 1067—1073).—Ozonolysis of a butadiene (I) polymeride obtained from (I) in aq. emulsion without a catalyst gives $(CH_2{\cdot}CO_2H)_2$, butane-αβδ-tricarboxylic acid, and resinous acids. Hence (I) under these conditions polymerises by all the possible additive mechanisms; it shows a greater disposition to αδ addition than when polymerised with Na. F. L. U.

Butadiene co-polymerides: elucidation of structure by ozonolysis. R. Hill, J. R. Lewis, and J. L. Simonsen (Trans. Faraday Soc., 1939, **35**, 1073—1079).—Polymerisation of an equimol. mixture of butadiene (I) with CH_2:CMe·CO_2Me (II) in aq. emulsion gives a C_6H_6-sol. rubber-like product which is essentially linear. The major product of ozonolysis is β-methylbutane-αβδ-tricarboxylic acid, with smaller amounts of $(CH_2{\cdot}CO_2H)_2$, $C_8H_{14}(CO_2H)_4$, and a more complex product; > half the polymeride is composed of alternate units of (I) and (II), (I) polymerising mainly by αδ addition. There are also sections where 2, and others where 3 or more, (II) units are adjacent to one another. Contiguity of (I) units is comparatively rare. A theory of the reaction is proposed which correlates the differences in structure and properties between the co-polymeride and the (I) polymeride (cf. preceding abstract) prepared under comparable conditions. F. L. U.

Homogeneous catalytic formation of mono- and di-vinylacetylene from acetylene.—See A., 1939, I, 478.

Chemical properties of tetranitromethane, and its probable constitution. C. Krauz and J. Štěpánek (Chem. Obzor, 1936, **11**, 153—155; Chem. Zentr., 1937, i, 1923; cf. A., 1937, II, 43).—$C(NO_2)_4$ has m.p. 13°, b.p. 126°. Its reactions indicate the constitution $(NO_2)_2$C:NO·O·O·NO. A. J. E. W.

Controlled sulphochromic oxidation of organic compounds containing oxygen. M. Polonovski and A. Lindenberg (Compt. rend., 1939, **209**, 46—47; cf. A., 1924, i, 364).—0·02N-$K_2Cr_2O_7$ in cold 20% H_2SO_4 does not react with $EtCO_2H$, $Pr^{\alpha}CO_2H$, or $Bu^{\alpha}CO_2H$ but oxidises $CH_2Alk{\cdot}OH$ and AlkCHO to acids. The amount of $K_2Cr_2O_7$ used indicates that the C chain suffers some oxidation before the fatty acids are formed. J. L. D.

Alcohols $C_8H_{14(16)}O$ and $C_{10}H_{18(20)}O$ from *Thesium virgatum*.—See A., 1939, III, 884.

Partially methylated hexitols. II. Synthesis of αβγεζ-pentamethyldulcitol. R. S. Tipson and P. A. Levene (J. Biol. Chem., 1939, **129**, 575—585; cf. A., 1939, II, 137).—Methylgalactofuranoside and Me_2SO_4–aq. NaOH–$COMe_2$, then Purdie's reagents, give tetramethylmethylgalactofuranoside (I), b.p. 89°/0·5 mm. (first fractionation gives a mixture of α- and β-forms), containing some tetramethylmethyl-

galactopyranoside (II); its rate of hydrolysis by 0·1N-HCl at 100° is determined. Hydrolysis of (I) gives tetramethyl-*d*-galactofuranose (III) and some (II). No "autocondensation" to octamethyldigalactose was noted. Hydrogenation (Raney Ni) of (III) in H_2O gives *αβδε-tetramethyldulcitol* (IV), m.p. 83—84°, $[\alpha]_D^{25}$ —26·8° in H_2O, also obtained from (I) without isolating (III). (IV) and CPh_3Cl–C_5H_5N at room temp. for 7 days (no moisture) afford ζ-triphenylmethyl-αβδε-tetramethyldulcitol, converted into its γ-benzoate, and thence by boiling 80% aq. AcOH into *αβδε-tetramethyldulcitol γ-benzoate* (V), b.p. 167—169°/0·25 mm., $[\alpha]_D^{25}$ —1·2° in $COMe_2$, and some Bz_2 derivative, b.p. 183°/0·1 mm., $[\alpha]_D^{25}$ —22·1° in $COMe_2$. Methylation (MeI–Ag_2O) of (V) gives *αβγεζ-pentamethyldulcitol γ-benzoate*, b.p. 142°/0·1 mm., $[\alpha]_D^{28}$ ±0·5° in $COMe_2$, hydrolysed by $Ba(OH)_2$-aq. EtOH to *αβγεζ-pentamethyldulcitol*, m.p. 23·5°, b.p. 93°/2 mm., $[\alpha]_D^{30}$ —17·1° in EtOH. A. T. P.

Chemical and biochemical hydrolysis of diose phosphate. Analytical applications. P. Fleury and J. Courtois (Compt. rend., 1939, **209**, 219—221).—0·1N-α-Glycerophosphate (I) with 0·05N-HIO_4 gives phosphoglycollaldehyde (II), which is hydrolysed (2N-H_2SO_4 at 100°/12 min.) 600 times as rapidly as unoxidised (I). (II) is hydrolysed (N-NaOH at 100° or 37°) to give about 50% of the free PO_4''' theoretically obtainable. (II) when hydrolysed by H_2SO_4 or the phosphatase of sweet almonds at about p_H 5·5 gives H_3PO_4 and an aldehyde, oxidised (HIO_4) to CH_2O and HCO_2H. Both (II) and its hydrolytic product obtained at room temp. show equal reducing properties. (I) and the β-form are in equilibrium in solution (cf. Bailly, A., 1938, II, 353), and as (I) is rapidly oxidised by HIO_4 (cf. Fleury and Paris, A., 1933, 696), and (II) is readily hydrolysed by acid, either (I) or (II) can be determined. J. L. D.

Ring structure in certain aliphatic organic compounds. H. A. Smith and J. P. McReynolds (J. Amer. Chem. Soc., 1939, **61**, 1963—1970).—Ring formation, similar to that postulated to explain the effect of the alkyl chain length of *n*-aliphatic acids on the velocity of esterification in MeOH (A., 1939, I, 206, 376), gives a satisfactory explanation of the effect of the character of an alkyl side-chain on the processes of esterification and hydrolysis, on acid dissociation consts., and on optical activity. The ortho-effect is attributed to the same type of structure. W. R. A.

Recognition of carboxylic acids as ureides with aid of carbodi-imides. IV. Detection of αβ-substituted acids. F. Zetzsche and G. Röttger (Ber., 1939, **72**, [*B*], 1599—1612).—*N*-Acyl-*NN'*-di-*p*-dimethylaminophenylcarbamides (I) are darkest when derived from CHR:CH·CO_2H, somewhat paler if obtained from CRR':CH·CO_2H, and so little coloured if derived from CHR:CR'·CO_2H or CH_2:CR'·CO_2H (α-effect) that the limit of visibility is often not reached. The following (I) are described in which the acyl group is: *acrylyl*, m.p. 144·5° after softening at 141°; *α-crotonyl*, m.p. 150° (corr.); *Δ^α-hexenoyl*, m.p. 139° (softens at 137°); *Δ^α-octadecenoyl*, m.p. 115° (softens at 113)°; *Δ^α-hentriacontenoyl*, m.p. 103—104°; cyclo*hexylideneacetyl*, m.p. 151° (softens at 149°); *sorbyl*, yellow *form*, m.p. 147° (softens at 145°), and orange *variety* passing into yellow form at 100°; *geranyl*, m.p. 126—127°; *fumaryl*, m.p. 168° (slight decomp.) (softens at 166°); *cinnamoyl*, m.p. 155·5° (softens at 153°); *furfuracrylyl*, m.p. 153—154° (corr.); *piperyl*, m.p. 154° (softens at 153°), re-solidifying at 155° and again melting at ~185°; *acetylenecarboxyl*, m.p. 132° (softens at 129°); *phenylpropiolyl*, m.p. 151° (softens at 149°); *Δ^β-hexenoyl*, m.p. 146° (corr.) (softens at 144°); *γ-phenyl-Δ^β-butenoyl*, m.p. 150—152°; *Δ^β-butene-αδ-dicarboxyl*, m.p. 210°; *Δ^γ-pentenoyl*, m.p. 148—149° (corr.); cis-*Δ^χ-tetracosenoyl*, m.p. 96—97°; trans-*Δ^χ-tetracosenoyl*, m.p. 110—111·5°; α-cyclo*geranyl*, m.p. 142—143°; *chaulmoogryl*, m.p. 116·5° (softens at 115°); *α-methylacrylyl*, m.p. 143·5° (softens at 140°); *tiglyl*, m.p. 137° (softens at 135°); *atropyl*, m.p. 134—135°; *α-methylcinnamoyl*, m.p. 139° (softens at 135°); *α-phenylcinnamoyl*, m.p. 152·5° (softens at 151°); *$\Delta^{1:4}$-dihydrobenzoyl*, m.p. 148—149° (decomp.); *benzoyl*, m.p. between 198° and 218° according to rate of heating; p-*toluoyl*, m.p. 147—148°; *anisoyl*, m.p. 151—153°; *piperonoyl*, m.p. 135—136°; β-*phenylpropionyl*, m.p. 155—156°; *terephthalyl*, becomes discoloured at ~180°, darkens at 200°, softens at ~240°, and decomposes at 320°, which passes in boiling *sec.*-C_8H_{17}·OH into *terephthalyldi*-p-*dimethylaminophenylimide*, decomp. 340°; iso*phthalyl*, m.p. 205—215° (decomp.) (softens at 162° and becomes hard again at ~190°), whence iso*phthalyldi*-p-*dimethylaminophenylimide*, m.p. 244—247° (decomp.) (softens at ~240°); 1-, m.p. 162° (decomp.), and 2-, m.p. 185—190°, *-naphthoyl*; *anthracene*-9-*carboxyl*, m.p. 180° (softens at 177°); 9 : 10-*dihydroanthracene*-9-*carboxyl*, m.p. 119—121°; *diphenylacetyl*, m.p. 154—155° and ~180° after resolidification; 2' : 4'-*dimethoxybenzophenone*-2-*carboxyl*, m.p. 154—155·5°; β-1-*pyrenoylpropionyl*; γ-1-*pyrenylbutyryl*, m.p. 153—155°; *furan*-2-*carboxyl*, m.p. 141° (softens at 136°); *thiophen*-2-*carboxyl*, m.p. 136·5—137°; *nicotinoyl*, m.p. 150° (softens at 128°); *pyridine*-2-*carboxyl*, m.p. 154° (softens at 150°); *cyanoacetyl*, m.p. 262° (softens at 255°). H. W.

Trifluoroacetates.—See A., 1939, I, 482.

Electrolysis of potassium tiglate. A. D. Petrov and D. A. Vjachirev (J. Gen. Chem. Russ., 1939, **9**, 513—515).—Electrolysis of K tiglate gives $(CHMe:)_2$ and *α-methyl-Δ^α-propenyl tiglate*, b.p. 170—195°. 74% of the current is used for the reaction of oxidation of tiglic acid to CO_2 and H_2O. R. T.

Polymerisation of styrene and methyl methacrylate.—See A., 1939, I, 479.

Re-esterification of stearic acid esters with higher fatty acids and re-esterification of tristearin with triolein. Y. Toyama (J. Soc. Chem. Ind. Japan, 1939, **42**, 218B).—Heating an equimol. mixture of Me stearate (I) with oleic acid (II) at 280±5° for 2 hr. caused re-esterification and the conversion of 40% of (II) into Me oleate. With (I) and lauric acid, about 30—40% of each constituent reacted analogously. Similarly, considerable re-esterification (30—50%) occurred with mixtures of tristearin (1 mol.) with (II) (3 mols.) or with (II) and

behenic acid. Mixed glycerides were produced by heating an equimol. mixture of tristearin and triolein. E. L.

Acetylation of 9:10-dihydrostearic acids, and diastereoisomeric transformations of these acids when treated with acetic anhydride. V. I. ESAFOV (J. Gen. Chem. Russ., 1939, 9, 503—505).—The isomeride of m.p. 95° is more difficult to acetylate (with Ac_2O) than is that of m.p. 132°, thus confirming the supposition that the OH of the former isomeride are in corresponding positions. The products are in both cases mixtures of the acetates of the two forms. R. T.

Electrolysis of acid–ester salts in non-aqueous solutions, and mechanism of the Crum-Brown–Walker synthesis.—See A., 1939, I, 480.

Separation of [constituents of] mixtures of dicarboxylic acids. F. RENNKAMP (Z. physiol. Chem., 1939, **260**, 276—278; cf. Klenk, A., 1936, 1225).—A mixture of azelaic and sebacic acid is esterified with MeOH + H_2SO_4, the mixture is fractionally distilled at 125—140°/0·01—0·02 mm., the fractions are hydrolysed with KOH in MeOH, the K salts are converted into free acids, and these are crystallised from MeOH. W. McC.

Polarometric study of the action of heat on aqueous solutions of *l*-malic acid. R. DESCHAMPS (Bull. Soc. chim. Belg., 1939, **48**, 201—228).—Owing to the formation of dehydration products the *l*-rotation of dil. solutions of *l*-malic acid (I) and the *d*-rotation of conc. solutions each change when the solutions are kept at 75°. The rotations gradually approach new const. vals. characteristic for each concn. Conflicting optical data recorded in the literature for solutions of (I) are attributed to the difficulty of separating the acid from optically active dehydration products. The sign of the rotation of the solutions is reversed within the concn. range 29·5—30·5 wt.-%. The Darmois rule appears to apply to the solutions investigated. J. W. S.

Molecular and electronic effects of substituent on optical activity of tartaric acid. See A., 1939, I, 357.

Infra-red absorption spectra of acetaldehyde, paraldehyde, α- and β-trithioacetaldehyde.—See A., 1939, I, 402.

Raman spectra of α- and β-trithioacetaldehyde and of monothioparaldehyde.—See A., 1939, I, 403.

Crotonaldehyde condensation; condensation with acid amides. H. L. DU MONT and G. RÄTZEL (Ber., 1939, **72**, [*B*], 1500—1505).—The condensation of CHMe:CH·CHO (I) with $HCO·NH_2$ gives C_5H_5N in very small amount probably because only the *cis*-form of (I) can act in this direction and it is present only in a very small proportion in technical (I). In the reaction between (I) and NH_2Ac the reactions of the *cis*- and *trans*-forms of (I) are concurrent. The attempted isomerisation to the *cis*-form by irradiation resulted in a general acceleration of the reaction. *o*-$C_6H_4Me·CHO$ which has preformed Me in the *cis*-position does not give the desired *iso*quinoline or 3-methyl*iso*quinoline with $HCO·NH_2$ or NH_2Ac, probably because the activating effect of CHO is not so well transmitted through an aromatic nuclear double linking as through a simple vinyl group. $Bu^{\beta}CHO$ and $HCO·NH_2$ do not appear to afford C_5H_5N, dihydropyridine, or piperidine, and nitrogenous products are not derived from NH_2Ac. $CH_2Cl·CH_2·CHO$ and $CHMeCl·CH_2·CHO$ tend to intramol. loss of HCl with formation of the unsaturated aldehyde rather than to elimination of HCl between the Cl of the aldehyde and H from NH_2Ac; the latter functions essentially as acceptor for the acid and therefore forms diacetamide hydrochloride in both cases. Heterocyclic compounds are not obtained from $CH_2Cl·CO·NH_2$ and EtCHO. H. W.

Catalytic preparation of acetone. A. TIAN and (MLLE.) S. VIAN (Bull. Soc. chim., 1939, [v], **6**, 1436—1447).—The yield of $COMe_2$ from AcOH passed over $Ca(OAc)_2$ or $Ba(OAc)_2$ on pumice is max. (81%) at ~620°. From 600° to 900°, CO_2 formed decreases and CO and CH_4 increase. $Pb(OAc)_2$ is unsatisfactory as a catalyst, being reduced. E. W. W.

Mutarotation of xylose.—See A., 1939, I, 478.

Elucidation of the configuration at the glucosidic carbon atom in sugars by formation of ammonium salts. K. HESS and K. E. HEUMANN (Ber., 1939, **72**, [*B*], 1495—1499).—Exceptions are noted to Micheel's rule according to which only α-1-halogenoacetyl sugars react with NMe_3 with production of quaternary bases, which occurs with Walden inversion. It is uncertain whether halogeno-derivatives of furanose sugars and those of pyranose forms react essentially in opposite directions or whether Micheel's rule cannot be generalised. 4-Chloro-2 : 3 : 6-trimethyl-*d*-glucofuranose 5-*p*-toluenesulphonate in C_6H_6 is converted by NMe_3 in abs. EtOH at −80° and then at room temp. into *trimethyl*-5-p-*toluenesulphonyl*-2 : 3 : 6-*trimethyl*-β-d-*glucofuranosidoammonium chloride* (I), m.p. 133°, $[\alpha]_D^{20}$ −48·9° in MeOH, −47·1° in H_2O, −45·7° in $CHCl_3$ (apparently unaccompanied by any dextrorotatory material), and 2 : 3 : 6-*trimethyl*-1-*ethyl*-α-d-*glucofuranoside* 5-p-*toluenesulphonate* (II), $[\alpha]_D^{20}$ +60·6° in MeOH, +59·8° in $CHCl_3$, +57·7° in C_6H_6. Na and 80% EtOH at room temp. transform (I) into trimethyl-2 : 3 : 6-trimethyl-β-*d*-glucofuranosidoammonium chloride, m.p. 165°, $[\alpha]_D^{20}$ +67·7° in H_2O, whereas when similarly treated (II) gives 2 : 3 : 6-*trimethyl*-1-*ethyl*-α-d-*glucofuranoside*, $[\alpha]_D^{20}$ +66·6° in $CHCl_3$, +65·6° in C_6H_6, +63·4° in MeOH. H. W.

Esters of methanesulphonic acid in the sugar group. B. HELFERICH, H. DRESSLER, and R. GRIEBEL (J. pr. Chem., 1939, [ii], **153**, 285—299).—Gradual addition of $MeSO_2Cl$ to anhyd. glucose in C_5H_5N at −20°, keeping the mixture at 0°, and subsequent treatment with Ac_2O affords β-*d*-glucose tetra-acetate 6-methanesulphonate (I), m.p. 156°, $[\alpha]_D$ +10·1° in $CHCl_3$, in ~29% yield. (I) is converted by anhyd. NaI in $COMe_2$ at 100° into β-d-*glucose tetra-acetate* 6-*iodohydrin*, m.p. 152—153°, $[\alpha]_D^{20}$ +9·1° in $CHCl_3$. Analogously the by-product in the prep. of (I) gives α-d-*glucose tetra-acetate* 6-*iodohydrin*, m.p. 180—181° (corr.), $[\alpha]_D^{20}$ +101·0° in $CHCl_3$. This is

transformed by Zn dust and 70% AcOH at 80—85° into α-d-iso*rhamnose tetra-acetate*, m.p. 119·5° (corr.), $[\alpha]_D^{20}$ +123·8° in $CHCl_3$, which with HBr–AcOH at 0° gives acetobromo-*d-iso*rhamnose, m.p. 143·5—144° (corr.), $[\alpha]_D^{18}$ +247° in $CHCl_3$. 1 : 2-5 : 6-Di*iso*propylideneglucose is transformed by $MeSO_2Cl$ in C_5H_5N into 1 : 2-5 : 6-di*iso*propylideneglucose 3-*methanesulphonate* (II), m.p. 83—84° (corr.), $[\alpha]_D^{19}$ −50·0° in $CHCl_3$, which with H_2SO_4–aq. MeOH affords d-*glucose* 3-*methanesulphonate*, m.p. 133—134° (corr.), $[\alpha]_D^{20}$ +77·0° to +56·9° in H_2O during 2 days. This is converted by Ac_2O and NaOAc at 100° into β-d-*glucose tetra-acetate* 3-*methanesulphonate*, m.p. 169—170° (corr.), $[\alpha]_D^{19}$ +1·5° in $CHCl_3$, transformed by HBr–AcOH containing Ac_2O into α-d-*bromoglucose* 2 : 4 : 6-*triacetate* 3-*methanesulphonate*, (III) $[\alpha]_D^{19}$ +160° in $CHCl_3$. (II) is converted similarly into α-d-*bromoglucose* 2 : 6-*diacetate* 3-*methanesulphonate* (IV), m.p. 136—137° (corr.; decomp.), $[\alpha]_D^{19}$ +170° in $CHCl_3$. Ag_2CO_3 and MeOH transform (III) into *methyl*-β-d-*glucoside triacetate* 3-*methanesulphonate*, m.p. 128—128·5° (corr.), $[\alpha]_D^{19}$ −21·7° in $CHCl_3$, and (IV) into *methyl*-β-d-*glucoside* 2 : 6-*diacetate* 3-*methanesulphonate*, m.p. 105° (corr.), $[\alpha]_D^{19}$ −56·8° in $CHCl_3$. PhOH, KOH, and (IV) yield *phenyl*-β-d-*glucoside* 2 : 6-*diacetate* 3-*methanesulphonate* (V), m.p. 134·5—135° (corr.), $[\alpha]_D^{19}$ −56·6° in $CHCl_3$, which gives *phenyl*-β-d-*glucoside* 2 : 4 : 6-*triacetate* 3-*methanesulphonate*, m.p. 154—154·5°, $[\alpha]_D^{18}$ −27·0° in $CHCl_3$. Deacetylation of (V) by NaOMe in $CHCl_3$–MeOH affords *phenyl*-β-d-*glucoside* 3-*methanesulphonate*, m.p. 175° (corr.; decomp.), $[\alpha]_D^{19}$ −28·2° in C_5H_5N. (II) is hydrolysed by aq. AcOH to non-cryst. 1 : 2-iso*propylideneglucofuranose* 3-*methanesulphonate*, $[\alpha]_D^{18}$ −20·6° in H_2O, converted by Ac_2O–C_5H_5N into 1 : 2-iso*propylideneglucofuranose* 5 : 6-*diacetate* 5-*methanesulphonate*, m.p. 136—136·5° (corr.), $[\alpha]_D^{19}$ −2·3° in $CHCl_3$. This is transformed by HBr–AcOH containing Ac_2O into α-d-*bromoglucofuranose* 2 : 5 : 6-*triacetate* 3-*methanesulphonate*, m.p. 123—123·5° (corr.), $[\alpha]_D^{19}$ +191·5° in $CHCl_3$. Di*iso*propylidenegalactose and $MeSO_2Cl$ in C_5H_5N at 0° yield 1 : 2 : 3 : 4-di*iso*propylidenegalactopyranose 6-*methanesulphonate*, m.p. 122°, $[\alpha]_D^{20}$ −62·0° in $CHCl_3$. H. W.

Acyl migration in a derivative of galactose. J. S. D. Bacon, D. J. Bell, and H. W. Kosterlitz (J.C.S., 1939, 1245—1250).—4 : 6-Benzylidene-β-methylgalactoside (improved prep.) is converted by BzCl–C_5H_5N–C_6H_6 at 38° for 24 hr. into 4 : 6-*benzylidene*-β-*methylgalactoside* 2 : 3-*dibenzoate* (I), m.p. 195—196°, $[\alpha]_D^{17}$ +156·1° (all in $CHCl_3$ unless stated otherwise), which with boiling $COMe_2$–0·25N-HCl gives β-*methylgalactoside* 2 : 3-*dibenzoate* (II), m.p. 136·5—138·5°, $[\alpha]_D$ +101·9°, or (+1$CHCl_3$), m.p. 80°, $[\alpha]_D$ +80·6° [PhCHO–$ZnCl_2$ gives (I), m.p. 198°]. (II) and BzCl–C_5H_5N–C_6H_6 afford β-*methylgalactoside* 2 : 3 : 6-*tribenzoate* (III), m.p. 143—144°, $[\alpha]_D^{18}$ +56·1° [its 4-p-*toluenesulphonate* (IV), m.p. 175°, $[\alpha]_D^{20}$ +58·9°, is unaffected by NaI–$COMe_2$ at 100°]. Methylation (Purdie's reagents) (method: Levene *et al.*, A., 1932, 1115) of (III) gives a dimethylhexose tribenzoate, debenzoylated (Zemplén) to an amorphous product (OMe 27%) and 2-methyl-β-methylgalacoside, m.p. 132—133°, $[\alpha]_D^{18}$ +1·2° (cf. Oldham *et al.*, A., 1938, II, 127). This acyl migration in the galactose series is discussed. *iso*Propylidene-β-methylgalactoside and CPh_3Cl–C_5H_5N (method: Bell *et al.*, 1938, II, 393) give a product, converted by *p*-$C_6H_4Me{\cdot}SO_2Cl$–C_5H_5N at 38° for 48 hr. into 6-*triphenylmethyl*-3 : 4-iso*propylidene*-β-*methylgalactoside* 2-p-*toluenesulphonate*, m.p. 163—164°, $[\alpha]_D^{21}$ −8·4°. Change in α with a solution of (IV) in $COMe_2$–H_2O–N-HCl at 100° is very small; the resulting (after 220 min.) β-*methylgalactoside* 2-p-*toluenesulphonate* has m.p. 143—144°, $[\alpha]_D^{21}$ −23·7° in EtOH (3 : 4 : 6-*tribenzoate*, m.p. 143—144°, $[\alpha]_D^{18}$ +45·5°). A. T. P.

Syntheses of glycosides. XI. Cichoriin. F. S. H. Head and A. Robertson (J.C.S., 1939, 1266—1267; cf. A., 1931, 73).—Æsculetin and BzCl–aq. NaOH give 6-O-*benzoylæsculetin* (I), m.p. 198° (sinters at 185°), and the 6 : 7-*O*-dibenzoate, m.p. 186°. (I) and MeI–K_2CO_3–$COMe_2$ give 6-benzoyloxy-7-methoxycoumarin, m.p. 217—218° (*loc. cit.*), converted by NH_3–MeOH at 0°, then aq. HCl, into 7-*O*-methylæsculetin. (I), *O*-tetra-acetyl-α-glucosidyl bromide, and active Ag_2O give 7-O-*tetra-acetyl*-β-*glucosidoxy*-6-*benzoyloxycoumarin*, m.p. 218°, which with NH_3–MeOH at 0° gives 6-*hydroxy*-7-β-*glucosidoxycoumarin* (*cichoriin*), m.p. 213—214°, $[\alpha]_D^{20}$ −104° in aq. dioxan (*Ac*$_5$ derivative, m.p. 218°), identical with a natural specimen. A. T. P.

Chemical examination of the fruit of *Pittosporum undulatum*. J. W. Cornforth and J. C. Earl (J. Proc. Roy. Soc. New South Wales, 1939, **72**, 249—254).—Extraction of the dried fruit with Et_2O gives a small amount of unidentified material, m.p. 51—52°, and pentatriacontane, m.p. 73—75°. The alcoholic extract of the fruit gives a non-separable mixture of a saponin and an anthocyanidin. Addition of $CaCl_2$ to a solution of the evaporated extract in H_2O gives a ppt. rich in leucoanthocyanin which is hydrolysed by HCl–H_2O–EtOH to cyanidin. Hydrolysis of the alcoholic extract affords a mixture from which $CHCl_3$ removes *pittosapogenin*, $C_{30}H_{50}O_7$, m.p. 308—310°, $[\alpha]_D$ 27·8° in $CHCl_3$–MeOH (*acetate*, m.p. 252—254°). Glucose (I), galactose (II), and a little mannose are formed during the hydrolysis; pentoses, glycuronic acid, and ketoses are absent. The separation of (I) and (II) by $NPhMe{\cdot}NH_2$ is greatly improved by allowing the galactosephenylmethylhydrazone to crystallise for two days in the ice-chest instead of for 6 hr. at room temp. H. W.

Gentiopicrin. II. Y. Asahina and Y. Sakurai (Ber., 1939, **72**, [*B*], 1534—1540; cf. A., 1936, 731).—The maximal formation of eugentiogenin (I) accompanied by an almost equal amount of Tanret's gentiogenin (II) is observed when the enzymic hydrolyses of gentiopicrin (III) takes place at 35—37° and p_H 3·4. At p_H 7·2 the production of (II) reaches its max. at the expense of (I), so that primarily formed (I) appears to pass in the presence of emulsin into (II). Continuous extraction with Et_2O of a solution containing (III) and emulsin gives optically inactive *mesogentiogenin* (IV) as a viscous, yellow oil which polymerises within a few days to an amorphous mass. It gives a blue colour with $FeCl_3$. It is $C_{10}H_{10}O_4$ since it passes into *tetrahydromesogentiogenin* (V), $C_{10}H_{14}O_4$, m.p. 103°. In H_2O in presence of emulsin (IV)

passes into (I) and (II). Takadiastase converts (IV) into (II). Hence (IV) is probably the primary product of the hydrolysis of (III). In respect of its optical inactivity and formation of (V) there is a difference between (IV) and the hypothetical protogentiogenin attributed to spontaneous at. displacements at the moment of elimination of the sugar. Gentiopicrin tetra-acetate (VI) is hydrogenated in EtOH or EtOAc to α- (VII), m.p. 208° $[\alpha]_D^{25}$ −48·06° in $CHCl_3$, and (possibly non-homogeneous) β- (VIII), m.p. 159°, $[\alpha]_D^{25}$ −98·80° in $CHCl_3$, *-tetrahydrogentiopicrin tetra-acetate*. Chlorination of a mixture of (VII) and (VIII) in $CHCl_3$ and crystallisation of the product leads to the isolation of *tetrahydrogentiopicrin tetra-acetate dichloride*, m.p. 161°, which is stable towards $KMnO_4$ in $COMe_2$; it is obtained almost quantitatively from (VII) whereas (VIII) affords essentially a non-cryst. product. Hydrogenation (Pd–C in AcOH) of (VI) gives *hexahydrogentiopicrin tetra-acetate* (IX), m.p. 154°, $[\alpha]_D^{20}$ −54·24° in $CHCl_3$, also obtained directly from (VII); under similar conditions (VIII) gives a non-homonegeous product from which (IX) can be isolated. The previous observation that (III) loses 1 mol. of AcOH when acted on by KOH–EtOH could not be confirmed. After removal of sugar the freshly prepared (IV) is heated under pressure with $Ba(OH)_2$, which causes the loss of 1 mol. each of CO_2 and HCO_2H. Since (III) does not give an additive product with maleic anhydride it does not appear to contain a conjugated double linking. (III) is unchanged when heated in EtOH at 220° or in boiling xylene. The salt obtained by the hydrolysis of (III) is unaffected by prolonged contact with cold alkali and (III) is regenerated by the addition of acid. H. W.

Kikyo root. VII. Mol. wt. and hydrolysis of platycodin. M. Tsujimoto and T. Matsumoto (J. Agric. Chem. Soc. Japan, 1939, **15**, 690—695).—Platycodin, $C_{42}H_{68}O_{17}$, is completely hydrolysed to *platycodigenin*, $C_{30}H_{48}O_7$, and glucose in 20 hr. by boiling 5% EtOH–HCl or in 100 hr. by boiling 5% EtOH–H_2SO_4. J. N. A.

Composition and properties of soluble starch. C. Dumazert and G. Santoni (Compt. rend., 1939, **209**, 127—129).—A solution of starch from wheat, arrowroot, maize, potato, and rice after treatment with cold NaOH has $[\alpha]_D$ +189° and does not gel when cooled. It gives a Ac_3 derivative and is oxidised by I in an alkaline medium, from the extent of which, before and after hydrolysis, the min. mol. wt. is calc. to be 3258. J. L. D.

"Faults" in cellulose molecules. H. Staudinger and A. W. Sohn (Naturwiss., 1939, **27**, 548—549).—Two forms of cellulose (I) chain are distinguished: (i) the normal, containing an uninterrupted series of pyranoid glucose units and represented by repptd. (I), in which the degree of polymerisation in Schweizer's reagent equals that of the nitrate (II); (ii) a second form containing reactive "faults" of an ester nature which suffer fission with alkali but not with conc. HNO_3; this can be formed from normal (I) by oxidation of a glucose unit to a product containing CO_2H. Oxycellulose in Schweizer's reagent has therefore a much smaller degree of polymerisation than (II), due to degradation by the reagent. Treatment of (II) with dil. alkali, however, lowers the degree of polymerisation to that of the former. The technical implications of this are discussed. S. H. H.

System cellulose–sodium hydroxide–water.—See A., 1939, I, 512.

Condensation products of aldehydes with amines.—See A., 1939, I, 510.

Microscopy of the amino-acids and their compounds. IV. Picrolonates. R. Dunn, K. Inouye, and P. L. Kirk (Mikrochem., 1939, 154—160; cf. A., 1937, II, 314).—Characteristic crystal habits and optical data are described for the salts of picrolonic acid with 27 NH_2-acids. The predominant crystal habit is acicular, the needles being usually arranged in rosettes. In nearly all cases the *n* of the crystals can serve for identification. J. W. S.

Nickel salts of amino-acids: their solubility. K. Lang (Biochem. Z., 1939, **301**, 368—370).—The salts (2 mols. acid residue to 1 Ni) are prepared by boiling aq. solutions of the acids with $NiCO_3$ until evolution of CO_2 ceases. The *l*(+)-valine salt is anhyd. but the salts of glycine, *dl*-alanine, *dl*-aminobutyric acid, *l*-leucine, *dl-iso*leucine, and *l*-proline contain $2H_2O$. The solubilities of the salts in H_2O and MeOH are recorded. Although considerable differences in solubility exist, the separation of NH_2-acids (*e.g.*, from protein hydrolysates) by means of the salts is not practicable. W. McC.

Cosubstrates in proteolysis. O. K. Behrens and M. Bergmann (J. Biol. Chem., 1939, **129**, 587—602; cf. A., 1939, II, 463).—*Carbobenzyloxy*-l-, m.p. 122—123°, and -d-*leucineamide*, m.p. 123—124°, are hydrogenated (Pd-black; AcOH–MeOH) to l- (I), m.p. 125—126°, $[\alpha]_D^{27}$ +9·25° in H_2O, and d-*leucineamide acetate*, m.p. 125—127°, $[\alpha]_D^{26}$ −9·3° in H_2O, respectively. (I) and *l*-leucineanilide (II) are hydrolysed slowly by cysteine-activated papain (*A*) (citrate buffer, p_H 5·0); *e.g.*, (I) shows a 75% fission (optimum at p_H 5) at 40° in 5 days, and (II), 57% in 6 days. *d*-Leucineamide shows no fission after 4 days at 40°. The action of various papain preps. on (I) and carbobenzyloxy-*l-iso*glutamine is compared. Carbobenzyloxy-*l*-glutamic acid, N-NaOH, NH_2Ph, and (*A*) at 40° give the anilide, m.p. 193—195°, $[\alpha]_D^{26}$ −15·3° in 95% EtOH, hydrogenated to glutam-monoanilide (III), m.p. 193—194°. Glycine-amide (IV) or -anilide (V), or (III), is resistant to (*A*); the anilides are, however, hydrolysed slowly (17 and 41% fission in 4 days, respectively) in presence of horse serum (has no effect alone), which thus produces substances enabling (*A*) to effect hydrolysis. (IV) (35% in 6 days) or (V) or (III) is hydrolysed by (*A*) when acetyl-*dl*-phenylalanylglycine (VI) (cosubstrate) is present; thus (V) gives acetyl-*l*-phenylalanylglycineanilide (VII), m.p. 207—208°, acetylphenylalanylglycylglycineanilide, m.p. 242—243°, (VI), NH_2Ph, and glycine. (V) and acetyl-*l*-phenylalanylglycine probably first give acetyl-*l*-phenylalanylglycylglycineanilide, hydrolysed to glycine and NH_2Ph, some of the latter then forming acetyl-*l*-phenylalanylglycineanilide. Acetyl-*dl*-phenylalanine (V), and (*A*) show no reaction. (V)

(as acetate) and carbobenzyloxy-*l*- (VIII) or -*d*-phenylalanylglycine in presence of (*A*) (7 days) gives a nearly quant. yield of *carbobenzyloxy*-l-, m.p. 213°, $[\alpha]_D^{27}$ −3·3° in AcOH, or -d-*phenylalanylglycylglycineanilide*, m.p. 213—214°, $[\alpha]_D^{27}$ +3·1° in AcOH, respectively (not attacked by enzyme solution). (V) and benzoyl-*dl*-phenylalanylglycine similarly give (l + dl-)*benzoylphenylalanylglycylglycineanilide*, m.p. 236—240°. (VIII), (III), and (*A*) give *carbobenzyloxy*-l-*phenylalanylglycyl*-l-*glutam-monoanilide*, m.p. 213—215°. Carbobenzyloxyglycine and (III) + (*A*) give *carbobenzyloxyglycyl*-l-*glutamanilide*, m.p. 182°. Glycyl-*l*-leucine is not hydrolysed by (*A*), but catalysis by (VI) gives, through acetylphenylalanyldiglycyl-leucine, free glycine and *l*-leucine; 88% of (VI) is recovered and there is 65% hydrolysis in 29 hr., almost complete in a few days; the mechanism is discussed. (V) is slowly split by (*A*) when proteins, *e.g.*, blood fibrin, gelatin, casein, are present, and these, on hydrolysis, give products which act as "cosubstrates." Carbobenzyloxytyrosineamide is hydrogenated to l-*tyrosineamide acetate* (IX), m.p. 177°, which with (VIII) and (*A*) give *carbobenzyloxy*-l-*phenylalanylglycyl*-l-*tyrosineamide*, m.p. 248° (decomp.) (darkens at 243°). (IX), (VI), and (*A*) give free tyrosine (80% hydrolysis). Glycine anhydride and acetamidocinnamic acid azlactone, in aq. NaOH–$COMe_2$, give *acetyldehydrophenylalanylglycylglycine*, m.p. 223—224°, hydrogenated (Pd-black; AcOH–MeOH) to *acetyl*-dl-*phenylalanylglycylglycine* (XI), m.p. 183—184° [57% hydrolysis by (*A*) in 3 days] [*amide* (XII), m.p. 203—206°, from (XIII)]. (XI) and CH_2N_2–MeOH–Et_2O give the *Me* ester (XIII), m.p. 158—159°, converted by N_2H_4,H_2O–EtOH into *acetyl*-dl-*phenylalanylglycylglycine hydrazide*, m.p. 200—202°, which through the azide affords the *anilide*, m.p. 229—231°. This is hydrolysed slowly by (*A*) (16% of each of the peptide bonds in 3 days), but (XII) is hydrolysed more readily to acetylphenylalanylglycine, glycine, and NH_3. (XI), NH_2Ph, and (*A*) give (VII). A. T. P.

Physico-chemical analysis of reactions of organic amides with acids. Carbamide with fatty acids.—See A., 1939, I, 524.

Preparation of cyanogen iodide.—See A., 1939, I, 483.

Amidines and amidoximes with trypanocidal activity. I. D. Lamb and A. C. White (J.C.S., 1939, 1253—1257; cf. King *et al.*, A., 1938, III, 63).—Alkylenedicarbonamidoximes, $[CH_2]_n[C(NH_2):N\cdot OH]_2$, are prepared (readily when $n = 5$ or 10—13; with difficulty when $n = 7$—9) from $[CH_2]_n(CN)_2$ (*A*) and NH_2OH by Tiemann's method (A., 1884, 734). The following are described: *pentane*-αε-*, m.p. 142—144° (*dihydrochloride*, m.p. 150—155°), *heptane*-αη-*, m.p. 156°, *nonane*-αι-, m.p. 167°, *decane*-ακ-†, m.p. 184—186° (decomp.) (*dihydrochloride*, m.p. 149—158°; Ac_2 derivative, m.p. 129°), *undecane*-αλ-† (I), m.p. 166° (*dihydrochloride*, m.p. 178°), and *tridecane*-αν-*dicarbonamidoxime* † (II), m.p. 170° (*dihydrochloride*, m.p. 158—160°). *Diphenyl*-, m.p. 245° (decomp.) [*dihydrochloride*, m.p. 290° (decomp.)], *diphenylmethane*-, m.p. 215° (previous sintering) (*dihydrochloride*, decomp. 220°), *dibenzyl*-, decomp. ~243° (*dihydrochloride*), and *stilbene*-4 : 4′-*dicarbonamidoxime*, m.p. >320° (decomp.) (*dihydrochloride*, chars ~300°), are similarly prepared. α-*Carbamyl*-*, m.p. 157—158° (*hydrochloride*, m.p. 144°), and α-*cyano-undecane*-λ-*carbonamidoxime* *, m.p. 87—88° (*hydrochloride*, m.p. 84°), accompany (I) and α-*cyanotridecane*-ν-*carbonamidoxime* *, m.p. 98° (*hydrochloride*, m.p. 96°), is formed with (II). κ-*Cyanoundecoamide*, m.p. 87°, λ-*cyanododecoamide*, m.p. 101°, and ν-*cyanotetradecoamide*, m.p. 103—104°, are formed as by-products during prep. of (*A*) from $[CH_2]_nBr_2$ and KCN. 4 : 4′-*Dicyanostilbene*, m.p. ~278° (after sintering), is obtained from the $(NH_2)_2$- [prep. from less fusible $(NO_2)_2$-]derivative. The following are prepared by the method of Easson *et al.* (A., 1932, 55): *decane*-αδ-*dicarbonamidine dihydrochloride*, m.p. 227—228° (decomp.), and picrate, m.p. 233°; *decanebis*-(NN′-*diphenyl*-*, m.p. 163—165°, and (-N-cyclo*hexyl-carbonamidine* *), m.p. 122° (*dihydrochloride*, m.p. 273°); undecane-αλ-dicarbonamidine (III) (dihydrochloride, m.p. 150—151°); tridecane-αν-dicarbonamidine (dihydrochloride, m.p. 165—167°; picrate, m.p. 190—191°), accompanied by the -αν-*dicarboxylamide*, m.p. 176°; α-*carbamyltridecane*-ν-*carbonamidine hydrochloride* *, m.p. 164—165°; tetradecanemonocarbonamidine [*hydrochloride* *, m.p. 138° (after sintering); picrate, m.p. 166°]. ακ-*Di*-(4 : 5-*dihydro*-2-*glyoxalinyl*)*decane*, m.p. 181° (*hydrochloride*, m.p. 183°; picrate, m.p. 223—224°), is obtained from decanedicarboniminoethyl ether hydrochloride and EtOH–$(CH_2\cdot NH_2)_2$ at 70°.

Compounds marked † have considerable activity against experimental mouse trypanosomiasis (*T. equiperdum*) but are less active than (III). Some of the compounds described possess slight activity, but those marked * are inactive. H. B.

Thermal decomposition of azomethane.—See A., 1939, I, 476.

Mechanism of the attack of trimethylarsine and some quaternary arsonium salts by sulphuric acid. G. Petit (Compt. rend., 1939, **209**, 111—113; cf. A., 1937, II, 449).—The action of H_2SO_4 (*d* 1·83) on $AsMe_3$ at <250° yields $AsMe_3O$, which undergoes further degradation to $As(OH)_3$, without formation of intermediate compounds, at >280°. $(AsMe_4)_2SO_4$ is converted directly to $As(OH)_3$ in 6 hr. at 320°. $[AsMe_3(C_2H_4\cdot OH)]_2SO_4$ reacts similarly (45 min. at 320°), the reaction occurring by scission and destruction of the $C_2H_4\cdot OH$ group followed by oxidation and degradation of the resulting $AsMe_3$. A similar process occurs with $[AsMe_3(CH_2\cdot CO_2H)]_2SO_4$. The org. groups are eliminated with formation of CO_2, SO_2, and H_2O in each case. A. J. E. W.

Complex nickel salts with quadri- and sexavalent central atom. H. Glaser and P. Pfeiffer [with W. Rühlmann] (J. pr. Chem., 1939, [ii], **153**, 300—312).—The *Ni* compounds richest in amine from $(CH_2\cdot NH_2)_2$ (= en) and $NHEt\cdot[CH_2]_2\cdot NH_2$ (X) have the composition [Ni en_2]$(ClO_4)_2$,0·5H_2O and $[NiX_3](ClO_4)_2$, which in colour and constitution agree with the other Ni hexamine salts. The *salts* [Ni $en_2(OH_2)_2$]$(ClO_4)_2$ and $[Ni\{CH_2\cdot NHEt)_2\}_2(OH_2)_2](ClO_4)_2$ (II) are diaquo-compounds since their violet-blue colour changes to

orange when they are dehydrated. These latter salts contain Ni^{IV}. The orange salts immediately absorb H_2O from the air. (I) dissolves unchanged in MeOH whereas in hot MeOH (II) becomes dehydrated. The tendency to form salts with Ni^{IV} attains its max. in the salt, $[Ni(NH_2{\cdot}[CH_2]_2{\cdot}NEt_2)_2](ClO_4)_2$, which does not yield an aquo-salt. This is converted by KCNS in MeOH into the violet-blue *salt*, $[Ni(NH_2{\cdot}[CH_2]_2{\cdot}NEt_2)_2(CNS)_2]$, which loses 1 mol. of base when heated and passes into the green *compound*, $[Ni(NH_2{\cdot}[CH_2]_2{\cdot}NEt_2)[CNS)_2]$. H. W.

Ammonio-mannito-dimolybdic complexes.—See A., 1939, I, 484.

Dimerisation reactions of unsaturated hydrocarbons. E. Bergmann (Trans. Faraday Soc., 1939, **35**, 1025—1034).—Dimerisation of olefines gives *cyclo*butane derivatives by irradiation only; under the influence of catalysts it proceeds by migration of a H atom. Experimental evidence in support of these conclusions is reviewed. F. L. U.

Homogeneous thermal decomposition of cyclic hydrocarbons. L. Küchler (Trans. Faraday Soc., 1939, **35**, 874—880).—Thermal decomp. of *cyclo*hexene at 758—838° K/<200 mm. yields 80—90% of C_2H_4 + butadiene (I) and a negligible amount of C_6H_6; addition of H_2 (equal amount) or NO neither inhibits nor catalyses the reaction to any extent, indicating absence of radical chain mechanism. *cyclo*Hexane (II) decomposes more slowly, but contrary to Pease and Morton (A., 1933, 1017) does not give methyl*cyclo*pentane (III). The chief products are H_2, C_2H_4, C_3H_6, and (I), indicating two mechanisms, $C_6H_{12} \rightarrow 2C_3H_6$, and $\rightarrow H_2+C_6H_{10} \rightarrow H_2+C_2H_4$ + (I). NO has no influence on the velocity of decomp. and no explanation can be given for the period of negligible pressure change at the start of the reaction. The results for (III) were similar to those for (II), although the initial lag was less marked. F. R. G.

Preparation of [sodium] *cyclo*pentylalkanesulphonates. S. Pilat and N. Turkiewicz (Ber., 1939, **72**, [*B*], 1527—1531).—Aq. solutions of $C_5H_9{\cdot}[CH_2]_n{\cdot}SO_3Na$ have a larger surface activity when n is small and are more active than alkylated *cyclo*hexane derivatives. β-*cyclo*Pentylethanol (modified prep. from *cyclo*pentyl chloride) is converted into β-*cyclo*pentylethyl chloride and thence by cryst. Na_2SO_3 at 200° into *Na* β-cyclo*pentylethanesulphonate*. δ-*cyclo*Pentylbutanol, obtained in 5% yield from Mg *cyclo*pentylmethyl chloride and $[CH_2]_3O$ or in 68% yield from Mg β-*cyclo*pentylethyl bromide and $[CH_2]_2O$, is transformed by HBr and conc. H_2SO_4 into δ-*cyclo*pentylbutyl bromide (I) and thence into *Na* δ-cyclo*pentylbutanesulphonate*. The Grignard compound of (I) and p-$C_6H_4Me{\cdot}SO_3{\cdot}[CH_2]_3{\cdot}Cl$ yield η-*cyclo*pentylheptyl chloride, whence *Na* η-cyclo*pentylheptanesulphonate*. Menthol is converted successively into menthyl bromide, β-menthylethanol, b.p. 132—136°/10 mm., β-menthylethyl chloride, b.p. 120—125°/10 mm., and *Na* β-*menthylethanesulphonate*. Et fencholate is reduced to the corresponding alcohol, which is converted into the chloride (II) and thence into *Na dihydrofenchylsulphonate*. (II) by successive condensation with $CHNa(CO_2Et)_2$, hydrolysis, and decarboxylation yields *dihydrofenchylacetic acid*, b.p. 165—166°/10 mm., the *Et* ester, b.p. 146—148°/10 mm., of which is reduced to β-*dihydrofenchylethanol*, b.p. 134—135°/10 mm., whence β-dihydrofencholethyl chloride, b.p. 120—126°/10 mm., and *Na dihydrofenchylethanesulphonate*. H. W.

***n*-Octyl*cyclo*hexane, b.p. 117—119°/11 mm.**—See A., 1939, I, 516.

Catalytic ring-closure of open-chain hydrocarbons.—See A., 1939, I, 530.

Cyclisation (aromatisation) of aliphatic hydrocarbons. H. Hoog, J. Verheus, and F. J. Zuiderweg (Trans. Faraday Soc., 1939, **35**, 993—1006).—Quant. analysis of the products obtained by passing a large no. of hydrocarbons over Cr_2O_3 at 465° and 1 atm. (contact time 20 sec.) shows that aromatisation occurs to a marked extent only with those hydrocarbons with structure permitting direct formation of a 6-C ring. *sec.* C atoms preferentially take part in ring closure. Cyclisation of paraffins and olefines containing ≮8 C also involves cracking, which increases with the no. of C atoms. The degree of aromatisation increases in the order paraffins < olefines < 6-ring naphthenes < 6-ring *cyclo*olefines. Cr_2O_3 promotes shift of the double bond in an olefine to a more central position. A general conclusion is that cyclisation of a paraffin proceeds largely through dehydrogenation to the corresponding olefine. F. L. U.

Ozonisation of allyl-, propenyl-, and α-methylvinyl-benzene.—See A., 1939, I, 401.

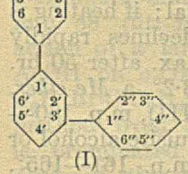
Aryl iodochlorides. I. R. Neu (Ber., 1939, **72**, [*B*], 1505—1512).—$ArICl_2$ most closely resemble metallic halides; the ArI portion is very similar to a metal in a higher state of oxidation from which it readily passes into a lower state. $PhI(OAc)_2$ is best obtained by the interaction of $PhICl_2$ and $Pb(OAc)_2$ in AcOH containing 10% of Ac_2O. $PhICl_2$ and $Pb(CNS)_2$ in $CHCl_3$, CCl_4, or CH_2Cl_2 give a solution of CNS, which converts NH_2Ph into p-*thiocyanoaniline*, m.p. 56—57°, PhOH into p-*thiocyanophenol*, m.p. 59—60°, $NPhMe_2$ into p-*thiocyanodimethylaniline*, m.p. 73—74°, o-$NH_2{\cdot}C_6H_4{\cdot}OH$ into 2-*amino*-5-*thiocyanophenol*, m.p. 98°, and m-$NH_2{\cdot}C_6H_4{\cdot}OH$ into 3-*amino*-6-*thiocyanophenol*, m.p. 107—109°. Similar treatment of p-$NH_2{\cdot}C_6H_4{\cdot}OH$ gives black, non-homogeneous products. o-$C_6H_4(OH)_2$ in EtOAc and CNS in CH_2Cl_2 afford 1 : 2 : 4-$C_6H_3(OH)_2{\cdot}CNS$, m.p. 142°. Dithiocyanobenzidine decomposes at >365° (lit. 250°). o-$OH{\cdot}C_6H_4{\cdot}CO_2H$ does not appear to be attacked by CNS, prolonged contact giving $(CNS)_n$; the use of Fe as catalyst in Et_2O, EtOAc, or AcOH brings no advantage. p-$NH_2{\cdot}C_6H_4{\cdot}OEt$ and CNS in $CHCl_3$ at room temp. afford 1-amino-5-ethoxybenzthiazole, m.p. 164°, whilst thymol and CNS in CCl_4 yield 6-*thiocyano*-4-iso*propyl*-m-*cresol*, m.p. 108—109°. o-$NH_2{\cdot}C_6H_4{\cdot}CO_2H$ gives 5-*thiocyanoanthranilic acid*, m.p. 173—174°. 1-*Thiocyano*-2-*naphthol*, m.p. 113°, and 1-*thiocyano*-2-*naphthylamine* or 1-*aminonaphthothiazole*, m.p. 260°, are derived from β-$C_{10}H_7{\cdot}OH$ and β-$C_{10}H_7{\cdot}NH_2$, respectively. $PhICl_2$ and PhOH, NHPhAc, o-$OH{\cdot}C_6H_4{\cdot}CO_2H$, and β-$C_{10}H_7{\cdot}OH$ in suitable media give, respectively, p-$C_6H_4Cl{\cdot}OH$, (after hydrolysis) p-$C_6H_4Cl{\cdot}NH_2$, 2 : 5 : 1-$OH{\cdot}C_6H_3Cl{\cdot}CO_2H$, and 1 : 2-$C_{10}H_6Cl{\cdot}OH$. $PhI(OAc)_2$ converts NH_2Ph

in C_6H_6 at room temp. into azobenzene; an ill-defined product, possibly 3 : 7-diethoxyphenazine, is derived from $PhI(OAc)_2$ and *p*-NH_2·C_6H_4·OEt in AcOH. H. W.

Isomerisation of carotenes. III. Change of β-carotene into ψ-α-carotene. G. P. Carter and A. E. Gillam (Biochem. J., 1939, **33**, 1325—1331; cf. A., 1937, II, 405; Zechmeister *et al.*, A., 1938, II, 400).—The conversion of β- (I) into ψ-α- (II) -carotene is spontaneous and not due to adsorption on Al_2O_3 or $Ca(OH)_2$. The final product is an equilibrium mixture containing ~31% of (II). The rate of transformation in C_6H_6–light petroleum is slow at −2° (2·5% isomerisation in 12 weeks) and ~20° (11% in 7 weeks) but equilibrium is attained in 3 hr. at 80°. The reverse change is more rapid (5—6% in 8 weeks at −2°, 31% in ~0·5 hr. at 80°). (I) is separated from (II) by crystallisation (after boiling) or adsorption on Al_2O_3 or $Ca(OH)_2$. If absorption spectra are used for control, α-carotene and (II) can be chromatographically differentiated and separated. W. McC.

Reversible isomerisation of carotenoids by iodine catalysis. L. Zechmeister and P. Tuzson (Ber., 1939, **72**, [*B*], 1340—1346; cf. A., 1938, II, 400).—Under the influence of I or heat the following reversible isomerisations are recorded: lycopene ⇌ neolycopene; β- to ψ-α-carotene; kryptoxanthin to neokryptoxanthin; lutein (xanthophyll) to neolutein-*A* and -*B*; zeaxanthin to neozeaxanthin-*A*, -*B*, and -*C*; taraxanthin to neotaraxanthin-*A*, -*B*, and -*C*. The absorption of the products lies in a region of shorter λ than that of the initial materials. In the case of the hydrocarbons and kryptoxanthin the newly formed zones lie close beneath those of the unchanged pigment. If, however, at least two OH are present in the mol., the isomerised fraction has a greatly enhanced adsorption affinity and remains in the topmost zone, whereas, on development, the initial material passes much lower, whilst the new colour zone consists of two or three components which remain close to one another. The processes of isomerisation are in all cases reversible. The phenomena cannot at present be explained and the nomenclature is therefore provisional. Probably *cis–trans* displacements play a decisive part and, possibly, differences in configuration of >CH·OH in the polyene alcohols. H. W.

Terphenyl series. III. Preparation and nitration of *m*-terphenyl [*m*-diphenylbenzene]. H. France, I. M. Heilbron, and D. H. Hey (J.C.S., 1939, 1288—1292).—5-Chloro-3-phenyl-Δ^5-*cyclo*hexenone is reduced (H_2, colloidal Pd, EtOH, room temp.) to 3-phenyl*cyclo*hexanone, converted by MgPhBr into a carbinol, which is dehydrated (98% HCO_2H) to 1 : 3-*diphenyl*-Δ^3- and/or -Δ^2-cyclo*hexene*, b.p. 198—200°/18 mm. This is dehydrogenated (S in boiling quinoline) to *m*-terphenyl (I), m.p. 89°. *m*-C_6H_4Ph·NO_2 (63% yield from *m*-NO_2·C_6H_4·NAc·NO and C_6H_6) is converted (usual methods) into *m*-C_6H_4Ph·NAc·NO, which with C_6H_6 gives (I). Nitration of (I) is reinvestigated (cf. Wardner *et al.*, A., 1932, 940). HNO_3 (*d* 1·42)–AcOH at 85—90° affords 4′-*nitro*-m-*terphenyl* [4-*nitro*-1 : 3-*diphenylbenzene*] (II), distils at 80°/10^{-2} mm. (whence 4′-amino- and 4′-*acetamido*-m-*terphenyl*, m.p. 116—117°); HNO_3 (*d* 1·42) at 80—90° gives the ? 4 : 4′- or 4′ : 4″-$(NO_2)_2$-derivative, m.p. 213—215° [oxidised (CrO_3, AcOH) to *p*-NO_2·C_6H_4·CO_2H], whilst HNO_3 (*d* 1·5)–AcOH at 40—100° yields (probably) the 4 : 4′ : 4″-$(NO_2)_3$-derivative, m.p. 199—200° [also from (II) and HNO_3 (*d* 1·5)–AcOH at 30—90°]. Oxidation (CrO_3, AcOH) of (II) gives 2-*nitrodiphenyl*-5-*carboxylic acid*, m.p. 220—221°, similarly obtained from 2-*nitro*-5-*methyldiphenyl*, m.p. 86—87° (from 2 : 4 : 1-NO_2·C_6H_3Me·NAc·NO and C_6H_6 at 35°). H. B.



(I)

Absorption spectra and structure of compounds containing chains of benzene nuclei.—See A., 1939, I, 449.

Hydrogenation of naphthylamines.—See B., 1939, 917.

Formation of aryltrimethylammonium iodides in methyl-alcoholic solution.—See A., 1939, I, 527.

Kinetics of the formation of *o*-substituted phenyltrimethylammonium iodides in methyl-alcoholic solution.—See A., 1939, I, 527.

Optical inversion of the benzyl derivatives of *d*-cysteine and *d*-homocysteine *in vivo*.—See A., 1939, III, 936.

Benzyl*iso*thiocarbamide and its application to the identification of organic acids. S. Veibel and K. Ottung (Bull. Soc. chim., 1939, [v], **6**, 1434—1435).—By the method previously described (A., 1938, II, 390; cf. also Donleavy, A., 1936, 1005), the following benzyl*iso*thiocarbamide salts are obtained: dl-*malate*, m.p. 159—160°; *mucate*, m.p. 194—195°; *mono*-, m.p. 159—160°, *di*-, m.p. 178—179°, and *tri-chloroacetate*, m.p. 148—149°; α-*bromopropionate*, m.p. 158—159°; *azelate*, m.p. 163—164°; *o*-toluate, new m.p. 145—146°; p-*hydroxybenzoate*, m.p. 143—145°; α-, m.p. 158—159°, and β-*hydroxynaphthoate*, m.p. 216—217°; phthalate, new m.p. 157—158°; *H* iso*phthalate*, m.p. 215—216°; *terephthalate*, m.p. 202—206°; *pyromucate*, m.p. 211—212°. E. W. W.

Sulphanilhydroxylamide.—See B., 1939, 995.

***cis*-Azo-compounds. II.** A. H. Cook and D. G. Jones (J.C.S., 1939, 1309—1315).—The following are obtained by the procedure previously described (A., 1938, II, 317): cis-m-*methyl*-, oil, -m-*nitro*-, m.p. 70° (unchanged when kept in light petroleum in diffuse light for several days), -p-*nitro*-, m.p. 128°, -3 : 3′-*dimethyl*-, oil, -3 : 3′-*dinitro*-, m.p. 144°, -4 : 4′-, -2 : 4-, oil, and -2 : 6-*dimethoxy*-, oil, -p-chloro-, m.p. 32° (cf. *loc. cit.*), -p-*bromo*-, m.p. 39°, and -p-*iodo*-, m.p. 62°, -*azobenzenes* and cis-*benzeneazo*-α-*naphthyl Me ether*, m.p. 70°. The *cis*-configuration is based on analogy with previous examples and the easy reversion to the *trans*-form on fusion. They show varying degrees of stability in inert solvents at room temp. in the dark; the electronic nature of the substituents is insufficient to account for the differences. Short irradiation only is necessary for *cis–trans* equilibrium in solid *m*-nitroazobenzene and the *cis*-form is obtained directly (in appreciable amounts) from crude or old preps. by adsorption. *p*-NO_2·C_6H_4·NH_2 (I) in C_6H_6 with aq. NaOCl gives (cf. Meigen *et al.*, A., 1900, i, 702)

4 : 2 : 6 : 1-NO_2·$C_6H_2Cl_2$·NH_2 and a *tetrachloro*-4 : 4′-*dinitroazoxybenzene*, m.p. 267°, or (shorter reaction time) 2 : 2′-dichloro-4 : 4′-dinitroazobenzene and a ? *dichloro*-4 : 4′-*dinitroazoxybenzene*, m.p. 144°. 4 : 4′-Dinitroazobenzene* is obtained from (I) and $K_2S_2O_8$ in aq. H_2SO_4 at 60—70°. It is unlikely that α- and β-4 : 4′-dihydroxyazobenzene hydrates are *cis–trans*-isomerides (cf. Willstätter *et al.*, A., 1907, i, 566) since they are unchanged (spectra) after prolonged irradiation; they both give the α-hydrate on fusion, yield a mixture of the green and orange forms of the anhyd. α-compound when distilled at 170°/0·002 mm., afford the same *picrate* (+H_2O), m.p. 183°, appear to give the same diacetate, and are methylated (Me_2SO_4 or CH_2N_2) to *trans*-4 : 4′-dimethoxyazobenzene. 2-*Hydroxy*-2′-*methoxy*-, m.p. 110°, and 2 : 2′-dimethoxy-* azobenzene are formed by successive treatment of the $(OH)_2$-derivative with Me_2SO_4–aq. NaOH. The isomerism of *p*-hydroxybenzeneazophloroglucinol is physical; both forms with CH_2N_2 give the same *Me*$_4$ *ether*, m.p. 118°. The trans-*Me ether*, m.p. 94°, of 1-*o*-*iodobenzeneazo*-β-*naphthol*, m.p. 176°, affords a labile isomeride, as does 2-*methoxy*-2′-*methyl*-1 : 1′-*azonaphthalene*, m.p. 72° (from 2 : 1-$C_{10}H_6Me$·N_2Cl and β-$C_{10}H_7$·OH with subsequent methylation). Reduction (Na_2SnO_2) of *o*-C_6H_4I·NO_2 gives 2 : 2′-*di-iodoazoxybenzene*, m.p. 148°, which with 4% Na–Hg in EtOH–$COMe_2$ followed by a little H_2O_2 affords (:NPh)$_2$. Irradiation of *p*-C_6H_4(N:NPh)$_2$ (to which is ascribed a *trans-trans*-configuration) gives (probably) the cis-trans-*isomeride*, m.p. 136°, and *cis-cis*-form; cis-cis- and cis-trans-4 : 4′-*bisbenzeneazodiphenyls* are similarly obtained. 4 : 4′-Bis(benzeneazo)azobenzene appears to give at least one isomeride. *trans*-Benzeneazo-β-naphthyl Me ether, *o*-nitro- and 2 : 2′-dinitro-azobenzene, and compounds marked * are unaffected by irradiation.

The 3 : 3′-azotoluene of A., 1938, II, 317 is the 2 : 2′-compound and the compound, $C_{14}H_{14}ON_2$, is *trans*-2 : 2′-azoxytoluene. H. B.

Azo-chromophore. VIII. J. S. P. Blumberger (Chem. Weekblad, 1939, **36**, 574—578; cf. A., 1938, II, 180).—Spectroscopic data on a large no. of *o*-hydroxy- or -amino-azo dyes show that negative substituents in the *m*-position usually have a hypsochromic effect in acid and a bathochromic effect in alkaline media. The effect is usually intensified in presence of *o*-OMe groups but in some cases the effects neutralise one another. The total effect is approx. the algebraic sum of the effects of each substituent separately. The tendency to dissociation of the proton is decreased by the introduction of positive groups into the azo-chromophore and increased by introduction of negative groups in the *m*- or *p*-positions. The effects are explained by the $\pi 2p$-electron shell of the ·N:N· group assuming a higher quantum level, which predominates over the negative effect expected from the suppression of polarisation. S. C.

Azo-dyes from naphthidine (4 : 4′-diamino-1 : 1′-dinaphthyl). P. P. T. Sah and K. H. Yuin (Rec. trav. chim., 1939, **58**, 751—757).—*Azo-dyes* are obtained from tetrazotised naphthidine and the following components (2 mols.): *o*-OH·C_6H_4·CO_2H (orange-yellow on wool and cotton), 4 : 1-NH_2·$C_{10}H_6$·SO_3H (red on wool, silk, and cotton), 2 : 6-OH·$C_{10}H_6$·SO_3H (violet-red on wool and silk, violet on cotton), *m*-$C_6H_4(OH)_2$ (brownish-red on wool, yellow-orange on silk, red-violet on cotton), 1-phenyl-3-methyl-5-pyrazolone (orange on cotton). J. D. R.

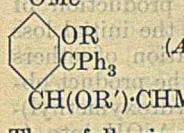
Phenyl phosphoric esters. E. J. King and T. F. Nicholson (Biochem. J., 1939, **33**, 1182—1184).—Mol. proportions of a phenol and $POCl_3$ react rapidly in C_5H_5N without prolonged heating. The prep. is described by this means of Na_2PhPO_4, $BaPhPO_4$(+2H_2O), Ba *o*-*tolyl* (+1H_2O), *Ba* p-*bromophenyl*, *Ba* p-*nitrophenyl*, and K_2 cyclo*hexyl phosphate*. P. G. M.

Terphenyl series. II. Hydroxy- and methyl-*p*-terphenyls. H. France, I. M. Heilbron, and D. H. Hey (J.C.S., 1939, 1283—1287; cf. A., 1938, II, 437, for nomenclature).—*p*-C_6H_4Ph·NAc·NO (I) and PhOMe at 18° for 48 hr. give 2- (II) and 4- (III) -*methoxy*-p-*terphenyl*, m.p. 118—119° and 223—224°, respectively, demethylated (HI) to 2- (IV) and 4-*hydroxy*-p-*terphenyl*, m.p. 176—177° and 264—265° (sublimes partly at 260°), respectively. 2-Amino-*p*-terphenyl is converted (diazo-method) into (IV), which is methylated (MeI, EtOH–KOH) to (II). 4′-Acetamido-4-methoxydiphenyl with nitrous fumes in AcOH–Ac_2O at 8°/2 hr. affords the N-*NO*-derivative, detonates at 103°, which with C_6H_6 yields (III). *p*-$C_6H_4(OMe)_2$ (IV) and (I), first at 50—55° and then up to 90°, give 2 : 5-dimethoxy-, new m.p. 159—160°, and thence 2 : 5-dihydroxy-*p*-terphenyl, new m.p. 173—174°. *p*-C_6H_4(NAc·NO)$_2$ (V) and (IV) similarly afford 2 : 5 : 2″ : 5″-*tetramethoxy*-p-*terphenyl*, m.p. 159—160°. Attempted nitrosation of 2-*methoxy*-NN′-*diacetyl*-p-*phenylenediamine*, m.p. 220—222°, in AcOH–Ac_2O–P_2O_5 at 8° gives the 5-*NO*$_2$-derivative, m.p. 258—259°. PhMe and (I) give 2- (VI), m.p. 91—92°, and 3-, m.p. 169—170°, -*methyl*-p-*terphenyl* together with the 4-isomeride (VII), m.p. 207—208°. 4-Nitrosoacetamido-2′- and -4′-methyldiphenyl with C_6H_6 afford (VI) and (VII), respectively, which are oxidised (CrO_3, dil. AcOH) to ? 2-*methyldiphenyl*-4′-, m.p. 173—175°, and *p*-terphenyl-4-carboxylic acid, respectively. 4-Nitro-2′- and -4′-methyldiphenyl are prepared from *p*-NO_2·C_6H_4·N_2Cl, PhMe, and aq. NaOH. *p*-Xylene and (V) at 50—55° and then 90° give 2 : 5 : 2″ : 5″-*tetramethyl*-p-*terphenyl*, m.p. 112—113°. H. B.

Attempted applications of camphor oil. I. Diphenylmethyl derivatives of *iso*chavibetol. I. E. Funakubo and G. Kawasaki (Ber., 1939, **72**, [*B*], 1518—1523).—*iso*Chavibetol and $CHPh_2Cl$ in C_5H_5N at 150° give iso*chavibetol CHPh*$_2$ *ether* (I), m.p. 105—106°, *diphenylmethyl*iso*chavibetol* (II), m.p. 154·8—155·8°, and its *CHPh*$_2$ *ether*, m.p. 160—161°. After 20 hr. the yields of (I) and (II) are equal; if heating is more prolonged the yield of (I) declines rapidly whereas that of (II) increases to a max. after 50 hr. (II) yields an *acetate*, m.p. 122·7—123·2°, a *Me ether*, m.p. 115·5—116·5°, and a *dibromide* (III), m.p. 160—160·5°. (III) is converted by the requisite alcohol or by AcOH into β-*bromo*-α-*methoxy*-, m.p. 161—165°, -α-*ethoxy*-, m.p. 124·2—126·2°, and -α-*acetoxy*-, m.p.

153·7—154·8° (decomp.), *-diphenylmethyldihydro*iso*chavibetol*. (II) is unchanged by KOH in aq. EtOH at 200—238°. H. W.

Introduction of the triphenylmethyl group. VII, VIII. Mobility of the bromine atom in triphenylmethyl*iso*chavibetol and in its derivatives. III, IV. E. Funakubo and T. Hirotani (Ber., 1939, **72**, [*B*], 1513—1515, 1516—1517).—VII. Triphenylmethyl*iso*chavibetol dibromide (I) is converted by boiling aq. $COMe_2$ into β-*bromo*-α-*hydroxytriphenylmethyldihydro*iso*chavibetol* (*A*, R = R′ = H), m.p. 187° (decomp.), the structure of which is proved by its inability to give CHI_3 when oxidised with I in alkaline solution.



(*A*.)

The following β-*bromo*-α-*hydroxytriphenylmethyldihydro*iso*chavibetol alkyl ethers* (*A*; R = alkyl; R′ = H) are described: *Me*, m.p. 164° (decomp.); *Et*, m.p. 164—165° (slow decomp.); *Pr*$^{\alpha}$, m.p. 168—169° (slow decomp.); *Pr*$^{\beta}$, m.p. 159—160° (slow decomp.); *Bu*$^{\alpha}$, m.p. 139—140°; *Bu*$^{\beta}$, m.p. 134—135° after becoming opaque at 124—127° [formed with a *substance* (? *Bu*$^{\gamma}$ *ether*), $C_{33}H_{35}O_3Br$, m.p. 124° (slow decomp.) after becoming opaque at 114°]; iso*amyl*, m.p. 155—157° (slow decomp.).

VIII. (I) is converted by the requisite hot alcohol into the corresponding β-*bromo*-α-*alkoxytriphenylmethyldihydro*iso*chavibetol* [*A*, R = H; R′ = *Pr*$^{\alpha}$, m.p. 160—161° (slow decomp.); *Pr*$^{\beta}$, m.p. 159—160° (slow decomp.); *Bu*$^{\alpha}$, m.p. 145—146° (slow decomp.); *Bu*$^{\beta}$, m.p. 160° (slow decomp.); *Bu*$^{\gamma}$, m.p. 179—180° (decomp.); n-*amyl*, m.p. 159—160°; iso*amyl*, m.p. 116°; n-*hexyl*, m.p. 135—137°]. H. W.

Duroquinol monophytyl ether.—See B., 1939, 997.

Bromination of 2-methoxydiphenyl ether. F. Lions and A. M. Willison (J. Proc. Roy. Soc. New South Wales, 1939, **72**, 257—272).—Gradual addition of Br in AcOH to *o*-OPh·C_6H_4·OMe in AcOH gives 5-*bromo*- (I), m.p. 71°, 5 : 4′-*dibromo*- (II), m.p. 64°, and 4 : 5 : 4′-*tribromo*-, m.p. 131°, *-2-methoxydiphenyl ether*. If the AcOH solution after bromination is heated at 75° for several hr., the OMe is partly hydrolysed and the phenols thus formed may be removed from the oily reaction product by extraction of its solution in Et_2O by alkali hydroxide; *2-hydroxydiphenyl ether*, m.p. 106°, and *5-bromo*-2-3′ : 5′-*dinitrobenzoyloxydiphenyl ether*, m.p. 102°, are thus isolated. Further amounts of (I) can be obtained as the unchanged portion when oily residues from the bromination are nitrated. The synthesis of (I) from 5 : 2 : 1-NH_2·C_6H_3(OMe)·OPh is recorded; 4′-*bromo*-2-*methoxydiphenyl ether* (III), b.p. 195—197°/15 mm., m.p. 38°, is obtained from the 4′-NH_2-compound. 5-Bromo-4′-amino-2-methoxydiphenyl ether (IV) has m.p. 88° (lit. 105°). (II) is readily obtained by the action of a larger proportion (see above) of Br in AcOH on *o*-OPh·C_6H_4·OMe, by bromination of *p*-C_6H_4Br·O·C_6H_4·OMe-*o* in AcOH, or by Gattermann's method from (IV). 5 : 2 : 1-NHAc·C_6H_3(OMe)·OPh is brominated to (?) 5-*acetbromoamido*-2-*methoxydiphenyl ether*, highest observed m.p. 158° (decomp.), readily transformed by aq. or hydroxylic solvents into 4-*bromo*-5-*acetamido*-2-*methoxydiphenyl ether*, m.p. 100°, which is hydrolysed by boiling 15% KOH–MeOH to the 5-NH_2-derivative, m.p. 68°, converted (diazo-method) into 4 : 5-*dibromo*-2-*methoxydiphenyl ether*, b.p. 230—232°/15 mm., m.p. 83°. 5-*Bromo*-4 : 4′-*dinitro*-2-*methoxydiphenyl ether*, m.p. 170°, is obtained by the action of fuming HNO_3 on (I) in AcOH–Ac_2O, from (I) and warm HNO_3 (*d* 1·42), and from 5-bromo-4-nitro-2-methoxydiphenyl ether and HNO_3 (*d* 1·5) in AcOH–Ac_2O; it is readily converted into 4 : 4′-*dinitro*-5-*morpholyl*-2-*methoxydiphenyl ether*, m.p. 191°. 4′-*Bromo*-5-*nitro*-2-*methoxydiphenyl ether*, m.p. 150°, is prepared by bromination of 5 : 2 : 1-NO_2·C_6H_3(OMe)·OPh or from HNO_3 (*d* 1·42) and (III). 4 : 2 : 1-NO_2·C_6H_3(OMe)·OPh has m.p. 59°. H. W.

Aminoaryl alkyl sulphones.—See B., 1939, 916.

Epimeric alcohols of the *cyclo*hexane series. II. 4-Methyl- and 4-*iso*propyl-*cyclo*hexylcarbinols. R. G. Cooke and A. K. Macbeth (J.C.S., 1939, 1245—1247).—*p*-$C_6H_4Pr^{\beta}$·CO_2H is reduced by H_2–PtO_2 in warm AcOH to cis-*hexahydrocuminic acid*, b.p. 133°/2·5 mm. (*Et*, b.p. 94°/2·5 mm., p-*chlorophenacyl*, m.p. 61°, and p-*bromophenacyl*, m.p. 85°, esters), and by H_2–Raney Ni in 10% NaOH at 200°/150—200 atm. to *trans*-hexahydrocuminic acid (*Et*, b.p. 100°/2 mm., p-*chlorophenacyl*, m.p. 97·5°, and p-*bromophenacyl*, m.p. 108°, esters); *cis*- and *trans*-hexahydro-*p*-toluic acids (Et, b.p. 64°/3 mm., and 71°/2 mm., respectively, p-*chlorophenacyl*, m.p. 90° and 105°, respectively, and p-*bromophenacyl* esters, m.p. 100° and 135°, respectively) are similarly prepared. Hydrogenolysis (H_2, Cu–Ba–Cr oxide, 250°/~200 atm.) of the appropriate Et ester gives *cis*-4 methyl*cyclo*hexylcarbinol, b.p. 75°/2·5 mm. (*H phthalate*, m.p. 127°; α-*naphthylcarbamate*, m.p. 72—73°), *trans*-4-methyl*cyclo*hexylcarbinol, b.p. 74°/3 mm. (*H phthalate*, m.p. 147—148°; p-*nitrobenzoate*, m.p. 57°; 3 : 5-*dinitrobenzoate*, m.p. 112°; *phenylcarbamate*, m.p. 82·5°; α-*naphthylcarbamate*, m.p. 110·5°), cis-4-iso*propyl*cyclo*hexylcarbinol*, b.p. 101°/2 mm. (*H phthalate*, m.p. 107—108°; p-*nitrobenzoate*, m.p. 54—55°; 3 : 5-*dinitrobenzoate*, m.p. 72°; α-*naphthylcarbamate*, m.p. 72—73°), and trans-4-iso*propyl*cyclo*hexylcarbinol*, b.p. 98°/2 mm. (*H phthalate*, m.p. 107—108°; p-*nitrobenzoate*, m.p. 47·5°; 3 : 5-*dinitrobenzoate*, m.p. 95°; *phenylcarbamate*, m.p. 74°; α-*naphthylcarbamate*, m.p. 93°). Physical consts. are in agreement with the Auwers–Skita rule. The *cis*-alcohols are contaminated by small amounts of the *trans*-compounds, which are readily obtained pure through the H phthalates. H. B.

Phenylpropoxyethyl alcohol. A. Halasz (Compt. rend., 1939, **209**, 319—321; cf. A., 1939, II, 155).—β-(γ-Phenylpropoxy)ethyl alcohol (I) has a somewhat greater solubility in H_2O and a lower η than Ph·$[CH_2]_3$·OH. (I) is stable to dil. acid or alkali, but with Cr_2O_3, H_2O_2, or PbO it yields Ph·$[CH_2]_2$·CHO, MeCHO, and the corresponding acids. (I) with HI (Zeisel) gives EtI (39% yield). The following are prepared by the usual methods: β-(γ-*phenylpropoxy*)*ethyl formate*, b.p. 161—162°/18 mm., *propionate*, b.p. 140—141°/1 mm., iso*butyrate*, b.p. 154—155°/3 mm., *benzoate*, b.p. 204—205°/4

mm., *chloride*, b.p. 146—147°/18 mm., *bromide*, b.p. 155—156°/15 mm., and *iodide*, b.p. 171—172°/19 mm., *Me*, b.p. 134—136°/20 mm., *Et*, b.p. 141—143°/18 mm., *Pr*, b.p. 154—155°/20 mm., *benzyl*, b.p. 183—185°/1 mm., *triphenylmethyl*, m.p. 80—80·5°, and ? β-*hydroxyethyl ether*, b.p. 190—192°/18 mm. J. L. D.

***cis-* and *trans-l-* and *-dl*-3-Methylcyclopentanol. I—IV.** M. Godchot, (Mlle.) G. Cauquil, and R. Calas (Bull. Soc. chim., 1939, [v], **6**, 1353—1358, 1358—1365, 1366—1370, 1370—1374).—I. *d*-β-Methyladipic acid in Ac_2O at ≯170° yields *d*-3-methylcyclopentanone (I), new (higher) $[\alpha]_{5893}^{20}$ +152·84°.

II. With H_2–Pt (Adams) in AcOH, (I) gives cis-l-3-*methyl*cyclo*pentanol* (II), b.p. 60°/15 mm., $[\alpha]_{5893}^{28}$ −6·55° [*H phthalate*, non-cryst.; p-*nitrobenzoate* (III), m.p. 37°; $[\alpha]_{5893}^{21}$ +4·88° in MeOH; *phenylurethane*, m.p. 78°, $[\alpha]_{5893}^{21}$ +0·92° in EtOH; *acetate*, b.p. 61·5°/16 mm., $[\alpha]_{5893}^{19}$ −0·42°]. With Na in aq. Et_2O, (I) gives trans-l-3-*methyl*cyclo*pentanol* (IV), b.p. 62·5°/15 mm., $[\alpha]_{5893}^{28}$ −6·50° [*H phthalate*, non-cryst.; p-*nitrobenzoate* (V), m.p. 41°; $[\alpha]_{5893}^{21}$ +0·65° in MeOH; *phenylurethane*, m.p. 82°, $[\alpha]_{5893}^{21}$ +0·62° in EtOH; *acetate*, b.p. 63°/15 mm., $[\alpha]_{5893}^{20}$ −0·95°]. The *cis-* and *trans*-structures are assigned because (V) is hydrolysed more rapidly than (III), and (IV) is more viscous than (II). Both (II) and (IV) are oxidised (CrO_3–AcOH) to (I).

III. *dl*-β-Methyladipic acid heated with 5% $BaCO_3$ gives *dl*-3-methyl*cyclo*pentanone (VI), which with H_2–Pt gives cis-dl-3-*methyl*cyclo*pentanol* (VII), b.p. 65°/23 mm. (cf. A., 1913, i, 873) [p-*nitrobenzoate* (VIII), m.p. 70°; *phenylurethane*, m.p. 80°]. With Na in aq. Et_2O, (VI) gives (VII) and its trans-*isomeride* (IX), b.p. 70°/24 mm. [p-*nitrobenzoate* (X), m.p. 44°; *phenylurethane*, m.p. 78°]. Both (VII) and (IX) are oxidised to (VI).

IV. The rates of hydrolysis of (III), (V), (VIII), and (X), with other physical data on the above isomerides, are tabulated. E. W. W.

Isolation of phenol dialcohols from reaction mixtures. F. Seebach (Ber., 1939, **72**, [*B*], 1635—1638).—MgO slowly dissolves in a cold mixture of PhOH and 30% CH_2O and after a further period the *compound*, $(C_8H_9O_3)_2Mg,H_2O$, crystallises. It is readily converted by AcOH into 1 : 2 : 6-$OH{\cdot}C_6H_3(CH_2{\cdot}OH)_2$ (*triacetate*, m.p. 87°), the constitution of which follows from its methylation and subsequent oxidation to 2 : 1 : 3-$OMe{\cdot}C_6H_3(CO_2H)_2$. Similarly, *m*-cresol affords the *compound*, $C_{18}H_{26}O_8Mg$, which yields 2 : 4-di(hydroxymethyl)-*m*-cresol. Similar Pb and Mn^{III} salts are formed. H. W.

Hardening process of phenol–formaldehyde resins. II. F. Hanus and E. Fuchs [with E. Ziegler] (J. pr. Chem., 1939, [ii], **153**, 327—336).—*p*-$C_6H_4Et{\cdot}OH$, 10% NaOH, and 40% CH_2O at room temp. give 4-*ethyl*-2 : 6-*di*(*hydroxymethyl*)*phenol* (p-*ethylphenol dialcohol*), m.p. 85·8—86·6° (*Na* salt; p-*toluenesulphonate*, m.p. 130—131°). 4-n-*Propyl*-, m.p. 85·4—85·8°, -n-*butyl*-, m.p. 67—67·4°, and -tert.-*butyl*-, m.p. 74—75° (p-*toluenesulphonate*, m.p. 140°), -2 : 6-*di*(*hydroxymethyl*)*phenol* are described. When these compounds are heated the amount of H_2O liberated predominates at lower and of CH_2O at higher temp. The incidence of elimination of CH_2O appears to depend on the size of the *para*-substituent. With increasing size the stepwise elimination becomes more distinct independently of the m.p. of the dialcohol. Nearly all the compounds investigated lose H_2O at ~110—130°; loss of CH_2O commences at a temp. which increases with the sum of the atoms in the *para*-substituent. The influence of constitution is apparent in the behaviour of the Bu^{α} and Bu^{γ} compounds in which loss of H_2O and CH_2O occurs more readily from the latter, which is therefore particularly suited to the production of artificial resins. The hypothesis that the initial loss of H_2O is accompanied by the formation of ethers is supported by the observation that the product obtained from 4-*cyclo*hexyl-2 : 6-di(hydroxymethyl)-phenol at 140° is converted by HBr–AcOH into 4-cyclo*hexyl*-2 : 6-*di*(*bromomethyl*)*phenol*, m.p. 81·8°. Analogously, 4-methyl-2 : 6-di(hydroxymethyl)phenyl *p*-toluenesulphonate when heated at 204° and then treated with AcOH–HBr yields 4-*methyl*-2 : 6-*di*-(*bromomethyl*)*phenyl* p-*toluenesulphonate*, m.p. 122·3—122·5°. H. W.

Constituents of natural phenolic resins. XVI. Synthesis of lignan diols. R. D. Haworth and D. Woodcock (J.C.S., 1939, 1237—1241; cf. A., 1937, II, 497).—Reduction (4% Na–Hg) of 1 : 2 : 3-$C_{10}H_5Ph(CO_2H)_2$ gives a mixture (*A*), m.p. 170—180°, of stereoisomeric 1-phenyl-1 : 2 : 3 : 4-tetrahydronaphthalene-2 : 3-dicarboxylic acids; a homogeneous form (I), new m.p. 209° (decomp.) [converted by hot AcCl into an anhydride (II), new m.p. 155—156°, which is sulphonated by cold conc. H_2SO_4], is isolable by repeated crystallisation from $COMe_2$. Alkaline hydrolysis of (II) affords an isomeride, m.p. 219°, of (I). Esterification (Ag salt method) of (*A*) gives solid (III), m.p. 106—109°, and liquid (IV), b.p. 190—195°/1 mm., Me_2 esters; boiling MeOH–HCl or –H_2SO_4 also affords (III) and (IV) after 4 hr. but (IV) only after 12 hr. The configuration of the ester is thus modified by mineral acid. Distillation of (III) also gives (IV). Bouveault–Blanc reduction of (III), (IV), or the Et_2 ester, b.p. 210—215°/1·5 mm., yields ~20% of 1-phenyl-2 : 3-di(hydroxymethyl)-1 : 2 : 3 : 4-tetrahydronaphthalene (probably a mixture of stereoisomeric forms), dehydrated ($KHSO_4$ at 180°) to a little of an *anhydro*-derivative, m.p. 103—104°. 6 : 7-Dimethoxy-1-3′ : 4′-dimethoxyphenyl-1 : 2 : 3 : 4-tetrahydronaphthalene-2 : 3-dicarboxylic acid, crude, m.p. 140—155°, homogeneous *form*, m.p. 155—157° [Me_2 ester (+MeOH), m.p. 110° (using MeOH–acid), m.p. (MeOH-free) 146° (from Ag salt)], with EtOH–H_2SO_4 gives *Et H*, m.p. 122°, and solid, m.p. 116—117°, and liquid, b.p. 270—275°/3 mm., Et_2 esters. Reduction of the Et_2 ester affords 40% of a mixture of 6 : 7-dimethoxy-1-3′ : 4′-dimethoxyphenyl-2 : 3-di-(hydroxymethyl)-1 : 2 : 3 : 4-tetrahydronaphthalene; this in Et_2O slowly deposits a little of a *form* (V), m.p. 155—158°, the *anhydro*-derivative, m.p. 126—127°, of which is dehydrogenated by AcOH–$Pb(OAc)_4$ at 70° to dehydroanhydro*iso*lariciresinol Me_2 ether [also obtained by the same procedures from the material from the mother-liquors after separation of (V)].

The oil obtained in 37% yield by reduction of the Et_2 ester, b.p. 260—265°/1·5 mm., of 6 : 7-methylenedioxy-1-3′ : 4′-methylenedioxyphenyl-1 : 2 : 3 : 4-tetrahydronaphthalene-2 : 3-dicarboxylic acid (inseparable mixture) similarly deposits a little 6 : 7-*methylenedioxy*-1-3′ : 4′-*methylenedioxyphenyl*-2 : 3-*di*(*hydroxymethyl*)-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 183—184° (? 187°) (*anhydro*-derivative, m.p. 137°). Configurational change during Bouveault–Blanc reduction is confirmed by the observation that Et_2 meso- (VI), m.p. 114—115° (Me_2 ester has m.p. 136—137°), dl- (VII), oil (Me_2 ester, m.p. 65—66°), d-, m.p. 65—66°, $[\alpha]_D^{17}$ +26·4° in $CHCl_3$, and l-, m.p. 65—66°, $[\alpha]_D^{17}$ −26·2° in $CHCl_3$, -*αα′-di*-(3 : 4-*dimethoxybenzyl*)*succinates* [from the Ag salts of the respective acids (A., 1939, II, 122)] all yield an oily, inactive *αδ-di*-(3 : 4-*dimethoxyphenyl*)-*βγ-di*(*hydroxymethyl*)*butane*, distils/2 mm. (*diformate*, m.p. 131—132°; *anhydro*-derivative, m.p. 118—119°), which is oxidised (NaOBr) to *dl*-matairesinol Me_2 ether. The ester not reduced also undergoes stereochemical change since, *e.g.*, *meso*- and *dl*-acid are recovered from both (VI) and (VII). H. B.

Mobility of the *cyclo*heptane ring and configuration of the *cyclo*heptane-1 : 2-diols. J. Böeseken (Rec. trav. chim., 1939, **58**, 856—862).—The results of Hermans and Maan (A., 1938, II, 320) on the steric analysis of *cis*- (I) and *trans*- (II) -*cyclo*heptane-1 : 2-diols are discussed in connexion with ring formation with H_3BO_3 by (I) and (II), and the non-formation of a ring by *cis-cyclo*hexane-1 : 2-diol. The phenomena observed with *cyclo*diols agree satisfactorily with the hypothesis of intramol. movements of a vibratory character. J. D. R.

Molecular compounds of bile acids with sterols. IV. Cholesterol. H. Rheinboldt [with A. Lauber] (Z. physiol. Chem., 1939, **260**, 279—284; cf. A., 1929, 925; Partington, J.C.S., 1911, **99**, 313).—M.p. curves for binary mixtures of cholesterol (I) with palmitic, stearic, stearolic, brassidic, and behenolic acid show that no cryst. compounds, but possibly mixed crystals, are produced. In each case a single eutectic mixture is obtained, the m.p. and % of (I) being 56°, 25; 63·5°, 27; 44°, 14; 55°, 19; and 52°, 14 respectively. W. McC.

Reactions of α- and β-cholesteryl benzoate oxides. F. S. Spring and G. Swain (J.C.S., 1939, 1356—1359).—Cholesteryl benzoate and BzO_2H in $CHCl_3$ at 0°/12 hr. and 20°/4 days give ~50% of α- (I), m.p. 168—169°, $[\alpha]_D^{20}$ −31·3°, and ~40% of β- (II), m.p. 151—152°, $[\alpha]_D^{20}$ +3·8°, -*cholesteryl benzoate oxide*, hydrolysed (EtOH–KOH) to α- (III) and β- (IV) -cholesterol oxide, respectively. 3 : 5 : 6-Trihydroxycholestane and BzCl (excess) in C_5H_5N at 100° (bath) afford a Cl-containing gelatinous product; with Bz_2O–C_5H_5N the 3-*monobenzoate*, m.p. 222—223°, $[\alpha]_D^{25}$ −4·9° [also obtained from (I) and hot C_6H_6–66% H_2SO_4], and (I) are produced. 6-*Chloro*-5-*hydroxy*-3-*benzoyloxycholestane*, m.p. 202—203° (decomp.), $[\alpha]_D^{20}$ −19·5° [from (III) and BzCl–C_5H_5N or (I) and EtOH–C_6H_6–HCl (*d* 1·16) or $CHCl_3$–HCl], is converted by short treatment with quinoline at 180° into (I), and by $SOCl_2$–C_5H_5N at 0° into 6-*chloro*-3-*benzoyloxy*-Δ⁴-*cholestene*, m.p. 127—128°, $[\alpha]_D^{20}$ −79·4°. 5-*Chloro*-6-*hydroxy*-3-*benzoyloxycholestane*, m.p. 206—207° (decomp.), $[\alpha]_D^{20}$ ±0° [from (II) and HCl (as above)], and BzCl–C_5H_5N give the 3 : 6-dibenzoate, new m.p. 184°, $[\alpha]_D^{20}$ −68·6°, which is also formed from (II) or (IV) and BzCl–C_5H_5N. 6-Ketocholestanyl benzoate is obtained from (I) and anhyd. alum at 180°/0·1 mm. or P_2O_5 in boiling xylene. The (I), m.p. 181°, of Lettré *et al.* (A., 1937, II, 455) could not be prepared. $[\alpha]_D$ are in $CHCl_3$. H. B.

Photochemical dehydrogenation of ergosterol and 7-dehydrocholesterol. T. Ando (Bull. Chem. Soc. Japan, 1939, **14**, 285—290).—The same ergopinacone (diacetate, new m.p. 207—207·5°) and 7-dehydrocholesterolpinacone (I), $C_{54}H_{86}O_2,H_2O$, m.p. 184·5—185·5° (diacetate, new m.p. 190—190·5°; dibenzoate, m.p. 183—183·5°, obtained from 7-dehydrocholesteryl benzoate), are obtained from ergosterol and 7-dehydrocholesterol (II), respectively, when the EtOH–C_6H_6–eosin solutions are freed from air either by CO_2 or by boiling (cf. Schenck *et al.*, A., 1937, II, 59) prior to insolation. Shorter exposure of (II) to sunlight appears to give ? (I), m.p. 192·5—193·5° (cf. *loc. cit.*). M.p. are corr. with decomp. S. H. H.

17-Amino-Δ⁵-androsten-, m.p. 164—166·5°, and -androstan-3-ol, m.p. 174°.—See B., 1939, 995.

Basic esters of aralkylacetic acids and their spasmolytic properties. T. Wagner-Jauregg, H. Arnold, and P. Born (Ber., 1939, **72**, [*B*], 1551—1561).—Muscular spasmolytic action greatly exceeding that of papaverine is observed in the β-diethylaminoethyl esters of disubstituted acetic acids. In this group, the atropine-like, neural spasmolytic effect diminishes with increasing mol. wt. Substances with high papaverine vals. have usually small atropine vals. A very favourable combination of neural and powerful muscular action is observed in β-diethylaminoethyl αβ-diphenylpropionate and β-phenyl-α-*iso*propylpropionate. The following are described: β-diethylaminoethyl γ-phenyl-α-β′-phenylethylbutyrate, b.p. 200—210°/1 mm. (*hydrochloride*, m.p. 94—95°; *ethobromide*, m.p. 126—127°), and β-phenyl-α-benzylpropionate (*hydrochloride*, m.p. 142—144°; *octabromide*, m.p. 103—105°); *γ-diethylamino*-n-*propyl*, m.p. 109—111°, *β-dimethylaminoethyl*, m.p. 105—108°, and *tropine*, m.p. 247—249°, *β-phenyl-α-benzylpropionate hydrochloride*; *β-diethylaminoethyl αβ-diphenylpropionate hydrochloride*, m.p. 111—112° (free *ester*, b.p. 190—195°/1 mm.); β-diethylaminoethyl β-anisyl-α-benzylpropionate, b.p. 220—230°/0·05 mm. (*hydrochloride*, m.p. 73—74°); β-diethylaminoethyl γ-*cyclo*hexyl-α-β′-*cyclo*hexylethylbutyrate, b.p. 220—230°/0·1 mm. (*hydrochloride*, m.p. 135—136°); *β-diethylaminoethyl diphenylacetate benzylobromide* (+H_2O), m.p. 105—106°. All m.p. are corr. H. W.

Isomerisation of methyl *allo*cinnamate by hydrogen bromide and the influence of oxygen. O. Simamura (Bull. Chem. Soc. Japan, 1939, **14**, 294—296; cf. A., 1939, II, 139).—Me *allo*cinnamate (I) and HBr, in absence of air, in the dark at room temp., afford Me cinnamate (II), the isomerisation being slower in CCl_4. It is accelerated by O_2, the

action of which is suppressed by *o*-$C_6H_4(OH)_2$. (I) and HCl at 55° slowly afford (II), but there is no isomerisation in CCl_4 even in presence of O_2. Piperidine also causes 34% conversion of (I) into (II) during 24 hr. S. H. H.

Condensation of aldehydes with malonic acid. XII. Influence of groups and other factors. K. C. Pandya, T. S. Sodhi, and (in part) D. S. Mittal (Proc. Indian Acad. Sci., 1939, 9, A, 511—517; cf. A., 1938, II, 363).—3 : 4 : 1-$C_6H_3(OH)_2$·CHO, -OMe·C_6H_3(OH)·CHO, and -$C_6H_3(OMe)_2$·CHO with $CH_2(CO_2H)_2$ (equimol. proportions) at 70—100° yield respectively 17, 62, and 87%, or in presence of C_5H_5N, 44, 51, and 60% yields of the corresponding cinnamic acids; with 2 mols. of $CH_2(CO_2H)_2$, C_5H_5N (6 mols.), and a trace of piperidine (I) at 10—25° for 3 weeks the yields are 83, 71, and [without (I)] 82% respectively. Conc. H_2SO_4 and EtOH–HCl are less effective as condensing agents. *o*-, *m*-, and *p*-NO_2·C_6H_4·CHO with $CH_2(CO_2H)_2$, alone (yield ~52%) and in presence of C_5H_5N, (I), and quinoline (yield 75—91%), give the corresponding *trans*-nitrocinnamic acids. A. Li.

Condensation of aldehydes. III. *p*-Tolualdehyde with amides. XI. *p*-Tolualdehyde with malonic and malonanilic acid. R. K. Mehra and K. C. Pandya (Proc. Indian Acad. Sci., 1939, 9, A, 508—510; cf. A., 1938, II, 363, 365).—III. *p*-C_6H_4Me·CHO with HCO·NH_2 and a trace of C_5H_5N at 175—180° yields p-*tolylidenebisformamide*, m.p. 287°. Other amides react at 120—130° with or without C_5H_5N, giving p-*tolylidenebis-acetamide*, m.p. 274°, *-propionamide*, m.p. 232°, *-benzamide*, m.p. 230°, and *-phenylacetamide*, m.p. 238°.

XI. *p*-C_6H_4Me·CHO heated with $CH_2(CO_2H)_2$ and CO_2H·CH_2·CO·NHPh in presence of C_5H_5N yields *p*-methyl-cinnamic acid and *-cinnamanilide*, m.p. 184°, respectively. A. Li.

Condensation of piperonal with succinic acid derivatives. J. W. Cornforth, G. K. Hughes, and F. Lions (J. Proc. Roy. Soc. New South Wales, 1939, 72, 228—232).—Piperonal (I), Ac_2O, and Na_2 succinate at 125° for 3 hr. give a mixture of 3 : 4-*methylenedioxyphenyl-paraconic* (II), m.p. 164—165°, and *-iso*crotonic acid (III), m.p. 117—118°. When heated above its m.p. (II) gives (III) and CO_2 quantitatively. Pyrolysis of (III) at 260° under atm. or somewhat diminished pressure, prolonged boiling of (III) with Ac_2O, or treatment with $POCl_3$ at 100° gives intractable tars or unchanged material. (I), Et_2 succinate, and NaOEt in hot EtOH afford 3 : 4-*methylenedioxyphenylitaconic acid* (IV), m.p. 194—195°, in 90% yield, also obtained less advantageously from Zn turnings, (I), and Et_2 bromosuccinate in dry C_6H_6; its *Et H ester*, long needles or rhombic plates, m.p. 130—131°, is pyrolysed in "calol" at 290° to C_2H_4 and (IV). H. W.

Effect of polar groups on esterification velocities of substituted benzoic acids with *cyclo*hexanol.—See A., 1939, I, 529.

Reaction of 3 : 5-dinitrobenzoic acid with alkali. I. Isolation and constitution of the compound giving a red colour with alkali. A. Bolliger and F. Reuter (J. Proc. Roy. Sci. New South Wales, 1939, 72, 329—334).—Exposure of a mixture of 3 : 5 : 1-$(NO_2)_2C_6H_3$·CO_2H and 12N-NaOH at 40° to the light of a 75-w. lamp, particularly in presence of traces of heavy metals such as Fe, gives a 10% yield of 5-*nitro*-2 : 3-*dihydroxybenzoic acid*, m.p. 223—224° [*K* (+ $3H_2O$) (I) and NH_4 (II) salts]. (I) in 2N-NaOH with Me_2SO_4 gives 5-*nitro*-3-*methoxysalicylic acid*, m.p. 220°, and its *Me* ester, m.p. 138—139°. (II) is transformed by CaO at 250°/20 mm. into 4 : 2 : 1-NO_2·$C_6H_3(OH)_2$. H. W.

Alkaline hydrolysis of ethyl anthranilate.—See A., 1939, I, 527.

Theory of allyl isomerisation. III. O. Mumm and J. Diederichsen (Ber., 1939, 72, [*B*], 1523—1527).—The product obtained (A., 1939, II, 113) by the isomerisation of Me 2-Δ^{β}-pentenyloxy- and 2-α-ethylallyloxy-*m*-toluate is shown to be Me 2-hydroxy-5-Δ^{β}-pentenyl-*m*-toluate. This is hydrolysed and decarboxylated to 5-Δ^{β}-pentenyl-*o*-cresol (I), the *Me ether*, b.p. 140°/12 mm., of which is ozonised to 4-methoxy-3-methylphenylacetaldehyde (*semicarbazone*, m.p. 162°). Similarly (I) is transformed into its acetate, which is ozonised to 2-methyl-4-aldehydomethylphenoxyacetic acid [*semicarbazone*, m.p. 184° (decomp.)]. H. W.

Syntheses in the phenyl*cyclo*hexane series. D. Bodroux and R. Thomassin (Bull. Soc. chim., 1939, [v], 6, 1411—1416).—Phenyl*cyclo*hexane (I) treated slowly with Br in presence of I gives *p*-bromophenyl*cyclo*hexane (II) (80% yield), new b.p. 153—155°/10 mm. (cf. Truffault, A., 1938, II, 476), the Mg derivative (III) of which is converted by solid CO_2, followed by dil. HCl, into *p-cyclo*hexylbenzoic acid, and by $CH(OEt)_3$ into 53% of *p-cyclo*hexylbenzaldehyde (anil, new m.p. 117—118°; cf. von Braun *et al.*, A., 1933, 1283). The last is also obtained by action of boiling aq. $Cu(NO_3)_2$ or $Pb(NO_3)_2$ on a saline emulsion of p-cyclo*hexylbenzyl chloride* (IV), b.p. 162—164°/12 mm. [from (I), $(CH_2O)_3$, and HCl, in presence of $ZnCl_2$]. A by-product in the prep. of (III) is 4 : 4′-*dicyclohexyldiphenyl*, m.p. 202—203°, not obtained from (II) and Na in Et_2O or Bu^{α}_2O. With Na in Et_2O (IV) gives 4 : 4′-*dicyclohexyl*-αβ-*diphenylethane*, m.p. 148—149°, which is also a by-product in the prep. from (IV) of its Mg derivative (V). In Et_2O, (V) gives, with air, *p-cyclo*hexylbenzyl alcohol, and with CO_2, slowly *p*-cyclo*hexylphenylacetic acid*, m.p. 78·5°, which is oxidised by alkaline $KMnO_4$ to *p*-$C_6H_4(CO_2H)_2$. E. W. W.

Synthesis of 1 : 12-dimethyl-7-*iso*propyloctahydrophenanthrene-1-carboxylic acid. R. D. Haworth and R. L. Barker (J.C.S., 1939, 1299—1303).—The product from Et 2-methyl*cyclo*hexanone-2-carboxylate and Et_2O–CH_2Ph·CH_2·MgBr (I) is dehydrated ($KHSO_4$) to *Et* 1-β-*phenylethyl*-2-*methyl*-Δ^6-cyclo*hexene*-2-*carboxylate*, b.p. 160—163°/3 mm. (free *acid*, m.p. 97—98°), converted by boiling AcOH–conc. H_2SO_4 into 1-*methyl*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydrophenanthrene*-1-*carboxylic acid*, m.p. 187—188°, which, like its *Me* ester, m.p. 75—76°, is dehydrogenated (Se at 280—290° and then 320°) to 1-methylphenanthrene (II). *Et* 2 : 6-*dimethyl*cyclo*hexanone*-2-

carboxylate (III), b.p. 111—112°/15 mm. (from the 6-Me derivative, EtOH–NaOEt, and MeI), and (I) similarly give *Et* 1-β-*phenylethyl*-2 : 6-*dimethyl*-Δ^6-cyclo*hexene*-2-*carboxylate*, b.p. 175—180°/4 mm. (free *acid*, m.p. 121—122°), cyclised (best with AcOH–H_2SO_4) to 1 : 12-*dimethyloctahydrophenanthrene*-1-*carboxylic acid*, m.p. 232—233° [*Me* ester, m.p. 128—129°, dehydrogenated to (II)].

m-$C_6H_4Pr^{\beta}$·MgBr and $(CH_2)_2O$ at 15° (in Et_2O) and then at 100° (no Et_2O) give β-m-iso*propylphenylethyl alcohol*, b.p. 134—138°/20 mm. The Grignard reagent from the *bromide*, b.p. 130—132°/20 mm., with (III) affords (after dehydration) *Et* 1-β-m-iso*propylphenylethyl*-2 : 6-*dimethyl*-Δ^6-cyclo*hexene*-2-*carboxylate*, b.p. 173—180°/20 mm., cyclised to 1 : 12-*dimethyl*-7-iso*propyloctahydrophenanthrene*-1-*carboxylic acid* (IV), m.p. 202—203° (*Me* ester, m.p. 91—92°), which is dehydrogenated (Se) to retene. The absorption spectrum of (IV) resembles that of dehydroabietic acid (V); (IV) may be *dl*-(V) or a diastereoisomeride. Prep. of $PhPr^{\beta}$ from C_6H_6, $Pr^{\beta}Br$, and $AlCl_3$ is improved. *p*-$C_6H_4Pr^{\beta}$·NHAc and Br–AcOH at 55—60° give 3-*bromo*-4-*acetamidocumene*, m.p. 129—130°, hydrolysed (EtOH–conc. HCl) to the 4-NH_2-derivative, b.p. 139—141°/20 mm., which is deaminated (diazonium sulphate in aq. EtOH with Cu-bronze) to m-*bromocumene*, b.p. 94—96°/20 mm. [oxidised ($KMnO_4$) to *m*-$C_6H_4Br·CO_2H$]. H. B.

Complex phthalates. G. J. Burrows and E. Ritchie (J. Proc. Roy. Soc. New South Wales, 1939, **72**, 175—178).—$Cu(OH)_2$ and $Co(OH)_2$ dissolve almost quantitatively in hot dil. *o*-$CO_2H·C_6H_4·CO_2Na$ (I) giving thermostable solutions which yield the complex *salts*, $Na_2[C_6H_4(CO_2)_2Cu(CO_2)_2C_6H_4],2H_2O$ and $Na_2[C_6H_4(CO_2)Co(CO_2)_2C_6H_4],2H_2O$, which are stable in air but are readily decomposed by dil. acids or alkalis. $Ni(OH)_2$ dissolves readily in dil. (I) to a complex Ni phthalate which is stable in solution but breaks up at the point of crystallisation into $C_6H_4(CO_2Na)_2$ and $C_6H_4(CO_2)_2Ni$. Very unstable solutions of a complex Cr salt are obtained by dissolving $Cr(OH)_3$ in hot dil. (I) or by adding an excess of $C_6H_4(CO_2Na)_2$ to a $Cr^{\cdots}$ salt. The complex $Fe^{\cdots}$ salt is decomposed when the solution is warmed or concentrated. Hg, Al, and $Sn^{\cdots\cdot}$ show no tendency towards formation of complex phthalates. H. W.

Metabolic products of *Aspergillus ochraceus*. III. Synthesis of *iso*ochracin. T. Tamura (J. Agric. Chem. Soc. Japan, 1939, **15**, 685—689; cf. A., 1935, 619).—3 : 1 : 2-$NO_2·C_6H_3(CO)_2O$ heated with $(EtCO)_2O$ and $EtCO_2Na$ yields 3-*nitro*-α-*ethylidenephthalide*, which with dil. NaOH gives 6-*nitro*-2-*propionylbenzoic acid*. This is reduced by Na–Hg to 6-*amino*-2-α-*hydroxypropylbenzoic acid*, which on treatment with HCl is converted into 3-*amino*-α-*ethylphthalide*. 3-Hydroxy-α-ethylphthalide, identical with *iso*ochracin, is obtained from this by the diazo-reaction. Similarly 3 : 1 : 2-$OMe·C_6H_3(CO)_2O$ yields (probably) 6-*methoxy*-α-*ethylidenephthalide* and -*ethylphthalide*, m.p. 58°. J. N. A.

Lichen substances. XCIV. Occurrence of thelephoric acid in lichens. Y. Asahina and S. Shibata (Ber., 1939, **72**, [*B*], 1531—1533).—Continuous extraction of *Lobaria retigera*, Trev., with hot $COMe_2$ gives thelephoric acid (I), $C_{20}H_{12}O_9,H_2O$, m.p. >350°, further identified by conversion by boiling Ac_2O containing a drop of conc. H_2SO_4 into the *triacetate*, decomp. 330°, and by Zn dust, NaOAc, and Ac_2O into *leucothelephoric acid penta-acetate*, m.p. >340° after becoming brown at 320°. (I) is also obtained from *Thelephora palmata*. H. W.

Structure of bile acids and their colour reactions. Benzaldehyde test for hyo- and anthropo-deoxycholic acid. G. Saba (J. Biochem. Japan, 1939, **29**, 371—375).—Colour reactions for 33 bile acids are tabulated and correlated with the structure of the acids. The differentiation of hyo- and anthropo-deoxycholic acid by a modified PhCHO test of Shimada (A., 1938, II, 365) is described. F. O. H.

Choleic acids. V. Choleic acids containing aliphatic hydrocarbons. H. Rheinboldt [with P. Braun, E. Flume, O. König, and A. Lauber] (J. pr. Chem., 1939, [ii], **153**, 313—326).—*Choleic acids* from the following hydrocarbons and deoxycholic acid (mol. proportions in parentheses) are described: *n*-undecane (I) (1 : 6), m.p. 183°; *n*-dodecane (II), m.p. 184—185°; *n*-tridecane (III), m.p. 186°; *n*-tetradecane (IV), m.p. 188°; *n*-pentadecane (V) (1 : 8), m.p. 189·5—190°; *n*-hexadecane (VI) (1 : 8), m.p. 191·5—192°; *n*-pentatriacontane (VII) (1 : 8), m.p. ~201·5°; *n*-tritetracontane (VIII) (1 : 8), m.p. ~201°; Δ^a-*n*-hexadecene (IX), (1 : 8), m.p. 190°; Δ^{ν}-*n*-heptacosene (X) (1 : 8), m.p. 195·5—196·5°; *n*-hexadecylbenzene (1 : 8), m.p. 189—189·5°. *apo*Cholic acid affords similar *compounds* with (I), m.p. 181·5°; (II), m.p. 183°; (III), m.p. 185°; (IV), m.p. 187°; (V), m.p. 188·5—189°; (VI) (1 : 8), m.p. 190—190·5°; (VII) (1 : 8), m.p. ~194°; (VIII) (1 : 8), m.p. ~195°; (IX) (1 : 8), m.p. 189·5—190°; (X) (1 : 8), m.p. 194°; *p*-hydroxyphenyl-*n*-octadecane (1 : 8), m.p. 171°. (VIII) does not appear to form a compound with picric acid. H. W.

Manufacture of aldehydes.—See B., 1939, 918.

Exchange of amine residues in the internally complex salts of Schiff's bases. P. Pfeiffer and H. Glaser [with E. Milz] (J. pr. Chem., 1939, [ii], **153**, 265—284).—In the *o*-$OH·C_6H_4·CHO$ series the imine residues are replaceable readily in the direction of the arrows: :NPh → :NMe → *o*-$C_6H_4(N:)_2$ → $C_2H_4(N:)_2$ but not in the reverse direction. The same series is met among 2 : 1-$OH·C_{10}H_6·CHO$ compounds except that :NPh and :NMe are mutually interconvertible. These results combined with those on the replaceability of the central metallic atom show that the tricyclic Cu salicylaldehyde-ethylenedi-imine is the most stable compound of the series. Addition of aq. $Cu(OAc)_2$ to *o*-$OH·C_6H_4·CHO$ and 25% NH_2Me in MeOH at 60° yields Cu salicylaldehydemethylimine, green needles, m.p. 158° (also $+1C_5H_5N$); in an individual, non-reproducible experiment the compound was isolated as brown leaflets which pass into the green needles when mixed with $CHCl_3$ and cannot be used as seed material for further quantities of the brown compound. Cu salicylaldehydeanil has m.p. 234—236°. The exchange experiments are performed by mixing the requisite salt and an excess of amine in boiling alcohol. Addition of 50% aq. $(CH_2·NH_2)_2$ to a

suspension of Cu 2-hydroxy-1-naphthaldehyde in MeOH yields *Cu 2-hydroxy-1-naphthaldehyde-ethylene-di-imine*, m.p. >250°. The corresponding *-propylene-di-imine*, *-o-phenylenedi-imine*, m.p. >250°, *-imine*, m.p. 246—248°, *-methylimine*, brown and green *forms*, m.p. 233—234°, *-ethylimine*, *-benzylimine*, and *-anil*, m.p. 237—238°, are described. H. W.

Phototropism of semicarbazones and phenylhydrazones of ethylenic ketones. IV. C. V. Gheorghiu and V. Matei (Bull. Soc. chim., 1939, [v], **6**, 1324—1334; cf. A., 1934, 656, 774).—Styryl ketones give non-phototropic (pyrazoline-forming) and phototropic phenylhydrazones, to which the *syn-* (*A*) and *anti-* (*B*) -structures are attributed respectively,

CHPh:CH·CR CHPh:CH·CR
NHPh·N (*A*.) N·NHPh (*B*.)

with similar structures for isomeric semicarbazones. COMeBu$^{\beta}$ and piperonal in EtOH–NaOH give 3 : 4-*methylenedioxystyryl Bu$^{\beta}$ ketone*, m.p. 64—65°. This gives two isomeric *semicarbazones*, α (I),* m.p. 190—191°, and γ (II),* m.p. 190—191°; a *δ-phenylsemicarbazone*,* m.p. 185°; and a *phenylhydrazone*,* m.p. 110—111°. β-$C_{10}H_7$ *styryl ketone*, m.p. 104° (syn-*semicarbazone*, m.p. 185°), with NHPh·NH_2 (III) at 145° gives 1 : 5-*diphenyl*-3-β-*naphthylpyrazoline*, m.p. 180—181°. β-$C_{10}H_7$ p-*methoxystyryl ketone*, m.p. 96° (syn-*semicarbazone*, m.p. 188°), with (III) at 160° gives 1-*phenyl*-5-p-*anisyl*-3-β-*naphthylpyrazoline*, m.p. 141—142°. β-$C_{10}H_7$ 3 : 4-*methylenedioxystyryl ketone*, m.p. 142—144°, gives a syn-*semicarbazone*, m.p. 203—204°. The compounds marked * are phototropic, as are the (*anti*) phenylhydrazones of CHPh:CH·COEt and CHPh:CH·COPr^{a}, but not the (*syn*) phenylhydrazones of CHPh:CMe·COMe or CHPh:CEt·COMe. Phototropism of (I) [more stable to light than (II)] is attributed to admixed (II). E. W. W.

Pinacols and the pinacolone rearrangement. II. E. Bergmann (Rec. trav. chim., 1939, **58**, 863—870).—αα-Diphenyl-ββ-di-*p*-tolylethane-αβ-diol when treated successively with MgEtBr and H_2O is recovered unchanged, indicating non-dissociation of the central C·C linking (cf. Gomberg *et al.*, A., 1927, 245, 1190). The theory that the rearrangement involves an ionic compound, formation of which is favoured by the high dielectric const. of the usual acidic reagents, is not supported by the fact that PhNCO acts as a dehydrating agent [forming $CO(NHPh)_2$]. Fluorenonepinacol thus gives diphenylenephenanthrone (also formed in boiling PhOEt), *p*-chlorobenzophenonepinacol gives impure *p*-$C_6H_4Cl·CPh_2·CO·C_6H_4Cl$-*p*, benzylhydroanisoin gives CH_2Ph 4 : 4′-dimethoxybenzhydryl ketone, but benzylhydrobenzoin (I) yields its cyclic *carbonate*, m.p. 119—120° [also formed from (I) and $COCl_2$ in PhMe–quinoline], probably by way of $CH_2Ph·CPh(OH)·CHPh·CO_2·NHPh$ and loss of NH_2Ph. *o-Fluorobenzophenonepinacol*, m.p. 188—195°, from *o*-$C_6H_4F·COPh$ and Zn–AcOH, is rearranged (boiling AcOH–I; not AcCl) with difficulty to *o-fluorophenyl o-fluorotriphenylmethyl ketone*, m.p. 132—133°, hydrolysed by MeOH–KOH to *o-fluorotriphenylmethane* (II), m.p. 85—87°. *o*-$C_6H_4F·CO_2Me$ with PhBr and Mg yields *o-fluorotriphenylcarbinol*, m.p. 116°, converted by AcCl–HCl in C_6H_6 into *o-fluorotriphenylmethyl chloride*, m.p. 110—111°, which with Na–Hg in Et_2O yields (II). The difficulty of rearrangement of pinacols from *o*-$C_6H_4Hal·COPh$ is considered to be due to electron sharing between the halogen and adjacent OH groups rather than to steric hindrance. Data on the thermal decomp. (in PhOEt at 136·8°/285 mm. to 155°/515 mm.) of $(·CPh_2·OH)_2$ and $(o\text{-}C_6H_4R·CPh·OH)_2$ (R = F, Cl, Br, Me) are given. J. D. R.

Pyrocatechol alkyl ketones.—See B., 1939, 918.

Identification of 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrophenanthrene. F. Bergmann and E. Bergmann (J.C.S., 1939, 1364).—The assumed 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrophenanthrene (A., 1939, II, 363) is identified by converting it and an authentic specimen into the same 9-*Ac* derivative, m.p. 52—53° (*semicarbazone*, m.p. 201—203°), by AcCl and $AlCl_3$ in $PhNO_2$ at 0—5°. H. B.

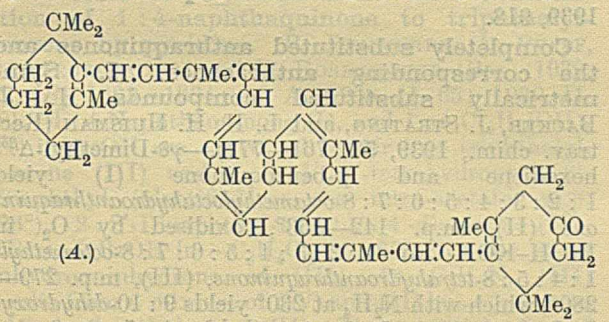
Preparation of substituted *cyclo*pentanones. I. H. A. Weidlich and G. H. Daniels (Ber., 1939, **72**, [*B*], 1590—1598).—*cyclo*Pentenones (I) are obtained by the successive addition of an acylacetic ester and α-Br-ketone to powdered Na under Et_2O whereby, after heating, the undistillable ester is almost quantitatively obtained and is then hydrolysed by 2% aq. NaOH; further quantities of (I) are obtained by acidifying the alkaline filtrates. (I) is hydrogenated in EtOH containing Pd-sponge or, preferably, PdO_2. The following are described: 3-*phenyl*-2-*methyl*-Δ^2-cyclo*pentenone* b.p. 163°/11 mm., m.p. 47—48° [*semicarbazone*, m.p. 238° (decomp.)], from $COEt·CH_2·CO_2Et$ and $COPh·CH_2Br$, hydrogenated to 3-*phenyl*-2-*methyl*cyclo*pentanone*, b.p. 158°/15 mm. [*semicarbazone*, m.p. 209—210° (decomp.)]; 3-*phenyl*-5-*methyl*-Δ^2-cyclo*pentenone*, b.p. 130°/0·4 mm., m.p. 41° [*semicarbazone*, m.p. 211° (decomp.)], whence 3-*phenyl*-5-*methyl*cyclo*pentanone*, b.p. 110—114°/0·6 mm. (*semicarbazone*, m.p. 162°); 5-phenyl-2 : 3-dimethylfuran, b.p. 110—115°/0·4 mm., obtained by rapid heating of $CH_2Ph·CO·CMeAc·CO_2Et$ with NaOH, and identified as the *adduct*, $C_{16}H_{14}O_4$, m.p. 195°, with maleic anhydride; (?) 3-bromo-2 : 4-diphenylfuran, m.p. 122°; 3-*phenyl*-4-*methyl*-Δ^2-cyclo*pentenone*, m.p. 73° (*semicarbazone*, m.p. 203°), reduced to 3-*phenyl*-4-*methyl*cyclo*pentanone*, b.p. 100—104°/0·3 mm. (*semicarbazone*, m.p. 162°). 3-Phenyl*cyclo*pentanone is transformed by successive treatments with Na in liquid NH_3 and $CH_2Cl·CO_2Et$ into *phenyl*cyclo*pentylidenephenyl*cyclo*pentanone*, b.p. 184°/0·4 mm., m.p. 113—114°. $CHAcNa·CO_2Et$ and 2-$C_{10}H_7·CO·CH_2Br$ yield *Et* 2-*naphthacylacetoacetate*, m.p. 64—65°, cyclised (dil. alkali) to a mixture of 3-*hydroxy*-3-β-*naphthyl*-cyclo*pentanone*, m.p. 83—84°, and 3-β-*naphthyl*-Δ^2-cyclo*pentenone*, m.p. 126—127° [*semicarbazone*, m.p. 244° (decomp.)], reduced to 3-β-*naphthyl*cyclo*pentanone*, b.p. 150—153°/0·2 mm., m.p. 61° [*semicarbazone*, m.p. 196—197°; (:*CHPh*)$_2$ derivative, m.p. 211—212°]. $COEt·CH_2·CO_2Et$ and 2-$C_{10}H_7·CO·CH_2Br$ afford *Et* 2-*naphthacylpropionylacetate*, m.p. 70—71° (with small amounts of 2 : 4-*diketo*-3-*propionyl*-3 : 5-*di*-β-*naphthacyl*-6-*ethyl*-2 : 3-*dihydropyran*, m.p. 209—214°), cyclised to 3-β-*naphthyl*-2-*methyl*-Δ^2-cyclo-

pentenone, m.p. 128—129°, which is reduced to 3-β-*naphthyl*-2-*methyl*cyclo*pentanone*, m.p. 84·5° (*semicarbazone*, m.p. 213—214°). An incomplete cyclisation led to *Et* 5-β-*naphthyl*-2-*ethylfuran*-3-*carboxylate*, m.p. 61—62° (*acid*, m.p. 196°).

[With H. KNAUBER and F. KÜBLER.] The ester obtained from $CHAcNa{\cdot}CO_2Et$ and 2-bromo-1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene is converted by distillation or boiling with HCl (1 : 1) into *Et* 1-*methyl*-3 : 4-*dihydro*-5 : 6-*benzcoumarone*-2-*carboxylate*, b.p. 152°/0·4 mm. (*acid*, m.p. 225—226°), and by NH_3 in excess of AcOH into *Et* 2-*methyl*-4 : 5-*dihydro*-6 : 7-*benzoindole*-3-*carboxylate*, m.p. 156—157°. H. W.

Oxidation of *cyclo*pentenones. I. J. RINKES (Rec. trav. chim., 1939, **58**, 722—724).—Oxidation of 2-*n*-hexyl-Δ^2-*cyclo*pentenone with $KMnO_4$ in $COMe_2$ yields γδ-*diketoundecoic acid*, m.p. 99—100° (*dioxime*, m.p. 174°). Similarly, 2-*n*-butyl-Δ^2-*cyclo*pentenone gives γδ-*diketononoic acid*, m.p. 96°. J. D. R.

Carotenoids of fresh-water algæ. VII. Polyene pigments of the blue alga *Aphanizomenon flos-aquæ*. II. J. TISCHER (Z. physiol. Chem., 1939, **260**, 257—271; cf. A., 1938, III, 360).—Aphanin (I) (probably *A*), m.p. 180° (corr.) [*oxime*, m.p. 208° (corr.), spectrum very similar to that of (I)], is optically inactive. It contains 6 :CMe, 11 C:C, and 1 CO but no $:CMe_2$ and hence is not a derivative of γ-carotene. (I) in C_6H_6+$Pr^{\beta}OH$ and $Al(OPr^{\beta})_3$ give aphanol and other products separated by adsorption



(*A*.)

on Al_2O_3. Aphanicin (II), $C_{80}H_{106}O_3$, m.p. 195° (corr.) (*oxime*, m.p. 241°), which also contains 1 CO (not in the conjugated system) and 11 C:C, is reduced by $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ to aphanicol. Possibly (II) is made up of 2 mols. of (I) (less 2 H) united by O and contains only one non-substituted β-ionone ring. Aphanizophyll (III) (possibly related to lycopene) yields an oxime (CO not in conjugated system) and a palmitate. 2·25 kg. of the dry alga contain 1·3 g. of palmitic acid, which accompanies (III). W. McC.

Synthesis of derivatives of fluorene from 1-hydrindone via the "Mannich" reaction. R. H. HARRADENCE and F. LIONS (J. Proc. Roy. Soc. New South Wales, 1939, **72**, 284—292).—1-Hydrindone, morpholine hydrochloride, and paraformaldehyde in boiling abs. EtOH give 2-*morpholinomethyl*-1-*hydrindone* (I), b.p. 130—152°/3·5 mm. (considerable decomp.) (*hydrochloride*, m.p. 162°; *picrate*, m.p. 146°), and a *by-product*, $C_{24}H_{25}O_3N$, m.p. 143° (*picrate*, m.p. 169°). The successive action of MeI and $CHAcNa{\cdot}CO_2Et$ on (I) leads to *Et* 3-*keto*-1 : 2 : 3 : 10-*tetrahydrofluorene*-2-*carboxylate* (II), m.p. 157° (*dinitrophenylhydrazone*, m.p. 185°; *pyrazolone*, $C_{20}H_{16}ON_2$, m.p. 288°). (II) is converted by boiling KOH–MeOH into tarry products but is hydrolysed and decarboxylated in glycerol containing 10% of H_2O at 180—190° to 3-*keto*-1 : 2 : 3 : 10-*tetrahydrofluorene* (III), b.p. 170—173°/2 mm., m.p. 100° (*dinitrophenylhydrazone*, m.p. 248°; *semicarbazone*, m.p. 234°). This is hydrogenated (Pd–norit) to 3-*keto*-1 : 2 : 3 : 4 : 10 : 11-*hexahydrofluorene*, b.p. 142—144°/1·3 mm. (*dinitrophenylhydrazone*, m.p. 215°; *semicarbazone*, m.p. 220°). Na and EtOH reduce (III) to 3-*hydroxy*-1 : 2 : 3 : 4 : 10 : 11-*hexahydrofluorene* (IV), b.p. 135—140°/1·2 mm., which does not give a cryst. acetate, *p*-nitrobenzoate, or phenylurethane. When heated with Pd–C at 330—335° (III) gives 3-*hydroxyfluorene*, m.p. 137°. Zn–Hg and boiling HCl reduce (IV) to 1 : 2 : 3 : 4 : 10 : 11-*hexahydrofluorene*, b.p. 136—138°/23 mm. Dimethoxy-1-hydrindone analogously gives 5 : 6-*dimethoxy*-2-*morpholinomethyl*-1-*hydrindone hydrochloride*, m.p. 183° (corresponding *picrate*, m.p. 185—186°). A "Mannich" base could not be prepared from 2-hydrindone. H. W.

Separation and purification of ketones of the sterol series.—See B., 1939, 995.

Δ^1-Unsaturated steroid ketones. A. BUTENANDT, L. MAMOLI, H. DANNENBERG, L. W. MASCH, and J. PALAND (Ber., 1939, **72**, [*B*], 1617—1623).—The compounds previously designated (lit. 1935—1938) Δ^1-cholestenone, m.p. 111—112°, Δ^1-3-ketobisnor*allo*cholenic acid, m.p. 235°, Δ^1-*allo*pregnenedione, m.p. 140°, Δ^1-androstenedione, m.p. 139—140°, and Δ^1-androstenolone, m.p. 158—159°, and obtained by the action of KOAc in AcOH at 180—200° on the requisite 2-Br-ketones (I) do not possess the structures indicated and are provisionally termed "*hetero*-Δ^1-ketones." The normal Δ^1-unsaturated steroid ketones are obtained in good yield and certain structure from (I) and boiling collidine (II). Thus 2-bromocholestanone gives Δ^1-*cholestenone*, m.p. 95°, $[\alpha]_D^{20}$ +64·5° in EtOH, hydrogenated (Pd–$CaCO_3$–MeOH) to cholestanone. 2-Bromo*allo*pregnanedione (III) affords a *pyridinium bromide*, m.p. 286° (decomp.), which passes at 270—280°/14 mm. into Δ^1-*allopregnenedione*, m.p. 202—204°, $[\alpha]_D^{21}$ +126° in $CHCl_3$ [also from (III) and boiling (II)], hydrogenated (Pt in AcOH) to *allo*pregnanedione, m.p. 200°. 2-Bromoandrostane-3 : 17-dione yields Δ^1-*androstene*-3 : 17-*dione*, m.p. 138—139°, $[\alpha]_D^{23}$ +148·5° [*dioxime*, m.p. 258—264° (decomp.)], whence androstane-3 : 17-dione. 2 : 4-Dibromocholestanone gives $\Delta^{1:4}$-cholestadienone, m.p. 108—110°, $[\alpha]_D^{22}$ +31°. H. W.

Behaviour of dehydro*iso*androsterone and androsterone in the *m*-dinitrobenzene reaction. G. O. LANGSTROTH and N. B. TALBOT (J. Biol. Chem., 1939, **129**, 759—768; cf. A., 1939, II, 378).—Absorption spectra (λ 3100—6500 A.) show that androsterone and dehydro*iso*androsterone give identical results. A. T. P.

Degradation of hyodeoxycholic acid to bisnorhyodeoxycholic acid and pregnane-3 : 6-diol-20-one. T. KIMURA and G. SUGIYAMA (J. Biochem. Japan, 1939, **29**, 409—419).—Me hyodeoxycholate

with MgMeI gives the corresponding *dimethylcarbinol*, m.p. 215—216°, the *diacetate* (I), m.p. 110°, of which is oxidised (CrO_3) to the Ac_2 derivative (II), m.p. 140°, of *norhyodeoxycholic acid*, m.p. 209°, $[\alpha]_D^{20}$ +6·32° in EtOH [*dehydro*-derivative, m.p. 211°; *Me* (+0·5H_2O), m.p. 115°, and *Et* ester, m.p. 124°], which, similarly treated, yields the *dimethylcarbinol*, m.p. 241° [*diacetate* (III), m.p. 151°], and Ac_2 derivative of *bisnorhyodeoxycholic acid*, $C_{22}H_{36}O_4$, m.p. 238°, $[\alpha]_D^{15}$ −12·9° in EtOH [*Me* ester (IV), m.p. 137°]. Partial oxidation (CrO_3) of (I) gives a *ketone diacetate*, $C_{29}H_{46}O_5,H_2O$, m.p. 163°, further oxidised to some (II) and hydrolysed to a 3 : 6-*dihydroxyketone*, $C_{25}H_{42}O_3,0{\cdot}5H_2O$, m.p. 183°, $[\alpha]_D^{15}$ +19·81° in EtOH, whilst (III) gives a *ketone diacetate*, m.p. 178°, hydrolysed to a 3 : 6-*dihydroxyketone*, $C_{24}H_{40}O_3,H_2O$, m.p. 233°, $[\alpha]_D^{28}$ −3·17° in EtOH. The *diethylcarbinol* (+H_2O), m.p. 195°, from (IV) and MgEtBr, is successively acetylated, oxidised, and hydrolysed to *pregnane*-3 : 6-*diol*-20-*one*, m.p. 198°, $[\alpha]_D$ +6·52° in EtOH. F. O. H.

Degradation of deoxycholic acid to a dihydroxyketone, $C_{19}H_{32}O_3$, and 3 : 12-diketo-22-methyl-Δ^{20}-norcholene. T. Kazuno and T. Shimizu (J. Biochem. Japan, 1939, 29, 421—433).—Me deoxycholate with MgMeI and MgEtI affords the corresponding carbinols, non-cryst. and m.p. 115°, (sinters at 85—87°) respectively, the respective diacetate (I), m.p. 107—110°, and triacetate (II), m.p. 149°, of which are oxidised (CrO_3) to *nordeoxycholic acid diacetate*, m.p. 206—207·5° (*Me* ester, m.p. 157°), hydrolysed to *nordeoxycholic acid*, m.p. 211—212°, $[\alpha]_D^{30}$ +57·68° in EtOH [*Me* ester (III), m.p. 110—112°]. (III) with MgMeI yields the corresponding dimethylcarbinol, the triacetate of which is oxidised and then hydrolysed to *bisnordeoxycholic acid*, m.p. 235—237° (sinters at 200°), $[\alpha]_D^{20}$ +53·14° in EtOH [*Me* ester, m.p. 167°; dimethylcarbinol (IV) and *diphenylcarbinol* derivative (+0·5H_2O), m.p. 227°]; a by-product is a ketone diacetate, m.p. 148—150°. Oxidation (CrO_3–AcOH) of acetylated (IV) yields 3 : 12-*diacetoxy*-22-*methyl*-Δ^{20}-*norcholene*, m.p. 166°, hydrolysed to the 3 : 12-(*OH*)$_2$-derivative, m.p. 206° (oxidised to the 3 : 12-*diketo*-derivative, m.p. 181—182°). Oxidation of (I) also gives a *ketone diacetate*, $C_{29}H_{46}O_5$, m.p. 141°, and (II) affords a *ketone diacetate*, $C_{23}H_{34}O_5$, m.p. 205—206°, and a *ketone triacetate*, $C_{34}H_{54}O_7$, m.p. 180°. Direct oxidation of deoxycholic acid gives a dihydroxyketone, $C_{19}H_{32}O_3$, oxidised to a 3 : 12 : 17-triketone. Structures of the above neutral by-products are given. F. O. H.

Δ^{16}-*allo*Pregnene-3 : 20-dione. A. Butenandt, L. Mamoli, and A. Heusner (Ber., 1939, 72, [*B*], 1614—1617).—Androsterone acetate in EtOH is transformed by KCN and AcOH into the corresponding cyanohydrin, decomp. 192°, which with $POCl_3$ in C_5H_5N gives the Δ^{16}-*acetoxynitrile*, m.p. 198—200°. This is transformed by MgMeBr into Δ^{16}-epiallo*pregnen*-3-*ol*-20-*one*, m.p. 226°, $[\alpha]_D^{24}$ +54° in $CHCl_3$ (*acetate*, m.p. 159°, $[\alpha]_D^{24}$ +57° in $CHCl_3$), which is oxidised by CrO_3 in AcOH to Δ^{16}-allo*pregnene*-3 : 20-*dione*, m.p. 205—208°, $[\alpha]_D^{24}$ +72° in $CHCl_3$ (*dioxime*, decomp. 198—202°). H. W.

Derivatives of pregnane- and pregnene-dione.—See B., 1939, 996.

Vitamin-K_1, $C_{32}H_{48\text{-}50}O_2$, and -$K_2$, $C_{40}H_{54\text{-}56}O_2$. α-Phylloquinone, $C_{30}H_{44(46)}O_2$ or $C_{32}H_{48(50)}O_2$, and diacetyl-α-dihydrophylloquinone. Vitamin-K_1 dihydro-diacetate, $C_{36}H_{54\text{-}56}O_4$, m.p. 59°, and vitamin-$K_2$ dihydro-diacetate, $C_{44}H_{60\text{-}62}O_4$, m.p. 57—58°.—See A., 1939, III, 853.

Chemical nature of the substance secreted by the eggs of *Arbacia pustulosa* to allure the spermatozoa. R. Kuhn and K. Wallenfels (Ber., 1939, 72, [*B*], 1407—1413).—The ovaries are triturated with sand in the presence of aq. $COMe_2$ containing a little AcOH, extracted with $COMe_2$–HCl, and the dark red extract + H_2O is exhaustively treated with Et_2O. The Et_2O solution yields to aq. $NaHCO_3$ *echinochrome* A (I), $C_{12}H_{10}O_7$, m.p. 220° (decomp.). Reductive acetylation (Zn dust and Ac_2O in presence of C_5H_5N) converts (I) into *dihydroechinochrome* A *hepta-acetate*, $C_{26}H_{26}O_{14}$, decomp. 240—245°, whilst Et_2O–EtOH–CH_2N_2 yields *trimethylechinochrome* A, m.p. 129—130° (Berl) (insol. in $NaHCO_3$; blue-violet solution in dil. NaOH). Distillation with Zn dust yields a small amount of $C_{10}H_8$ and oxidation with CrO_3 affords $EtCO_2H$. It is therefore probable that leucoechinochrome *A* is 1 : 3 : 4 : 5 : 6 : 7 : 8-heptahydroxy-2-ethylnaphthalene and that the pigment is the related 1 : 4- or 5 : 8-quinone. H. W.

1 : 4 : 5 : 8-Tetra-aminoanthraquinone.—See B., 1939, 918.

Completely substituted anthraquinones and the corresponding anthracenes. I. Symmetrically substituted compounds. H. J. Backer, J. Strating, and L. H. H. Huisman (Rec. trav. chim., 1939, 58, 761—777).—γδ-Dimethyl-$\Delta^{\beta\delta}$-hexadiene and *p*-benzoquinone (I) yield 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octamethyloctahydroanthraquinone* (II), m.p. 142—153°, oxidised by O_2 in EtOH–KOH to 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octamethyl*-1 : 4 : 5 : 8-*tetrahydroanthraquinone*, (III), m.p. 279—280°, which with N_2H_4 at 230° yields 9 : 10-*dihydroxy*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octamethyl*-1 : 4 : 5 : 8 : 9 : 10-*hexahydroanthracene* (IV), m.p. 310° [oxidised by air in EtOH–KOH to (III)], together with the *quinhydrone*, m.p. 303° [prep. also from (III) and (IV)]. Oxidation of (II) with O_2 in NaOBu–BuOH yields *octamethylanthraquinone*, m.p. 303°, reduced by red P and HI to *octamethylanthrone*, m.p. 251—252°, and (Clemmensen) to *octamethyl*-9 : 10-*dihydroanthracene*, m.p. 283—284°, which is dehydrogenated by Se in $C_{10}H_8$ at 230° to 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octamethylanthracene*, m.p. 299—300° [*picrate*, decomp. ~233°; $C_6H_3(NO_2)_3$ *compound*, decomp. ~265°]. Di-Δ^1-*cyclo*pentenyl (2 mols.) and (I) in BuOH give 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-tetra*cyclo*penteno-octahydroanthraquinone (improved yield), m.p. 146—151° (lit. 153°), which is oxidised by O_2 in NaOBu–BuOH to *tetra*cyclo*pentenoanthraquinone*, m.p. 362°, reduced (Clemmensen) to *tetra*cyclo*penteno*-9 : 10-*dihydroanthracene*, m.p. 377—378°, which is dehydrogenated (Se) to *tetra*cyclo*pentenoanthracene*, decomp. >300°. Di-Δ^1-*cyclo*hexenyl and (I) in C_6H_6 followed by fractional crystallisation yield three *stereoisomerides*

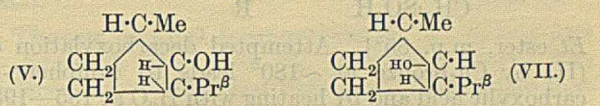
of 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-tetra*cyclo*hexeno-octahydroanthraquinone, m.p. 217—217·5°, 303—304°, and 136·5—137·5°. In PhMe, another *isomeride*, m.p. 249—250°, is obtained. The mixture of isomerides is oxidised by O_2 in NaOBu–BuOH to 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*tetra*cyclo*hexenoanthraquinone*, m.p. 362°, which is reduced to *tetra*cyclo*hexeno*-9 : 10-*dihydroanthracene*, m.p. 382—383°, dehydrogenated by Se in $C_{10}H_8$ at 230° to *tetra*cyclo*hexeno*-*anthracene*, m.p. >380°. J. D. R.

Hypericin, the photodynamically active pigment of *Hypericum perforatum*. H. Brockmann, M. N. Haschad, K. Maier, and F. Pohl (Naturwiss., 1939, **27**, 550).—*Hypericin* (I), $C_{28}H_{10}O_2(OH)_6$, the red pigment of *H. perforatum* (St. John's wort), is isolated in cryst. form, decomp. ~330° (? *hexa-acetate*, decomp. when heated, and *-benzoate*, m.p. 224—226°). (I) in solution exhibits a red fluorescence, and in EtOAc has absorption max. at 597, 554, and 516, and in C_5H_5N, 603, 559, and 520 mμ. Solutions in alkali hydroxide, conc. H_2SO_4, and Ac_2O + boroacetic anhydride exhibit a green colour. (I) is probably a *hexahydroxy*meso*dianthrone*. (I) is responsible for the photodynamic activity of *H. perforatum* producing hypericismus in grazing animals. (I) injected into, or fed to, rats or mice with subsequent illumination produces the characteristic alteration of body temp. and final death. S. H. H.

Processes of polymerisation. III. Condensation of 1 : 4-naphthaquinone to triphthalylbenzene by pyridine. R. Pummerer, A. Pfaff, G. Riegelbauer, and E. Rosenhauer (Ber., 1939, **72**, [*B*], 1623—1634; cf. A., 1938, II, 65; 1939, II, 78).—1 : 4-Naphthaquinone (I), and 1 : 4-$C_{10}H_6(OH)_2$ (II) in AcOH are converted by air into triphthalylbenzene (III) and 1 : 4 : 1′ : 4′-tetrahydroxy-2 : 2′-dinaphthyl (identified as the tetra-acetate, m.p. 226°). 2 : 2′-Dinaphthyl-1 : 4 : 1′ : 4′-diquinone (IV), (II), and BzOH in *o*-$C_6H_4Cl_2$ at 185° give the green anhydroquinhydrone of (III). In C_5H_5N, (III) results from a mixture of (IV) and (II) but appears to be derived entirely from (II) without participation of (IV). (IV), obtained in 65—70% yield by the polymerisation of (I) in EtOH containing some AcOH and quinoline, with N_2H_4,H_2O in $PhNO_2$ (suspension) gives a *monohydrazone*, decomp. ~300°. (IV) is isomerised in boiling 1-$C_{10}H_7$·NO_2 to 4′-*hydroxy*-2 : 2′-*dinaphtha*-3 : 1′-*furan*-1 : 4-*quinone* (V), decomp. >360° (sealed tube) (*o*-*chlorobenzoate*, m.p. 379—380° after softening at 376° if placed in bath at 250°). Reducing acetylation of (V) affords a colourless *dihydrotriacetate*, m.p. 297° (corr.; decomp.) when placed in Cu block preheated to 260°. (III) is reduced by HI to trinaphthylene, a violet *quinone*, $C_{30}H_{14}O_3$, m.p. 362° (*leucodiacetate*, decomp. 328° in bath preheated to 310°), and a blue *dihydroxyquinone*, $C_{30}H_{16}O_4$ (*diacetate*). (III) and N_2H_4,H_2O in boiling C_5H_5N–$PhNO_2$ afford *triphthalylbenzenebisdiazine*, $C_{30}H_{12}O_2N_4$, decomp. >420°. H. W.

Camphorphorone and pulegenone : hydrogenation products and their structure. I. II. Hydrogenation by sodium in presence of aqueous ether or of absolute alcohol. III. Hydrogenation in presence of metallic catalysts. R. Calas (Bull. Soc. chim., 1939, [v], **6**, 1374—1382, 1382—1391, 1391—1401).—I. *Th* d-*camphorate* at 300—400° (vac.) gives camphorphorone (2-methyl-5-*iso*propylidene*cyclo*pentanone) (I) (41% yield), with a smaller amount of pulegenone (2-methyl-5-*iso*propyl-Δ^4-*cyclo*pentenone) (II), $[\alpha]_{5461}^{20}$ +0·73°, and some 2-methyl-*cyclo*pentanone.

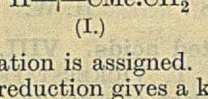
II. In aq. Et_2O, Na reduces (I) to approx. equal quantities of 1 : 1′-*dihydroxy*-2 : 2′-*dimethyl*-5 : 5′-*di*-iso*propyldi*cyclo*pentyl* (III), m.p. 182—183° [not the di*iso*propylidene compound, as stated by Kerp (A., 1896, i, 447)], and a mixture, b.p. 81—82°/14 mm. This yields the *H phthalate* (IV), m.p. 114°, of cis- (V) (p-*nitrobenzoyl* derivative, m.p. 71°) and, in larger proportion, the *H phthalate* (VI), m.p. 84°, of trans-*dihydrocamphorol* (VII) (p-*nitrobenzoyl* derivative, m.p. 58°). (V) and (VII) are oxidised by CrO_3 to dihydro-



camphorphorone. The *cis*- and *trans*-structures are respectively assigned because (VI) is formed in larger quantity, and is hydrolysed much more rapidly by dil. H_2SO_4 than is (IV); also (VII) is more viscous than (V). The mol. refraction of (V) is, however, greater than that of (VII). Parachors are almost identical. Reduction of (II) similarly gives (III), (V), and (VII). With Na in anhyd. EtOH, (I) gives (VII), a smaller proportion of (V) than before, and very little (III). (II) behaves similarly.

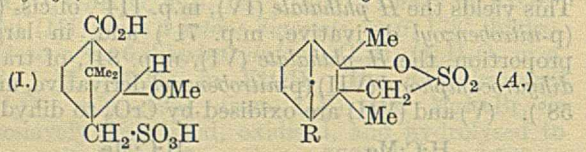
III. With H_2 and Raney Ni in EtOH (neutral or alkaline), (I) and (II) both give a mixture of cis- and trans-*dihydrocamphorphorone* (*semicarbazones*, m.p. 209° and 198°) (cf. Godchot *et al.*, A., 1913, i, 348). E. W. W.

Menthone series. XVI. (*d*-neo)*iso*Pulegol. A. G. Short and J. H. Read (J.C.S., 1939, 1306—1309).—Reduction of *d*-pulegone by the Ponndorf reagent gives a mixture of pulegols and *iso*pulegols, from which, after treatment with 3 : 5-dinitrobenzoyl chloride, can be separated (d-*neo*)iso*pulegyl* 3 : 5-*dinitrobenzoate*, m.p. 138—139°, $[\alpha]_D^{16}$ +45·0° in $CHCl_3$, hydrolysed to (d-*neo*)iso*pulegol* (I), b.p. 95°/17 mm., $[\alpha]_D^{15}$ +39·3° in EtOH. Catalytic hydrogenation converts (I) exclusively into *d*-neomenthol and the mol. configuration is assigned. The unesterified portion from the reduction gives a ketone (2 : 4-*dinitrophenylhydrazone*, m.p. 149—150°, $[\alpha]_D^{19}$ +116·0° in $CHCl_3$) containing some *d-iso*pulegone. F. R. S.



Action of sulphuric acid on camphenecarboxylic acids. Y. Asahina and H. Kawahata (Ber., 1939, **72**, [*B*], 1540—1548).—In general, OH introduced by addition of H_2SO_4 at the CH_2 double linking of 1-substituted camphene derivatives immediately undergoes the Nametkin isomerisation followed by reaction with SO_3H to yield the sultone, whereas the Wagner isomerisation is preferred by 4-substituted camphene compounds. The behaviour of camphene-1-carboxylamide is exceptional. *d*-Camphene-1-carboxylic acid is converted by conc. HCl into 2-*chloro*-

camphane-4-carboxylic acid, m.p. 164—165°, $[\alpha]_D^{19}$ +32·2° in EtOH, transformed by boiling aq. K_2CO_3 into *2-hydroxycamphane-4-carboxylic acid*, m.p. 221—222° (decomp.), $[\alpha]_D^{19}$ +18·8° in EtOAc, which is converted by boiling 0·1N-H_2SO_4 into Dl-*camphene-4-carboxylic acid*, m.p. 158—159°, $[\alpha]_D^{19}$ −56·5° in EtOH. Conc. H_2SO_4 and Ac_2O convert this into *isobornylacetato-4-carboxylic-ω-sulphonic acid* (I) (*Me*$_2$ ester, m.p. 91°, $[\alpha]_D^{24}$ −3·82° in EtOH). *Dd*-Camphene-1-carboxylic acid, conc. H_2SO_4, and Ac_2O give camphenehydrato-4-carboxylo-π-sulphonolactone (II) (*A*; R = CO_2H) [*Me* ester, m.p. 179—180°, $[\alpha]_D^{13}$ −16·18° in C_6H_6 (does not react with NH_3–MeOH at 100°);



Et ester, m.p. 85°]. Attempted decarboxylation of (II) by Cu-bronze at ~180° leads to camphene-1-carboxylic acid and by heating with H_2O at 185—195° to the optically inactive r-*camphene-4-carboxylic acid*, m.p. 131°. (II) is transformed by $SOCl_2$ into the *chloride* (*A*; R = COCl), m.p. 199—200°, which with conc. aq. NH_3 affords the *amide* (*A*; R = CO·NH_2), m.p. 191—192°, $[\alpha]_D^{15}$ +10·03° in EtOH. Addition of Br to this compound in NaOMe–MeOH yields the *sultonyl-4-urethane* (*A*; R = NH·CO_2Me), m.p. 136—138°, which could not be converted into the corresponding amine by dissolution in conc. H_2SO_4 or by heating with HCl. The *sultonyl-4-carbimide*, m.p. 184°, $[\alpha]_D^{15}$ −34·15° in C_6H_6, is converted by conc. H_2SO_4 at 0° into 4-aminosultone (*A*; R = NH_2), m.p. 74—75° (*Bz* derivative, m.p. 209°). Conc. H_2SO_4, Ac_2O, and camphene-1-nitrile yield the *sultone-4-nitrile* (*A*; R = CN), m.p. 236°, $[\alpha]_D^{16}$ −58° in $COMe_2$. Addition of camphene-1-carboxylamide to conc. H_2SO_4–Ac_2O leads to *camphene-4-carboxylamide-π-sulphonic acid*, m.p. 236° (decomp.), $[\alpha]_D^{18}$ −65·78° in H_2O. Camphene-1-carboxyl chloride, b.p. 94°/7 mm., and NaN_3 in C_6H_6 at 90—100° give *camphenyl-1-carbimide*, m.p. 234° after becoming discoloured at ~200°, transformed by conc. H_2SO_4 at 0° and subsequently at room temp. into 4-aminocamphene, m.p. 130—133° (hydrochloride, decomp. ~291° after becoming discoloured at ~250°, $[\alpha]_D^{18}$ −49·1° in H_2O). *Dicamphenylcarbamide* has m.p. 288°. H. W.

Triterpene resinols and related acids. VIII. E. S. Ewen, F. S. Spring, and T. Vickerstaff (J.C.S., 1939, 1303—1306).—Reduction of α-amyrenonol (I) with Na–EtOH gives a *compound*, $C_{32}H_{56}O_3$, m.p. 231°, formed by reduction of CO to the diol and addition of EtOH to the ethylenic linking; the compound is acetylated or benzoylated to α-amyradienyl acetate or benzoate. Similar reduction of (I) with Na–C_5H_{11}·OH affords a *compound*, $C_{35}H_{62}O_3$, m.p. 225—226°, $[\alpha]_D^{20}$ +41·5° in $CHCl_3$ (cf. Ruzicka *et al.*, A., 1939, II, 330), hydrolysed (KOH) to α-amyradienol (II) and oxidised (CrO_3–AcOH) to α-amyrenedione. If the concn. of Na amyloxide be sufficiently great, this reduction leads to the direct formation of (II), the intermediate compound spontaneously decomp. with loss of C_5H_{11}·OH and H_2O. F. R. S.

Polyterpenoid compounds. I. Betulic acid from *Cornus florida*, L. A. Robertson, G. Soliman, and (in part) E. C. Owen (J.C.S., 1939, 1267—1273; cf. Ruzicka *et al.*, A., 1939, II, 29).—The acid obtained from the bark has been shown to be identical with betulic acid (I) (*Na* salt). Acetylation (Ac_2O–C_5H_5N) of (I) gives the mixed *anhydride*, m.p. 194—196°, of *O*-acetylbetulic acid and AcOH, which does not react with CH_2N_2. Similarly (I) and *p*-NO_2·C_6H_4·COCl afford a product, hydrolysed to the *p-nitrobenzoate*, m.p. >320°, of (I). Esterification of (I) takes place only with CH_2N_2 and $C_2H_4N_2$: Me [*p-nitrobenzoate*, m.p. 232—233°; *p-toluenesulphonate*, m.p. 172—174° (decomp.)] and *Et betulate*, m.p. 201—202°, $[\alpha]_{5461}^{22}$ +11·44° in $CHCl_3$ (*acetate*, m.p. 185—186°, $[\alpha]_{5461}^{22}$ +14·33° in $CHCl_3$). Esterification of dihydrobetulic acid yields *Me dihydrobetulate*, m.p. 238—240°. Hydrogenation of Et *O*-acetyl- gives *Et O-acetyldihydrobetulate*, m.p. 205°, hydrolysed to *Et dihydrobetulate*, m.p. 208°. BzO_2H and Me *O*-acetylbetulate afford the *oxide*, m.p. 202°. HBr–AcOH and (I) yield a *lactone acetate*, m.p. >350°, which is hydrolysed to a saturated *lactone* (A), $C_{30}H_{48}O_3$, m.p. >320°, $[\alpha]_{5461}^{22}$ +75·18° in $CHCl_3$. CH_2O_2 and (I) give the *formate*, m.p. >350°, which is hydrolysed to the *lactone* (B), $C_{30}H_{48}O_3$, m.p. >330°, $[\alpha]_{5461}^{22}$ +59·05° in $CHCl_3$. Both lactones show a high degree of stability, and it seems probable that the ethylenic linking in (I) is in the βγ- or γδ-position to the ·CO_2H. *O*-Acetylbetulic acid and Br in AcOH afford the *lactone* of *O*-acetylbromobetulic acid, m.p. 290° (decomp.), whilst with AcOH–H_2O, the corresponding Br_2-compound, m.p. 290—295° (decomp.), is obtained. The formation of these substances is discussed. F. R. S.

Pigment, $C_{15}H_{10}O_6$, m.p. 273° (tetra-acetate, m.p. 187°), from *Penicillium citreo-roseum*.—See A., 1939, III, 872.

Pigments in root-bark of *Celastrus scandens*. O. Gisvold (J. Amer. Pharm. Assoc., 1939, **28**, 440—443).—The root-bark, which contains no β-carotene, yields a red, optically inactive ($CHCl_3$) pigment, *celastrol*, $C_{23}H_{36}O_3$ (?), m.p. 205° [*Ac* derivative, m.p. 241°, $[\alpha]_D^{25}$ −54·2° in $CHCl_3$; *Me ether*, m.p. 217·5—218° (*acetate*, m.p. 132—133°)], oxidised (alkaline $KMnO_4$) to a product, m.p. 252°. The I val. indicates 3 double linkings. F. O. H.

Vegetable tannins in Formosa. IV. Y. Osima (J. Agric. Chem. Soc. Japan, 1939, **15**, 636—638).—*Casuarin*, m.p. 182°, α_D +19·7° in $COMe_2$–H_2O (1 : 1), +9° in EtOH (*hexa-acetate*, m.p. 127—128°, α_D +34·3° in $COMe_2$, *Me*$_5$ *ether*, m.p. 156—158°, α_D +29·2° in $COMe_2$), a stereoisomeride of the gallocatechin in tea leaves, has been isolated from the bark of *Casuarina equisetifolia*. J. N. A.

Hibiscic acid, $C_6H_6O_7$.—See B., 1939, 993.

Constituents of derris root. II. T. M. Meyer and D. R. Koolhaas (Rec. trav. chim., 1939, **58**, 875—884; cf. A., 1939, II, 176).—Hydrolysis of derride (I) with KOH–EtOH yields Buckley's compound (B., 1936, 1117), whilst dehydroderride, under the same conditions, gives *derridic acid*, $C_{20}H_{18}O_8$, m.p. 188°, which when oxidised with H_2O_2 gives *derric acid*,

$C_{12}H_{14}O_7$, m.p. 160°, and when oxidised with $KMnO_4$ gives rissic acid. Oxidation of (I) with CrO_3 in AcOH yields a *ketone* ("*derridenone*"), $C_{20}H_{12}O_7$, m.p. 318° (*hydrazone*, m.p. 260—262°), and a *OH-acid*, $C_9H_6O_4$. Catalytic hydrogenation of (I) yields a *substance*, $C_{20}H_{26}O_5$, m.p. 161—162°, whilst with NaOAc and I in EtOH, *dehydroderride*. $C_{20}H_{14}O_6$, m.p. 242·5—244°, is formed. It is suggested that (I) is the optically active precursor of Buckley's compound, and is a normal constituent of derris root, and not a degradation product of deguelin as suggested by Cahn and Boam (A., 1939, II, 33). J. D. R.

Pechmann dyes. Formation of an ester of an acid isomeric with the yellow mono-acid. P. Chovin (Compt. rend., 1939, **209**, 169—171; cf. A., 1938, II, 333).—The mono-acid of Pechmann's dye with CH_2N_2 gives a gum whilst the di-acid gives a cryst. Me_2 ester which loses MeOH to give 2-*keto*-5-*phenyl*-3-α-*carboxy*-β-*benzoylethylidene*-2 : 3-*dihydrofuran* (I), m.p. 165° (block), which when heated above its m.p. in vac. is converted into the yellow isomeride (II) of Pechmann's dye. Hydrolysis of (I) gives the di-acid. In solution (I) is converted into (II). Attempts to form Ac derivatives of the mono- and di-acids with keten result in cyclisation. J. L. D.

Action of mixed organomagnesium compounds on *N*-substituted 2-furoamides. N. Maxim, I. Zugravescu, and I. Fulga (Bull. Soc. chim., 1939, [v], **6**, 1339—1347).—2-Furoyl chloride and NHPhMe (I), NHPhEt (II), and $NHPh_2$ (III) in C_6H_6 give 2-*furo-methyl-* (IV), m.p. 120°, and *-ethylanilide* (V), m.p. 127°, and *-diphenylamide* (VI), m.p. 157°. With MgEtBr or $MgBu^{\beta}Br$ in Et_2O, (IV), (V), and (VI) give 2-furyl Et ketone [semicarbazone, m.p. 172° (cf. A., 1930, 1442; Asahina *et al.*, A., 1915, i, 430; Mironesco *et al.*, A., 1935, 1503)] or Bu^{β} ketone, with (I), (II), and (III), respectively. With MgPhBr, (IV) and (VI) yield Ph 2-furyl ketone (VII) and (I) and (III), respectively, but (V) gives, as well as (II) and (VII), N-(2-*furyldiphenylmethyl*)*ethylaniline*, m.p. 181°. *o*-C_6H_4Me·MgBr with (V) or (VI) gives o-*tolyl* 2-*furyl ketone*, b.p. 177°/22 mm., and (II) or (III), respectively. E. W. W.

Fixation of aromatic double bonds in hydroxychromones and -coumarins. Formation of azo-dyes. S. Rangaswami and T. R. Seshadri (Proc. Indian Acad. Sci., 1939, **9**, **A**, 526—530; cf. A., 1938, II, 198; 1939, II, 221).—The coupling of *p*-NO_2·C_6H_4·N_2Cl with 7-hydroxy-3-methoxy-2-methylchromone (I) and 7-hydroxyflavone in aq. NaOH, and with 7-hydroxy- and 7-hydroxy-4-methylcoumarin in aq. Na_2CO_3, is described. With excess of reagent, (I) gives wholly the bis-, but the other three give chiefly the mono-, with some bis-azo dye. The coumarins readily give bis-azo dyes in NaOH solution, owing to ring-opening. These results indicate no rigid fixation of the double bonds. A. Li.

Psoralen and the electro-reduction of naphthalimide. E. Späth and R. Hillel (Ber., 1939, **72**, [*B*], 1577—1580).—Contrary to Okahara (A., 1936, 1121), ficusin (I), obtained in 2·35% yield by a modified procedure from the air-dried leaves of *Ficus carica*, L., has m.p. 166—167° (corr.) and dihydroficusin has m.p. 204° (corr.). The failure of (I) to attain the m.p. of synthetic psoralen is attributed to the difficulty of the complete separation of coumarins of similar constitution. The failure of Sakurai (A., 1939, II, 388) to repeat the authors' electro-reduction of naphthalimide is possibly due to the use of unsuitable electrode material. H. W.

***iso*Flavones from soya bean.** K. Okano and I. Beppu (J. Agric. Chem. Soc. Japan, 1939, **15**, 645—652).—5 : 4′-*Dihydroxy-* ("tatoin"), m.p. 318°, and 5 : 7 : 4′-*trihydroxy*-8-*methyliso*flavone ("methylgenistein"), m.p. 298°, a *glucoside* of 5 : 7 : 2′-*trihydroxy*-8-*methylisoflavone* ("methyl*iso*genistin"), m.p. 255°, and a *glucoside* of 5 : 7 : 2′-*trihydroxy*iso*flavone* ("*iso*genistin"), m.p. 265°, have been isolated from the by-product of the EtOH extract of soya bean. J. N. A.

Theory of allyl isomerisation. E. Späth and F. Kuffner (Ber., 1939, **72**, [*B*], 1580—1581).—The observation of Späth and Holzen (A., 1933, 1056) that $COMe_2$ is obtained by the ozonisation of *allo*imperatorin (I) and *iso*hexoic acid by the oxidation of hexahydro*allo*imperatorin shows that the ·CH_2·CH:CMe_2 which wanders during the isomerisation of imperatorin to (I) is attached by the same C to the remainder of each mol. This result precedes the similar observation of Mumm and Möller (A., 1938, II, 21). H. W.

Alkylene βδ-glycol formals.—See B., 1939, 915.

Aluminium chloride, new reagent for the condensation of β-ketonic esters with phenols. IV. Condensation of 4-acylresorcinols with ethyl acetoacetate. C. V. Deliwala and N. M. Shah (J.C.S., 1939, 1250—1253).—Respropiophenone and CH_2Ac·CO_2Et (I) give ($AlCl_3$) 5-*hydroxy*-6-*propionyl*-4-*methylcoumarin* (II), m.p. 164—165° (*Ac* derivative, m.p. 167—168°; *oxime*, m.p. 257—258°), identical with the Fries transformation product of 5-*propionoxy*-4-*methylcoumarin*, m.p. 100—101°, prepared from the OH-compound. Acetylation (Ac_2O–NaOAc) of (II) yields 2′ : 3′ : 4-*trimethylchromono*-7′ : 8′ : 6 : 5-α-*pyrone*, m.p. 241—242°, and reduction (Zn–Hg–HCl) affords 5-*hydroxy*-4-*methyl*-6-*propylcoumarin*, m.p. 152°. A similar series of reactions with resbutyrophenone gives 5-*hydroxy*-6-*butyryl*-4-*methylcoumarin*, m.p. 141—142° (*Ac* derivative, m.p. 167°; *Me ether*, m.p. 83—84°; *oxime*, m.p. 210°), 5-*butyroxy*-4-*methylcoumarin*, m.p. 100—101°, 4 : 2′-*dimethyl*-3′-*ethylchromono*-7′ : 8′ : 6 : 5-α-*pyrone*, m.p. 201—202°, and 5-*hydroxy*-4-*methyl*-6-*butylcoumarin*, m.p. 145—146°. 2 : 4-$(OH)_2C_6H_3$·CO·CH_2Ph and (I) form 5-*hydroxy*-6-*phenylacetyl*-4-*methylcoumarin*, m.p. 172—173° (*Ac* derivative, m.p. 142°; *Me ether*, m.p. 78—79°; *oxime*, m.p. 257°), acetylated (Ac_2O–NaOAc) to 3′-*phenyl*-4 : 2′-*dimethylchromono*-7′ : 8′ : 6 : 5-α-*pyrone*, m.p. 237—238°. 4-*p*-Toluoylresorcinol and (I) yield 5-*hydroxy*-6-p-*toluoyl*-4-*methylcoumarin*, m.p. 204—205° (*Ac* derivative, m.p. 192—193°), acetylated to 4′-p-*tolyl*-4-*methylcoumarino*-7′ : 8′ : 6 : 5-α-*pyrone*, m.p. 238—239°. F. R. S.

Rottlerin. III. T. Backhouse and A. Robertson (J.C.S., 1939, 1257—1261).—5 : 7-Dihydroxy-

2 : 2-dimethylchroman (I) and AcCN with $ZnCl_2$ give 5 : 7-*dihydroxy*-8-*acetyl*-2 : 2-*dimethylchroman* (II), m.p. 150° (2 : 4-*dinitrophenylhydrazone*, m.p. 228·5°), and small amounts of the 6-*Ac* compound (III), m.p. 229° (2 : 4-*dinitrophenylhydrazone*, m.p. 227·5°); with $AlCl_3$, (III) only is formed. MeI–KC_2O_3 and (II) afford the 7-*hydroxy*-5-*methoxy*-derivative, m.p. 78°, which condenses with EtOAc–Na to form the 8-acetoacetyl compound, cyclised to 5′-*methoxy*-2 : 2′ : 2′-*trimethylchromano*-8′ : 7′ : 5 : 6-*γ*-*pyrone*, m.p. 168°. Condensation of (II) with PhCHO yields 5 : 7-*dihydroxy*-8-*cinnamoyl*-2 : 2-*dimethylchroman*, m.p. 176—177°, reduced (H_2–Pd–C) to the -8-β-*phenylpropionyl* compound (IV), m.p. 172°.

$CH_2Ph{\cdot}CH_2{\cdot}CO{\cdot}CN$ and (I) give (IV) and 5 : 7-*dihydroxy*-6-β-*phenylpropionyl*-2 : 2-*dimethylchroman*, m.p. 171° (*oxime*, m.p. 129·5°), neither of which is identical with tetrahydrorottlerone (cf. McGookin *et al.*, A., 1938, II, 199). Methylation (MeI–K_2CO_3) of (IV) yields 7-*hydroxy*-5-*methoxy*-8-p-*phenylpropionyl*-2 : 2-*dimethylchroman*, m.p. 104°, which is further methylated to the 5 : 7-$(OMe)_2$-compound, m.p. 74°. Benzylation of (IV) affords the 7-*hydroxy*-5-*benzyloxy*-derivative, m.p. 112—113°, methylated to the 7-*OMe*-compound, m.p. 67·5°, which is debenzylated to 5-*hydroxy*-7-*methoxy*-8-β-*phenylpropionyl*-2 : 2-*dimethylchroman*, m.p. 158°. Oximation of 5 : 7-dimethoxy-6-formyl-2 : 2-dimethylchroman gives the *oxime*, m.p. 184°, dehydrated to the *nitrile*, m.p. 126—127°, which does not react satisfactorily with $Ph{\cdot}[CH_2]_2{\cdot}MgBr$. F. R. S.

Picrotoxin. IV. R. W. H. O'Donnell, A. Robertson, and (in part) J. C. Harland (J.C.S., 1939, 1261—1266).—Hydrogenation of picrotoxinin (Pd catalyst) gives a mixed product, the constituents of which appear to depend on the solvent; with Pd–C in EtOAc, a product containing β-dihydropicrotoxinin (*acetate*, m.p. 177°), also picrotonol (I) and dihydropicrotoxic acid, are obtained. With Pd–C in EtOH, a substance, $C_{15}H_{18}O_6$, m.p. 219—220°, is separated, together with an *acid* ($+H_2O$), m.p. 183° (efferv.) [$(OMe)_2$-ester, m.p. 164°]. When Pd–C is used in AcOH with a trace of HCl, the product is a mixture of α-dihydropicrotoxinin and a substance, m.p. 232° (*acetate*, m.p. 190°), which is the precursor of (I). As tested by hydrogenation and ozonolysis methods, α- and β-bromopicrotoxinin, α- and β-bromopicrotoxinic acids, and β-picrotoxinic acid do not contain a double bond. α-Picrotoxinic acid contains a CMe_2: system, since on ozonolysis it yields a product which with HI–P gives a ketone, $C_{13}H_{16}O_2$, and nor- and hydroxynor-picrotic acid. F. R. S.

Cyclic sulphones formed by the addition of sulphur dioxide to butadienes. H. J. Backer, J. Strating, and C. M. H. Kool (Rec. trav. chim., 1939, **58**, 778—784).—$CHMe{:}CH{\cdot}CMe{:}CH_2$ and SO_2 in Et_2O at 100° yield 2 : 4-*dimethyl*-Δ^3-*thia*cyclo*pentene* 1 : 1-*dioxide*, m.p. 39·5—40° (*dibromide*, m.p. 121—122°). Similarly, $(CHMe{:}CH)_2$ gives 2 : 5-*dimethyl*-Δ^3-*thia*cyclo*pentene* 1 : 1-*dioxide*, m.p. 43—43·5°. From myrcene a sulphone is similarly formed, which with Br (2 atoms) in CCl_4 yields 3-(*γδ-dibromo*-δ-*methylamyl*)-Δ^3-*thia*cyclo*pentene* 1 : 1-*dioxide*, m.p. 105°, and this with more Br (2 atoms) gives 3 : 4-*dibromo*-3-(*γδ*-*dibromo*-δ-*methylamyl*)*thia*cyclo*pentane* 1 : 1-*dioxide*, m.p. 131°. $(CHPh{:}CH)_2$ does not react with SO_2. J. D. R.

Action of ammonia on γ-substituted αε-dibromopentane. M. Plantanida (J. pr. Chem., 1939, [ii], **153**, 257—262).—Hydrogenation (PtO_2 in EtOH or AcOH respectively) of the requisite CH_2 derivative affords 4-α-*ethylpropyl*- (I), b.p. 197—198°, and 4-*benzhydryl*- (II), m.p. 138°, -*tetrahydropyran* (with a by-product, m.p. 107°). 4-*iso*Propyltetrahydropyran is transformed by 70% HBr at 100—110° into αε-*dibromo*-γ-iso*propylpentane* (I), b.p. 128—130°/10 mm. αε-*Dibromo*-γ-α-*ethylpropyl*-, b.p. 178—180°/23 mm., 157—159°/18 mm., and -γ-*benzhydryl*-, m.p. 82°, -*pentane* are obtained analogously. 20% NH_3–MeOH at 130—140° transforms (I) into 4-iso*propylpiperidine*, b.p. 62—64°/10 mm. (yield 26%) (*picrate*, m.p. 154°; *platinichloride*, decomp. 180°), and 4 : 4′-*di*iso*propylbispiperidiniumspiran bromide*, decomp. ~280°. 4-α-*Ethylpropylpiperidine*, b.p. 71°/2 mm. (*picrate*, m.p. 150·5°; *platinichloride*, decomp. ~180°), and 4 : 4′-*di*-(α-*ethylpropyl*)*bispiperidiniumspiran bromide*, decomp. ~300°, are obtained analogously. 4-*Benzhydrylpiperidine*, m.p. 99° (*picrate*, decomp. ~130°; *platinichloride*), and 4 : 4′-*dibenzhydrylbispiperidiniumspiran bromide*, decomp. >300°, are described. H. W.

Pyridinium compounds.—See B., 1939, 919.

Pyridine and quinoline derivatives. XLI. Chlorination of pyridine. J. P. Wibaut and J. R. Nicolaï. **XLII. Formation of (4-pyridyl)pyridinium compounds from 4-chloro- and 4-bromopyridine.** J. P. Wibaut and F. W. Brockman (Rec. trav. chim., 1939, **58**, 709—721, 885—894).—XLI. Interaction of Cl_2 and C_5H_5N in a glass tube at 240—420° gives 2-chloro- (I) and 2 : 6-dichloropyridine (II). At 270°, (I) is formed in good yield, with a little (II) and a pyridylpyridinium compound which gives 2-$C_5H_4N{\cdot}NH_2$ (III) with NaOH. At 400°, (II) is the main product. At 200° chlorination is slow and 3 : 5-di- (IV) and 3 : 4 : 5-tri-chloropyridine (V) are formed. Chlorination of fused C_5H_5N,HCl at 170° gives (IV) in good yield, with small quantities of (V) and C_5Cl_5N. When heated with aq. NH_3 and $CuSO_4$, (I) gives (III) and (II) gives 6-chloro-2-aminopyridine.

XLII. 4-Chloropyridine (VI) (improved prep.) when kept passes into N-(4-*pyridyl*)-4′-*chloropyridinium chloride*, which with HCl yields *N*-(4′-pyridyl)-4-pyridone dihydrochloride; 4-bromopyridine (improved prep.) behaves in the same way as (VI). J. D. R.

Formation of β-hydroxypyridine derivatives from hexoses and ammonium salts. I. K. Aso (J. Agric. Chem. Soc. Japan, 1939, **15**, 629—633).—5-Hydroxy-2-methylpyridine, a substance probably 5 : 6-dihydroxy-2-(or -3-)methylpyridine, and a *substance*, $C_6H_7O_2N$, m.p. 124—125° (*picrate*, m.p. 182—183°), probably 5-hydroxy-2-hydroxymethylpyridine, have been isolated from the reaction between aq. glucose or sucrose and NH_4 salts in an autoclave. J. N. A.

Synthesis of 2 : 6-dimethylpyridines substituted in position 3. A. Dornow (Ber., 1939, **72**, [*B*], 1548—1550).—β-Ethoxycrotonaldehyde Et_2 acetal (I) and Et aminocrotonate at 100° slowly yield Et 2 : 6-dimethylpyridine-3-carboxylate, b.p. 132°/25 mm., in 40% yield (picrate, m.p. 137—138°). Acetylacetoneimine and (I) at 100° give 3-*acetyl*-2 : 6-*dimethylpyridine*, b.p. 108°/12 mm. (also *dihydrate*, m.p. 41—42°, and *picrate*, m.p. 129—130°). Similarly diacetonitrile affords 3-*cyano*-2 : 6-*dimethylpyridine*, m.p. 83° (*picrate*, m.p. 179—180°), and benzoylacetoneimine yields 3-*benzoyl*-2 : 6-*dimethylpyridine*, b.p. 170—173°/12 mm. (*perchlorate*, m.p. 171—172°).

H. W.

Synthesis of adermin. R. Kuhn, K. Westphal, G. Wendt, and O. Westphal (Naturwiss., 1939, **37**, 469—470).—3-Methoxy-2-methylpyridine-4 : 5-dicarboxylic acid (cf. A., 1939, II, 177), obtained by oxidation of 4-methoxy-3-methyl*iso*quinoline, is converted through its diamide into 4 : 5-*dicyano*-3-*methoxy*-2-*methylpyridine*, m.p. 80°, which on catalytic hydrogenation yields 3-*methoxy*-2-*methyl*-4 : 5-*di*-(*aminomethyl*)*pyridine*. When treated with HNO_2, this base yields 3-methoxy-2-methyl-4 : 5-di-(hydroxymethyl)pyridine, m.p. 90°, of which the hydrochloride, m.p. 150°, is identical with adermin Me ether hydrochloride (cf. A., 1938, II, 373). When boiled with HBr this Me ether gives 3-hydroxy-2-methyl-4 : 5-di(bromomethyl)pyridine, converted by AgOAc into the $(OH\cdot CH_2)_2$ compound, of which the hydrochloride, m.p. 203—204°, is identical with adermin hydrochloride. Biological tests have confirmed the identity of the synthetic compound with the natural anti-dermatitis vitamin (cf. Möller *et al.*, A., 1939, III, 704).

W. O. K.

Vitamin-B_6. Synthesis of 3-methoxy-2-methylpyridine-4 : 5-dicarboxylic acid. A. Ichiba and K. Michi (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1939, **36**, 173—177; cf. A., 1939, II, 280). —A mixture of o-$C_6H_4(CO)_2NK$ and $CHMeBr\cdot CO_2Et$ at 150—160° gives *Et* α-*phthalimidopropionate*, m.p. 61—63°, which with NaOMe in boiling MeOH gives 4-*hydroxy*-1-*keto*-3-*methyl*-1 : 2-*dihydro*isoquinoline (I), m.p. 240° after sintering at 180°. With hot xylene (I) gives a product which with excess of $POCl_3$ at 120°/1 hr. is converted into 1 : 4-dichloro-3-methyl- and 1-*chloro*-4-*hydroxy*-3-*methyl*-iso*quinoline*, m.p. 163°, which with MeI–NaOMe in boiling MeOH gives 1-*chloro*-4-*methoxy*-3-*methyl*isoquinoline (II), m.p. 49°. With Sn–HCl at 70—80°/10 hr. (II) gives 4-methoxy-3-methyl*iso*quinoline [*hydrochloride*, m.p. 179—180° (decomp.)], which with aq. $KMnO_4$ at 60° gives 3-*methoxy*-2-*methylpyridine*-4 : 5-*dicarboxylic acid*, m.p. 218—220° (decomp.), identical with the product, $C_9H_9O_5N$, from *O*-methyladermin and therefore confirming the structure of vitamin-B_6 (cf. Kuhn and Wendt, A., 1939, II, 177).

J. L. D.

Constitution of the so-called "norlupinane *B*." V. Prelog and R. Seiwerth (Ber., 1939, **72**, [*B*], 1638—1642).—Et δ-ethoxyvalerate is reduced by Na and abs. EtOH to ε-ethoxyamyl alcohol, b.p. 90°/9 mm., converted by PBr_3 and C_5H_5N into ε-*ethoxyamyl bromide*, m.p. 85°/14 mm. This is transformed by $OEt\cdot[CH_2]_3\cdot CNa(CO_2Et)_2$ into *Et*$_2$ γ-*ethoxypropyl*-ε-*ethoxyamylmalonate*, b.p. 207—210°/14 mm. The corresponding acid is decarboxylated at 180° to α-*diethoxynonane*-δ-*carboxylic acid*, b.p. 162—163°/0·03 mm., which is transformed by NaN_3 and conc. H_2SO_4 into δ-*amino*-α-*diethoxynonane*, b.p. 160—161°/17 mm. The hydrobromide is converted by successive treatment with 69% HBr at 100° and 0·1N-NaOH at 50° into 1-*aza*dicyclo-[0, 3, 5]-*decane*, $CH_2<\begin{matrix}CH_2\cdot CH_2\cdot CH\cdot CH_2\\CH_2\cdot CH_2\cdot N—CH_2\end{matrix}>CH_2$, b.p. 80°/14 mm. [picrate, m.p. 213—214° (corr.); picrolonate, m.p. 191·5° (corr.); methiodide (I), m.p. 282·5—283° (corr.)], identical with norlupinane *B* (Clemo *et al.*, A., 1931, 499). (I) is transformed by treatment with Ag_2O, followed by distillation and hydrogenation, into 1-methylaza*cyclo*decane, m.p. 89—90°/20 mm.

H. W.

Action of mixed organo-magnesium compounds on the phenylhydrazones of cyclanones. P. Grammaticakis (Compt. rend., 1939, **209**, 317—319; cf. A., 1937, II, 287; 1938, II, 283).—*cyclo*Hexanonephenylhydrazone with MgPhBr in Et_2O affords 1 : 2 : 3 : 4-tetrahydrocarbazole and 1-*phenylhydrazino*-1-*phenyl*cyclo*hexane*, m.p. 113° [*hydrochloride*, m.p. 215° (decomp.); *oxalate*, m.p. 186°; *phenylcarbamyl* derivative, m.p. 172°], converted by O_2 in Et_2O or EtOH into 1-*benzeneazo*-1-*phenyl*cyclo*hexane*, m.p. 60°. Similarly 2-methyl*cyclo*hexanonephenylhydrazone (I) with MgPhBr gives 1- (II) and 5-methyl-1 : 2 : 3 : 4-tetrahydrocarbazole (III), and 2-*phenyl*-2 : 3-*tetramethylene*-3- or -1′-*methyl*-2 : 3-*dihydroindole*, m.p. 102° [*hydrochloride*, m.p. 258° (decomp.); *oxalate*, m.p. 166°; *Ac*, m.p. 93°, and *phenylcarbamyl* derivative, m.p. 168°]. 3-Methyl*cyclo*hexanonephenylhydrazone with MgEtBr, MgPhBr, or $CH_2Ph\cdot MgCl$ gives 2-methyl-1 : 2 : 3 : 4-tetrahydrocarbazole and other condensation products. (I) with MgMeI gives (II) and (III). *cyclo*Pentanonephenylhydrazone with MgPhBr gives, besides other substances, 2 : 3-*trimethyleneindole*, m.p. 109°, b.p. 160—162°/<1 mm. Some unchanged phenylhydrazone, NH_2Ph, $NHPh\cdot NH_2$, and cyclanone are always obtained.

J. L. D.

Homogeneous catalytic hydrogenation.—See A., 1939, I, 529.

Quinoline derivatives.—See B., 1939, 996.

Fate in the animal body of *N*-substituted amino-acids. III. Fate of *ON*-dimethyltyrosine in the rabbit and dog. T. Tō (Z. physiol. Chem., 1939, **260**, 175—180; cf. A., 1939, III, 296).—Methylhydantoin hydrochloride and anisaldehyde heated at 105—120° for 4 hr. with NaOAc and Ac_2O give 85·5% of 4-*anisylidene*-3-*methylhydantoin*, decomp. 225°, which is reduced by Na–Hg in 0·5N-NaOH to 90% of ON-*dimethyltyrosinylhydantoin*, decomp. 149—150°; this is hydrolysed in 12 hr. by boiling aq. $Ba(OH)_2$ to 75% of dl-ON-*dimethyltyrosine* (I), decomp. 235°. Creatinine, anisaldehyde, NaOAc, and Ac_2O heated at 130—140° for 90 min. give 91% of *anisylidenecreatinine*, decomp. 195—200°, which in 0·5N-NaOH is reduced by Na–Hg to ~86% of *dihydroanisylidenecreatinine*, decomp. 258°; this also is hydrolysed to 80% of (I) by boiling aq. $Ba(OH)_2$. After subcutaneous injection of the Na salt of (I) into

rabbits the urine contains the *d*-form, m.p. 240°, $[\alpha]_D^{20}$ +21·87°, of the acid, together with smaller amounts of unchanged *dl*-acid and of *p*-methoxyphenylpyruvic acid probably derived from the *l*-acid. When dogs are used in place of rabbits unchanged material only is found in the urine. W. McC.

Structure of murexides and alloxantines. N. M. Winslow (J. Amer. Chem. Soc., 1939, **61**, 2089—2092).—1- (I) and 1′-*phenylmurexide* (II) exist as different individuals, which does not accord with resonance colour theories. $CH_2(CO_2H)_2$, NHPh·CO·NH_2, and Ac_2O in boiling $CHCl_3$ give 1-phenylbarbituric acid (III) (40%), *malonyldi*(*phenylcarbamide*) [hydrolysed by hot 0·6M-Na_2CO_3 to NHPh·CO·NH_2 and (III)], and some NHPh·CO·NHAc. Conversion of (III) into Na phenylviolurate by aq. $NaNO_2$ at 50°, followed by reduction by H_2S–HCl at 45°, gives 1-*phenyluramil* (IV), which with HNO_3 (*d* 1·42) at 0° gives 60—90% of 1-*phenylalloxan* (V). Alloxan hydrate (VI) and (IV) in H_2O at 50° give 1-phenylalloxantine, hydrolysed by hot, aq. NaOAc to Na 1-phenyldialurate (74·5%) or slowly by KOAc to K dialurate (VII). Dialuric acid [prep. *in situ* from (VI) by H_2S at 98°] and (V) in H_2O give 1′-phenylalloxantine (VIII), hydrolysed at once by KOAc to (VII) (~67%). In hot 20% aq. $(NH_4)_2CO_3$, (VI) and (IV) give (I), hydrolysed by approx. M-HCl to 1-phenyluramil and (VI) (determined by reduction to alloxantine). A similar method did not give (II), which, however, was obtained from (VIII) by NH_3 in dry C_6H_6 at 50° and is hydrolysed by M-HCl to uramil, the (V) also formed being decomposed. R. S. C.

Pyrazolones.—See A., 1939, 996.

Salts of thiolbenziminazole.—See A., 1939, I, 532.

Derivatives of 1-hydroxy-1 : 2 : 3-benztriazole. B. Vis (Rec. trav. chim., 1939, **58**, 847—855).—Interaction of N_2H_4 and 1 : 3 : 4 : 5-$C_6H_2Cl_2(NO_2)_2$ (I) in EtOH yields the *hydrazine* salt, m.p. indef. (loses N_2H_4), of 4 : 6-*dichloro*-1-*hydroxy*-1 : 2 : 3-*benztriazole* (II), m.p. 193°. Similarly from 1 : 3 : 4 : 5-$C_6H_2Br_2(NO_2)_2$ (III) is produced the N_2H_4 salt, m.p. 222° after losing N_2H_4, of 4 : 6-*dibromo*-1-*hydroxy*-1 : 2 : 3-*benztriazole* (IV), m.p. 222°. With NHMe·NH_2 (V), (I) gives 4 : 6-*dichloro*-3-*methyl*-1 : 2 : 3-*benztriazole* 1-*oxide*, m.p. 141°, the structure of which is confirmed by a depression of m.p. when mixed with the isomeric 4 : 6-*dichloro*-1-*methoxy*-1 : 2 : 3-*benztriazole*, m.p. 110—140°, which is formed from the *Ag* salt of (II) with MeI. From (III) and (V) in EtOH is formed 4 : 6-*dibromo*-3-*methyl*-1 : 2 : 3-*benztriazole* 1-*oxide*, m.p. 189°, not identical with 4 : 6-*dibromo*-1-*methoxy*-1 : 2 : 3-*benztriazole*, m.p. 120°, formed from the *Ag* salt of (IV) and MeI. Interaction of 4 : 2 : 6 : 1-$C_6H_2Cl(NO_2)_2$·OMe (VI) and N_2H_4 in EtOH yields the N_2H_4 salt, m.p. 190°, of 6-*chloro*-4-*nitro*-1-*hydroxy*-1 : 2 : 3-*benztriazole*, m.p. 190°, whilst with NHMe·NH_2 (VI) gives 6 : 6′-*dichloro*-3 : 3′-*dimethyl*-1 : 2 : 3 : 1′ : 2′ : 3′-*azoxydibenztriazole* 1 : 1′-*dioxide*, m.p. 194°. J. D. R.

Catalytic properties of phthalocyanines in oxidations. C. Paquot (Compt. rend., 1939, **209**, 171—173).—When O_2 is bubbled through a suspension of Fe, Co (I), or Ni (II) phthalocyanine (0·25—0·5%) in α-pinene (III) at 50—100°/8—40 hr., verbenone (10—25%), active pineol hydrate (1—3%), and unchanged (III) (40—70%) are formed. With (I) at 100°, verbenene (2—7%), verbenol (2%), and a viscous residue (10—35%) of condensation products of (III) result. (I) is considerably inactivated after being used once, but the other two catalysts can be used repeatedly. *cyclo*Hexene containing (II) (0·4%) with O_2 at 65°/60 hr. gives Δ^2-*cyclo*hexenone (17%), Δ^2-*cyclo*hexenol (6%), $\Delta^{1:3}$-*cyclo*hexadiene (2%), 1 : 2-oxido*cyclo*hexane (2%), and *cis*-*cyclo*hexane-1 : 2-diol (4%). J. L. D.

Indoles. IX. Reaction of phenylhydrazine with "Mannich" bases. (Miss) R. H. Harradence and F. Lions (J. Proc. Roy. Soc. New South Wales, 1939, **73**, 14—21).—With NHPh·NH_2 (I), 2-morpholinomethyl*cyclo*hexanone gives its *phenylhydrazone*, m.p. 112°, which with dry HCl in cold EtOH gives the *hydrochloride*, m.p. 211°, of 11-*morpholinomethyl*-1 : 2 : 3 : 4-*tetrahydrocarbazolenine*, m.p. 112° (*picrate*, m.p. 193°). The product from 2-piperidinomethyl*cyclo*hexanone and (I) with EtOH–HCl followed by alkali gives 11-*piperidinomethyl*-1 : 2 : 3 : 4-*tetrahydrocarbazolenine*, m.p. 95° (*picrate*, m.p. 207°). 11-*Diethylaminomethyl*- (*picrate*, m.p. 158°), and 11-*dimethylaminomethyl*-1 : 2 : 3 : 4-*tetrahydrocarbazolenine* (*picrate*, m.p. 175°) are obtained similarly. With (I), 2-morpholinomethyl*cyclo*pentanone gives its *phenylhydrazone*, m.p. 103° (*picrate*, m.p. 160°), which with EtOH–HCl gives the *hydrochloride*, m.p. 241°, of 3-*morpholinomethyl*-2 : 3-*trimethyleneindolenine*, m.p. 103° (*picrate*, m.p. 194°). $COEt_2$, $(CH_2O)_3$, and morpholine hydrochloride (100°; 5 hr.) give the *hydrochloride*, m.p. 131°, of β-*morpholinomethylpentan*-γ-*one*, b.p. 95—100°/2 mm. (*picrate*, m.p. 132°), of which the reaction product with (I) gives with EtOH–HCl an uncrystallisable product. E. W. W.

Morpholinomethyl alkyl ethers. (Miss) R. H. Harradence and F. Lions (J. Proc. Roy. Soc. New South Wales, 1939, **73**, 22—28).—Morpholine (I), 40% CH_2O (II), and K_2CO_3 give *dimorpholinomethane*, b.p. 139—140°/29 mm. By the method of McLeod and Robinson (J.C.S., 1921, **119**, 1472), (I), (II), and the appropriate alcohol give the following ethers: *morpholinomethyl* Pr^{β}, b.p. 185—195°, Bu^{α}, b.p. 218—222°/760 mm., cyclo*hexyl*, b.p. 140—150°/30 mm. (impure), and β-*phenylethyl ether*, b.p. 184°/25 mm.; *di*(*morpholinomethyl*) αβ-*dimethylene*, b.p. 205—209°/26 mm., and αγ-*trimethylene diether*, b.p. 218—221°/27 mm. The following cetyl ethers were also prepared for possible use as emulsifiers: *morpholinomethyl*, b.p. 198—202°/1 mm. (of which the *methiodide*, m.p. 160°, and the *methosulphate* have emulsifying properties but are not sufficiently stable to be of val.); *piperidinomethyl*, b.p. 200—202°/1·5 mm. (*methiodide*, m.p. 124°), *diethylaminomethyl*, b.p. 183—185°/1·7 mm. (*methiodide*, m.p. 105°), and *hexahydronicotinyl cetyl ether*, b.p. 250—255°/2 mm. (gummy unstable *methiodide* and *picrate*). E. W. W.

Ammines with thiolbenzthiazole. G. Spacu and C. G. Macarovici (Bull. Acad. Sci.

Roumaine, 1939, **21**, 173—187).—The following *compounds* (X = $C_7H_4NS_2$) derived from thiolbenzthiazole are described: $X_4Sn,4H_2O$; X_4Sn; $X_2[Ni(NH_3)_2]$; $X_2[Zn(NH_3)_2]$; $X_2[Co(C_5H_5N)_2]$; $X_2[Ni(C_5H_5N)_2]$; $X_2[Cd(C_5H_5N)_2]$; $X_2[Zn(C_5H_5N)_2]$; $X_2[Co(NH_2Ph)_2],H_2O$; $X_2[Ni(NH_2Ph)_2],H_2O$; $X_2[Cd\ en]$; $X_2[Zn\ en]$; $X_2[Co\ en_2Cl(H_2O)]$; $X[Co\ en_2(SCN)_2]$; $X_3[Co\ en_2(NH_3)_2]$; $X_6[Co((HO)_2Co\ en_2)_3],4H_2O$; $X_3[Cr\ en_3]$; $X_2[Ni\ en_3]$; $X_2[Cu\ en_2]$; $X_3[Co\ en_3],H_2O$; $X_3[Co(NH_3)_6],3H_2O$.

F. J. G.

Cyanine dyes.—See B., 1939, 920.

Synthesis of 5-substituted rubans. G. R. Clemo and E. Hoggarth (J.C.S., 1939, 1241—1244).—3-Ketoquinuclidine (I) and PhCHO give (trace $C_5H_{11}N$) 2-*benzylidene*-3-*ketoquinuclidine*, m.p. 133° (*phenylhydrazone*, m.p. 184°). Quinoline-4-aldehyde [improved prep.; *picrate* (+EtOH), m.p. 179°] and (I) afford (HCl or piperidine acetate) 5-*keto*-6 : 9-*rubanene* (II), m.p. 153° (*picrate*, m.p. 209°; *platinichloride*, decomp. >260°), which is hydrogenated (MeOH–Pd–C) to 5-*ketoruban*, m.p. 125—126° (*phenylhydrazone*, m.p. 198°; *picrate*, m.p. 168°). This compound is reduced [$Pr^{\beta}OH$–$Al(OPr^{\beta})_3$] to *ruban*-5-*ol*, m.p. 198° (*picrate*, m.p. 188—189°), and with MgEtI gives 5-*ethylruban*-5-*ol*, m.p. 139° (*picrate*, m.p. 161°). MgEtI and (II) yield a *compound*, $C_{19}H_{22}ON_2$, m.p. 164° (*picrate*, m.p. 150°). F. R. S.

Modified cinchona alkaloids. VII. Constitution of niquidine. E. M. Gibbs and T. A. Henry (J.C.S., 1939, 1294—1299; cf. A., 1939, II, 187).—Oxidation (ice-cold $KMnO_4$) of "niquidine" gives MeCHO, quininic acid (I), and small quantities of a *substance* E, $C_{17}H_{14}O_4N_2$, m.p. >300° (*Me* ester, m.p. 168°), and a *substance* F, $C_{17}H_{20}O_4N_2$, m.p. 247° (decomp.); it is suggested that *E* is converted into *F* by oxidation of $C_5H_{11}N$ to C_5H_5N. Dihydroniquidine is oxidised (H_2O_2) to (I), its *amine oxide*, m.p. 268° (decomp.), and β-propylglutaric acid, m.p. 50° (*diamide*, m.p. 195°; *dianilide*, m.p. 219°), identical with the synthetic acid. Similar oxidation (H_2O_2) of dihydroquinidine gives (I) and its amine oxide and *ω-ethylmethanetriacetic acid*, m.p. 120°, $[\alpha]_D$ −1·3° in H_2O [*di*-, m.p. 222°, and tri-anilide, m.p. 280° (decomp.)], also obtained by the hydrolysis of the CN-ester prepared from CN·CHEt·CO_2Et and Et glutaconate. These experiments confirm the constitutions previously assigned. F. R. S.

[Strychnine and brucine. Re-examination of the action of bromine on diketonucidine and its bearing on the structure of the alkaloids.] H. Leuchs (Ber., 1939, **72**, [*B*], 1588—1589).—A reply to Holmes and Robinson (A., 1939, II, 290).

H. W.

***Strychnos* alkaloids. CVII. Transformation of the nitroquinones from *ψ*-brucine and dihydro-*ψ*-brucine.** H. Leuchs and H. L. Louis (Ber., 1939, **72**, [*B*], 1483—1487).—The dark red isomeride (I) of the nitroquinone from *ψ*-brucine is unchanged by H_2SO_3 at 100° and converted into a dark red resin at 130—140°; it does not react with NH_2OH and does not afford well-defined products with CH_2N_2. Catalytic reduction followed by crystallisation of the product from $COMe_2$ gives the *product*, $C_{24}H_{29}O_6N_3,HClO_4$, blackens at 220—290°, which is the :CMe_2 derivative of an NH_2-phenol $C_{21}H_{25}O_6N_3,HClO_4$. Reduction of (I) with Sn and 12N-HCl gives the *substance*, $C_{21}H_{23}O_6N_3,HCl,0{\cdot}5H_2O$, whereby it appears that NO_2 is reduced but C:C is left untouched. Zn dust and Ac_2O transform (I) into the *substance*, $C_{27}H_{29}O_9N_3,HClO_4$ (Ac_3 derivative of $C_{21}H_{23}O_6N_3$). Catalytic hydrogenation of *ψ*-brucine in 50% AcOH continues after the consumption of 3 H and the product contains dihydrobrucine (*perchlorate*). Interruption at a suitable point permits the isolation of dihydro-*ψ*-brucine, converted by successive treatments with 5N-HNO_3 and H_2SO_3 into the quinol (*perchlorate*, $C_{21}H_{24}O_5N_2,HClO_4$). This is oxidised by HNO_3 to the *nitroquinone hydrate* (II) [*perchlorate* (III), $C_{21}H_{23}O_8N_3,HClO_4$]; the corresponding *oxime hydrochloride* and *semicarbazone perchlorate* are described. (II) is reduced by H_2SO_3 to the nitroquinol (*perchlorate*, $C_{21}H_{25}O_8N_3,HClO_4$). H_2O at 80° converts (III) into the dark red amorphous *compound*, $C_{21}H_{23}O_8N_3$, the *perchlorate* of which is hydrogenated and converted by $COMe_2$ into the *perchlorate*, $C_{24}H_{29}O_6N_3,HClO_4$.

H. W.

Amino-morphides and -codides. L. Small and F. S. Palmer (J. Amer. Chem. Soc., 1939, **61**, 2186—2190).—Interaction of 6- or 8-halogeno-derivatives of morphine or codeine with bases involves in each case an allylic shift. Structures are assigned by behaviour on catalytic hydrogenation. The basic substituents reduce the physiological (especially the analgesic) action. 8-Diethylaminomorphide, m.p. 201—204° (vac.) (lit., 203°), $[\alpha]_D^{21}$ +49·1° in MeOH [*dihydriodide*, +1·5H_2O, m.p. 87—93° (vac.), $[\alpha]_D^{25}$ +2·6° in H_2O; *diperchlorate*, m.p. 114—116° (vac.), $[\alpha]_D^{19}$ +4·4° in H_2O], is described. 8-*Piperidinomorphide* (I) (prepared from α-chloromorphide and piperidine at 100°), m.p. 222—224° (vac.), $[\alpha]_D^{24}$ +28·7° in MeOH [*dihydriodide*, m.p. 208—214° (vac.), $[\alpha]_D^{23}$ +14·9° in H_2O; *methiodide*, m.p. 243—245° (vac.), $[\alpha]_D^{23}$ +23·7° in 50% (vol.) EtOH], is hydrogenated (PtO_2 in this and other cases) in 5% AcOH to phenolic 8-*piperidinotetrahydromorphide*, m.p. 270—280° (vac.; decomp.), $[\alpha]_D^{26}$ +45·1° in 10% AcOH (green $FeCl_3$ colour) (*acetate*, m.p. 172—178°). 8-Diethylaminocodide, m.p. 101—103° (lit., 102°), $[\alpha]_D^{23}$ +42·6° in MeOH (*diperchlorate*, m.p. 180·5—183°, $[\alpha]_D^{19}$ +3·3° in H_2O; *dihydriodide*, m.p. 179—182°, $[\alpha]_D^{26}$ +22·9° in abs. EtOH), is hydrogenated in EtOH to 8-*diethylaminotetrahydrocodide*, m.p. 154—157°, $[\alpha]_D^{25}$ +31·5° in MeOH, or (? +xH_2O), m.p. 116—119° (gas) [*perchlorate*, m.p. 234—238° (vac.), $[\alpha]_D^{26}$ +18·3° in H_2O]. Hydrogenation of 8-piperidinocodide [obtained from (I) and CH_2N_2 or from α-chlorocodide (II)], m.p. 116—117° (lit., 118°), $[\alpha]_D^{22}$ +25·8° in MeOH [H_2 *disulphate*, m.p. 161—163·5° (vac.), $[\alpha]_D^{25}$ +19·8° in H_2O; *mono*-, m.p. 234—237° (vac.), $[\alpha]_D^{24}$ +13·3° in H_2O, and impure *di-hydriodide*; methiodide, $[\alpha]_D^{25}$ +22·0° in H_2O; *diperchlorate*, m.p. 181—183°, $[\alpha]_D^{23}$ +13·2° in 50% (vol.) EtOH], in EtOH gives the phenolic H_4-derivative, m.p. ~125°, $[\alpha]_D^{25}$ +36·7° in MeOH (green $FeCl_3$ colour), but that of the hydrochloride in AcOH gives mostly the non-phenolic H_2-derivative, m.p. 167—169°, $[\alpha]_D^{23}$ −1·2° in MeOH. Liquid NH_3 and (II) at 50° give 8-*aminocodide*, m.p. 128·5—129°, $[\alpha]_D^{21}$

—79·2° in EtOH [*dihydrochloride*, m.p. 300—305° (vac.; corr.), $[\alpha]_D^{24}$ —40·7° in H_2O; Ac_2 derivative, +*x*EtOAc, m.p. 218—220° or, in vac., 165—175°, solidifies, remelts at 205°, $[\alpha]_D^{24}$ —83·1° in EtOH], which by hydrogenation in MeOH gives the phenolic H_4-derivative, m.p. 138·5—140°, $[\alpha]_D^{24}$ —9·7° in EtOH (green $FeCl_3$ colour; *dihydrochloride*, $[\alpha]_D^{24}$ +6·6° in H_2O), or, as dihydrochloride in AcOH, the H_2-derivative, a glass, $[\alpha]_D^{21}$ —28·7° in EtOH [*dihydrochloride*, +H_2O, m.p. 274—277° (vac.), $[\alpha]_D^{24}$ —14·7° in H_2O]. Bromomorphide (III) and piperidine at 100° give 6-*piperidinomorphide* (IV), m.p. 216—217° (vac.), $[\alpha]_D^{23}$ —234·8° in MeOH [*methiodide*, m.p. 236—241° (vac.; corr.), $[\alpha]_D^{23}$ —145·8° in 50% (vol.) EtOH], which is hydrogenated in EtOH to the H_2-derivative (V), m.p. 215—217°, $[\alpha]_D^{24}$ —155·9° in MeOH. 6-*Piperidinocodide*, m.p. 75—80°, $[\alpha]_D^{23}$ —233·9° in MeOH (*diperchlorate*, m.p. 172—175°, $[\alpha]_D^{23}$ —113·4° in H_2O), is obtained by piperidine from (III) at 100° or β-chlorocodide at 130° or by CH_2N_2 from (IV); when hydrogenated, it absorbed 2 H to give an oil; CH_2N_2 and (V) also give an oil. Liquid NH_3 and (III) at 50° give a mixture. The bases sublime in a high vac. R. S. C.

Veratrine alkaloids. VI. Oxidation of cevine. L. C. Craig and W. A. Jacobs (J. Amer. Chem. Soc., 1939, **61**, 2252—2253; cf. A., 1938, II, 515; 1939, II, 459).—CrO_3 in dil. H_2SO_4 oxidises cevine to a mixture, including acids, which at 180° give CO_2 and a *lactonic acid* (I), $C_{14}H_{14}O_6$, m.p. 273—278° $[\alpha]_D^{25}$ +47·6° in C_5H_5N (reddish-purple $FeCl_3$ colour). CH_2N_2 gives a *product* (II), $C_{14}H_{12}O_4(OMe)_2$, m.p. 165—166°. (I) neutralises 2 NaOH–EtOH in the cold; (II) neutralises 1 NaOH–EtOH in the cold and a second mol. when boiled. *p*-$SO_3H{\cdot}C_6H_4{\cdot}N_2Cl$ couples with (I) or (II). (I) absorbs 3 H_2 (PtO_2) to give an oil (III), which does not give the colour reactions and may be a tetrahydronaphthalene derivative; however, as, with acid, (III) liberates CO_2 (to give cryst. products), (I) may be a ketone. (I) is derived from that part of the mol. not related to octahydropyridocoline. R. S. C.

Sulphophenylarsinic acids and their derivatives. II. *p*-Sulphonamidophenylarsinic acid. J. F. Oneto and E. L. Way (J. Amer. Chem. Soc., 1939, **61**, 2105—2106; cf. A., 1938, II, 464).—p-*Sulphonamidophenylarsinic acid* (I) (*Ag* salt; "*anhydride*" formed at 185—190°/vac.) is obtained from *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ by the Bart reaction and from p-*sulphonamidophenylarsine oxide* (II) by 30% H_2O_2 at 100°. With HI, (I) gives p-*sulphonamidophenyldiiodoarsine*, m.p. 192—193°, with HBr–SO_2 and a trace of HI gives p-*sulphonamidophenyldibromoarsine* (III), m.p. 191—192°, and with HCl–SO_2 and a trace of HI or with PCl_3 gives p-*sulphonamidophenyldichloroarsine*, m.p. 176—177°, also obtained from (II) by hot HCl. *p*-$SO_3Na{\cdot}C_6H_4{\cdot}AsO_3H_2$ with PCl_5–PCl_3 gives p-*chlorosulphonylphenyldichloroarsine*, m.p. 84—85°, which with conc., aq. NH_3 gives (II) [also obtained from (III) by hot, aq. NH_3] and with Cl_2–$CHCl_3$ gives p-*chlorosulphonylphenylarsinic acid* (*sulphonanilido-acid* obtained by NH_2Ph at 100°). R. S. C.

Arsinic acids.—See B., 1939, 997.

Preparation of *p*-tolylstibinic acid. G. J. Burrows and E. Ritchie (J. Proc. Roy. Soc. New South Wales, 1939, **72**, 118—119).—A diazotised solution of *p*-$C_6H_4Me{\cdot}NH_2$ is added slowly and with good stirring at 0° to a solution of Na_3SbO_3 obtained by mixing $SbCl_3$ in conc. HCl and glycerol with aq. NaOH; excessive frothing is prevented by occasional addition of Et_2O. After keeping overnight, the mixture is filtered from coloured by-products, nearly neutralised with dil. HCl, and treated with CO_2 until Sb_2O_3 is no longer pptd.; this is filtered off and the filtrate is treated with HCl, whereby *p*-tolylstibinic acid is pptd. in 45—50% yield. H. W.

Device for avoiding sucking back with the Parnas–Wagner micro-Kjeldahl apparatus.—See A., 1939, I, 540.

Micro-method for potentiometric formaldehyde titration. A. Janke and E. Mikschik (Mikrochem., 1939, **27**, 176—179).—A thin glass bulb, coated externally with Ag and mounted in insulating and protective material, serves as a glass electrode and as titration vessel. A 0·01N-HCl–quinhydrone electrode is used as reference. The glass electrode vessel is placed in the axis of a loud-speaker magnet to ensure agitation of the solution. For determination of NH_2 in NH_2-acids and peptides 0·1—0·3 c.c. of the sample is introduced into the electrode and titrated with NaOH to p_H 7. 0·1—0·3 c.c. of CH_2O is then added and the solution further titrated to p_H 9. The wt. of N present is deduced from the vol. of NaOH required for the titration between p_H 7 and 9, after correction ascertained by a blank test with the same CH_2O. J. W. S.

Oxidation of aldoses by hypoiodite. III. K. Myrbäck (Svensk Kem. Tidskr., 1939, **51**, 149—158; cf. A., 1939, II, 244).—The rate of oxidation of glucose and maltose with I in KI in presence of alkali is high in 0·031N-NaOH and in N-Na_2CO_3, but low in more conc. NaOH or in presence of $NaHCO_3$. In conc. NaOH the results obtained after long keeping are high owing to further stages of oxidation, whilst in Na_2CO_3 oxidation is incomplete owing to formation of IO_3'. The reaction becomes more complete in very dil. sugar solutions. For accurate determinations the method of Willstätter and Schudel must be followed closely. J. W. S.

Methionine. III. Comparison of oxidative reactions of methionine, cysteine, and cystine. Determination of methionine by hydrogen peroxide oxidation. G. Toennies and T. P. Callan (J. Biol. Chem., 1939, **129**, 481—490; cf. A., 1939, II, 302).—Methionine (I) is much more reactive towards H_2O_2 than cystine (II) or cysteine (III), and it may be possible to use this factor to determine (I) among the products of protein hydrolysis. Oxidation of (I) is limited to the sulphoxide stage, except in presence of MoO_4^{--}, when it proceeds further; Cu^{++} has no effect. Oxidation velocity of (I) or (II) increases with increasing acidity, whilst that of (III) decreases. Oxidation of (III) is also influenced by Cu^{++}. A. T. P.