BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

SEPTEMBER, 1938.

Structural definition of auxochromes and chromophores. M. Artinet (Bull. Soc. chim., 1938, [v], **5**, 1033—1042).—The at. groups causative of coloration or selective absorption can be divided into auxochromes and chromophores and this distinction appears advisable. To each of these groups can be given a definition based on the consideration of their structure and from which it can be predicted that the accumulation in a single mol. solely of chromophores or solely of auxochromes is much less favourable to the development of colour than the simultaneous presence of members of each of the two groups. H. W.

Deuterium and optical activity. C. Buchanan (Chem. and Ind., 1938, 748—751).—A review. A. Li.

Kinetics of the thermal decomposition of *n*-butane.—See A., 1938, I, 403.

Synthesis of *n*-heptane. V. V. Tischtschenko and M. A. Belopolski (J. Appl. Chem. Russ., 1938, **11**, 638—642).—BuOH is oxidised to PrCHO, and this to $PrCO_2H$, by known catalytic methods. $PrCO_2H$ is passed over ThO_2 gel at 400° to give $COPr_2$, which is hydrogenated (MoS_3 catalyst, at 350°/100—110 atm.) to yield *n*-heptane, by the reactions: $COPr_2 \rightarrow CHPr_2{\cdot}OH \rightarrow CHEt{:}CHPr \rightarrow n\text{-}C_7H_{16}$. R. T.

Peroxide effect in the addition of reagents to unsaturated compounds. XV. Correction. F. R. Mayo (J. Org. Chem., 1938, **2**, 577; cf. A., 1938, II, 122). R. S. C.

Influence of substituents on the spontaneous or thermal polymerisation of olefines. F. Eirich (Österr. Chem.-Ztg., 1938, **41**, 251—254).—A lecture. E. S. H.

Mercury-photosensitised hydrogenation of ethylene, tetradeuteroethylene, and partly deuterated ethylenes.—See A., 1938, I, 408.

Explosive decomposition of acetylene with ignition. A. Gross (Compt. rend., 1938, **206**, 1654—1656; cf. A., 1928, 28).—C_2H_2, pure or diluted with an inert gas, when passed through certain tubes (listed) of various diameters and at different temp. does not ignite. Using other tubes (*e.g.*, Pyrex, SiO_2, Fe, graphite), white fumes changing to yellow and then to brown issue from the tube, and there is periodic ignition of the gas, and a deposit of C. The temp. at which the phenomenon occurs varies from 550—600° and 850—900° depending on the tube. The period of ignition varies with the temp. and rate of flow of C_2H_2 and is independent of the dilution of C_2H_2. The phenomenon is probably due to two reactions, polymerisation and decomp. of C_2H_2, and is catalysed by the material of the tube. The reaction is not a chain reaction because the presence of inert gas is without effect. J. L. D.

Fluorination method. A. L. Henne (J. Amer. Chem. Soc., 1938, **60**, 1569—1571).—Passing HF into a stirred mixture of red HgO and an org. substance leads to smooth replacement of Cl or Br in the org. substance by F, if efficient cooling is provided. Yields, usually >70%, are often improved by cooling, *e.g.*, to −20°. Indifferent solvents may be used. Complete exchange occurs with CH_2Cl_2, $CH_2Br{\cdot}CH_2{\cdot}OAc$, $CHBr_2{\cdot}CH_2{\cdot}OAc$, $CHMeCl_2$, $n\text{-}C_6H_{13}{\cdot}CHCl_2$, CPh_2Cl_2, and CPh_3Cl. $CHCl_3$ gives $CHClF_2$. $(CCl_2F)_2$ gives $(CClF_2)_2$. $CHCl_2{\cdot}CClF_2$ or $CHF_2{\cdot}CCl_3$ gives $CHF_2{\cdot}CClF_2$. A quant. method of recovering the Hg is described. R. S. C.

Photochemical polymerisation of chloroprene and related molecules.—See A., 1938, I, 408.

Peroxide effect in the addition of reagents to unsaturated compounds. XVII. Addition of hydrogen sulphite. M. S. Kharasch, E. M. May, and F. R. Mayo (Chem. and Ind., 1938, 774—775).—O_2 and peroxides catalyse the addition of $NaHSO_3$ to allyl alcohol, styrene, and $CHPh{:}CH{\cdot}CH_2{\cdot}OH$; in their absence very little action occurs. A chain mechanism is proposed. H. W.

Scission of primary and secondary β-ethylenic alcohols. C. Prévost and O. K. Houo (Compt. rend., 1938, **206**, 1661—1662; cf. A., 1928, 1211).—Alcohols $R{\cdot}CH(OH){\cdot}CH_2{\cdot}CH{:}CH_2$ (R = H, Me, Et, or $\cdot CH{:}CH_2$) at 340—360° in presence of Al_2O_3 are largely (50%) unaltered, a little H_2O and conjugated dienes are formed, and about 40% splits to give CH_2O, MeCHO, EtCHO, and acraldehyde, respectively, with $CHMe{:}CH_2$ in each case. $CH_2Ph{\cdot}CH_2{\cdot}OH$ and $CH_2Ph{\cdot}CHMe{\cdot}OH$ similarly afford $CHPh{:}CH_2$ and CHPh:CHMe, respectively. J. L. D.

"Leaf alcohol." [*trans*-Δ$^\gamma$-hexenol]. I. Occurrence in plants. S. Takei, Y. Sakato, M. Ono, and Y. Kuroiwa. **II. Synthetic perfumes from "leaf alcohol."** S. Takei, M. Ono, Y. Kuroiwa, T. Takahata, and T. Sima (J. Agric. Chem. Soc. Japan, 1938, **14**, 709—716, 717—723).—I. The leaf oils from tea, ivy, clover, oak, wheat, mulberry, and black radish contain Δ$^\alpha$-hexenal with *trans*-Δ$^\gamma$-*hexenol* (I) (4′-*iodophenylurethane*, m.p. 157°; 3 : 5-*dinitrobenzoate*, m.p. 49°; *Ag* salt of *phthalic ester*, m.p. 126°; *allophanate*, m.p. 146°; *anthraquinone*-2-*carboxylate*, m.p. 68°). In general

(I) occurs in the free state, but in Japanese peppermint oil it is present as the phenylacetate. Oxidation of (I) with CrO_3 gives the *aldehyde* (2 : 4-*dinitrophenylhydrazone*, m.p. 144°; *semicarbazone*, m.p. 173°).

II. (I) is converted into Δ^{γ}-hexenyl bromide by PBr_3 and condensation of this with acraldehyde yields $\alpha\zeta$-*nonadien-γ-ol* (II) (4′-*iododiphenylurethane*, m.p. 122°; *allophanate*, m.p. 125°), which has an odour of cypress leaves or sea-cucumber. (II) by the successive action of PBr_3, AgOBz, and KOH is converted into trans-trans-$\Delta^{\beta\zeta}$-*nonadienol* (4′-*iododiphenylurethane*, m.p. 137°; *allophanate*, m.p. 140°), which also has an odour of cypress leaves. Oxidation with CrO_3 yielded trans-trans-$\Delta^{\alpha\epsilon}$-*nonadienol* (*semicarbazone*, m.p. 157·5°; 2 : 4-*dinitrophenylhydrazone*, m.p. 113°) identical with the natural violet leaf aldehyde. *Nonan-γ-ol* (4′-*iododiphenylurethane*, m.p. 146°; *allophanate*, m.p. 135°) has a characteristic woody or Japanese lacquer odour. J. N. A.

Preparation of unsaturated alcohols by Grignard synthesis from α-diketones and allyl bromide. J. I. Juschtschenko (Mem. Inst. Chem. Ukrain. Acad. Sci., 1938, **5**, 101—113).—Ac_2 or benzil and Mg allyl bromide in Et_2O yield δε-*dimethyl*-, m.p. 70—70·7°, or δε-*diphenyl-octa*-$\Delta^{\alpha\eta}$-*diene*-δε-*diol*, m.p. 141·5°. R. T.

Synthesis of adonitol. R. Lespieau (Compt. rend., 1938, **206**, 1773—1775).—*dl*-Arabitol pentaacetate (I) synthesised as described previously (cf. A., 1936, 1229) is mixed with an oil which, when distilled in vac., affords some cryst. (I), which with boiling MeOH–HCl gives *dl*-arabitol (II), and an oil, hydrolysed (boiling MeOH–HCl) to adonitol (III). As all the OH in (III) are in the *cis*-positions to one another it follows that the OH in γδε-trihydroxy-Δ^{α}-pentinene (*loc. cit.*) are similarly related. The simultaneous formation of (II) and (III) is also explained on this assumption. No xylitol is isolated, but the considerable unworkable residues do not exclude its presence. J. L. D.

Hydrogenation of the furan nucleus in presence of Raney nickel. Application to the preparation of αδ-epoxides (alkyltetrahydrofurans); αδ-dibromides. R. Paul (Bull. Soc. chim., 1938, [v], **5**, 1053—1062).—Furylethylene, obtained by dicarboxylation of furylacrylic acid by quinoline containing anhyd. $CuSO_4$, is hydrogenated (Raney Ni) to αδ-*oxido*-n-*hexane* [η-*ethyltetrahydrofuran*], b.p. 108° (corr.)/758 mm.; reaction ceases when 90% of the calc. amount of H has been absorbed and the product is purified by cautious treatment with Br and final contact with K–Na. The mixture of furylpropane and -propene obtained by dehydration of furylethylcarbinol is similarly hydrogenated to αδ-*oxido*-n-*heptane* [η-*propyltetrahydrofuran*], b.p. 135°/773 mm. αδ-*Oxido*-n-*octane*, b.p. 159—160°/768 mm., and αδ-*oxido*-n-*nonane*, b.p. 70—71°/14 mm., are described. Phenylfurylcarbinol is reduced (Na and abs. EtOH) to 2-*benzylfuran*, b.p. 104°/12 mm., hydrogenated (118°/65 atm.) to αδ-*oxido*-ε-*phenyl*-n-*pentane*, b.p. 109—110°/10 mm. The requisite oxide is dissolved in AcOH and the solution is saturated with HBr at room temp. and then heated in a sealed tube at 120—130°, whereby the following dibromides are obtained: αδ-*dibromo*-n-*heptane*, b.p. 110—112°/11 mm.; αδ-*dibromo*-n-*octane*, b.p. 125—126°/11 mm.; αδ-*dibromo*-n-*nonane*, b.p. 139—140°/11 mm.; αδ-*dibromo*-ε-*phenylpentane*, b.p. 153—155°/4 mm. H. W.

Esterification of acetic acid at high pressure.—See A., 1938, I, 405.

Catalytic preparation of *iso*amyl acetate. IV. M. B. Turova-Polak and L. A. Vorotnikova (J. Appl. Chem. Russ., 1938, **11**, 643—645).—The highest yield of C_5H_{11}·OAc from *iso*-C_5H_{11}·OH and AcOH is obtained at 100—120° ($C-H_3PO_4$ catalyst). The yield falls abruptly as the temp. exceeds 170°, owing to dehydration of the alcohol to yield amylene. R. T.

Preparation and properties of esters of β-methoxy*iso*butyl alcohol. L. E. Thomas [with R. E. Nelson] (J. Org. Chem., 1938, **2**, 506—507).—β-Methoxy*iso*butyl alcohol, the appropriate acid anhydride, and a little H_2SO_4 give, when warmed, the *acetate*, b.p. 162·7—162·8°/733·69 mm., 58—58·5°/15 mm., *propionate*, b.p. 176·1—176·7°/733·69 mm., 78—78·5°/20 mm., and *butyrate*, b.p. 193·4—193·5°/733·69 mm., 87·5—88°/20 mm. R. S. C.

Conversion of stearic acid into oleic acid by catalytic dehydrogenation. L. Margaillan and X. Angeli (Compt. rend., 1938, **206**, 1662—1663).—Me stearate vapour in C_2H_4 when passed over reduced Ni at 220° affords some Me oleate (23%), H_2, and C_2H_6. The reaction proceeds in the liquid ester with $C_{10}H_8$ acting as a H acceptor, though less efficiently than in the vapour state. Me palmitate is not dehydrogenated similarly. J. L. D.

Dehydration of ricinoleic acid, and polymerisation of the triglyceride of Δ^{9x}-octadecadienecarboxylic acid. P. M. Bogatirev, S. M. Dridze, and I. A. Kuziuberdin (Prom. Org. Chim., 1938, **5**, 327—333).—The action of metallic catalysts (Zn, Cu) in the dehydration of ricinoleic acid (I) (in castor oil) at 280° is ascribed to formation of fatty acid salts of these metals; the process is thus one of homogeneous catalysis. Both formation of these salts and subsequent formation and decomp. of *O*-esters of (I) to yield dienic acid glycerides (II) are ascribed to formation of acid products of thermolysis [chiefly $C_{11}H_{23}$·CO_2H (III)], the process being thus a special case of the Crafts reaction. Addition of acids accelerates the process, and lowers the yield of by-products [(III), C_7H_{15}·CHO], in the following diminishing order of efficacy: oxalic, boric, phthalic, stearic, oleic, and abietic acid. Under optimal conditions ≯85% of the (I) content of castor oil is dehydrated. The (II) formed polymerises almost immediately. A structural formula, based on theoretical considerations, is proposed for the polymeride. R. T.

Fats. LXI. Constitution of parinaric acid. H. P. Kaufmann, J. Baltes, and S. Funke (Fette u. Seifen, 1938, **45**, 302—304).—The spectral absorption curve of recryst. parinaric acid, m.p. 83°, from the fat of *Parinarium laurinum*, in abs. EtOH shows max. at λ 320, 307, and 292 mμ. (log E = 4·5 to 4·8)

and is very similar to that of decatetraene; this evidence supports the formula $Et\cdot[CH{:}CH]_4\cdot[CH_2]_7\cdot CO_2H$ (cf. Farmer and Sunderland, A., 1935, 1041). E. L.

Linoleic acid and its isomerides. J. W. McCutcheon (Canad. J. Res., 1938, **16**, B, 158—175).—A prep. of fatty acids from sunflower seed oil is brominated by a modification of Rollett's method (A., 1909, i, 759) and the tetrabromide (I), m.p. 115·2° (yield 50%), of linoleic acid is isolated, free from the liquid isomeride (details given). (I) is debrominated with Zn and then boiled with 4N-HCl in EtOH to give Et linoleate, b.p. 212°/12 mm., hydrolysed at room temp. to linoleic acid (II), m.p. −8° to −9° [dimorphous form (?), m.p. −13° to −14°] (*amide*, m.p. 57—58°, decomposes slightly after some weeks to give an amber-coloured liquid). Pure (II) with Br in light petroleum at −10° to −2° affords (I) and a liquid tetrabromide, converted by debromination and esterification into Et linoleate, b.p. 215°/12 mm., identical with the product obtained from (I). The acids derived from the solid and liquid tetrabromides when oxidised with alkaline $KMnO_4$ and H_2O_2–AcOH, respectively, yield two pairs of sativic acids, m.p. 173° and 155° and m.p. 146° and 126° (cf. A., 1935, 998), respectively, so that the linoleic acids derived from the isomeric tetrabromides are not *cis–trans*-isomerides. The structures of the two tetrabromides are discussed. The preps. of the different products are described in detail. J. L. D.

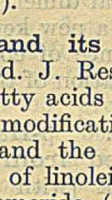
Action of antimony trisulphide on hydroxy-acids. Y. Volmar and E. Weil (Compt. rend., 1938, **206**, 1904—1905; cf. A., 1934, 187).—0·1N solutions of $OH\cdot CH_2\cdot CO_2H$ and $OH\cdot CHMe\cdot CO_2H$ react with Sb_2S_3 under the conditions described by Volmar and Betz (A., 1933, 948) with elimination of H_2S. Sb_2S_3 reacts exactly like Sb_2O_3 and max. yields are obtained with equimol. proportions of the reactants. Sb_2S_3 and K tartrate afford tartar emetic in good yield. β-OH-acids do not react. J. L. D.

Chemistry of the synthesis of acetoacetic ester. F. Arndt and B. Eistert (Ber., 1938, **71**, [*B*], 1547—1549).—The acetoacetic ester synthesis comprises an initial, reversible phase in which the anion of the Na_1 compound of the "methylene component" is intruded into the "directed" CO group of the ester component and a second, irreversible phase in which a proton and [OR] anion are removed under the influence of more alkali and the eliminated R·OH is immediately transformed into NaOR. H. W.

Hydrogenation using colloidal rhodium. C. Zenghelis and K. Stathis (Monatsh., 1938, **72**, 58—62).—The rates of absorption of H_2, using colloidal Rh in neutral solution at room temp. and atm. pressure, in the cases of $COMe_2$, C_6H_6, $PhNO_2$, PhCN, NH_2Ph, NPh:NPh, and maleic, fumaric, and cinnamic acids, indicate the superiority of this catalyst to Ni and metals of the Pt group, under the conditions used. A. T. P.

Effect of chlorophyll on the autoxidation of ascorbic acid.—See A., 1938, III, 744.

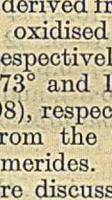
Preparation, electrometry, and ultra-violet spectrography of *d*-araboascorbic acid. G. Carpéni (Compt. rend., 1938, **206**, 1816—1818; cf. A., 1938, I, 399).—d-*Araboascorbic acid* (I), m.p. 164°,



(I.)

has been prepared from fructose, which is converted successively into β-di*iso*propylidenefructose, K di*iso*propylidene-α-ketogluconate, Me α-ketogluconate, and the Na salt of (I). Electrometric titration of (I) gives $p_{K_1} = 4{\cdot}23 \pm 0{\cdot}02$, p_{K_2} ~11—12; *d*-oxyaraboascorbic acid, the I oxidation product of (I), has p_{K_0} ~8·8. The undissociated mol. of (I) and its uni- and bivalent ions give absorption max. at 2420, 2645, and 2990 A., respectively. These results show that the steric isomerism of *l*-ascorbic acid and (I) does not affect the properties of the enediol-α-keto-group. A. J. E. W.

Preparation, electrometry, and ultra-violet spectrography of glucoheptoascorbic acid. G. Carpéni (Compt. rend., 1938, **206**, 1376—1378).—*Glucoheptoascorbic acid* (I) has been prepared from



(I.)

α-glucoheptose by successive conversion into the osazone, osone, and nitrile, followed by acid hydrolysis. (I) cannot be cryst. from aq. solution, probably owing to suppression of the growth of micro-crystals by traces of impurity. Electrometric titration of (I) gives $p_{K_1} = 4{\cdot}30 \pm 0{\cdot}05$, p_{K_2} ~11—12; the I oxidation product of (I) has p_{K_0} ~8·8. Absorption max., λ_M (at 2430—2980 A.), of aq. solutions of (I) of different p_H are recorded; the inflexion in the λ_M–p_H curve corresponds with p_{K_2} ~12. The length of the C chain has little effect on the dissociation consts. and absorption spectra of the enediol-α-keto-group. A. J. E. W.

Electrolytic preparation of calcium gluconate and other salts of aldonic acids. C. G. Fink and D. B. Summers (Trans. Electrochem. Soc., 1938, **74**, Preprint 7, 24 pp.).—An alkaline solution of glucose containing KBr or NaBr is electrolysed with a graphite anode and a graphite or Fe cathode, and the liquid neutralised with intermittent additions of $CaCO_3$. The effect of variations in numerous factors has been investigated, the optimum conditions for a semi-plant scale being: 1M-glucose in 2% NaBr; c.d. 1—2 amp. per sq. dm.; 40°; no diaphragm. Loss of Br, which normally increases with time, can be considerably reduced by changing the current direction approx. every 15 min. Salts of other acids can be prepared by electrolysing other aldoses. Salts other than KBr and NaBr were investigated but only KI and $K_3Fe(CN)_6$ showed any considerable efficiency. Ca gluconate (I) can also be prepared by electrolysing a solution containing 20% of glucose and 5% of (I), using a Hg anode and a graphite cathode, at 96—100°, with a c.d. 1·2—1·4 amp. per sq. dm., and adding $CaCO_3$ intermittently. C. R. H.

Peroxide effect in the addition of reagents to unsaturated compounds. XVI. Addition of thiolacetic acid to styrene and *iso*butene. M. S. Kharasch, A. T. Read, and F. R. Mayo (Chem. and Ind., 1938, 752).—At room temp. in presence of

ascaridole, $SH{\cdot}CH_2{\cdot}CO_2H$ gives (abnormally) with styrene, $Ph{\cdot}[CH_2]_2{\cdot}S{\cdot}CH_2{\cdot}CO_2H$, and with $CMe_2{:}CH_2$, $SBu^{\beta}{\cdot}CH_2{\cdot}CO_2H$, but in presence of p-$C_6H_4(OH)_2$ in vac. it does not react with either. A chain mechanism for O_2 or peroxide catalysis is suggested.

A. Li.

Reactions of formaldehydesulphoxylic acid. L. Spitzer (Annali Chim. Appl., 1938, **28**, 227—229).—The Na salt with $Hg(OAc)_2$ gives a black ppt. which is black or greenish-yellow after boiling and white with HCl (the colour change depending on the amount of reagent used); CH_2O–$NaHSO_3$, however, gives a yellow solution and, on boiling, a reddish ppt. $HgCl_2$ is reduced to HgCl. $CuSO_4$ gives a green solution which deposits Cu on boiling; no ppt. of Cu is produced by CH_2O–$NaHSO_3$.

F. O. H.

Purification of the alcoholate of the trimeride of hydroxypyruvaldehyde. W. E. Evans, jun., C. J. Carr, and J. C. Krantz, jun. (J. Amer. Chem. Soc., 1938, **60**, 1628—1629).—$CO(CH_2{\cdot}OH)_2$ and $Cu(OAc)_2$ give 64% of the pure, amorphous trimeride (+EtOH), m.p. 155—160°, of $OH{\cdot}CH_2{\cdot}CO{\cdot}CHO$, which gives the quinoxaline derivative, m.p. 250—251° (lit. 165°), and dioxime, m.p. 134—135° (lit. 168°).

R. S. C.

Keto–enol tautomerism in light and heavy (deuterium) solvents. F. C. Nachod (Z. physikal. Chem., 1938, **182**, 193—219).—The keto–enol equilibria of CH_2Ac_2 and $CHMeAc_2$ have been studied in H_2O and D_2O and in MeOH and MeOD. The proportion of enol is considerably reduced in D_2O as compared with H_2O. A similar though smaller reduction occurs in MeOD as compared with MeOH but for CH_2Ac_2 in these solvents it is within the limits of experimental error. The proportion of the keto-forms increases greatly in 0·1N-HCl in EtOH. The effect is considerably less in aq. acid. The solubilities of various org. compounds have been determined in H_2O and D_2O and the rate of enolisation of $CHMeAc_2$ has been studied in H_2O and EtOH. The differences between the rates for light substances in light solvents and heavy substances in heavy solvents are explained.

T. H. G.

Photochemical interaction between ketones and secondary alcohols.—See A., 1938, I, 408.

Photochemical interaction between ketones and alcohols. C. Weizmann, E. Bergmann, and Y. Hirshberg (J. Amer. Chem. Soc., 1938, **60**, 1530—1533).—When irradiated by a Hg arc, COPhMe and $Bu^{\alpha}OH$ give $Pr^{\alpha}CHO$ (50%) and both stereo-isomeric forms of $(CPhMe{\cdot}OH)_2$. The same pinacols are similarly obtained from COPhMe and *cyclo*hexanol (I) [gives 80% of the ketone (II)] or $CHPhMe{\cdot}OH$. $COMe_2$ and $Pr^{\beta}OH$ give $(CMe_2{\cdot}OH)_2$. (I) and (II) give only a poor yield of *cyclo*hexanonepinacol, which was not isolated, but its presence is inferred by conversion into di*cyclo*hexenyl. $COMe_2$ and $Bu^{\alpha}OH$ give $Pr^{\beta}OH$, $Pr^{\alpha}CHO$ and its trimeride, and *forms*, m.p. 121° and b.p. 95°/0·3 mm., respectively, of *octane-δε-diol*. The reaction depends on the presence of H attached to C in CH·OH, but this H is not detached during reaction as $CHPhMe{\cdot}OH$ is not racemised by irradiation. COPhMe and *d*-$CHPhMe{\cdot}OH$ give inactive pinacols, and reaction thus proceeds by activation of CORR′ to ·CRR′·O·, formation of ·CRR′·OH (from the ketone) and ·CR″R‴·OH (from the alcohol), and finally symmetrical or asymmetrical dimerisation to the pinacol or further oxidation to a new ketone. Conversion of ergosterol in the presence of eosin into the pinacol similarly involves activation of the H at $C_{(3)}$.

R. S. C.

Keto-ethers. III. β-Halogenoethoxyethyl alkyl ketones derived from ethylene bromohydrin. J. H. Clark [with H. R. Henze] (J. Org. Chem., 1938, **2**, 508—513; cf. A., 1937, II, 177).—Passing HCl into $Br{\cdot}[CH_2]_2{\cdot}OH$ and $(MeCHO)_3$ at 0° gives 69% of *α-chloroethyl β-bromoethyl ether*, b.p. 84·2°/37 mm., converted by CuCN, best in C_6H_6, into *α-β′-bromoethoxypropionitrile*, b.p. 69°/3 mm., which with the appropriate Mg alkyl bromide affords *Me*, b.p. 63·5°/2 mm. [*semicarbazone*, m.p. 124·5° (decomp.)]; and *Et α-β′-bromoethoxyethyl ketone*, b.p. 91°/6·5 mm. (*semicarbazone*, m.p. 99·5°), *α-β′-bromoethoxyethyl* n-, b.p. 82·5—83·5°/2·5 mm. (*semicarbazone*, m.p. 112·5°), and iso-*propyl*, b.p. 80—81°/2·5 mm., n-, b.p. 102—102·5°/4 mm. (*semicarbazone*, m.p. 117·7°), iso-, b.p. 91—92°/2 mm., and sec.-*butyl*, b.p. 89·5°/2·5 mm., n-, b.p. 119·5—120°/5·5 mm. (*semicarbazone*, m.p. 106·3°), and iso-*amyl ketone*, b.p. 100·5—101°/2·5 mm. (*semicarbazone*, m.p. 83°). Temp. are corr.

R. S. C.

Suggestion for naming the higher carbon sugars. C. S. Hudson (J. Amer. Chem. Soc., 1938, **60**, 1537—1541).—It is suggested that $>C_6$ sugars should be named by relating the 4 CH·OH adjacent to the $CH_2{\cdot}OH$ and the 4 CH·OH adjacent to the CHO each to the appropriate hexose. *E.g.*, *α-D-α*-glucoheptose (I) is termed *D*-gluco-*D*-guloheptose. Numerous examples of naming heptoses, octoses, and

$$OH{\cdot}CH_2{\cdot}\underset{OH}{\overset{H}{C}}—\underset{OH}{\overset{H}{C}}—\underset{H}{\overset{OH}{C}}—\underset{OH}{\overset{H}{C}}—\underset{OH}{\overset{H}{C}}{\cdot}CHO \quad \text{(I.)}$$

their derivatives on this system are given. 2-Keto-heptoses are named heptuloses. 7-Deoxyheptoses are best named methyloheptoses. The α- and β-nomenclature is retained only for glucosides. The disadvantages of other systems, particularly that of Isbell, are stressed.

R. S. C.

Preparation of 2 : 3-, 3 : 4-, and 3 : 6-anhydromethylhexosides from 3-*p*-toluenesulphonylmethylglucoside. S. Peat and L. F. Wiggins (J.C.S., 1938, 1088—1097).—Alkaline hydrolysis of β-methylglucoside 3-*p*-toluenesulphonate to anhydrosugars proceeds partly with and partly without Walden inversion. Inversion accompanies alkaline fission of dimethyl-3 : 4-anhydro-β-methylalloside. Hydrolysis of sugar *p*-toluenesulphonates may occur without anhydro-ring formation, but in these cases no inversion occurs. *iso*Propylideneglucose 3-*p*-toluenesulphonate and hot 2% HCl–MeOH give a mixture of glucosides (*A*), converted by Ac_2O–C_5H_5N at 36° or NaOAc–Ac_2O into β- (I), m.p. 138°, $[\alpha]_D^{19}$ −19·5° in $CHCl_3$ (cf. Freudenberg and Ivers, A., 1922, i, 523), and *α-methylglucoside* 2 : 4 : 6-*triacetate* 3-p-*toluenesulphonate*, m.p. 97°, $[\alpha]_D^{16}$ +87·1° in $CHCl_3$. With NaOMe–MeOH–$CHCl_3$ at room temp. (I) gives a

mixture, $[\alpha]_D^{20}$ −80° to −90° in EtOAc, which with PhCHO and P_2O_5 in $CHCl_3$ gives 4 : 6-*benzylidene*-2 : 3-*anhydro*-β-*methylalloside*, m.p. 138°, $[\alpha]_D^{19}$ −15·6° in $CHCl_3$, and a syrup, converted by MeI–Ag_2O into 2 : 6-*dimethyl*-3 : 4-*anhydro*-β-*methylalloside* (II), m.p. 46°, $[\alpha]_D^{21}$ −144·5° in $CHCl_3$, and impure 2 : 4-*dimethyl*-3 : 6-*anhydro*-β-*methylglucoside* (III). (II) and 5% NaOMe–MeOH at 95° give 2 : 3 : 6-*trimethyl*-β-*methylglucoside* (IV), m.p. 59—60°, $[\alpha]_D^{19}$ −48° in $CHCl_3$, $[\alpha]_D^{17}$ −33·4° in H_2O, and impure, oily 2 : 4 : 6-*trimethyl*-β-*methyl*-d-*gulopyranoside* (V). Three methylations of (IV) with Ag_2O–MeI give tetramethyl-β-methylglucopyranoside, hydrolysed to tetramethyl-α-*d*-glucopyranose. Hydrolysis of (IV) gives 2 : 3 : 6-trimethylglucose, oxidised by Br to trimethylgluconic acid. Methylation of (V) gives a *tetramethyl*-β-*methylhexoside*, b.p. 85—90° (bath)/0·01 mm., $[\alpha]_D^{17}$ −69° in $CHCl_3$, hydrolysed by 6% HCl to *tetramethyl*-d-*gulose*, an oil, $[\alpha]_D^{16}$ +8·25° in H_2O, which with Br gives *tetramethyl*-d-*gulonolactone*, $[\alpha]_D^{15}$ +64·6° → +22° in H_2O in 32 hr. (very rapid hydrolysis indicates the δ-lactone structure), oxidised by HNO_3 to *i*-$(OMe{\cdot}CH{\cdot}CO_2H)_2$ and *l*-arabotrimethoxyglutaric acid; these products all contained some of the derivatives from (V) and i-*trimethoxyxyloglutaromethylamide*, m.p. 166°, was incidentally isolated. The pyranoside structure of (V) is also supported by its rapid hydrolysis by HCl. Purification of (III) by further methylation, acetylation, and distillation gives an oil, $[\alpha]_D^{15}$ −1·68° in $CHCl_3$; this is stable to 2·5N-KOH in 75% EtOH, is merely converted into the α-glucoside by hot 6% HCl–MeOH, but with cold, dil. aq. HCl yields 2 : 4-*dimethyl*-3 : 6-*anhydroglucose* (VI), $[\alpha]_D^{18}$ −1·1° → +61·9° in 300 hr. (VI) gives the *anilide*, m.p. 96°, and with Br affords 2 : 4-*dimethyl*-3 : 6-*anhydrogluconolactone*, $[\alpha]_D$ +90·9° → +64·2° in H_2O in 180 hr., yielding 2 : 4-*dimethyl*-3 : 6-*anhydrogluconamide*, m.p. 91—92°. The mixture (*A*), when hydrolysed by NaOMe at room temp. and then methylated, yields a mixture, containing 4 : 6-dimethyl-2 : 3-anhydro-α-methylalloside, m.p. 63°, $[\alpha]_D^{18}$ +187°; the crude hydrolysis product yields 4 : 6-ethylidene-, m.p. 128°, $[\alpha]_D^{18}$ +100° in $CHCl_3$, and 4 : 6-benzylidene-2 : 3-anhydro-α-methylalloside, m.p. 198°, $[\alpha]_D^{20}$ +161°, the latter product giving by H_2–Pd–C in EtOH–$COMe_2$ at 1·5 atm. 2 : 3-*anhydro*-β-*methylalloside*, m.p. 60—62°, $[\alpha]_D^{17}$ −6·1° in EtOAc, hygroscopic (4 : 6-*Me*$_2$, m.p. 50—51°, $[\alpha]_D^{19}$ +35·3° in $CHCl_3$, and 4 : 6-*benzylidene* derivative, m.p. 188°, $[\alpha]_D$ −62·9° in $COMe_2$). β-Methylglucoside 3 : 4 : 6-triacetate 2-*p*-toluenesulphonate and NaOMe give 2 : 3-anhydro-β-methylmannoside, $[\alpha]_D^{19}$ −28·8° (4 : 6-benzylidene derivative, m.p. 183°, $[\alpha]_D^{18}$ −30·7° in $CHCl_3$). 5% HCl at 95° (not room temp.) converts 4 : 6-dimethyl-2 : 3-anhydro-α-methylalloside into a *chlorodimethylhexose*, $[\alpha]_D^{20}$ +67·5° in 5% HCl, but (II) is hydrolysed in the cold to an oily *chlorodimethylhexose*, $[\alpha]_D^{20}$ −76·6° in 5% HCl (yields an oily *chlorodimethylmethylhexoside acetate*, $[\alpha]_D^{20}$ −41·4° in $CHCl_3$). *iso*Propylideneglucose 3-*p*-toluenesulphonate or 1 : 2-*iso*propylideneglucofuranose 5 : 6-diacetate 3-*p*-toluenesulphonate (VII) with cold NaOMe give slowly *iso*propylideneglucose without anhydro-ring formation or inversion. Attempts to replace the $ArSO_2$ of (VII) by Ac failed. R. S. C.

Pyranose–furanose interconversions with reference to the mutarotations of galactose, lævulose, lactulose, and turanose. H. S. Isbell and W. W. Pigman (J. Res. Nat. Bur. Stand., 1938, **20**, 773—798).—Measurements of [α], mol. vol., and mol. refraction in buffered solutions show that the mutarotations of lævulose (I) (pyranose form of *d*-fructose), lactulose (II), and turanose (III) are similar to the rapid mutarotation reactions of α-*d*-galactose and other sugars. The large variation of [α] with temp., the comparable heats of reaction, and the high sensitivity of the reaction rates to acids and bases confirm this. Since the fructose liberated from sucrose by invertase has a mutarotation rate equal and opposite to that of (I), it is concluded that these reactions are furanose–pyranose interconversions, that (II) is a furanose, and that the O-bridge of (III) is not attached to the 5th or 6th C, but probably (since the osazone differs from those of maltose and cellobiose) to the 3rd. A. Li.

Biochemistry of carbohydrates. XXXI. Determination of acetyl groups in carbohydrate complexes by the Friedrich–Rapoport–Sternberg method. Hydrolysis of ethereal sulphate. M. Suzuki. **XXXII. Glucosamine and chondrosamine.** H. Hisamura and M. Kusuno (J. Biochem. Japan, 1938, **27**, 367—373, 375—379).—XXXI. Improvements in the method are suggested (cf. A., 1936, 968). The liberation of SO_4'' from chondroitinsulphuric acid in N-HCl at 100° requires at least 7 hr. for completion.

XXXII. Glucosamine yields a Bz_5 derivative, m.p. 216° (corr.), $[\alpha]_D^{15}$ +45·06° in C_5H_5N (cf. Levene, A., 1916, i, 713). *Pentabenzoylchondrosamine*, m.p. 199—201°, $[\alpha]_D^{22}$ +95·82° in C_5H_5N, was also prepared. Glucosamine prepared by Breuer's method (A., 1898, i, 620) is the β-isomeride, the hydrochloride of which has initial (extrapolated) $[\alpha]_D^{17}$ +20·0° in H_2O. F. O. H.

Formation of di*iso*propylideneglucose diethyl mercaptal. Kinetics of the reaction. R. Sutra (Bull. Soc. chim., 1938, [v], **5**, 1048—1052).—*Di-iso*propylidene-d-*glucose* Et_2 *mercaptal* is obtained as a non-distillable liquid, $[\alpha]_{578}$ −47·5° in $COMe_2$, by the action of $COMe_2$ containing H_2SO_4 and anhyd. $CuSO_4$ on *d*-glucose Et_2 mercaptal. The product formed has at first an anticatalytic effect on the change which, subsequently, is of the first order. H. W.

Oxidation of methylated derivatives of sorbose with nitric acid. (Mme.) Y. Khouvine and G. Arragon (Compt. rend., 1938, **206**, 1659—1661).—Oxidation of α-tetramethyl-*l*-sorbose with HNO_3 affords *d*-dimethoxysuccinic acid (cf. A., 1937, II, 485). α- or β-Tetramethyl-*l*-sorbose or α- or β-tetramethyl-*l*-methylsorboside with HNO_3 (*d* 1·49) (conditions described) at 100° affords $H_2C_2O_4$ (removed with H_2O_2) and a syrup which when methylated (MeI–Ag_2O followed by Me_2SO_4) and fractionally distilled at 10^{-4} mm. gives fractions converted by NH_2Me into *d*-dimethoxysuccinmethyldiamide and xylotrimethoxyglutarmethyldiamide. The latter indicates the existence of a pyranoid structure in the original sugars. α-*l*-Methylsorboside tetra-acetate, α-*l*-methylsorboside, and α-*l*-sorbose have pyranoid

structures as the last can be converted into the first two. J. L. D.

Oxidation of tetramethyl-α-*d*-methyltagatoside with nitric acid. (Mme.) Y. Khouvine, G. Arragon, and Y. Tomoda (Compt. rend., 1938, **206**, 1823—1824).—α-*d*-Methyltagatoside (I) with Me_2SO_4–NaOH at 60° affords tetramethyl-α-*d*-methyltagatoside (II) (cf. A., 1938, II, 84) which with HNO_3 (*d* 1·49) at room temp. and then at 100° affords $H_2C_2O_4$ and an oil converted by MeI–Ag_2O and by Me_2SO_4 into an oil which when fractionally distilled affords *l*-dimethoxysuccindi(methylamide) and *d*-arabotrimethoxyglutardi(methylamide), indicating that (I) and (II) have pyranose structures. J. L. D.

Catalytic hydrogenation of disaccharides. I. Cane sugar. T. Tanno (Bull. Inst. Phys. Chem. Res. Japan, 1938, **17**, 447—472).—Sucrose (I) with H_2 under high pressure and reduced Ni at 170—175° affords *d*-mannitol (II) and *d*-sorbitol (III) in equal amounts corresponding with 25% of (I), glycerol (IV), and OH·CHMe·CH_2·OH (V). At 155—160°, (II), (III), and a syrup are formed. With fructose (VI) at 170—175°, (II) and (III) only are rapidly formed, which indicates that (IV) and (V) are formed because of the glucosido-group in (I) and further that (I) is converted into (VI) during the reaction. J. L. D.

Theory of mutarotation; mutarotation and catalytic hydrogenation of the glucosides of secondary amines. R. Kuhn and L. Birkofer (Ber., 1938, **71**, [*B*], 1535—1541).—Contrary to expectation, the glucosides of piperidine (I) and $NH(CH_2Ph)_2$ are mutarotatory and, although the possibility of its passage into a Schiff's base is excluded, piperidine-*d*-glucoside is reduced (Ni) at 75° to N-1′-*sorbitylpiperidine*, m.p. 115—116°, $[\alpha]_D^{21}$ −22° in C_5H_5N (*penta-acetate*, b.p. 145—150°/10^{-3} mm.). At 100° (Ni) piperidine-*d*-glucoside undergoes reductive fission to (I) and sorbitol. The rate of mutarotation is very greatly increased by the addition of small amounts of H_2O. The relationship is diametrically opposed to that of the glucosides of other *sec.* amines. Addition of H_2O probably occurs and the cations undergo transformation. These can pass into ammonium bases (salts) which contain the double linking essential to mutarotation and hydrogenation. The rate of mutarotation is more markedly influenced by traces of HCl than of H_2O. Apparently the basicity of the amine is important. Ring–double linking desmotropy is therefore the essential of mutarotation. The formation of Schiff's bases and of CO-compounds (keto–*cyclo* desmotropy) are individual cases subordinate to the main principle. H. W.

2-Naphthylamine-*d*-glucoside. V. Cuculescu (Bull. Soc. chim., 1938, [v], **5**, 970—973).—Glucose and β-$C_{10}H_7$·NH_2 in boiling MeOH or EtOH afford 2-*naphthylamine*-β-d-*glucopyranoside* (+1H_2O), m.p. (indef.) 113—114·5° (decomp.), $[\alpha]_D^{22}$ −136·3°±0·7° diminishing slowly on account of decomp. It cannot be obtained anhyd. since loss of H_2O under diminished pressure is accompanied by decomp. It is transformed by C_5H_5N and Ac_2O into 2-*naphthylamine*-β-d-*glucospyranoside* 2 : 3 : 4 : 6-*tetra-acetate*, m.p. 172·5—173°, $[\alpha]_D^{22}$ −114·0°±0·7°, also obtained from β-$C_{10}H_7$·NH_2 and acetobromoglucose in CCl_4 containing Ag_2CO_3. H. W.

Fruit of *Sophora japonica*, L. I. Sophoricoside. C. Charaux and J. Rabaté. **II. Rutoside and sophoraflavanoloside. III. Holodiglucoside from sophoraflavanoloside.** J. Rabaté and J. Dussy (Bull. Soc. Chim. biol., 1938, **20**, 454—458, 459—466, 467—470).—I. The green fruit contains 2% of a glucoside, *sophoricoside*, m.p. 297·5°, $[\alpha]_D^{20}$ −32·2° in C_5H_5N, −46·7° in 0·02N-NaOH (*hexa-acetate*, m.p. 230°). Since hydrolysis by dil. H_2SO_4 in presence of AcOH yields 43·8% of glucose and 60·8% of genisteol, it is a β-glucoside of genisteol which differs in its physical consts. from genistin.

II. In addition to sophoricoside, extracts of the fresh fruit contain 0·6% of both *rutoside*, a heteroside, m.p. 202—203°, $[\alpha]_D^{20}$ −30° in 50% EtOH, which yields glucose, rhamnose, and quercetin on hydrolysis with 3% H_2SO_4, and *sophoraflavanoloside* (I), m.p. 207—208°, $[\alpha]_D^{20}$ −61° (for anhyd. product), which yields glucose and kaempferol on hydrolysis with 3% H_2SO_4.

III. *Sophorose*, a reducing α-diglucoside (+1H_2O), has been obtained by hydrolysis of (I) with 0·5% H_2SO_4. It has m.p. 195—196°, $[\alpha]_D^{20}$ +37° → +22·6°, and yields glucose on further hydrolysis with 1·5% H_2SO_4. It does not form a typical osazone. P. G. M.

Dextran synthesised by *Leuconostoc dextranicus*.—See A., 1938, III, 699.

Röntgenographic investigation of Schardinger's α-dextrin. O. Kratky and B. Schneidmesser (Ber., 1938, **71**, [*B*], 1413—1414).—The results confirm Freudenberg's conception of the presence of a large ring with five glucose residues. H. W.

Exchange reaction between cellulose and heavy water. Hydration of cellulose. G. Champetier and R. Viallard (Bull. Soc. chim., 1938, [v], **5**, 1042—1048).—Ash-free filter-paper, cotton linters cellulose, and mercerised cotton linters cellulose have been immersed in 99·55% D_2O at temp. between 10° and 100° and the exchange has been measured from the diminution of *d* of the liquid. Invariably the change involves 3 OH per glucose unit, thus justifying the view that the D_2O has penetrated into the interior of the cellulose. Simple superficial adsorption on the micelles could only occasion an exchange reaction with the OH groups in contact with the D_2O and consequently the no. of H exchanged would be <3 per glucose unit. These results confirm the formulæ $2C_6H_{10}O_5,H_2O$ and $C_6H_{10}O_5,H_2O$ assigned previously to the hydrates of ordinary and mercerised cellulose respectively. H. W.

Separation of small amounts of racemic amino-acids into their optical antipodes through the salts of cholestenonesulphonic acid. G. Triem (Ber., 1938, **71**, [*B*], 1522—1524).—The NH_2-acid is treated with cholestenonesulphonic acid in EtOH. The salt thus produced is triturated with PbO and then shaken with H_2O. Pb cholestenonesulphonate is filtered off, the filtrate is treated with H_2S and C, filtered, and the filtrate is evaporated at a low temp. The resolution of *dl*-leucine, *dl*-

α-aminobutyric acid, *dl*-tyrosine, and (in part) that of *dl*-aspartic acid has been achieved. d(−)-*Leucine cholestenonesulphonate* has m.p. 192—193° (decomp.). H. W.

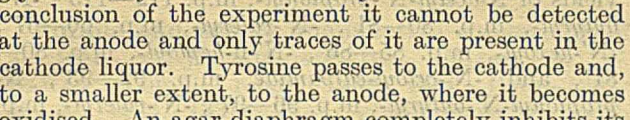
N-Methanesulphonyl derivatives of amino-acids. B. Helferich and R. Mittag (Ber., 1938, **71**, [*B*], 1480—1482).—$NH_2{\cdot}CH_2{\cdot}CO_2Et$ and $MeSO_2Cl$ in abs. Et_2O afford *Et methanesulphonamidoacetate*, m.p. 42·5° (corr.), hydrolysed by 2N-NaOH to *methanesulphonamidoacetic acid*, m.p. 174° (corr.), also obtained directly from $NH_2{\cdot}CH_2{\cdot}CO_2H$ and $MeSO_2Cl$ in presence of 2N-NaOH; it gives a *Na* salt, m.p. 220°. *Et α-methanesulphonamidopropionate*, b.p. 166°/4 mm., 140°/0·3 mm., and *α-methanesulphonamidopropionic acid*, m.p. 80°, are described. H. W.

Separation of diketopiperazines and amino-acids in the products of the hydrolysis of proteins by ionophoresis. III. N. I. Gavrilov, A. I. Paradaschvili, V. S. Balabusha-Popzova, and S. W. Ljapounzova. **IV.** V. S. Balabusha-Popzova, N. J. Gavrilov, A. I. Paradaschvili, and G. F. Jakunin (Bull. Soc. chim., 1938, [v], **5**, 973—978, 978—986).—III. Histidine anhydride passes entirely to the cathode without being decomposed and at a rate approaching that of the transport of free histidine. Hydrolysis or deamination does not occur. Aspartic anhydride under the experimental conditions (CO_2 at cathode) behaves like glycine anhydride and scarcely dissociates. At the conclusion of the experiment it cannot be detected at the anode and only traces of it are present in the cathode liquor. Tyrosine passes to the cathode and, to a smaller extent, to the anode, where it becomes oxidised. An agar diaphragm completely inhibits its transport to the anode. Deamination of glycine at a Ag cathode increases only the quantity of NH_3; it is due to an unsuitably high c.d. Prolongation of ionophoresis causes loss of N in other forms, evidently at the anode. The Ag cathode has not sp. deaminating properties but all those processes which occur at a Hg cathode are manifested in a greater degree. Mineral acid increases appreciably the production of NH_3 at the cathode.

IV. During ionophoresis of hexonic bases, of valine, and of glutamic and aspartic acid the c.d. should not exceed 10—15 ma. per sq. cm. The cathodic solution should be kept acid by a stream of CO_2; addition of mineral acid at the cathode increases the deamination of NH_2-acids. Aspartic acid migrates very slowly towards the cathode. In this case the customary acidification of the solution is inadequate; more powerful acidification is required and this involves a certain amount of deamination. Dipeptides during ionophoreses pass entirely to the cathode without being hydrolysed. If the conditions favourable for the ionophoreses of dipeptides are maintained (initial acidification with 0·1N-H_2SO_4 and passage of CO_2 through the cathodic solution) there is no liberation of NH_3 in the cathodic liquor at c.d. 10 ma. If the c.d. increases to 35—40 ma. per sq. cm. an insignificant deamination results; this is betrayed by the formation of small amounts of NH_3. H. W.

Hydrolysis of peptides of diaminosuccinic acid. T. Tamura (J. Biochem. Japan, 1938, **27**, 335—349).—*meso*-Diaminosuccinic acid (Et_2 ester *dihydrochloride*, m.p. 178°; Bz_2 derivative, m.p. 212°) with $CH_2Cl{\cdot}COCl$ gives meso-*dichloroacetamidosuccinic acid*, m.p. 205° [Et_2 ester (I), m.p. 156°], converted by NH_3 into meso-*diaminoacetamidosuccinic acid* (II), m.p. 275° (decomp.) [corresponding dl-*compounds*, m.p. 208° (Et_2 ester, m.p. 142°) and 245° (decomp.), respectively]. (I) with EtOH–NH_3 affords *diglycyl*-meso-*diaminosuccinic anhydride*, m.p. 183° (corresponding dl-*compound*, m.p. 167°). dl-*Dibenzamidosuccinic acid*, m.p. 152°, was also prepared. (II) is readily hydrolysed by erepsin (aminopolypeptidase action) and trypsin, but only slightly by papain. The above dibenzoyl-*meso*- and -*dl*-acids, and also benzoyl-aspartic and -glutamic acids, are not hydrolysed by histozyme. The anhydrides are not hydrolysed by proteases, due to non-dissociation of the ketopiperazine side-chains. Glycyl- and aspartyl-aspartic anhydrides are readily hydrolysed by glycerol extracts of dried pig's pancreas. The bearing of the results on the structure of the above compounds and on the related enzyme actions is discussed. F. O. H.

Complex salts of alkylenedi-α-amino-acids. P. Pfeiffer and W. Christeleit (Ber., 1938, **71**, [*B*], 1497—1504).—*dl*-Propylenediamine hydrochloride, KCN, and $COMe_2$ in H_2O give the corresponding dinitrile, hydrolysed (fuming HCl–conc. H_2SO_4 at 0°) to dl-*propylenedi-α-amino*isobutyric *acid*, m.p. 378° (decomp.), which gives a *tetrahydrated* and *anhyd. salt*,



d(−)-*Propylenedi-α-amino*isobutyric *acid*, $[M]_{6589}^{21}$ −2·8° in H_2O (other vals. recorded), gives a violet dehydrated and a blue anhyd. *Cu* salt, showing a pronounced Cotton effect. The *compounds*, $C_{11}H_{20}O_4N_2Cu$ + EtOH, + $2CH_2Ph{\cdot}OH$ + EtOH–H_2O and + PrOH–H_2O, are also described. The violet Cu salt of heptamethylenedi-α-amino*iso*butyric acid contains rather > 1 H_2O and gives a violet, anhyd. salt. Schlesinger's isomeric blue salt appears to contain 1 H_2O + 1 EtOH. *Diacetamidoheptamethylene* has m.p. 118°. H. W.

Possibility of the formation of cyclols from simple peptides. K. H. Meyer and W. Hohenemser (Nature, 1938, **141**, 1138—1139).—Glycyl-*l*-leucine and *l*-leucylglycine show no interchange of their constituent groups on mixing. Under the given conditions cyclol formation does not occur. This does not support the cyclol theory of Wrinch (A., 1937, II, 475; III, 296). L. S. T.

Multivalent amino-acids and peptides. X. Cystinyl peptides as substrates for amino-polypeptidase and dipeptidase. (Miss) J. P. Greenstein (J. Biol. Chem., 1938, **124**, 255—262).—Cystinylpeptides which yield an insol. NH_2-acid which can be filtered off and determined are convenient for determining peptidases. Glycine anhydride in 2N-NaOH and dicarbobenzyloxycystinyl chloride (adding 1N-NaOH) give *dicarbobenzyloxy-l-cystinylbisdiglycine*, m.p. 210°; this is reduced by Na in liquid NH_3 (cf. A., 1935, 1486), treated with H_2SO_4 and then with $HgSO_4$ reagent, and the Hg salt decom-

posed by H_2S, and $Ba(OH)_2$ added. The resulting solution is oxidised by air (Fe_2O_3) to give, after removal of $BaSO_4$ and addition of EtOH, *cystinylbisdiglycine* (I), m.p. ($+2H_2O$) 98°, anhyd. 145°, $[\alpha]_D^{20}$ −55° in 1N-HCl, hydrolysed by 5N-HCl to cystine, $[\alpha]_D^{20}$ −202° (showing that little or no racemisation occurs during synthesis). Aminopolypeptidase or crude erepsin at 30° hydrolyses (I) to cystine [in a new cryst. form (hexagonal prisms)], which is collected and determined; the amount remaining in solution is negligible. *l*-Cistinyldiglycine is also hydrolysed by erepsin, but only partly by aminopolypeptidase. Neither peptide is hydrolysed by carboxypeptidase; this, however, hydrolyses chloroacetyltyrosine to tyrosine, which may be filtered off and determined. E. W. W.

Physiological specificity of methionine in regard to the methylthiol group: synthesis of S-ethylhomocysteine (ethionine) and its availability for growth. H. M. Dyer (J. Biol. Chem., 1938, **124**, 519—524).—α-*Amino-γ-ethylthiolbutyric acid* [*ethionine*], m.p. 272° (N-$PhSO_2$ derivative, m.p. 80°), does not support growth of animals on a cystine-deficient diet, and appears to be toxic to rats. J. N. A.

ψ-Halogens. XXXIV. Reaction of hydrogen thiocyanate with cyanic acid and *iso*thiocyanoformamide. L. Birckenbach and K. Kraus (Ber., 1938, **71**, [*B*], 1492—1497).—Pure HCNS and pure NH:CO do not react at −80° or at −15° but in Et_2O at 0° give *thiocyanoformamide* (I), m.p. 69°, which is stable in the absence of moisture but is decomposed by warm H_2O into CO_2 and NH_4CNS. It is transformed by EtOH into *Et thioallophanate*, $NH_2{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}OEt$, decomp. 180°, which gives $CO(NH_2)_2$ and $CS(NH_2)_2$ when heated with NH_3, passes into EtCNS when heated alone, and affords O-*ethyl*iso*biuret*, $NH_2{\cdot}CO{\cdot}NH{\cdot}C(NH){\cdot}OEt$, m.p. 126—127°, with EtOH–NH_3. With NH_2Ph (I) immediately yields 1-*phenyl*-2-*thiobiuret*, $NH_2{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NHPh$, m.p. 161°, transformed by $AgNO_3$ into phenylbiuret and almost quantitatively converted by conc. aq. NH_3 into $NHPh{\cdot}CS{\cdot}NH_2$ and $CO(NH_2)_2$. H. W.

ψ-Halogens. XXXV. Cyanic acid. II. Cyanic and sulphuric acids. M. Linhard (Annalen, 1938, **535**, 267—284).—H_2SO_4,H_2O (1 mol.) and HNCO (1 mol.) in abs. Et_2O at −60° to −50° give mainly cryst. *carboxyaminosulphonic acid*, $CO_2H{\cdot}NH{\cdot}SO_3H$, which spontaneously loses CO_2 to give $NH_2{\cdot}SO_3H$. 2 mols. of HNCO and 1 mol. of H_2SO_4 give primarily $SO_2(NH{\cdot}CO_2H)_2$, which loses 1 CO_2 to give $NH_2{\cdot}SO_2{\cdot}NH{\cdot}CO_2H$ (also obtained to some extent from 1 mol. of each reagent). This product reacts usually rather as *carbamidosulphonic acid*, $NH_2{\cdot}CO{\cdot}NH{\cdot}SO_3H$, and probably has the zwitterion structure, $\overset{SO_2{\cdot}NH_3^+}{NH—CO}>O^-$. (I) gives an *$NH_4$*, m.p. 168° (decomp.) [hydrolysed by hot N-H_2SO_4 to $(NH_4)_2SO_4$ and $CO(NH_2)_2$], *K*, m.p. 201° (decomp.), *$NHEt_2$*, m.p. 156° (decomp.), and *NH_2Et* salt, m.p. 130°, (I) reacting in these cases as $\overset{CO{\cdot}NH_3^+}{NH—SO_2}>O^-$. With the weaker base, NH_2Ph, (I) gives *NH_4 phenylcarbamidosulphonate*, $NHPh{\cdot}CO{\cdot}NH{\cdot}SO_3NH_4$, decomp. about 135°, converted by KI into the *K* salt, $+H_2O$, decomp. about 137°, which with hot 17% HCl yields $KHSO_4$ and $NHPh{\cdot}CO{\cdot}NH_2$. With PhOH (I) gives *NH_4 phenylurethanesulphonate*, $OPh{\cdot}CO{\cdot}NH{\cdot}SO_3NH_4$, rapidly converted by EtOH into NH_4EtSO_4, $OPh{\cdot}CO{\cdot}NH_2$, HNCO, and PhOH. EtOH, $Bu^{\alpha}OH$, $Bu^{\beta}OH$, and $Bu^{\gamma}OH$ give the NH_4 alkyl sulphate and alkylurethane. *NH_4 Bu^{α} sulphate* melts at 222°. With H_2O (I) gives much CO_2, HNCO, and NH_4HSO_4, but in Et_2O slow addition of H_2O gives 80—90% of *$(NH_4)_2$ carbamidodisulphonate*, $CO(NH{\cdot}SO_3NH_4)_2$, $+H_2O$, decomp. 90—100°. The mechanism of the addition of HNCO and H_2SO_4 is discussed. R. S. C.

Diacylcarbamides. I. Preparation and properties of diacylcarbamides derived from normal aliphatic acids. R. W. Stoughton (J. Org. Chem., 1938, **2**, 514—521).—$CO(NH_2)_2$, $EtCO_2H$, and a little H_2SO_4 at 100° give exothermally *propionylcarbamide*, m.p. 210—211°. Adding the appropriate acyl chloride to $CO(NH_2)_2$ and 2 drops of H_2SO_4 in boiling C_6H_6 gives acetyl-, m.p. 216—217°, *n*-butyryl-, m.p. 173—174°, -octoyl, m.p. 191—192°, *-valeryl-*, m.p. 182—183°, *-hexoyl-*, m.p. 192—193°, and *-heptoyl-carbamide*, m.p. 191—192°. Heating the appropriate acylcarbamide, acyl chloride (best the lower member of the pair; the anhydride gives lower yields), and a little H_2SO_4 in C_6H_6 gives 75—85% yields of N-*acetyl*-N′-*propionyl-*, m.p. 112—113°, -N′-*butyryl-*, m.p. 80—81°, -N′-*valeryl-*, m.p. 66—67°, -N′-*hexoyl-*, m.p. 85—86°, -N′-n-*heptoyl-*, m.p. 80—81°, and -N′-*octoyl-carbamide*, m.p. 92—93°, N-*propionyl*-N′-*butyryl-*, m.p. 96—97°, -N′-*valeryl-*, m.p. 82—83°, and -N′-*heptoyl-carbamide*, m.p. 82—83°, N-*butyryl*-N′-*valeryl-*, m.p. 75—76°, N-*butyryl*-N′-n-*octoyl-*, m.p. 66—67°, N-*valeryl*-N′-n-*hexoyl-*, m.p. 80—81°, s-*dipropionyl-*, m.p. 105—106°, s-*dibutyryl-* (I), m.p. 86—87°, s-*divaleryl-*, m.p. 83—84°, s-*di*-n-*hexoyl-*, m.p. 87—88°, and s-*di*-n-*heptoyl-carbamide* (II), m.p. 89—90°. The diacylcarbamides are hydrolysed by hot (not cold) H_2O, slowly by acids, and very rapidly by alkali (in which they dissolve), the acyl of lower mol. wt. being most readily removed. With NaOEt at room temp. (I) gives NaCNO, $NH_2{\cdot}CO{\cdot}NH{\cdot}COPr$, and $PrCO_2Et$. At 160—200° (II) decomposes as to two thirds into CO_2, $C_6H_{13}{\cdot}CN$, and $C_6H_{13}{\cdot}CO{\cdot}NH_2$, and one third into $NH(COPr)_2$ and $(HCNO)_3$. When injected intravenously into white mice, the diacylcarbamides have hypnotic, sedative, and analgesic action without causing excitement. The C_6—C_8 compounds are most potent, the min. effective dose being 80—150 mg. per kg. of body wt. Anæsthesia is, however, very short (mean 1—2 min.), probably owing to hydrolysis, and intraperitoneal and oral administration are, perhaps for this reason, much less effective. The min. lethal dose is about 2—3 times the effective dose. M.p. are corr. R. S. C.

Synthesis of a radioactive organic compound: α-glycerophosphoric acid. E. Chargaff (J. Amer. Chem. Soc., 1938, **60**, 1700—1701).—Radioactive P, obtained by bombarding CS_2 with fast neutrons and evaporating the product, is mixed

with red P, converted into radioactive PCl_3 and thence into radioactive $POCl_3$ (by $KClO_3$), *iso*propylideneglycerophosphoric, and glycerophosphoric acid (Ba salt). The radioactivity of the final acid is less if measured as Na salt in H_2O than if ashed before measurement. R. S. C.

Determination of phosphoglyceric acid. O. Myerhof and W. Schulz (Biochem. Z., 1938, **297**, 60—65).—$[\alpha]_D^{20}$ of *d*(—)-3-phosphoglyceric acid in neutral solution is approx. +13·20° but is changed to —745° by addition of excess of MoO_4''. The concn. of the acid (< 0·05 mg. per c.c., *e.g.*, in muscle extract deproteinised with $CCl_3{\cdot}CO_2H$ and neutralised) is determined by measuring the rotation before and after the addition of MoO_4'', the difference corresponding with the amount of acid present. Interference due to inorg. PO_4''', excess of MoO_4'', and other factors is compensated by making a blank determination. Interference by other substances (*e.g.*, malic or tartaric acid, excess of lactic acid) is avoided by pptg. the phosphoglyceric acid with $Pb(OAc)_2$ and decomp. the ppt. with dil. H_2SO_4. The rotation of phosphoric esters without CO_2H (*e.g.*, α-glycerophosphoric, hexose-mono- and -di-phosphoric acid), d(+)-2-phosphoglyceric acid, and free sugars is only slightly or not at all affected by MoO_4''. The equilibrium 3-phosphoglyceric acid $\rightleftharpoons$ 2-phosphoglyceric acid is only slightly affected by temp. change between 0° and 60°. W. McC.

Simple and nearly quantitative conversion of β- into α-glycerophosphates. (Mlle.) M. C. Bailly (Compt. rend., 1938, **206**, 1902—1904; cf. A., 1934, 1331).—Na β-glycerophosphate with boiling 10% aq. H_2SO_4 or HCl is converted into the α-glycerophosphate (93% yield) which reduces HIO_4 (cf. A., 1933, 696) and can be isolated as the Na derivative. J. L. D.

Synthetic phosphatide acids. II. Preparation of monofatty-acylated glycerophosphoric acids. H. Arnold (Ber., 1938, **71**, [*B*], 1505—1510; cf. A., 1937, II, 365).—The products obtained by the action of chaulmoogric acid on α- or β-glycerophosphoric acid, or αβ- or αγ-glycerodiphosphoric acid or their Na salts in presence of excess of conc. H_3PO_4 or by phosphorylation of the mono- or di-fatty acid esters of glycerol with P_2O_5 have little uniformity. The following compounds are obtained by the action of the requsite acid chloride on a suspension of the anhyd. Na glycerophosphate in dry C_6H_6 containing C_5H_5N: *Na hydnocarpoyl-β-glycerophosphate* and the corresponding *Pb* salt, decomp. >300°; *Na chaulmoogroyl-α-glycerophosphate*, decomp. >200°, and the *Pb* salt, decomp. 190—200°; *Na mono-oleoyl-β-glycerophosphate*, m.p. 180—185° after softening at 150°, and the *Pb* salt; *Na monostearoyl-β-glycerophosphate*, m.p. 165—170°, and the *Pb* salt. αγ-Dichaulmoogrin is obtained from Na chaulmoograte suspended in xylene and $OH{\cdot}CH(CH_2Br)_2$ at 125°. H. W.

Esters of orthosilicic acid. M. N. Kalinin (Compt. rend. Acad. Sci. U.R.S.S., 1938, **18**, 433—434).—The use of C_6H_6 as solvent in the interaction of $SiCl_4$ and ROH increases the yield of esters $Si(OR)_4$, where R = Me, Et, Bu$^\alpha$, Bu$^\beta$, *iso*amyl. The prep. of $SiCl(OEt)_3$ is similarly facilitated. A. T. P.

Electrolysis of magnesium methyl iodide in pyridine solution. C. E. Thurston and K. A. Kobe (Philippine J. Sci., 1938, **65**, 139—142).—Using a divided cell and a Pt cathode, I is liberated at the anode and a brown powder (containing Mg and C_5H_5N) formed at the cathode with a small amount of unidentified gas. E. S. H.

New method of resolving a racemic compound. G. Karagunis and G. Coumoulos (Nature, 1938, **142**, 162—163; cf. A., 1938, II, 286).—Selective adsorption by powdered *d*- or *l*-quartz crystals in a Tswett column effects a partial resolution of $\{(Cr\ en_3)Cl_3 + 3{\cdot}5H_2O\}$. Using *d*-quartz, activated by heating, the first elutions are dextro- and the next lævo-rotatory and vice versa. L. S. T.

Lead alkyl compounds. G. Calingaert and H. Soroos (J. Org. Chem., 1938, **2**, 535—539).—$PbMe_4$ and I in Et_2O at —60° give 60% of *Pb trimethyl iodide*, which with $CHMeEt{\cdot}MgBr$ gives 50% of *Pb trimethyl* sec.-*butyl*, b.p. 59°/13 mm., 16% of $PbMe_4$, and 22% of $PbMe_2(CHMeEt)_2$. $PbMe_3Br$ gives a poorer yield of $PbMe_3$ derivative. $PbMe_3Br$ and $MgBu^\gamma Cl$ give $PbMe_4$ and Pb with some C_2Me_6 and (?) $CH_2Pr^\beta Bu^\gamma$, but $PbMe_3I$ gives 88% of *Pb trimethyl* tert.-*butyl*, m.p. 5·7°, b.p. 47—47·2°/13 mm. $PbCl_2$ and MgMeI at —5° to —8° give 61% of *Pb_2 hexamethyl*, m.p. 37—38°, obtained in only 7% yield from $PbMe_3I$ and Na in NH_3. The unexpected stability and crystal symmetry of $PbMe_3Bu^\gamma$ and Pb_2Me_6 are ascribed to their formal resemblance to C_2Me_6. R. S. C.

Organic osmium compounds. R. Criegee (Angew. Chem., 1938, **51**, 519—520).—A lecture. C. R. H.

1 : 2-Dimethyl-Δ^1- and -Δ^5-*cyclo*pentene and *cis*- and *trans*-1 : 2-dimethyl*cyclo*pentane. G. Chiurdoglu (Bull. Soc. chim. Belg., 1938, **47**, 363—381).—Dehydration of 1 : 2-dimethyl*cyclo*pentanol by 80·3% HCO_2H gives a mixture of 1 : 2-dimethyl-Δ^1-*cyclo*pentene (I), b.p. 105·03°/700 mm., m.p. —91·3°, and 1 : 2-dimethyl-Δ^5-*cyclo*pentene (II), b.p. 95·48—95·50°/760 mm., m.p. —118·1° (other consts. recorded). The constitution of (I) follows from its oxidation by $KMnO_4$ to δ-ketohexoic acid (semicarbazone, m.p. 178°) and heptane-βζ-dione, b.p. 96—97°/11 mm., m.p. about —30° (semicarbazone, decomp. 217°; oxime, m.p. 86°), whilst that of (II) is deduced from its oxidation to δ-keto-γ-methyl-*n*-hexoic acid, b.p. 164—168°/22 mm. (semicarbazone, decomp. 163·5° or m.p. 158° after softening at 153° when slowly heated). The acid is best obtained synthetically thus: $CH_2Ac{\cdot}CO_2Et \rightarrow$ $CHMeAc{\cdot}CO_2Et$, $CO_2Et{\cdot}CMeAc{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Et \rightarrow$ $CHMeAc{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$. Hydrogenation (Pt-black in AcOH at room temp.) gives trans-, b.p. 91·78°/760 mm., m.p. —119°, and cis-, b.p. 99·23°/760 mm., m.p. —52·5°, -1 : 2-*dimethyl*cyclo*pentane*, the configurations of which are decided by their physical properties. H. W.

Supposed isomeric forms of methyl*cyclo*hexane. J. P. Wibaut, S. L. Langedijk, J. Smit-

TENBERG, and H. HOOG (Chem. and Ind., 1938, 753).—The properties of pure methyl*cyclo*hexane (from PhMe) do not confirm VOGEL's observations (A., 1938, II, 268). A. LI.

Multiplanar forms of methyl*cyclo*hexane. A. I. VOGEL (Chem. and Ind., 1938, 772—773).—The work of Wibaut *et al.* (preceding abstract) is considered to confirm the author's observations by an entirely independent method. H. W.

Kinetics of aromatic nitration in nitromethane solution.—See A., 1938, I, 404.

Synthesis and hydrogenation of polyalkylated benzenes. H. KOCH and H. STEINBRINK (Brennstoff.-Chem., 1938, **19**, 277—285).—C_6Et_6 is not formed by the action of 96% H_2SO_4 and C_2H_4 on C_6H_6 and is produced only in very slight amount if Ag_2SO_4 and $NiSO_4$ are added to the acid; it is formed in 56—59% yield from C_6H_6, $AlCl_3$, and C_2H_4 under pressure. Hydrogenation (Ni–Mn–Al–SiO_2 at 235—240° in *cyclo*hexane) gives a mixture of the stereoisomeric *hexaethylcyclohexanes* (I) which has the properties of a spindle oil. Attempted further ethylation of (I) by EtCl–$AlCl_3$ or by BF_3–C_2H_4 in presence of Ni–SiO_2 gave inconclusive results. $C_6H_2Pr^{\beta}_4$, m.p. 118·5°, is not further alkylated by C_3H_6 and 96% H_2SO_4 in *cyclo*hexane or by BF_3–C_3H_6 under pressure. With $AlCl_3$ and AcCl it affords a *triisopropylacetophenone*, m.p. 105·6—106°, which does not react with NH_2·CO·NH·NH_2. C_6Et_6 does not suffer similar alkyl replacement when treated with $AlCl_3$ and AcCl. Hydrogenation (Ni–Al–Mn–SiO_2 in *cyclo*hexane) of $C_6H_2Pr^{\beta}_4$ gives the stereoisomeric *tetraisopropylcyclohexanes*, m.p. 125·2—125·8° and b.p. 150—153°/20 mm., each of which behaves as a spindle oil. The viscosity and ageing properties of C_6Et_6, $C_6H_6Et_6$, $C_6H_2Pr^{\beta}_4$, and $C_6H_8Pr^{\beta}_4$ are recorded. Exhaustive treatment of C_6H_6 and 96% H_2SO_4 with *iso*butene leads essentially to *p-ditert.-*butylbenzene, a large proportion of the gas being polymerised. AcCl and $AlCl_3$ in CS_2 transform it into tert.-*butylacetophenone* [*semicarbazone*, m.p. 225—227° (decomp.)]. It is hydrogenated (Ni–Mn–Al–SiO_2 in *cyclo*hexane) to a difficultly separable mixture of the stereoisomeric p-*ditert.-butylcyclohexanes*, one of which has m.p. 94·5—95°. The alkylation of C_6H_6 with Δ^{α}-butene, a pentene, and a decene fraction and of Ph_2 with C_2H_4 did not give homogeneous products. The products of the action of C_6H_6 on $Pr^{\alpha}Cl$, $Bu^{\alpha}Cl$, and *n*-amyl chloride in presence of $AlCl_3$ or H_2SO_4 are described. H. W.

Accessory products [formed during chlorination of toluene].—See A., 1938, I, 408.

Action of aluminium chloride on fluorinated compounds. A. L. HENNE and M. S. NEWMAN (J. Amer. Chem. Soc., 1938, **60**, 1697—1698).—$CPhF_3$, AcCl, and $AlCl_3$ give AlF_3 and $CPhCl_3$ in excellent yield; in the absence of AcCl much tar is formed, indicating participation of the AcCl–$AlCl_3$ complex in the reaction. Org. fluorides, $AlCl_3$, and ethylenes gives tars. In C_6H_6 $(CCl_2F)_2$, CCl_2F·$CClF_2$, $(CClF_2)_2$, $CHClF_2$, and $C_2Cl_2F_2$ give HCl, a little HF, AlF_3, and F-free, rubbery, polymerised substances. CCl_2F·$CClF_2$ and $AlCl_3$ (no C_6H_6) give AlF_3 and a little CCl_3·$CClF_2$ and higher-boiling, F-free material. $CHCl_2$·$CClF_2$ reacts more readily, giving HF, tars, and AlF_3. Thus, $AlCl_3$ cannot be used for Friedel–Crafts reactions with fluorides. R. S. C.

Nitration of phenylnitromethane, and a new isomeride of trinitrotoluene. T. URBAŃSKI and J. GIEDROYĆ (Rocz. Chem., 1938, **18**, 125—130).—CH_2Ph·NO_2 and 80% NHO_3 at 35—40° yield *m*-NO_2·C_6H_4·CH_2·NO_2, which with 1 : 1 HNO_3–20% oleum at ≯65° gives 3 : 5-*dinitrophenylnitromethane*, m.p. 130°; this is more readily detonated by shock, and less so by heat, than is $C_6H_2Me(NO_2)_3$ (I), although thermal decomp. begins at a lower temp. (200°). Its explosive power is equal to that of (I). R. T.

Prototropy of the nitromethanes. I. Chloro-, bromo-, and nitro-phenylnitromethanes. R. G. COOKE and A. K. MACBETH (J.C.S., 1938, 1024—1026).—The rate of the change, C_6H_4R·CH:NO·$O^- + H^+ \rightarrow C_6H_4R$·$CH_2$·$NO_2$, in 50% aq. EtOH at 0° is measured for substances in which R = *o*-, *m*-, and *p*-NO_2, -Br, and -Cl. In all cases, except that of *o*-NO_2 (where an *o*-effect is observed), the reaction mechanism is probably the same, as the graphs show first a curved and then a straight portion. The relative rates are NO_2 > Hal > H, and, for NO_2 only, *p* > *m*. The following are new: o-, b.p. 109°/10 mm., and m-, b.p. 128°/13 mm., m.p. 23°, *-chloro-*, *o-*, an oil, b.p. 139°/7 mm. (lit., m.p. 55—56°), and m-*bromophenylnitromethane*, m.p. 23—24°. R. S. C.

Stabilising action of quinol on the thermal polymerisation of styrene. J. W. BREITENBACH, A. SPRINGER, and K. HOREISCHY (Ber., 1938, **71**, [*B*], 1438—1441).—The polymerisation of styrene (I) by heat is almost entirely inhibited by quinol (II) in presence of O_2. A marked induction period is caused by O_2. Since at the beginning the rate is the same in the presence or absence of O_2 it appears that an additive compound first results from (I) and O_2 which then by decomp. or union with a further mol. of (I) gives a polymerisation nucleus. The stabilising effect of (II) is due to its reducing power. The similar influence of *p*-benzoquinone (III) on reaction and sp. viscosity of polymerisates show that its influence lies in increasing the rupture of the chain; it is consumed by the reaction, either being involved by the polystyrene or reduced to (II). During the course of the change the intensity of the colour in presence of (III) decreases gradually. H. W.

Cumulenes. II. Improved method of preparation. R. KUHN and K. WALLENFELS (Ber., 1938, **71**, [*B*], 1510—1512; cf. A., 1938, II, 226).—Treatment of diacetylenic glycols in Et_2O containing HCl with reducing agents (VCl_2, $CrCl_2$) gives cumulenes in excellent yield. Metals are unsuitable. The prep. of tetraphenyl- and didiphenlyene-hexapentaene is described. H. W.

Catalytic hydrogenation in the naphthalene series. L. PALFRAY (Compt. rend., 1938, **206**, 1976—1978).—α-$C_{10}H_7$·OH with H_2 (150 kg. pressure)–Raney Ni at 65° rapidly affords 1-hydroxy-1 : 2 : 3 : 4-tetrahydronaphthalene and tetrahydronaphthalene, which when further reduced (many hr.) afford 1-decahydronaphthol and decahydronaphthal-

ene, respectively. Similarly, β-$C_{10}H_7$·OH at 65° affords mainly 2-hydroxy-1 : 2 : 3 : 4-tetrahydronaphthalene (I) and a little decahydronaphthol. Further reduction of (I) at 125° affords a mixture of *cis*- and *trans*-2-decahydronaphthol from which the former is isolated. Similarly, $C_{10}H_8$ at 100° affords $C_{10}H_{12}$ which at 200° gives $C_{10}H_{18}$. J. L. D.

Dehydrogenation. I. S. C. Sengupta (J. pr. Chem., 1938, [ii], **151**, 82—96).—Addition of $AlCl_3$ to αα-dimethylsuccinic anhydride in C_6H_6 gives *β-benzoyl-αα-dimethylpropionic acid* (I), m.p. 170—171° (*semicarbazone*, m.p. 166°), the *Me* ester, m.p. 50°, of which is obtained by the successive action of $SOCl_2$ and $AlCl_3$ on the compound $COCl·CMe_2·CH_2·CO_2Me$. Zn–Hg and conc. HCl reduce (I) to *γ-phenyl-αα-dimethylbutyric acid*, b.p. 155—156°/6 mm., m.p. 98° (*anilide*, m.p. 113—114°), the *Et* ester, b.p. 114°/5 mm., of which could not be condensed with $Et_2C_2O_4$. The acid is cyclised by H_2SO_4 at 100° to 1-*keto*-2 : 2-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. 150°/27 mm. (*oxime*, m.p. 131—132°), which does not give a semicarbazone or phenylhydrazone; this is oxidised by $KMnO_4$–KOH to *o*-$C_6H_4(CO)_2O$ and reduced (Clemmensen) to 2 : 2-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. 123°/34 mm., which could not be dehydrogenated by Se at 280—340° in an open vessel but passes in a sealed tube at 300—320° into 2-$C_{10}H_7Me$. Similarly, *β-p-toluoyl-αα-dimethylpropionic acid*, m.p. 158—159° (*semicarbazone*, m.p. 166—167°; *Me* ester, b.p. 150°/7 mm.), gives successively *γ-p-tolyl-αα-dimethylbutyric acid*, m.p. 111—112° (*anilide*, m.p. 119°; *Et* ester, b.p. 120—121°/5 mm.), 1-*keto*-2 : 2 : 7-*trimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. 120—121°/5 mm. (*oxime*, m.p. 141—142°), 2 : 2 : 7-*trimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. 128°/23 mm., and 2 : 7-$C_{10}H_6Me_2$. *β-Benzoyl-αα-diethylpropionic acid*, m.p. 91—92° (*semicarbazone*, m.p. 114°; *Me* ester, b.p. 160—162°/8 mm.), gives *γ-phenyl-αα-diethylbutyric acid*, b.p. 185—186°/5 mm., m.p. 49—50° (*anilide*, m.p. 114—115°; *Et* ester, b.p. 95—96°/6 mm.), *α-keto*-2 : 2-*diethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. 148—150°/7 mm., 2 : 2-*diethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. 110°/4 mm., and 2-$C_{10}H_7Et$. H. W.

Chlorination of 2-methylnaphthalene. O. Achmatowicz and K. Lindenfeld (Rocz. Chem., 1938, **18**, 69—74).—The following substances were isolated from the complex mixture resulting from chlorination of 2-$C_{10}H_7Me$ at 220°, in diffused light: 1-*chloro*-2-*methylnaphthalene* (I), b.p. 162—164°/30 mm. [identical with Scherler's *eso*-chloro-β-methylnaphthalene (A., 1892, 493)], 2-$C_{10}H_7·CH_2Cl$, 1-*chloro*-2-*chloromethylnaphthalene* (II), m.p. 78—79°, and 2-*dichloromethylnapthhalene* (III), m.p. 114—115°. (I) is chlorinated at 225°, to yield (II), which gives with boiling aq. $Pb(NO_3)_2$ 1-*chloro*-2-*hydroxymethylnaphthalene*, m.p. 98—99° (*benzoate*, m.p. 68—69°), and this is oxidised ($KMnO_4$) to 1 : 2-$C_{10}H_6Cl·CO_2H$ (*Me* ester, m.p. 50°). (III) and H_2O at 140—150° (8 hr.) yield β-$C_{10}H_7$·CHO. R. T.

Hydrocarbons and hydrocarbon intermediates of high mol. wt. L. A. Mikeska, C. F. Smith, and E. Lieber (J. Org. Chem., 1938, **2**, 499—505).—Passing HCl into a boiling mixture of stearophenone (I) (modified prep.), m.p. 63·5—64·5°, mossy Zn–Hg, xylene, and conc. HCl gives a good yield of $Ph·C_{16}H_{33}$-*n* (II); other methods were less successful. H_2–PtO_2 reduces (II) in AcOH to n-*octadecyl*cyclo*hexane*, m.p. 40°, b.p. 204—210°/4 mm. $MgBu^aCl$ and (I) give *phenyl*-n-*butyl*-n-*heptadecylcarbinol*, b.p. 235—240°/2 mm., dehydrated by $H_2C_2O_4$ at 180—200° in CO_2 to α-n-*butyl*-n-Δ^a-*octadecenylbenzene*, b.p. 205—210°/1 mm., which is hydrogenated (PtO_2) in AcOH to α-n-*butyl*-n-*octadecylbenzene*, m.p. 38°, b.p. 200—201°/1 mm. Adding $AlCl_3$ to stearyl chloride (modified prep.) and Ph_2 in CS_2 gives *stearyldiphenyl*, m.p. 106—107°, reduced to n-*octadecyldiphenyl*, m.p. 79—81°, b.p. 270—275°/5 mm., and converted by $MgBu^aCl$ etc. into α-n-*butyl*-n-Δ^a-*octadecenyldiphenyl*, α-n-*butyl*-n-*octadecyldiphenyl*, m.p. 41·5—43°, and 1-cyclo*hexyl*-x-α-n-*butyl*-n-*octadecyl*cyclo*hexane*, b.p. 255—260°/1 mm. Similar reactions afford 1-*stearyl*-, m.p. 54·5—56°, 1-α-n-*butyl*-n-Δ^a-*octadecenyl*-, b.p. 232—240°/3 mm., and 1-α-n-*butyl*-n-*octadecyl*-*naphthalene*, m.p. 38°, b.p. 200—201°/2 mm., *stearyl*-, m.p. 49·5—50°, n-*octadecyl*- (III), an oil, α-n-*butyl*-n-Δ^a-*octadecenyl*-, b.p. 263—264°/4 mm., and α-n-*butyl*-n-*octadecyl*-*tetrahydronaphthalene* (IV), b.p. 235—245°/2 mm., and other products previously reported (B., 1936, 1077). Hydrogenation of (III) and (IV) yields n-*octadecyl*-, m.p. 43—47°, and α-n-*butyl*-n-*octadecyl*-*octahydronaphthalene*, b.p. 240—245°/3 mm., respectively. R. S. C.

Synthesis of condensed polynuclear hydrocarbons by the cyclodehydration of aromatic alcohols. VII. Cyclodehydration involving the Wagner rearrangement. D. Price, D. Davidson, and M. T. Bogert (J. Org. Chem., 1938, **2**, 540—545).—Cyclisation of $Ph·[CH_2]_n·CHBu^{\gamma}·OH$ ($n = 1$ or 2) by 90% H_2SO_4 involves a previous Wagner rearrangement. $CH_2Ph·CH_2·CHO$ and $MgBu^{\gamma}Cl$ in Et_2O at 2—10° give 70% of *ε-phenyl-ββ-dimethylpentan-γ-ol*, b.p. 90—91°/2 mm. (*phenylurethane*, m.p. 91°), converted by 90% H_2SO_4 at 2°—room temp. into 1 : 1 : 2-*trimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (55% yield), b.p. 77—77·5°/1 mm., 242°/760 mm., oxidised by $KMnO_4$ to *o*-$CO_2H·C_6H_4·CMe_2·CO_2H$, dehydrogenated by S to 1 : 2-$C_{10}H_6Me_2$, and obtained in 86% yield by the action of 90% H_2SO_4 on *ε-phenyl-βγ-dimethylpentan-γ-ol*, b.p. 118—119°/3 mm. (obtained in 50% yield from $CH_2Ph·CH_2·MgBr$ and $COMePr^{\beta}$). $CH_2Ph·CHO$ and $MgBu^{\gamma}Cl$ give *α-phenyl-γγ-dimethylbutan-β-ol*, b.p. 78·5°/2 mm., converted by H_2SO_4 at <5° into 1 : 1 : 2-trimethylindane (41%), b.p. 208°/760 mm., oxidised by CrO_3–AcOH to *Me* β-o-*carboxyphenyl*isopropyl *ketone*, m.p. 157·5° (corr.). R. S. C.

Comparison of three *meso*-anthracenic additive reactions; diene synthesis, photo-oxidation, and hydrogenation. C. Dufraisse, L. Velluz, and (Mme.) L. Velluz (Bull. Soc. chim., 1938, [v], **5**, 1073—1081).—A comparison of the conditions under which the maleic additive compounds and the photo-oxides of anthracene are produced and dissociate shows that the analogies noted previously are merely superficial and fortuitous and are limited without doubt to the *meso*-anthracenic structure.

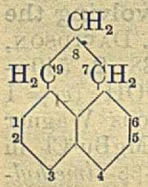
Comparison with the hydrides establishes the importance of the bridge position for the dissociability of a *meso*-anthracene additive product. 9 : 10-Dihydroanthracene cannot be photo-oxidised. This is also true of 9-phenyl-9 : 10-dihydroanthracene, whilst 9 : 10-diphenyl-9 : 10-dihydroanthracene is very stable towards heat and light and, in particular, is not photo-oxidisable. endo-9 : 10-αβ-*Anhydrodicarboxyethylene*-, m.p. 267° (block), -9-*phenyl*-, m.p. 290—291° (block), and -9 : 10-*diphenyl*-, m.p. 315—317° (block), -9 : 10-*dihydroanthracene* are obtained in the usual manner; the last-named is decomposed most easily and most completely into its components by heat.

H. W.

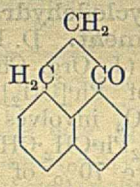
Factors affecting the addition of bromine to phenanthrene. M. S. Kharasch, P. C. White, and F. R. Mayo (J. Org. Chem., 1938, **2**, 574—576).—Addition of Br to phenanthrene is catalysed by intermittent, almost as much as by continuous, illumination, reaction being faster in air than in vac. Thus, Price measured a catalysed reaction (A., 1936, 1498; 1937, II, 12). Bz_2O_2 accelerates the reaction in the dark, but less so than does ascaridole (I). (I) is more effective with a low than with a high [Br].

R. S. C.

Synthesis of 3 : 4-benzpyrene derivatives. L. F. Fieser and E. B. Hershberg (J. Amer. Chem. Soc., 1938, **60**, 1658—1665).—The names, perinaphthane, perinaphthan-7-one, and perinaphthenone, for (I), (II), and (III), respectively, are preferred as being more systematic than those hitherto proposed. Convenient syntheses of substances in this and the benzpyrene series are described. Ring-closure of



(I.)



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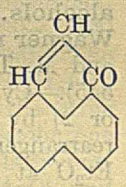
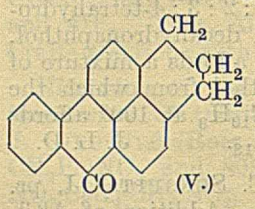


(III.)

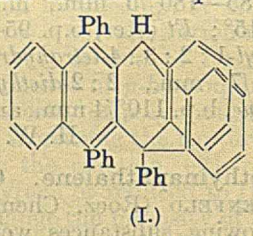
1-allylnaphthalene (prep. in 81% yield from 1-$C_{10}H_7Br$, Mg, and CH_2:CH·CH_2Br), b.p. 127·5—128·5°/8 mm. (*picrate*, m.p. 68—69°), could not be effected; distillation at 500—550°/15 mm. over activated Al_2O_3 gives 1-propenylnaphthalene, b.p. 139—140°/10 mm. (*picrate*, m.p. 110—111°; oxidised by $K_2Cr_2O_7$ to MeCHO and α-$C_{10}H_7$·CO_2H). β-$C_{10}H_7$·OH and glycerol are condensed and oxidised by NO_2·C_6H_4·SO_3Na in H_2SO_4 to (III) (26% yield), m.p. 156—156·5°, hydrogenated by H_2–Cu–Cr_2O_3 in dioxan or Et_2O, best at 250—260°/120 atm., to (I) (74% yield), m.p. 65·1—65·4° [*picrate*, m.p. 150—151°; $C_6H_3(NO_2)_3$ additive *compound*, m.p. 160—161°], with a little *perinaphthan-7-ol* (IV), m.p. 105·5—106° (*picrate*, m.p. 163·5—164·5°). (IV) is the main product (49%) obtained by means of H_2–Raney Ni in dry Et_2O–EtOH. H_2–PtO_2 in dry EtOH converts (III) into an unstable, bimol. *product*, $C_{26}H_{18-20}O_2$, m.p. 179—180° (decomp.). With the complex from $AlCl_3$ and BzCl in CS_2 (I) gives 3-*benzoylperinaphthane* (95% yield), m.p. 62—63°, b.p. 210—215°/2 mm., converted by NaCl–$AlCl_3$ in O_2 at 150—155° into 2 : 1′-*trimethylene*-1 : 9-*benzanthr*-10-*one* (V) (26% yield), m.p. 217—218°, which, when distilled with Zn dust at 1—2 atm., gives 3 : 4-benzpyrene (VI), m.p. 178·5—179° [best purified by way of the $C_6H_3(NO_2)_3$ additive *compound*, m.p. 226—227°]; the mother-liquor from (V) contains some further reduced benzanthrone derivative, converted into (VI) by Zn distillation, and a 50% yield of (VI) is obtained if isolation of (V) is omitted. The appropriate C_6H_4Me·COCl, (I), and $AlCl_3$ in CS_2 yield 3-o- (VII), m.p. 68—69°, b.p. 210—220°/0·2 mm., 3-m- (VIII), m.p. 86·5—87°, b.p. 225—230°/2 mm., and 3-p-*toluoylperinaphthane* (IX), m.p. 90—90·5°, b.p. 215—220°/0·5 mm. Ring-closure of (IX) gives 2′-*methyl*-3 : 4-*benzpyrene* (42% yield), m.p. 138—139° (after resolidification, 140—140·2°) [$C_6H_3(NO_2)_3$ additive *compound*, m.p. 211·5—212°; *picrate*, m.p. 184—185°]. (VII) and (VIII) give 22 and 14%, respectively, of 3′-*methyl*-3 : 4-*benzpyrene*, m.p. 146·5—147° (after resolidification, 147·6—148·1°) [$C_6H_3(NO_2)_3$ additive *compound*, m.p. 210·5—211°; *picrate*, m.p. 179·5—180°]. The rearrangement involved in the ring-closure of (VII) is discussed. Pure 1′ : 2′ : 3′ : 4′-tetrahydro-3 : 4-benzpyrene has m.p. 112·6—113·1° (cf. Fieser and Fieser, A., 1935, 741; Winterstein *et al.*, *ibid.*, 968). High-pressure hydrogenation thereof gives a mixture (cf. *loc. cit.*). M.p. are corr.



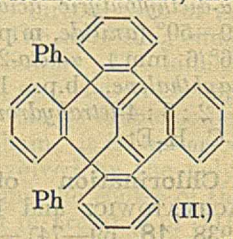
(V.)

R. S. C.

Dissociability of organic oxides. Transformations of tetra-arylnaphthacenes and their oxides. M. Enderlin (Ann. Chim., 1938, [xi], **10**, 5—116).—10 : 12-Diphenyl-9 : 11-di-*p*-tolylnaphthacene is converted by H_2SO_4 or HI into *ψ-diphenyldi-p-tolylnaphthacene*, form I, m.p. 294—295°, isomeride II, m.p. 271—272°. Analogously *ψ-diphenyldi-p-bromophenylnaphthacene* exists in two modifications, m.p. 345° (block) and 295°, respectively. The existence of these compounds in two isomeric forms, their



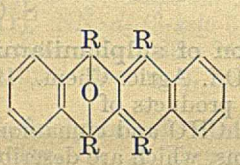
(I.)



(II.)

analogy to C_2Ph_6, and the occurrence of a single Ph_4 compound is best explained by the formulation (I). Dehydration of the requisite mono- or di-hydroxides affords 9 : 10-*diphenyl*-9 : 12 : 10 : 11-*diphenylene*-9:10-*dihydronaphthacene* (II), m.p. 430° (block), *phenyl*-p-*tolylphenylenemethylphenylenenaphthacene*, m.p. about 370°, and *phenyl*-p-*bromophenylphenylenebromophenylenenaphthacene*, m.p. 450° (block), respectively. The naphthacenes are converted into their monoxides by oxidation with dil. HNO_3, $KMnO_4$, or CrO_3, by reduction of the higher oxides by Zn and AcOH, and by dehydration of the requisite $(OH)_2$-compounds. They are stable to air and light, are not decomposed by heat, are readily reduced to the corresponding hydrocarbons, cannot be oxidised to the higher oxides, and do not react with Grignard reagents. 10 : 12-*Diphenyl*-9 : 11-*di*-p-*tolylnaphthacene oxide*, m.p. 265° or

($+C_6H_6$) m.p. 175°, and 10 : 12-*diphenyl*-9 : 11-*di*-p-*bromophenylnaphthacene oxide*, m.p. 274—276°, or ($+C_6H_6$), m.p. about 220°, are new. Dihydroxydihydrotetra-arylnaphthacenes are obtained by the action of Grignard's reagents, particularly MgEtBr, on the dissociable oxides but the method does not invariably lead to homogeneous products and oxidation of the hydrocarbons by $KMnO_4$ is preferable. They are colourless compounds with 2 active H (Zerevitinov); they do not dissociate when heated but lose H_2O at a moderate temp. with production of the monoxide. Further dehydration yields the diaryldiarylenenaphthacenes. They are readily reduced to the hydrocarbons. *Dihydroxy*-9 : 10 : 11 : 12-*tetraphenyldihydronaphthacene*, which when heated loses successively solvent and H_2O of crystallisation, *dihydroxy*-10 : 12-*diphenyl*-9 : 11-*di*-p-*tolyldihydronaphthacene*, m.p. 210—220° according to the mode of heating, and *dihydroxy*-10 : 12-*diphenyl*-9 : 11-*di*-p-*bromophenyldihydronaphthacene*, m.p. 220–230° (block; decomp.), are described. The dissociable oxides are transformed into the *iso*-oxides by Grignard's reagents or, more simply, by Mg salts; usually the products are difficultly separable mixtures. The *iso*oxides are colourless compounds which do not dissociate into O and hydrocarbon. Reduction leads to the hydrocarbon in poor yield and sometimes causes elimination of Ph. It appears impossible to transform them into a lower oxide or a diaryldiarylenenaphthacene. *Tetraphenylnaphthacene* iso*oxide*, m.p. 169—168° and 267—268°, *diphenyldi*-p-*tolylnaphthacene* iso*oxide*, m.p. 210° (block), and *diphenyldi*-p-*bromophenylnaphthacene* iso*oxide*, m.p. 258° (block), have been obtained.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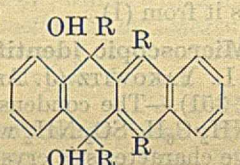
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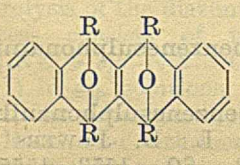
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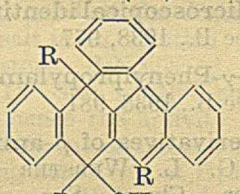

(VI.)

Tetraphenylnaphthacene peroxide is converted by 50% H_2SO_4 in C_6H_6 into *tetraphenylnaphthacene* ψ-*oxide*, $C_{42}H_{28}O_2$, decomp. 210° (block), which when solid or dissolved is rapidly transformed by light into a yellow resin. It readily liberates I from acidified KI, reacts vigorously with Grignard reagents (≡ 1 H), and is reduced by Zn and dil. AcOH to diphenyldiphenylenenaphthacene. The constitutions (III), (IV), (V), and (VI) are advanced for the monoxides, dihydroxides, *iso*oxides, and ψ-oxides, respectively. Support of these conclusions is found in the thermochemical behaviour of the hydrocarbons and their intermediate oxides and in their magnetic properties. H. W.

Catalytic hydrogenation of quaternary ammonium salts. O. Achmatowicz and K. Lindenfeld (Rocz. Chem., 1938, **18**, 75—87).—Catalytic hydrogenation (C–Pd catalyst) of quaternary NH_4 salts proceeds as follows, at 20 and 85° : $NMe_3RCl \rightarrow NMe_3 + RH + HCl$, in the cases R = allyl, Ph, $[CH_2]_n$·Ph (n = 1—4), and CHPh:CH·CH_2. $NMe_2Cl(CH_2Ph)_2$ yields PhMe, HCl, and NMe_2·CH_2Ph (further hydrogenated to PhMe and $NHMe_2$). The following new compounds were obtained incidentally, by the standard method : δ-*phenylbutyl*- (*aurichloride*, m.p. 149—150°), and 2-*naphthylmethyl*-*trimethylammonium chloride* (*aurichloride*, m.p. 188°; hydrogenation products, NMe_3, HCl, and a methyldihydronaphthalene, b.p. 226—228°). R. T.

Catalytic oxidation of aromatic amines and phenols by means of clay and similar substances. A. Eisenack (Naturwiss., 1938, **26**, 430).—Catalytic oxidation of the vapours of solid and liquid aromatic amines and phenols can be effected by the use of clay, fuller's earth, kaolin, flint, agate, pptd. Al and Mg silicates, permutit, SiO_2 gel, etc. $NPhMe_2$ gives crystal-violet and its leuco-base and colour base, and $NHPh_2$ gives diphenylbenzidine and a deep blue quinonoid derivative. A. J. M.

Organic catalysts. XIX. Esterase model. IV. W. Langenbeck and K. Hölscher (Ber., 1938, **71**, [*B*], 1465—1471).—Further examples are cited of the ready hydrolysis of acylcarbinyl esters and glycollarylamides. The following appear new : *acetoxyacet*-β-*naphthylamide*, m.p. 128°, -1-*bromo*-2-*naphthylamide*, m.p. 133°, -1-*methoxy*-2-*naphthylamide*, m.p. 125°, -3-*methoxy*-2-*naphthylamide*, m.p. 134°, -6-*methoxy*-2-*naphthylamide*, m.p. 147—148°, and 7-*methoxy*-2-*naphthylamide*, m.p. 134°; 9-, 2-, and 3-*phenanthroylcarbinyl acetate*, m.p. 122—123°, 117°, and 116—117°, respectively; 9- and 3-*phenanthroyldiazomethane*, m.p. 120° and 130—133° (decomp.), respectively. Reply is made to Ionescu and Cotani (A., 1938, III, 695). H. W.

New radical with quadrivalent nitrogen; phenyl-9-*trans*-decahydronaphthylnitrogen oxide. W. Hückel and W. Liegel (Ber., 1938, **71**, [*B*], 1442—1445).—9-Nitroso-*trans*-decahydronaphthalene (I) does not form azo- or azoxy-compounds with NH_2Ph, *cyclo*hexylamine, or NHPh·OH. It is converted smoothly by MgPhBr into *phenyl*-trans-9-*decahydronaphthylhydroxylamine* (II), m.p. 141—143° (decomp.) (*Ac*, m.p. 87°, *Bz*, m.p. 133°, and p-*nitrobenzoyl*, m.p. 142—143°, derivatives), which is reduced by Na and abs. EtOH or by H_2–Pd–$CaCO_3$ in EtOH to *phenyl*-trans-9-*decahydronaphthylamine* (III), m.p. 81°. This is transformed by $NaNO_2$ and conc. HCl into p-*nitrosophenyl*-trans-9-*decahydronaphthylamine*, m.p. 159°, hydrogenated, and then acetylated to the *compound*, $C_{18}H_{26}ON_2$, m.p. 212—213°. The mother-liquors from (II) contain *phenyl*-trans-9-*decahydronaphthylnitrogen oxide* Ph·N(:O)·$C_{10}H_{17}$, m.p. 83°, also obtained by autoxidation of (II) in C_6H_6; it is reduced (H_2–Pd–$CaCO_3$ in EtOH) to (III). MgMeI, Mg *cyclo*hexyl chloride, and $MgBu^{\gamma}Br$ essentially reduce (I) to (II). H. W.

Manufacture of substituted phenylcarbimides. —See B., 1938, 888.

Carbodiarylimides. F. Zetzsche, H. E. Meyer, H. Overbeck, and W. Nerger (Ber., 1938, **71**, [*B*], 1512—1516).—The desulphurisation of thiocarbamides to carbodiarylimides (I) is best effected by PbO in boiling PhMe, volatilisation of the H_2O diminishing the tendency towards the production of carbamides. The tendency of (I) towards polymerisation varies greatly, being most pronounced with the *p*-iodophenyl and least with the pyridyl derivative. The use of surface catalysts should be avoided. The following are described: carbodi-*p*-tolylimide, b.p. 202°/12 mm., m.p. 56°, readily converted by boiling H_2O, steam, or dil. H_2O_2 into the resinous form; *carbodi*-p-*bromo*-, b.p. 231—234°/12 mm., 188°/0·2 mm., m.p. 70—73°, and *-iodo-phenylimide*, m.p. (crude) 90°, which decomposes at 180° and is transformed into different polymerides by crystallisation from various solvents; *carbodi*-2-*pyridylimide*, m.p. 137° (*picrate*, decomp. 228°); *carbodi*-p-*dimethylaminophenylimide*, m.p. 86—88·5°. H. W.

Characterisation of carboxylic acids as ureides [acyldiarylcarbamides] by means of carbodiimides. II. F. Zetzsche, H. E. Meyer, H. Overbeck, and H. Lindlar (Ber., 1938, **71**, [*B*], 1516—1521).—BzOH does not react with carbodi-2-pyridylimide in boiling C_6H_6 or PhMe or in absence of solvent at 140°; at 180—200° 2-benzamidopyridine, m.p. 80° (picrate, m.p. 146°), is produced in 85% yield. The following *2-acyl-amidopyridines* are obtained analogously: *sebac*-, m.p. 139° (*picrate*, m.p. 193°); *cinnam*-, m.p. 139° (*picrate*, m.p. 199°); *α-croton*-, m.p. 79° (*picrate*, m.p. 137°); *stear*-, m.p. 78° (*picrate*, m.p. 114°); *palmit*-, m.p. 69° (*picrate*, m.p. 108°); *ole*-, m.p. 15—18° (*picrate*, m.p. 68°); *linole*- (*picrate*, m.p. 57°). Carbodi-*p*-dimethylaminophenylimide appears superior to the compounds described previously (A., 1938, II, 257) since it does not polymerise when solid and is less easily anhydrised. With AcOH in $COMe_2$ at room temp. it slowly affords *acetdi*-p-*dimethylaminophenylcarbamide*, m.p. 149°. The following *acyl-di*-p-*dimethylaminophenylcarbamides* are described: *propion*-, m.p. 162—163° after softening at 159°; *myrist*-, m.p. 120—120·5° after softening at 119° (*picrate*, m.p. 142—143°); *palmit*-, m.p. 120—122° after softening at 119° (*picrate*, m.p. 144—145°); *benz*-, m.p. 216—218° (*picrate*, m.p. 175°); *phellon*-, m.p. 160—163°; p-*azoxybenz*-, decomp. 292—298° (red at 190°); *lævul*-, m.p. 155°; *ole*-, m.p. 100—101° after softening at 98°; *linole*-, m.p. 88—89° (*picrate*, m.p. 129°); *linolen*-, m.p. 84—85°. The pyridines and carbamides are readily hydrolysed by conc. H_3PO_4 at 130—140° whereby $CO(NH{\cdot}C_6H_4{\cdot}NMe_2)$ is degraded to *p*-$NH_2{\cdot}C_6H_4{\cdot}NMe_2$. H. W.

Phenylthiocarbamides. The triad –N·C·S–. VI. Action of nitrous acid on *N*-phenyl-*N'*-methylthiocarbamide. VII. Some hydrolytic decompositions of phenylthiocarbamide. Action of sodium ethoxide on phenylthiocarbamide and of acetic anhydride and hydrolytic agents on *N*-phenyl-*N*- and -*N'*-methylthiocarbamide. K. B. Lal and H. Krall (J. Indian Chem. Soc., 1938, **15**, 217—220, 221—228).—VI. NHPh·CS·NHMe with $NaNO_2$ in aq. EtOH–AcOH yields *N'-nitroso*-N-*phenyl*-N'-*methylthiocarbamide*, m.p. 84° (decomp.). This with cold H_2O slowly yields NO, N_2, S, and PhNCS (the last slowly giving place to a non-basic solid, m.p. 137°), with cold NaOH yields PhNCS, and with warm dil. HCl gives NO, S, and a base (I), $C_{16}H_{18}N_4S$, m.p. 82°, which yields in EtOH a *picrate*, m.p. 195°, and in dil. HCl (usually) an isomeric *picrate*, m.p. 153—154°, and when heated gives PhNCS and a basic resinous substance. $NaNO_2$ in HCl partly oxidises NHPh·CS·NHMe to a base which deposits S, giving (I).

VII. The extent to which NHPh·CS·NH_2 is hydrolysed by NaOH, H_2O, and dil. HCl to NH_2Ph+HCNS, or to NH_3+PhNCS, has been studied. Traces of COS are always produced. HCNS is determined either by pptg. with $NiSO_4$ and C_5H_5N and determining excess of Ni, or by Volhard's method after decomp. NHPh·CS·NH_2 with NH_3–$AgNO_3$, and PhNCS by steam-distilling and heating the distillate with NH_3–$AgNO_3$. NHPh·CS·NH_2 and NaOEt heated in EtOH yield some Na_2S, but when heated dry give chiefly NaCNS. With Ac_2O, HCl, H_2O, or NaOH, NPhMe·CS·NH_2 yields (at varying rates) mainly NHPhMe+HCNS, whilst NHPh·CS·NHMe gives mainly NH_2Me + PhNCS. A. Li.

Identification of prontosil album, *p*-aminobenzenesulphonamide. F. Amelink (Pharm. Weekblad, 1938, **75**, 851—853).—*p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ gives characteristic crystals with the following reagents (sensitivity given in parentheses): $PtCl_4$–HCl; $PtCl_4$–NaBr (0·2%); picric (0·5%) and picrolonic acids (0·5%); Br (0·1%) [also given by *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_3H$ (I)]. The pine-shaving reaction (orange-yellow decolorised by NH_3 vapour) differentiates it from (I). S. C.

Microscopic identification of sulphanilamide. M. L. Yakowitz (J. Assoc. Off. Agric. Chem., 1938, **21**, 351).—The condensation products of *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ with PhCHO and cinnamon oil have characteristic cryst. forms, which are described. E. C. S.

Microscopical identification of sulphanilamide. —See B., 1938, 977.

***p*-γ-Phenylpropylaminobenzenesulphonamide.** —See B., 1938, 981.

Derivatives of *p*-aminobenzenesulphonanilide. I. G. L. Webster and L. D. Powers (J. Amer. Chem. Soc., 1938, **60**, 1553—1555).—*p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ (I) and $NO_2{\cdot}C_6H_4{\cdot}NH_2$ in hot $NPhMe_2$ give p-*acetamidobenzenesulphon*-o'-, m.p. 200—201°, -m'-, m.p. 236—237°, and -p'-*nitroanilide*, 237—238°, reduced by $FeSO_4$–NaOH to p-*acetamidobenzenesulphon*-o'- (II), m.p. 222—223°, -m'- (III), m.p. 217—218°, and -p'-*aminoanilide* (IV), m.p. 232°. $OH{\cdot}C_6H_4{\cdot}NH_2$ and (I) in hot $NPhMe_2$ or, better, aq. NaOAc at 75° give p-*acetamidobenzenesulphon*-o'-, m.p. 216—217°, -m'- (V), m.p. 217—218°, and -p'-*hydroxyanilide*, m.p. >260°. Hydrolysis by HCl–EtOH affords p-*aminobenzenesulphon*-m'-, m.p. 171—172°, and -p'-*nitro*-, m.p. 165—166°, -o'- m.p. 201—202°, -m'-, m.p. 176—177°, and -p'-*amino*-, m.p. 155—156° (*dihydrochloride*, decomp. from 200°), -o'-, m.p. 182—183°, -m'-, m.p. 195—196°, and -p'-*hydroxyanilide* (VI), m.p. 196—197°. With hot Ac_2O (IV)

gives p-*acetamidobenzenesulphon*-p′-*acetamidoanilide*, m.p. >260°. Diazotisation of (II), (III), and (IV) affords the *o-diazoimide*, decomp. 138—140°, (V), and (VI), respectively. (IV) is moderately effective against streptococcal infections in mice. R. S. C.

Influence of metal sulphates and vanadium pentoxide on sulphonation of α-naphthylamine.—See B., 1938, 884.

Coupling of methone with tetrazonium compounds. B. H. Iyer (J. Indian Inst. Sci., 1938, **21**, A, 65—75).—"Methone" (3-hydroxy-5 : 5-dimethyl-Δ²-*cyclo*hexenone) (I) couples with p-$C_6H_4R{\cdot}N_2Cl$ to yield the 2-p-*nitro*-, m.p. 215—216°, and 2-p-*acetamido-benzeneazo*- (II), m.p. 250—255°, -derivatives, respectively. (II) is hydrolysed (30% H_2SO_4) to the p-NH_2-compound (III), m.p. 225°, which when diazotised and coupled with (I) yields the corresponding p-*phenylenebisazo*-derivative, m.p. 275—280° (decomp.). Similarly, (I) coupled with tetrazotised benzidine, *o*-tolidine, and *o*-dianisidine yields *diphenylene*- (IV), m.p. 285° (decomp.), 3 : 3′-*dimethyldiphenylene*- (+$C_6H_4Me_2$), m.p. 263—265° (decomp.), and 3 : 3′-*dimethoxydiphenylene*-4 : 4′-*bisazo*-, m.p. 290—292° (decomp.), -derivatives of (I). Reduction of (IV) ($SnCl_2$–HCl) yields benzidine and 2-amino-5 : 5-dimethyldihydroresorcinol. The above dyes on silk and wool give yellow to orange shades fast to light and washing, but fugitive on cotton; (III) dyes leather light-fast yellow shades. With (I) (1 mol.) in EtOH, benzidine and *o*-tolidine yield respectively 3-(4′-*amino*)-, m.p. 217—218°, and 3-(4′-*amino*-3 : 3′-*dimethyl*)-p-*diphenylylamino*-5 : 5-*dimethyl*-Δ²-cyclo*hexenone*, m.p. 245°, whilst with 2 mols. of (I), NN′-*di*-(3-*keto*-5 : 5-*dimethyl*-Δ¹-cyclo*hexenyl*)-*benzidine*, m.p. 339—341° (decomp.), and -*o-tolidine*, m.p. 320° (decomp.), respectively, are formed.

J. D. R.

Hydrolysis of diazo-compounds, and their activity. A. A. Tscherkasski (Prom. Org. Chim., 1938, **5**, 322—325).—The readiness with which diazo-compounds undergo coupling parallels the degree of hydrolysis of the diazonium salt in aq. solution; this process consists of the steps R·NX:N ⇄ *syn*-R·N:NX → *syn*-R·N:N·OH (I). The relative concn. of (I) in aq. solutions, and hence the activity of a given diazo-compound, rises with increasing concn. of the latter, and with increasing negativity of R, for a series of compounds. R = *m*-C_6H_4Me and 3 : 5-$C_6H_3Me_2$ are exceptions to this rule. R. T.

Mechanism of the diazoaminobenzene conversion : addendum. H. V. Kidd (J. Org. Chem., 1938, **2**, 577; cf. A., 1937, II, 494). R. S. C

Preparation of 2 : 4-dinitro-6-*cyclo*hexylphenol.—See B., 1938, 888.

Thermal decomposition of diphenyl ether. E. Starokadomskaja (J. Appl. Chem. Russ., 1938, **11**, 646—651).—Decomp. of Ph_2O takes place only very slowly in glass vessels at <440°. R. T.

Isolation of guaiacol and pyrogallol 1 : 3-dimethyl ether from hardwood waste sulphite pulp liquor.—See B., 1938, 894.

Antisterility factor (vitamin-*E*). V. Synthetic antisterility factor. W. John and P. Günther (Z. physiol. Chem., 1938, **254**, 51—56).—2 : 3-Dimethyl-1 : 4-naphthaquinone was hydrogenated (colloidal Pt, AcOH) to 1 : 4-*dihydroxy*-2 : 3-*dimethyl*-5 : 6 : 7 : 8-*tetrahydronaphthalene*, m.p. 190—191°, absorption max. 288 mμ. (oxidised to the corresponding *quinone*, m.p. 121°), converted into the *mono*-, m.p. 78°, absorption max. 283 mμ., and *di*-n-*dodecyl ether*, m.p. 57°, absorption max. 296 mμ. The mono-ether is active in promoting fertility in female rats on a vitamin-*E*-free diet in doses of 60—80 mg., *i.e.*, it is 3—5% as active as α-tocopherol. The specificity of -*E* is discussed. F. O. H.

Synthetic substances with vitamin-*E* activity. F. von Werder and T. Moll (Z. physiol. Chem., 1938, **254**, 39—50).—The following were active in 100-mg. doses (increase in fertility of female rats on a vitamin-*E*-free diet) : duroquinone; 2 : 3-dimethylquinol; 1 : 4-*dihydroxy*-2 : 3-*dimethyl*-5 : 6 : 7 : 8-*tetrahydronaphthalene*, m.p. 190° [obtained by reduction (H_2, PtO_2, AcOH) of 2 : 3-dimethyl-1 : 4-naphthaquinone]; *mono*-, m.p. 81—82°, and *di*-n-*butyl*, m.p. 58°, *mono*-, m.p. 82°, and *di*-n-*hexyl*, m.p. 47°, *di*-n-*heptyl*, m.p. 56°, *mono*-, m.p. 88°, and *di*-n-*octyl*, m.p. 64°, *n*-dodecyl (*acetate*, m.p. 95—96°; *allophanate*, m.p. 223°), dihydrophytyl, benzyl (*acetate*, m.p. 118°) and *dihydrochaulmoogryl*, m.p. 89° (*acetate*, m.p. 60—61°), *ethers* of duroquinol; n-*hexyl*, m.p. 73°, and n-*dodecyl*, m.p. 81—82° (and its *acetate*, m.p. 47°, and *propionate*, m.p. 47°), *ethers* of ψ-cumoquinol. ψ-*Cumoquinol dihydrochaulmoogryl ether*, m.p. 61°, and *duroquinol* n-*dodecyl ether palmitate*, m.p. 86°, are active in 50-mg. doses whilst the n-*heptyl*, m.p. 82—83°, dibenzyl, and di-*n*-dodecyl ethers, and the n-*dodecyl ether propionate*, m.p. 80—80·5°, of duroquinol, and ψ-*cumoquinol di*-n-*dodecyl ether*, m.p. 47°, are inactive. No relationship between activity and structure of the above compounds is apparent.

F. O. H.

Hydroxyalkyl ethers of basic phenols. Antipneumococcic activity of some 8-quinolyl ethers. C. L. Butler and (Miss) A. G. Renfrew (J. Amer. Chem. Soc., 1938, **60**, 1582—1585).—p-$C_6H_4Me{\cdot}SO_3{\cdot}[CH_2]_2{\cdot}O{\cdot}CH_2Ph$ (I) and KOH–EtOH convert PhOH and $NHAc{\cdot}C_6H_4{\cdot}OH$ in good yield into *Ph*, b.p. 175°/3 mm., and p-*acetamidophenyl* β-*benzyloxyethyl ether*, m.p. 88°, respectively, the latter product with 11% HCl giving 80% of p-$NH_2{\cdot}C_6H_4{\cdot}O{\cdot}[CH_2]_2{\cdot}OH$, m.p. 73° ($Ac_2$ derivative, m.p. 128°). Similar alkylation and hydrolysis give good yields of 8-*quinolyl* β-*hydroxyethyl* (II), m.p. 83—84° (*hydrochloride*, m.p. 199—200°; *Ac* derivative, m.p. 153°), β-*hydroxyisopropyl*, m.p. 65° (*hydrochloride*; *Ac* derivative, m.p. 99°), and γ-*hydroxy*-n-*propyl ether*, m.p. 129° (*hydrochloride*; *Ac* derivative, an oil). p-$C_6H_4Me{\cdot}SO_3Et$ gives 8-ethoxyquinoline. p-$NH_2{\cdot}C_6H_4{\cdot}OH$ and (I) give a poor yield of p-β-benzyloxyethoxy-*NN*-di-β-benzyloxyethylaniline (*H sulphate*), hydrolysed to *N*-p-β-hydroxyethoxyphenylmorpholine (p-*toluenesulphonate*, amorphous; *acetate*, m.p. 118—119°). *m*-$NEt_2{\cdot}C_6H_4{\cdot}OH$ gives 62% of m-*diethylaminophenyl* β-*hydroxyethyl ether*, m.p. 41°, b.p. 148°/3 mm. (oily *Ac* derivative), by means of (I) or $CH_2Cl{\cdot}CH_2{\cdot}OH$

(III). (III) gives, however, only 19% of (II) and only 12·5% of OPh·$[CH_2]_2$·OH (cf. Rindfusz, A., 1919, i, 342). Failure of (III) to alkylate phenolic cinchona alkaloids smoothly is thus due to interference by the N. Alkylation reduces the pneumococcicidal activity and toxicity (mice) of 8-hydroxyquinoline, but the Et and OH·C_2H_4 ethers retain some activity. R. S. C.

Mobility of groups containing sulphur. V. D. T. Gibson (J.C.S., 1938, 983—986; cf. A., 1938, II, 135).—The rate of reaction of COPh·CH_2Ph (I) with $CH_2(SO_2Et)_2$, $CH_2Ac·CO_2Et$, and *p*-$C_6H_4Me·SO_2·CH_2·COMe$ (II) in presence of RCO_2Na is the greater the more alkaline is the solution, *i.e.*, R = Et>Me>H. Similarly, (I) and $(OMe·C_6H_3Cl·SO·)_2$ in presence of NaOAc give the mono-, whereas stronger alkali leads to the di-substitution product. The Brooker–Smiles reaction (A., 1926, 947) for various compounds is faster in C_5H_5N than in EtOH, indicating that conjugation of the lone pair of electrons on the entering S with the double linking of the enolised substitution product is a favouring, but not essential, factor in the reaction. The rates of reaction of Me and 2 : 5-$C_6H_3Cl_2$ camphorthiolsulphonates with $CH_2(COPh)_2$, $CH_2(CO_2Et)_2$, $CH_2(SO_2Et)_2$, and (II) in 85% $COMe_2$ + NaOAc (no reaction with HCO_2Na except in 80% C_5H_5N) show that S·$C_6H_3Cl_2$ enters more rapidly than SMe even when the possibility of conjugation is absent; the difference is least marked with (II) (development of conjugation with substitution). Previous results (*loc. cit.*) are supplemented.

p-$C_6H_4Me·SO_2·CH_2·NO_2$ is conveniently prepared from *p*-$C_6H_4Me·SO_2Na$ and $CH_2Br·NO_2$ in warm EtOH. R. S. C.

Reaction of α-naphthylamine-5-sulphonic acid with sodium hydrogen sulphite. I. M. Kogan and A. I. Nikolaeva (J. Appl. Chem. Russ., 1938, **11**, 652—659).—1 : 5-OH·$C_{10}H_6·SO_3Na$ is obtained in 85% yield from 1 : 5-$NH_2·C_{10}H_6·SO_3Na$ (1 mol.) and $NaHSO_3$ (20 mols.), at 100° and p_H 4·2. Smaller amounts of $NaHSO_3$ may be used provided this p_H is attained by addition of AcOH, $NaHSO_4$, or $Al_2(SO_4)_3$. R. T.

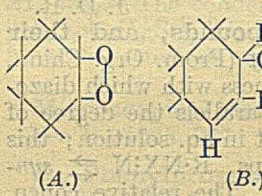
Bromination of optically active phenylmethyl- and phenylpropyl-carbinols. P. A. Levene and A. Rothen (Science, 1938, **87**, 510).—CHPhPr·OH (I) and higher homologues react predominantly with HBr (gas) without inversion. At 0° the reaction with (I) is practically instantaneous and the rotation of the CHPhPrBr (II) formed increases markedly with fall in temp. to −65°, with (I) and (II) rotating in the same direction. At temp. >−35°, the rotation of CHPhMeBr, formed from CHPhMe·OH under similar conditions, is opposite to that of the carbinol; the bromide shows a small increase in rotation at lower temp. At >−35° the rotation of the bromide changes sign, the reaction then proceeding without inversion. At each temp. two simultaneous reactions take place, one with and one without inversion; at lower temp., the latter predominates. L. S. T.

γγγ-Triphenylpropyl derivatives. C. B. Wooster, H. D. Segool, and T. T. Allan, jun. (J. Amer. Chem. Soc., 1938, **60**, 1666—1667).—The structure of γγγ-triphenyl-*n*-propyl alcohol (I) (A., 1934, 1095) is confirmed. It is obtained (m.p. 106·5—107·5°) from CPh_3Na and $(CH_2)_2O$ in liquid NH_3, is converted by HI into the known iodide, and by boiling Ac_2O into the *acetate*, m.p. 114—115° (also obtained from the iodide by AgOAc), whence it is regenerated by NaOH–aq. EtOH. BzCl gives (?) the benzoate, m.p. 134°. (I) is stable at 150—170° and gives no $CHPh_3$ with KNH_2 in liquid NH_3. R. S. C.

Magnesium derivative of bromopentamethylbenzene. H. Clement (Bull. Soc. chim., 1938, [v], **5**, 1011—1020).—A reprint of the paper by Savard and Hösögüt (A., 1938, II, 275). H. W.

Fission of alicyclic ethers. W. Hückel and H. Bretschneider (J. pr. Chem., 1938, [ii], **151**, 61—64).—PhOMe is hydrogenated (Ni, 170—180°/70 atm.) to hexahydroanisole (I); this gives a *compound*, m.p. —14°, with BF_3 which decomposes when warmed into a *methoxydimethyldodecahydrotriphenylene*, m.p. 159°. BzCl, (I), and $ZnCl_2$ in $CHCl_3$ yield MeCl, *cyclo*hexyl chloride and benzoate, and MeOBz. *l*-Menthol (II) is transformed by the successive action of $NaNH_2$ in PhMe and EtBr into *l*-menthyl Et ether (III), b.p. 87·5°/11 mm., $[\alpha]_D^{20}$ −100°. Addition of $HgEt_2$ or $PbEt_4$ in *cyclo*hexane (IV) to (III) + Na in (IV) yields (II) and 3-ethylmenthane (V). *d*-Neomenthyl Et ether, b.p. 84·5°/11 m.m., $[\alpha]_D^{20}$ +30·50°, similarly yields neomenthol and (V). Oxidation of (III) with CrO_2Cl_2 in CCl_4 gives *l*-menthone. H. W.

Autoxidation of hydrocarbons. *cyclo*Hexene peroxide, particularly its decomposition by alkalis. II. H. Hock and K. Gänicke (Ber., 1938, **71**, [*B*], 1430—1437).—*cyclo*Hexene peroxide (5 mols.) is disproportionated by aq. 1·5% NaOH to Δ^2-*cyclo*hexenol (I) (3 mols.) and acids (2 mols.) including CO_2, HCO_2H, AcOH, glutaric, adipic (II), and α-hydroxyadipic (III) acid, (II) and (III) appearing to be derived from the peroxide forms (*A*) and (*B*), respectively. The production of *trans-cyclo*hexane-1 : 2-diol, m.p. 103—104°, is established. Na_2CO_3 also causes the production of (I) but less acid is produced, the intermediate CO-compounds being resinified to a greater extent owing to the slower oxidation. The slow auto-decomp. of the peroxide in absence of acid or alkali probably proceeds similarly; the isolation of *p*-O:C_6H_4:O is of interest. H. W.



(*A.*) (*B.*)

Synthesis of compounds related to the antirachitic vitamins. **αβ-Di-Δ^1-*cyclo*hexenylethylene.** G. N. Burkhardt and N. C. Hindley (J.C.S., 1938, 987—991).—1-Acetylenyl*cyclo*hexanol (I), *cyclo*hexanone, and KOBu$^\gamma$ in boiling Et_2O give 70% of αβ-di-1-hydroxy*cyclo*hexylacetylene, m.p. 109°, the diacetate, m.p. 47°, b.p. 130—135°/0·5 mm., of which is unchanged by Cu at <180°, but with 1 mol. of H_2 in presence of Pd–$CaCO_3$ in MeOH gives αβ-*di*-1-*acetoxy*cyclo*hexylethylene* (II), b.p. 143—145°/1 mm. [hydrolysed to the $(OH)_2$-compound (III), m.p. 153°]. With Cu-bronze at 145—150°/30 mm. (II) gives AcOH and 80% of αβ-*di*-Δ^1-cyclo*hexenylethylene*, b.p. 110—115°/1 mm., m.p. 29°, unstable [absorption max. at

2595, 2690 (ε 42,600), and 2810 A.], converted at 255° in N_2 into an oily substance [absorption max. at 2600—2700 (ε 12,600) and 2800 A.], which with Se at 290—320° gives phenanthrene. With boiling, aq. $H_2C_2O_4$, $KHSO_4$ at 140°, I at 160°, or PBr_3 in C_5H_5N, (III) gives αβ-*di*cyclo*hexylethylene* 1 : 1′-*oxide*, b.p. 116—118°/10 mm. (*dibromide*, m.p. 96°), which absorbs 2 H_2 catalytically, probably with fission of the oxide ring. With $SOCl_2$ in Et_2O–C_5H_5N, (III) gives the *ester*, $[CH_2]_5>C<\begin{matrix}O\cdot SO\cdot O\\ CH=CH\end{matrix}>C<[CH_2]_5$, m.p. 83°, readily hydrolysed to (III). 2-Methyl*cyclo*hexanone (IV) gives, by Cook and Lawrence's method (A., 1938, II, 107), 2-methyl-1-acetenyl*cyclo*hexanol (V), b.p. 69—71°/10 mm., m.p. 57°, and stereoisomeric forms [one *form* (VI), m.p. 149°, obtained pure] of αβ-*di*-1-*hydroxy*-2-*methyl*cyclo*hexylacetylene*, obtained also from (IV), (V), and $NaNH_2$. (IV) and (V) or (I) and (IV) with $KOBu^{\gamma}$ give a crude product, containing (VI), indicating that the C_2H_2–ketone condensation is reversible. (IV) and (I) with $NaNH_2$ in Et_2O give a mixture of forms of α-1-*hydroxy*cyclo*hexyl*-β-1-*hydroxy*-2-*methyl*cyclo*hexylacetylene*, b.p. 186—189°/15 mm., whence one *form*, m.p. 97·5°, was obtained pure; (V) and *cyclo*hexanone give a poor yield of a similar mixture, also obtained from the Grignard derivative of (I). R. S. C.

Catalytic reduction of aryl alkyl ketones in presence of amines. Synthesis of ephedrine. P. Couturier (Compt. rend., 1938, **207**, 345—347).—COPhMe with Raney Ni in conc. NH_3–MeOH affords $CHPhMe\cdot NH_2$ (15%) and $CHPhMe\cdot OH$ (40%); *o*- and *p*-$OMe\cdot C_6H_4\cdot COMe$ react similarly but with difficulty. $CH_2Ph\cdot COMe$ (I) affords $CH_2Ph\cdot CHMe\cdot NH_2$ nearly quantitatively. *o*-$OH\cdot C_6H_4\cdot COEt$ (II) reacts like (I), but *m*-$OH\cdot C_6H_4\cdot COEt$ affords only *m*-$OH\cdot C_6H_4\cdot CHEt\cdot OH$, whilst the *p*-isomeride reacts very slowly; α-*o*- and -*p*-hydroxyphenylpropylamine [Bz_2 derivatives, m.p. 124—129° and 178—179° (decomp.), respectively] decompose when heated, or in cold HCl, to NH_3 and propenylphenols. (II) with a small excess of NH_2Et affords α-*o*-hydroxyphenylpropylethylamine, undistillable (Ac derivative, m.p. 108°). The reduction of $COPh\cdot COMe$ in presence of EtOH–Raney Ni containing NH_2Me affords *dl*-ephedrine because the CO adjacent to Ph reacts as in COPhMe whereas that adjacent to Me reacts as in (I) (cf. Skita *et al.*, A., 1933, 716). J. L. D.

Structure of nitrones. G. von Fodor and P. Csokán (Annalen, 1938, **535**, 284—290).—Absorption spectra indicate that products from RCHO and $OH\cdot CHAr\cdot CHMe\cdot NH\cdot OH$ are $O<\begin{matrix}CHAr\cdot CHMe\\ CHR=N\cdot OH\end{matrix}$, whereas those from $OAc\cdot CHAr\cdot CHMe\cdot NH\cdot OH$ have the nitrone structure, $OAc\cdot CHAr\cdot CHMe\cdot NO{:}CHR$. *o*-OH-aldehydes give products, $OH\cdot CHAr\cdot CHMe\cdot NO<\begin{matrix}CH_2\\ O\end{matrix}>C_6H_4$-*o*. R. S. C.

Phenanthrene series. XVII. Amino-alcohols derived from 9-hydroxy-1 : 2 : 3 : 4-tetrahydrophenanthrene. A. Burger (J. Amer. Chem. Soc., 1938, **60**, 1533—1536; cf. A., 1938, II, 321).—The *Me* ester, m.p. 42—43°, of β-4-methoxy-1-naphthoylpropionic acid in presence of 16% Pd–C in EtOH absorbs >2 H_2, giving esters of oily acids; it is not reduced by H_2–Cu–Cr_2O_3 at 100°, and at 156—210° gives (?) impure *methoxytetrahydronaphthylbutyrolactone*, m.p. 120—122°. The acid is reduced (modified Clemmensen) to γ-4-methoxy-1-naphthylbutyric acid in 50% yield. 1-*Keto*-9-*acetoxy*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (I), m.p. 159—160°, is obtained from the OH-compound, Ac_2O, and C_5H_5N. 1-Keto-9-methoxy-1 : 2 : 3 : 4-tetrahydrophenanthrene (II) and Br in Et_2O give the 2-*Br*-derivative, m.p. 174—175°, converted by $NHEt_2$ in boiling C_6H_6 into 2-diethylamino-1-keto-9-methoxy-1 : 2 : 3 : 4-tetrahydrophenanthrene (30% yield), m.p. (crude) 90—95° [*hydrochloride*, m.p. 128—138° (decomp.)], and 1-*hydroxy*-9-*methoxyphenanthrene*, m.p. 131—132° [*Ac* derivative, m.p. 154·5—155·5°, converted by 48% HBr–AcOH into 1 : 9-*dihydroxyphenanthrene*, m.p. 184—185° (evacuated tube; sinters at 181°) (*Ac_2* derivative, m.p. 154—155°; *Me_2 ether*, m.p. 113—114°)]. 2-*Bromo*-9-*hydroxy*-1-*keto*- (prep. by Br in $CHCl_3$–Et_2O), m.p. >330° (after decomp.), and 2-*piperidino*-1-*keto*-9-*methoxy*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (60% yield), m.p. 112—113° [*hydrochloride*, m.p. 258—261° (decomp.; sinters at 246°)], unstable in O_2, are similarly prepared. Hydrogenation of the NH_2-ketones could not be arrested at the alcohol stage. With paraformaldehyde and the appropriate *sec.* amine in *iso*-$C_5H_{11}\cdot OH$ (I) and (II) yield 20—70% of 1-keto-9-methoxy-2-1′ : 2′ : 3′ : 4′-tetrahydro*iso*quinolino- [*hydrochloride*, m.p. 176—177° (decomp.); *perchlorate*, m.p. 135—150° (decomp.)], and -2-*diethylamino-methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 83° (*hydrochloride*, m.p. 160—161°), 1-*keto*-9-*acetoxy*-2-1′ : 2′ : 3′ : 4′-*tetrahydro*isoquinolino-, m.p. 144° [*hydrochloride*, m.p. 167—168° (decomp.)], and 2-diethylamino-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene (*hydrochloride*, m.p. 146—147°), hydrogenated (PtO_2) in MeOH to 1-*hydroxy*-9-*methoxy*-, m.p. 137—138° [*hydrochloride*, m.p. 211°; *Ac* derivative *hydrochloride*, m.p. 200—201° (decomp.)], -9-*acetoxy*- [*hydrochloride*, m.p. 234—235° (decomp.)], and -9-*hydroxy*-2-1′ : 2′ : 3′ : 4′-*tetrahydro*isoquinolinomethyl-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 213° (decomp.; in vac.) [*hydrochloride*, m.p. 225—227° (decomp.)], and 1-hydroxy-9-methoxy-2-diethylaminomethyl-1 : 2 : 3 : 4-tetrahydrophenanthrene [*hydrochloride*, m.p. 190° (decomp.); *Ac* derivative *hydrochloride*, m.p. 165—166° (decomp.)]. The *oxime*, m.p. 174—175°, of (II) with Al–Hg in moist Et_2O gives 1-amino-9-methoxy-1 : 2 : 3 : 4-tetrahydrophenanthrene [*hydrochloride*, m.p. 291° (decomp.; in vac.)]. R. S. C.

Reactions in sunlight. I. [Acetophenone and aromatic hydrocarbons.] E. Oliveri-Mandalà. **II. [Aromatic hydrocarbons.]** E. Oliveri-Mandalà, G. Caronna, and E. Deleo (Gazzetta, 1938, **68**, 324—327, 327—331).—I. Acenaphthene and COPhMe (I) in sunlight (August, Palermo) give a *product*, $C_{20}H_{18}O$ [*phenylacenaphthylmethylcarbinol* (?)], m.p. 98—99°, and acenaphthylene. CH_2Ph_2 and (I) give a *product*, $C_{34}H_{30}O$ [*phenyl-ααββ-tetraphenylethylmethylcarbinol* (?)], m.p. 222—223°, and the pinacol of (I).

II. CH_2Ph_2 in C_6H_6 in sunlight (3 months) gives

$(CHPh_2)_2$. Fluorene similarly gives bisdiphenylene-ethane. Acenaphthene is unchanged, but in presence of Bz_2 yields a *product*, $C_{26}H_{20}O_2$, m.p. 234°.

E. W. W.

Micro-determination of cholesterol by a new colour reaction. S. Ohyama (J. Biochem. Japan, 1938, **27**, 395—404).—The substance (in $CHCl_3$) is treated with salicylaldehyde (in $CHCl_3$), H_2SO_4, and H_2O, the mixture well shaken for 2 hr., and the $CHCl_3$ layer compared with suitable standards. The reddish-violet colour produced is stable and the error for samples containing 0·3—1·2 mg. of cholesterol is <5%. The colours with other aldehydes etc. are studied. F. O. H.

Purification of crude sitosterol. P. Lobert (Bull. Soc. Chim. biol., 1938, **20**, 766—806).—Pure sitosterol (I) cannot be obtained from the unsaponifiable matter of oil of maize or barley rootlets by crystallisation. M.p. and $[\alpha]_D$ alone cannot be used as criteria of purity; spectrographic examination must also be made. When adsorption on Al_2O_3 + animal C (the column being examined in Wood's light) followed by acetylation and recrystallisation from EtOH is applied pure (I), m.p. 140·8—141°, $[\alpha]_D$ −38·8° in $CHCl_3$ (acetate, m.p. 140·2—140·4°, $[\alpha]_D$ −43·42° in $CHCl_3$), is obtained. In addition to (I), maize oil contains ergosterol (II) and a sterol having absorption max. at 2530, 2417, and 2354 A. and barley oil also contains (II), a sterol with absorption bands at 2530, 2417, and 2352 A., another with bands at 2707 A., and another with bands at 3365, 3245, and 3109 A. W. McC.

Sterols. XXXV. Carbinols from stallions' urine. R. E. Marker, E. J. Lawson, E. Rohrmann, and E. L. Wittle. **XXXVII. Uranediol from mares' pregnancy urine.** R. E. Marker, E. Rohrmann, and E. L. Wittle. **XXXVIII. Pregnenediol in mares' pregnancy urine. Its conversion into progesterone.** R. E. Marker and E. Rohrmann (J. Amer. Chem. Soc., 1938, **60**, 1555—1558, 1561—1564, 1655—1567; cf. A., 1938, II, 322).—XXXV. The neutral fraction from stallions' urine yields, besides a very little ketone (by Girard's reagent), carbinols from which digitonin ppts. β-*equistanol* (I), $C_{30}H_{54}O$, m.p. 133° (*acetate*, m.p. 124°; stable to Br; largely unaffected by Na in xylene), oxidised by CrO_3 in 90% AcOH to β-*equistanone*, $C_{30}H_{52}O$, m.p. 115°. (I) belongs to the *allo*-series, is probably a phytosterol or phytosterol derivative derived from the food, and may be identical with dihydro-α-tritisterol (Karrer *et al.*, *ibid.*, 13). The mother-liquors from which (I) is pptd. probably contain α-equistanol, since treatment with Na–xylene leads to more (I); they then yield also an allo-*triol*, $C_{21}H_{36}O_3$, m.p. 295° (*triacetate*, m.p. 140—145°), and an allo-*tetraol* (II), $C_{21}H_{36}O_4$, m.p. 290—295°, both giving insol. digitonides and thus being 3(β)-*allo*-compounds; their 3(α)-epimerides must have occurred in the urine. (II) may be *allo*pregnane-3(β) : 11 : 20 : 21-tetraol derived from corticosterone. The epimerised carbinol mixture, not pptd. by digitonin, gives, when oxidised, uranetrione, m.p. 247°. Stallions' urine thus probably contains the same uranetriol as does mares' pregnancy urine, and this triol is probably derived from the adrenal cortex or hormone of unknown function. β-Sitosterol and cholesterol are absent from stallions' urine.

XXXVII. The carbinol fraction of mares' pregnancy urine, freed from ketones, yields by digitonin *urane*-3(β) : 11-*diol* (III) (5 mg. per gal.), m.p. 210° (*diacetate*, m.p. 160°), largely unchanged by Na–xylene and thus normal at $C_{(5)}$, oxidised to uranedione, m.p. 177·5° [only *mono-semicarbazone*, m.p. 245° (decomp.), and -2 : 4-*dinitrophenylhydrazone*, m.p. 200° (decomp.)]. Hydrogenation (PtO_2) of the dione in AcOH affects only $C_{(3)}$, since Na–xylene destroys the product. Uranetriol and (III) are probably related to constituents of the adrenal cortex or to an unknown hormone. Examination of the mother-liquors from (III) indicates absence of other substances having a β-OH at $C_{(3)}$ and the coprostane structure at $C_{(5)}$.

XXXVIII. The carbinol fraction from mares' pregnancy urine also yields (after epimerisation) *allo*-pregnane-3(β) : 20(α)-diol (IV), m.p. 216° (oxidised to *allo*pregnanedione), *pregnene*-3(β) : 20(α)-*diol* (V), m.p. 172—176°, (I), and, possibly, uranediol. (V) absorbs Br to give a substance converted by CrO_3–AcOH followed by Zn dust into progesterone, obtained directly by heating with Cu at 230°/20 mm. and then subliming at 125°/high vac. With H_2–PtO_2 at 3 atm. in EtOH (V) yields (IV). Cholesterol is absent from mare's pregnancy urine. R. S. C.

Dialkylaminoalkyl esters of phenyl-substituted fatty acids.—See B., 1938, 981.

Salts of nitro-compounds. III. Reaction of the silver salt of phenylnitroacetonitrile with diphenylbromomethane. R. L. Shriner and G. B. Brown (J. Org. Chem., 1938, **2**, 560—568; cf. A., 1938, II, 88).—CN·CPh:NO·OAg and $CHPh_2Br$ in C_6H_6 at <20° give up to 18% of the *C*-alkylation product, α-nitro-αββ-triphenylpropionitrile (I) (cf. Wieland *et al.*, A., 1933, 1163), and 50% of the *O*-alkylation product, CN·CPh:NO·O·$CHPh_2$, which is not isolated as such but is indicated by its decomp. products, $COPh_2$ and CN·CPh:N·OH; $CHPh_2$·OH and $(CHPh_2)_2O$ (produced by hydrolysis of $CHPh_2Br$) and a (?) polymeride, m.p. 245—249° (after decomp.), of COPh·CN were also isolated. The structure of (I) follows from (*a*) its conversion by KOH–EtOH into KNO_2 and triphenylacrylonitrile (II), m.p. 165—166°, which is obtained also by HI–red P in AcOH and from $COPh_2$, CH_2Ph·CN, and $NaNH_2$, and (*b*) its hydrogenation (PtO_2) in AcOH to αββ-triphenylpropionitrile (III), m.p. 101·5—102° (obtained alone in EtOH), and acet-βγγ-triphenylpropylamide (IV), m.p. 143·5—144°. Conc. HCl at 170° hydrolyses (III) to the amide, also prepared from the acid (prep. from CHPhPr·CHBr·CO_2H, C_6H_6, and $AlCl_3$ at 60°). H_2–Raney Ni reduction of (III) at 120°/2500 lb. and acetylation give (IV). Pyrolysis of (I) at 160° gives NO_2, (II), C_2Ph_4, $COPh_2$, and BzOH; there is no evidence of dissociation of (I) into radicals; HI gives no CH_2Ph_2 and it is unaffected by O_2 in hot C_6H_6.

R. S. C.

Isomeric triazocinnamic acids and related compounds. K. A. N. Rao and P. R. Venkataraman (J. Indian Chem. Soc., 1938, **15**, 194—204).—Triazo-cinnamic and -benzoic acids are synthesised

from the diazotised NH_2-acids and NaN_3. o-*Triazocinnamic acid* (I), m.p. 186° (decomp.) [*dibromide*, m.p. 165—166° (decomp.)], is reduced by $(NH_4)_2S$ to the NH_2-acid, by Sn + HCl to carbostyril, and by Na–Hg to dihydrocarbostyril; m- (II), m.p. 165° (decomp.) (*dibromide*, m.p. 157°), and p-*triazocinnamic acid* (III), decomp. 195—196° (slight decomp. 160°) (*dibromide*, m.p. 140—141°), with Sn + HCl yield $NH_2{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO_2H$, and with Na–Hg, $NH_2{\cdot}C_6H_4{\cdot}[CH_2]_2{\cdot}CO_2H$. All three are oxidised (cold $KMnO_4$) to the $N_3{\cdot}C_6H_4{\cdot}CO_2H$. An *acid*, decomp. 268—270°, is a by-product in the prep. of (II). (III) and o-, m.p. 143—144°, m-, m.p. 160°, and p-, m.p. 180—181°, *-triazobenzoic acids* with conc. H_2SO_4 evolve $\frac{2}{3}$ of their N, whilst (I) and (II) evolve about $\frac{1}{2}$. The *p*-acid is the least stable of the cinnamic series, but the most stable of the benzoic series.

$Ph{\cdot}[CHBr]_2{\cdot}CO_2H$ with NaN_3 in EtOH–C_5H_5N yields an acidic *compound* (containing N but not the N_3 group), m.p. 217° (*dibromide*, m.p. 176°), and a little CHPh:CHBr. $Ph{\cdot}[CHBr]_2{\cdot}CO_2Me$ with NaN_3 in MeOH, followed by C_5H_5N, yields *Me* α- or β-*triazocinnamate* (oil). A. Li.

Condensation of aldehydes with malonic acid in presence of organic bases. X. Condensation of resorcylaldehyde. K. C. Pandya and T. S. Sodhi (Proc. Indian Acad. Sci., 1938, **7**, **A**, 381—383; cf. A., 1935, 353; 1937, II, 340).—Resorcylaldehyde (I) (1 mol.) with $CH_2(CO_2H)_2$ (1 mol.) and C_5H_5N (0·15 mol.) at 100° affords umbelliferone (II) (43%). The yield is diminished without C_5H_5N or in presence of piperidine. (I) with NaOAc and Ac_2O at 160—180° affords 7-acetoxycoumarin, hydrolysed (10% KOH) to umbellic acid (III). (I), $CH_2(CO_2H)_2$, and AcOH at 100° afford (III) (54%). Robinson and Shinoda's method (A., 1925, i, 1301) of condensation gave no isolable product. J. L. D.

Condensation of aldehydes with amides. I. Salicylaldehyde. K. C. Pandya and T. S. Sodhi. **II. Cinnamaldehyde.** R. K. Mehra and K. C. Pandya (Proc. Indian Acad. Sci., 1938, **7**, **A**, 361—368, 376—380).—I. o-$OH{\cdot}C_6H_4{\cdot}CHO$ (I) with NH_2Bz alone or with a trace of lutidine at 130—140° affords only the α-form of salicylidenebenzamide, whereas in the presence of anhyd. NaOAc, C_5H_5N, or piperidine, a mixture of the α- and β-forms results (cf. J.C.S., 1908, **93**, 1933). $R{\cdot}CO{\cdot}NH_2$ (R = H, Me, Et, CH_2Ph) and (I) similarly afford salicylidene-formamide, -acetamide, decomp. 160—170° (lit. 150°), *-propionamide*, decomp. 190—195°, and *-phenylacetamide*, m.p. 110—114°, respectively. The presence of the org. base gives a better yield of a purer product at a lower temp.

II (cf. J.C.S., 1921, **119**, 298). CHPh:CH·CHO (I) (1 mol.) with $CH_2Ph{\cdot}CO{\cdot}NH_2$ (2 mols.) at 130—140° affords cinnamylidenebisphenylacetamide in 18·7% yield, which is not improved by catalytic org. bases. (I) (1 mol.) with NH_2Ac (4 mols.) and C_5H_5N (0·15 mol.) at 120—125° affords *cinnamylidenebisacetamide* (52%), m.p. 234°. (I) (1 mol.) with NH_2Bz (2 mols.) at 110—140° affords *cinnamylidenebisbenzamide* (50·5%), m.p. 250°; C_5H_5N (0·15 mol.) improves the yield to 55%. Similarly, (I) and $EtCO{\cdot}NH_2$ at 100° afford *cinnamylidenebispropionamide* (46%), m.p. 220—221°, and $CH_2Ph{\cdot}CH_2{\cdot}CHO$ with NH_2Bz at 140—150° (no C_5H_5N) affords *γ-phenylpropylidenebisbenzamide* (39%), m.p. 244—245°. J. L. D.

Derivatives of β-amino-α-hydroxy-α-phenylpropionic acid. II. B. Ciocca and E. Broggi (Annali Chim. Appl., 1938, **28**, 230—238).—The following esters of β-dimethylamino-α-hydroxy-α-phenylpropionic acid were prepared (cf. A., 1936, 1377); *Et*, b.p. 120°/1 mm., *Bu*, b.p. 138—140°/0·8 mm., *Bu*$^{\beta}$, b.p. 140°/1·5 mm., and iso*amyl*, b.p. 140°/0·8 mm. The pharmacological properties of the corresponding *Ac* derivative *hydrochlorides*, m.p. 128°, 138°, 155°, and 135—136°, respectively, were studied in rabbits. The depressor action increases with increase in length of the mol. of esterifying alcohol with straight-chain alcohols but is considerably diminished with branched-chain alcohols. F. O. H.

Synthetic and hydrolytic experiments with chymotrypsin. M. Bergmann and J. S. Fruton (J. Biol. Chem., 1938, **124**, 321—329).—Cryst. chymotrypsin effects the synthesis of *benzoyl-l-tyrosylglycineanilide*, m.p. 226°, from benzoyl-*l*-tyrosine and glycineanilide at 37° and p_H 7·6, whilst under the same conditions no synthesis of benzoyl-*l*-tyrosineanilide from benzoyltyrosine and NH_2Ph occurs. Chymotrypsin does not hydrolyse *benzoyl*-l-*tyrosineamide*, m.p. 198°, $[\alpha]_D^{23}$ —24·6°, or *benzoyl*-d-, m.p. 215°, $[\alpha]_D^{22}$ +10·4°, or -dl-*tyrosylglycineamide*, whilst *benzoyl*-l-*tyrosylglycineamide*, m.p. 216°, $[\alpha]_D^{23}$ —10·2°, is split; the *dl*-compound is probably a very stable racemate. Benzoyl-*dl*-tyrosylglycineamide is stable to papain–HCN whilst the *l*-isomeride is completely hydrolysed at one peptide linking, and a similar effect, although not so marked, is observed with *l*- and *dl*-benzoylalanineamide. Benzoyl-*d*-tyrosylglycineamide is not attacked by papain and the *d*-tyrosyl residue has the same inhibitory influence as the *d*-amino-acid residue on the hydrolysis of carbobenzyloxy-*d*-leucylglycylglycine and on the enzymic anilide formation from benzoyl-*d*-phenylalanylglycine and from acetyl-*d*-phenylalanyl-*l*-glutamic acid. The following compounds were prepared and, in some cases, examined for chymotryptic and papain-hydrolysis. *Benzoyl-dehydrotyrosineamide*, m.p. 230°, dl-, m.p. 238°, and -d-*tyrosineamide*, m.p. 198—200°, $[\alpha]_D^{23}$ +24·4°, -d-*tyrosine Me ester*, m.p. 150—151°, -dl-*tyrosylglycine Et ester*, m.p. 157—158°, -d-, m.p. ~250°, and -l-*tyrosine hydrazide*, m.p. ~255°, -d-, m.p. 184°, and -l-*tyrosylglycine Et ester*, m.p. 184—185°, *-dehydrophenyl-alanineamide*, m.p. 164°, and *-alanylglycine Et ester*, m.p. 140°, -dl-*phenylalanylglycine-amide*, m.p. 179°, and *Et ester*, m.p. 162°. All [α] are in MeOH. T. F. D.

Enzymic synthesis of peptide linkings. M. Bergmann and H. Fraenkel-Conrat [with D. G. Doherty] (J. Biol. Chem., 1938, **124**, 1—6).—In presence of papain–cysteine (cf. A., 1938, III, 393), a peptide linking is formed between benzoyl-*l*-leucine and l-*leucineanilide acetate*, m.p. 121° (obtained by hydrogenating carbobenzyloxy-*l*-leucineanilide in MeOH–AcOH), which give *benzoyl*-l-*leucyl*-l-*leucineanilide*, m.p. 203°, $[\alpha]_D^{24}$ —44·5° in AcOH, also obtained from benzoyl-*l*-leucine azide (A., 1936, 596) and

l-leucineanilide (from its acetate, above). With papain–cysteine, *glycineanilide acetate*, m.p. 136—137° (from carbobenzyloxyglycineanilide, hydrogenated in MeOH–AcOH), and benzoyl-*l*-leucine give, by a new type of enzymic reaction, in which the last replaces the glycine residue, *benzoyl*-l-*leucineanilide*, m.p. 212·5°. Further peptide syntheses by papain–cysteine are the conversion, in presence of NH_2Ph, of acetyldehydrophenylalanylglutamic acid into its *anilide* (I), m.p. 204°, $[\alpha]_D^{22}$ —108·2° in C_5H_5N, and of acetyl-*l*-phenylalanyl-*l*-glutamic acid into its *anilide* (II), m.p. 230°, $[\alpha]_D^{22}$ —25·8° in C_5H_5N. Hydrogenation (Pd–MeOH–AcOH) of (I) gives a mixture of stereoisomeric *acetylphenylalanyl*-l-*glutamic acid anilides*, m.p. 231°, $[\alpha]_D^{22}$ —113·9° (+0·5H_2O), and —27·1° (anhyd.), both in C_5H_5N; the rotation of the last suggests its identity with (II). *p*-Toluenesulphonylglycine with NH_2Ph in presence of papain–cysteine and a citrate buffer slowly gives its *anilide*, m.p. 156—157°; thus enzymic synthesis is apparently possible when the CO·NH group of the substrate is replaced by SO_2·NH. E. W. W.

Asymmetric course of the enzymic synthesis of peptide linkings. M. Bergmann and O. K. Behrens [with D. G. Doherty] (J. Biol. Chem., 1938, **124**, 7—10).—Acetamidocinnamic acid azlactone and glycine in $COMe_2$ and 0·5N-NaOH give *acetyldehydrophenylalanylglycine* (*acetamidocinnamylglycine*), m.p. 194—195°, hydrogenated (Pd in MeOH–AcOH) to *acetyl*-dl-*phenylalanylglycine*, m.p. 178°. With this, papain–cysteine and NH_2Ph (citrate buffer) react only with the *l*-component, forming *acetyl*-l-*phenylalanylglycineanilide*, m.p. 208—209°, $[\alpha]_D^{24}$ +21·3° in AcOH. Acetamidocinnamylglycine under similar conditions gives its *anilide*, m.p. 207—212°, α 0°. E. W. W.

Synthesis of umbellularic acid. P. C. Guha and M. S. Muthanna (Current Sci., 1938, **6**, 605).—Et α′-carbethoxy-α-*iso*propylsuccinate is converted into the α′-*Br*-derivative, b.p. 155—156°/3 mm., which with $NPhEt_2$ yields Et carbethoxy*iso*propylfumarate, b.p. 135—140°/3 mm. This readily adds 1 mol. of CH_2N_2 to yield *Et* 2-iso*propyl*cyclo*propane*-1 : 1 : 2-*tricarboxylate*, b.p. 148—150°/3 mm., hydrolysed and decarboxylated by boiling 18% HCl to *trans*-umbellularic acid, m.p. 190—192°. L. S. T.

Shikimic acid and derivatives. II. Ammonium and substituted ammonium salts. H. H. Lei (J. Amer. Pharm. Assoc., 1938, **27**, 393—396; cf. A., 1938, II, 25).—The NH_4, NH_2Me, m.p. 163—164°, *NH_2·CH_2Ph*, m.p. 195—196°, *ephedrine*, m.p. 162—163°, NH_2Ph, new m.p. 194—195°, o-*toluidine*, m.p. 178—180°, N_2H_4, m.p. 147—148°, C_5H_5N, m.p. 184—185°, *quinine*, m.p. 221—222°, *quinidine*, m.p. 224—226°, *codeine*, m.p. 173—174° (sinters at 160°), and *strychnine*, m.p. 234—236° (sinters at 154°), salts are described (cf. Chen, A., 1930, 259). The *n*-propyl- and -amyl-amine salts were obtained as syrups. F. O. H.

Aminobenzoic esters of propanetriol [glycerol]. R. Jacquemain and (Mlle.) G. Devillers (Compt. rend., 1938, **207**, 241—243).—The appropriate nitrobenzoates are reduced according to the technique described previously (cf. A., 1938, II, 255). The following are described: *glyceryl* α-*benzoate* βγ-*di*-o-*aminobenzoate*, m.p. 96° [*hydrochloride*, m.p. 173—176°; *hydrobromide*, m.p. 200° (decomp.)], α-*benzoate* βγ-*di*-m-*aminobenzoate*, m.p. 88°, α-*benzoate* βγ-*di*-p-*aminobenzoate*, m.p. 138° [*hydrochloride*, m.p. 214° (decomp.); *hydrobromide*, m.p. 210° (decomp.); *picrate*, decomp. ~117°], αβγ-*tri*-o-*aminobenzoate*, m.p. 105° [*hydrochloride*, decomp. ~150°; *hydrobromide*, m.p. 188°; *hydriodide*, unstable; *picrate*, m.p. 102°], α-o-*aminobenzoate* βγ-*di*-p-*aminobenzoate*, m.p. 133°, βγ-*di*-o-*aminobenzoate* α-m-*aminobenzoate*, m.p. 115°, αβγ-*tri*-m-*aminobenzoate*, m.p. 82°, α-m-*aminobenzoate* βγ-*di*-p-*aminobenzoate*, m.p. 171° [*hydrochloride*, m.p. 200° (decomp.)], βγ-*di*-o-*aminobenzoate* α-p-*aminobenzoate*, m.p. 109° [*hydrochloride*, m.p. 175—180° (decomp.); *hydrobromide*, decomp. ~200°; *hydriodide*, decomp. ~150°], and αβγ-*tri*-p-*aminobenzoate*, m.p. 168°. J. L. D.

Retardation of chemical reactions. VIII. Darkening of alkaline solutions of sodium salicylate.—See B., 1938, 977.

Esters of *p*-hydroxybenzoic acid as preservatives.—See B., 1938, 884.

Cyclisation of phenyl-1-naphthylmethane-*o*-carboxylic [*o*-α-naphthylmethylbenzoic] acid according to Fieser and Hershberg. R. Scholl and K. Meyer (Ber., 1938, **71**, [*B*], 1482).—The cyclisation by small amounts of $ZnCl_2$ (Fieser *et al.*, A., 1937, II, 333) appears identical in principle with the use of small amounts of HI or HCl in boiling Ac_2O. H. W.

α- and β-Naphthoic acids. A. Wahl (Rev. Gén. Mat. Col., 1938, **42**, 285—286).—Partly a more detailed account of work previously reviewed (A., 1938, II, 143). Comparison of a series of pyrazolone dyes indicates that derivatives of α-naphthylpyrazolone show the best fastness to light and washing. 5 : 1-NH_2·$C_{10}H_6$·CO_2H, obtained by nitration of α-$C_{10}H_7$·CO_2H (I) and reduction of the 5-NO_2-derivative (Me ester, m.p. 66°), is converted (diazo-method) into 5 : 1-$C_{10}H_6Br$·CO_2H, m.p. 264—265° (Maquenne block), identical with the product obtained by direct bromination of (I). Corbellini and Barbaro's dibromoanthanthrone (A., 1933, 1054) is shown as follows to be the 2 : 7-derivative. *Me* 5-*bromo*-1-*naphthoate*, b.p. 210—212°/20 mm., m.p. 66°, with HNO_3 (*d* 1·45) at 15—20° yields the 8-*NO_2-derivative*, m.p. 125—126°, reduction (Sn + HCl) then giving 5-bromonaphthastyryl. This is converted into 2 : 7-dibromoanthanthrone which has tinctorial properties similar to those of the commercial product obtained by bromination of anthanthrone. R. J. W. R.

Carboxylation of alkali-metal salts of phenols.—See B., 1938, 888.

Hydroxy-acids and unsaturated acids of the *cyclo*pentanophenanthrene series.—See B., 1938, 982.

Determination of cholic acid. I. Fructose–hydrochloric acid method. Y. Ohyama (J. Biochem. Japan, 1938, **27**, 351—362).—The sample (≡ 0·1—1·0 mg. of cholic acid) is mixed with fructose (approx. equal to wt. of cholic acid) in EtOH,

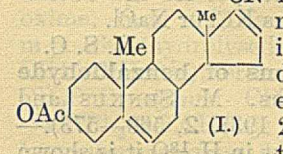
evaporated, and heated at 40° with conc. HCl (5 c.c.) for 20 min.; the red colour produced is compared with suitable standards or determined photometrically. The reaction is positive for tauro- and glyco-cholic and 7 : 12-dihydroxy-3-ketocholanic acids but negative for cholesterol and some derivatives of cholic acid. The application of the method to blood, bile, and liver is described. F. O. H.

Conversion of 7 : 12-dihydroxy-3-ketocholanic acid into cholic acid in the toad. T. S. Sihn (J. Biochem. Japan, 1938, **27**, 425—431).—Me triacetylcholate with N-KOH in MeOH yields 3-*hydroxy*-7 : 12-*diacetoxycholanic acid*, m.p. 203—204°, oxidised (CrO_3 in AcOH) to 3-*keto*-7 : 12-*diacetoxycholanic acid*, m.p. 197—198°, which is hydrolysed to 7 : 12-*dihydroxy*-3-*ketocholanic acid* (I), m.p. 121—123°. Subcutaneous injection of the Na salt of (I) in 0·9% NaCl into toads is followed by urinary excretion of cholic acid. The action of (I) in hæmolysing erythrocytes (ox, goat) and accelerating hydrolysis of fats by lipase is < that of cholic acid. F. O. H.

Colour reaction of deoxycholic acid. K. Kaziro and T. Shimada (Z. physiol. Chem., 1938, **254**, 57—60).—The acid, PhCHO, and 75% H_2SO_4 give a red colour, changed to green by addition of AcOH. The reaction is sp. for deoxycholic acid. F. O. H.

Systematic degradation of chenodeoxycholic acid. T. Ishihara (J. Biochem. Japan, 1938, **27**, 265—277).—Me chenodeoxycholate with MgMeI gives the corresponding dimethylcarbinol *derivative*, m.p. 178—179°, the *diacetate* (I), m.p. 153—157°, of which is oxidised (CrO_3) to the Ac_2 derivative, m.p. 213—214°, of norchenodeoxycholic acid [*Me* ester (+0·5H_2O), m.p. 85—87°], which, similarly treated, yields the dimethylcarbinol *derivative*, m.p. 182—183° [*diacetate* (II), m.p. 169—170°], and Ac_2 derivative, m.p. 226—227°, of *bisnorchenodeoxycholic acid*, $C_{22}H_{36}O_4$, m.p. 269—270°, $[\alpha]_D^{22}$ −18·88° in EtOH [*Me* ester (III), m.p. 173—174°]. Oxidation (CrO_3) of (II) also gives a *ketone diacetate*, m.p. 189—190°, hydrolysed to a *ketone*, $C_{24}H_{40}O_3$, H_2O, m.p. 160—161° (sinters at 85°), $[\alpha]_D^{22}$ +3·46° in EtOH. The *diethylcarbinol* (IV), m.p. 160—161°, from (III) and MgEtBr, acetylated and oxidised, affords 3 : 7-*dihydroxyætiocholane*-17-*carboxylic acid*, $C_{20}H_{32}O_4$, m.p. 165—166°. Oxidation (CrO_3) of (I) also gives a *ketone diacetate*, m.p. 132—133°, hydrolysed to a *ketone*, $C_{25}H_{42}O_3$, m.p. 175—176°, $[\alpha]_D^{22}$ +9·01° in EtOH. 7-*Hydroxypregnan*-3-*ol*-20-*one* (+0·5H_2O), m.p. 170—172° (*diacetate semicarbazone*, m.p. 271—272°), is also formed during the oxidation of (IV) (as Ac derivative). F. O. H.

Transformation of dehydroandrosterone into 3-hydroxy-Δ⁵-ætiocholenic acid; linking of the androsterone with the corticosterone group. A. Butenandt and J. Schmidt-Thomé (Ber., 1938, **71**, [*B*], 1487—1492; cf. A., 1938, II, 236).—Dehydroandrosterone is converted by KCN in boiling EtOH–AcOH into the corresponding *cyanohydrin*, decomp. between about 210° and 250° according to the method of crystallisation and rapidity of heating (*diacetate*, m.p. 207—208°). Simliarly dehydroandrosterone acetate affords the two epimeric *dehydroandrosterone cyanohydrin* 3-*acetates*, (*A*), prisms, m.p. 195° (decomp.), or needles, m.p. 195° (decomp.) after softening at about 185° (temp. of decomp. depends greatly on external factors), and (*B*), m.p. 203—206° (decomp.). The mixture of epimerides is dehydrated by $POCl_3$ in boiling C_5H_5N to 17-*cyano*-3-*acetoxy*-Δ$^{5:16}$-*androstadiene* (I), m.p. 210°, hydrolysed by NaOH–H_2O–EtOH at 180° to 3-*hydroxy*-Δ$^{5:16}$-*ætiocholadiene*-17-*carboxylic acid* (II), m.p. 256° (decomp.) [*acetate*, m.p. 253—254° (decomp.) after softening at about 230°]. Partial hydrogenation of (II) leads to 3-hydroxy-Δ⁵-ætiocholenic acid. H. W.



(I.)

Condensation of malonanilic acid with aromatic aldehydes. R. K. Mehra and K. C. Pandya (Proc. Indian Acad. Sci., 1938, **7**, **A**, 369—375).—Malonanilic acid (I), piperonal, and a C_5H_5N–piperidine mixture give, contrary to Ahluwalia *et al.* (cf. A., 1931, 1155), only piperonylidenemalonanilic acid (II) and no 3 : 4-methylenedioxycinnamanilide (III). At 60—70° and with longer heating, some (III) is formed. With C_5H_5N as condensing agent at 60°, only (II) is formed, but at 100° using either C_5H_5N or piperidine, (III) is the main product. Equimol. amounts of (I) and *o*-OH·C_6H_4·CHO at 100—104° afford coumarin-3-carboxylanilide in best yield when piperidine (0·15 mol.) is the condensing agent. Similarly, *m*- and *p*-OH·C_6H_4·CHO afford m- and p-*hydroxycinnamanilide*, m.p. 155—156° and 208°, respectively, and PhCHO affords cinnamanilide. (I) with *o*-NO_2·C_6H_4·CHO and C_5H_5N–piperidine (or either base separately) affords no *o*-nitrobenzylidenemalonanilic acid (cf. *loc. cit.*) but a mixture of a yellow, m.p. 190°, and a colourless, m.p. 172°, form of *o*-nitrocinnamanilide. Similarly, *m*- and *p*-NO_2·C_6H_4·CHO yield m- and p-*nitrocinnamanilides*, m.p. 194—195° and 208°, respectively. The yields obtained by using mixtures of C_5H_5N and piperidine, or of either base alone, are tabulated. J. L. D.

Luminescence phenomena during the oxidation of luminol. H. Thielert and P. Pfeiffer (Ber., 1938, **71**, [*B*], 1399—1403).—The intensity of the luminescence during the oxidation of 3-aminophthalhydrazide (luminol) in presence of salicylaldehyde-ethylenedi-imine ferrichloride (I) is about one third of that observed in the presence of hæmin but the effect lasts much longer. *Salicylaldehyde-o-phenylenedi-imine ferrichloride* causes pale blue luminosity of relatively small intensity whereas *salicylaldehydeanil ferrichloride* is completely inactive. *Fe*^{III} *salicylaldehyde-imine* and *-methylimine* provoke only a faint luminescence which persists for a few min. whilst *Fe*^{III} *salicylaldehyde* is almost without effect. The salt $\left[Fe\left(\begin{matrix}O\\O\cdot CO\end{matrix}>C_6H_4\right)_2\right]K,4H_2O$ has a powerful but transient action. Fe phthalocyanine, $[C_{32}H_{16}N_8Fe],6NH_2Ph$, is about as active as (I). H. W.

Preparation of ammonium aurintricarboxylate.—See A., 1938, I, 473.

Catalyst in the Gattermann reaction. R. T. Arnold and J. Sprung (J. Amer. Chem. Soc., 1938, **60**, 1699).—$Zn(CN)_2$ acts as catalyst for the Gattermann reaction only if it contains KCl or NaCl. R. S. C.

Oxygen exchange reactions of benzaldehyde and some other substances. M. Senkus and W. G. Brown (J. Org. Chem., 1938, **2**, 569—573).—By treatment with H_2O deficient in $H_2{}^{18}O$ it is shown that no exchange of O occurs with $CO(NH_2)_2$ or NaOAc at 25°. With citric acid exchange is catalysed by H_2SO_4. With PhCHO exchange is rapid and is catalysed by KOH or H_2SO_4. With $(OMe{\cdot}C_6H_4)_3C{\cdot}OH$, but not with Bu$^{\gamma}$OH, exchange is catalysed by H_2SO_4. There is no exchange with $CPh_2Me{\cdot}OH$ alone or in presence of KOH. With alloxan exchange proceeds in stages. R. S. C.

Synthesis of vanillin and other hydroxyaldehydes.—See B., 1938, 885.

Preferential demethylation of methoxyl ortho to a keto-group. W. A. Hutchins and T. S. Wheeler (Current Sci., 1938, **6**, 604—605).—2 : 4 : 6-Trimethoxyacetophenone (5 g.), HI (*d* 1·7; 40 c.c.), and Ac_2O (40 c.c.) after keeping in the cold for 24 hr. and dilution with aq. $NaHSO_3$ give 2-hydroxy-4 : 6-dimethoxyacetophenone (80%; $AlCl_3$ gives a 60% yield). Alkoxy-derivatives of *o*-anisyl styryl ketones can also be preferentially demethylated to *o*-OH-compounds in this way. L. S. T.

αβ-Ketols. K. von Auwers, H. Pötz, and W. Noll (Annalen, 1938, **535**, 219—251).—The structure of $COPh{\cdot}CHMe{\cdot}OH$ (I) (A., 1937, II, 64) is confirmed by conversion of its oxime by PCl_5 into PhCN. A *p*-OH, however, causes $COAr{\cdot}CHMe{\cdot}OH$ to be more stable than its isomeride, $OH{\cdot}CHAr{\cdot}COMe$. (I) gives a *thiosemicarbazone*, m.p. 143°. $OH{\cdot}CHPh{\cdot}COMe$ gives the thiosemicarbazone, m.p. 206°, and in HCl–MeOH a 2 : 4-*dinitrophenylhydrazone*, m.p. 182—183° (cf. *loc. cit.* and Hey, A., 1930, 935), also obtained from (I). $COPh{\cdot}COMe$ gives a *mono-*, m.p. 175—176° (red; decomp.), and *di-thiosemicarbazone*, m.p. 218—220° (decomp.). $EtCO_2Ph$ (best prepared from PhOH, $EtCO_2H$, and $SOCl_2$), b.p. 200—210°, or a mixture of $EtCO_2H$ + PhOH gives, best with BF_3, *p*-hydroxypropiophenone [*semicarbazone*, m.p. 168—170°; p-*nitro-*, *forms*, m.p. 187—188° and >155°, and 2 : 4-*dinitro-phenylhydrazone*, m.p. 233°; *Me ether*, m.p. 173—174° (p-*nitro-*, m.p. 148—149°, and 2 : 4-*dinitro-phenylhydrazone*, m.p. 192—193°)]. With Br–AcOH followed by Br–CS_2 this gives the α : 3-Br_2-, m.p. 144—145°, and αα(?β) : 3 : 5-Br_4-derivative, m.p. 79—80°, but in MeOH yields >90% of the 3 : 5-Br_2-derivative (II), new m.p. 114—115° [*semicarbazone*, m.p. 208—209°; *Ac* (III), m.p. 79·5—80·5°, and *Bz* derivative, m.p. 121—122°; *Me ether* (IV), m.p. 62—63° (*semicarbazone*, m.p. 193—194°)]. (II) and Br–$CHCl_3$ give the α : 3 : 5-Br_3-derivative, m.p. 162—163° (*Me ether*, m.p. 103°). With $C_5H_{11}{\cdot}NO_2$ and a little conc. HCl at 60—70° (III) gives 4 : 3 : 5-$OH{\cdot}C_6H_2Br_2{\cdot}CO_2H$ and 3 : 5-*dibromo-α-oximino-4-hydroxypropiophenone* (V), m.p. 158—159·5°, which is obtained having m.p. 171—172° from (II) or by oximation of αβ-*diketo-α*-3 : 5-*dibromo*-4-*hydroxyphenylpropane* (VI), m.p. 118—119°. (VI) is obtained from (V) by hot 18% HCl and gives the β-*phenylhydrazone*, m.p. 238—239° (O-*Bz* derivative, m.p. 153—154°), and β-*semicarbazone*, m.p. about 260° (decomp.); its *Me ether*, m.p. 107—108° (β-*semicarbazone*, m.p. 236°; β-*phenylhydrazone*, m.p. 229—230°), is obtained by hydrolysing the β-*oxime*, m.p. 149°, which is prepared from (IV) by $C_5H_{11}{\cdot}NO_2$ and HCl. α : 3 : 5-Tribromo-4-hydroxypropiophenone (VII) is converted, best by cold 2N-NaOH, into 3 : 5-*dibromo*-4-*hydroxybenzoylmethylcarbinol* [3 : 5-*dibromo*-α : 4-*dihydroxypropiophenone*] (VIII), m.p. (anhyd.) 112°, (+0·5C_6H_6) 93—94° [*phenylhydrazone*, m.p. 192°; impure *Bz*$_2$ derivative, an oil; *semicarbazone*, m.p. variable, 186—192°, hydrolysed by cold HNO_3 to (VIII); *oxime*, m.p. 162—163°, converted by PCl_5 in Et_2O into 4 : 3 : 5 : 1-$OH{\cdot}C_6H_2Br_2{\cdot}CN$]. (VIII) gives indefinite products with PCl_3, PBr_3, or $SOCl_2$; subsequent reduction by Zn dust and AcOH gives 4 : 3 : 5 : 1-$OH{\cdot}C_6H_2Br_2{\cdot}CH_2{\cdot}COMe$ (*semicarbazone*, m.p. 241°), isomerisation having occurred. CH_2N_2 (not MeI–NaOH) gives the 4-*Me ether*, b.p. 217—218°/16 mm., m.p. 77—79°, of (VIII); this gives, according to the conditions, its *semicarbazone*, m.p. 199—201°, or that of (VI), but gives only the phenylhydrazone of (VI). (VII) and KOAc in AcOH give the *Ac* derivative, m.p. 128°, of (VIII), the *semicarbazone*, m.p. 177°, of which is also obtained from the *Ac*$_2$ derivative, m.p. 89°, of (VIII). *p*-Hydroxyphenylacetone, b.p. 178—180°/13 mm. (lit., m.p. 35·5°), is best obtained from its Me ether by $AlBr_3$ in hot C_6H_6; it gives oily 3 : 5-Br_2- and α : 3 : 5-Br_3-derivatives. Ph α-bromopropionate (A., 1917, i, 37), b.p. 123—126°/10 mm., with $AlCl_3$ gives α-bromo-*p*- (IX), m.p. 95° (lit., 81°), and -*o*-hydroxypropiophenone, m.p. 36·5—37° (lit., 32°), b.p. 138—140°/12 mm. (identified by dehalogenation). Ph α-chloropropionate, b.p. 117—120°/14 mm., and α-*chloro*-p- (X), m.p. 81·5°, and -*o*-hydroxypropiophenone, b.p. 126—128°/10 mm., are similarly prepared. o-*Hydroxypropiophenonesemicarbazone* (?) has m.p. 206·5—207°. (IX) or, less well, (X) and 2N-NaOH give p-*hydroxybenzoylmethylcarbinol* [α : 4-*dihydroxypropiophenone*] (XI), m.p. 141° [*oxime*, m.p. 173·5°, and (?) a stereoisomeride thereof], which yields the *disemicarbazone*, m.p. 256—257° (decomp.), and 2 : 4-*dinitrophenylosazone*, decomp. 279—280° (sinters at about 260°), of αβ-diketo-α-*p*-hydroxyphenylpropane, and with Br gives (VIII). *p*-$OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CHMeBr$ and KOAc in AcOH give α-*acetoxy*-p-*methoxypropiophenone*, m.p. 72—73°, hydrolysed by $BaCO_3$ to p-*anisoylmethylcarbinol* [α-*hydroxy*-p-*methoxypropiophenone*] (XII), b.p. 158—160°/9·5 mm., obtained also in one step by 2N-NaOH. (XII) and PCl_3 give a product, reduced by Zn–AcOH to *p*-$OMe{\cdot}C_6H_4{\cdot}COEt$. (XII) gives its *semicarbazone*, m.p. 200°, and the *disemicarbazone*, m.p. 246°, of αβ-diketo-α-*p*-anisylpropane (XIII); it affords also the impure 2 : 4-*dinitrophenylhydrazone*, m.p. 258° after sintering, of (XIII). The structures assigned to (XI) and (XII) are supported by the large exaltation of [*n*]. R. S. C.

Friedel–Crafts reaction with diethers of resorcinol. D. C. Motwani, V. V. Bodani, and T. S. Wheeler (Current Sci., 1938, **6**, 604).—Cinnamoylation of *m*-$C_6H_4(OAlk)_2$ occurs at position 4 to give 1 : 3 : 4-$(OAlk)_2C_6H_3{\cdot}CO{\cdot}CH{:}CHPh$ identical with

those obtained from *OO*-dialkylresacetophenones and PhCHO (cf. A., 1927, 154). The styryl ketones from 2-acetyl-*OO*-dialkylresorcinols and PhCHO differ from those described by Simonis (*loc. cit.*). L. S. T.

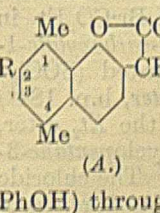
Preparation and properties of an ene-diol. β-Mesitoyl-α-phenylacetylene glycol [γ-keto-α-phenyl-γ-mesityl-Δ$^{\alpha}$-propene-αβ-diol]. R. P. Barnes and L. S. Green (J. Amer. Chem. Soc., 1938, **60**, 1549—1553).—An open-chain ene-diol is prepared, the relative stability being due to suitable activating groups. *p*-C_6H_4Br·COMe (I), HCO_2Et, and NaOEt in C_6H_6 give ω-hydroxymethylene-*p*-bromoacetophenone (II), m.p. 71° (67% enolic), yielding *Ac*, m.p. 125°, and *Bz* derivatives, m.p. 112°, which decolorise Br and $KMnO_4$, give only slowly a colour with $FeCl_3$–EtOH, and are hydrolysed by HCl–EtOH to (I) and EtOAc or EtOBz, respectively. With cold Br–$CHCl_3$ the Na derivative of (II) gives the α-*Br*-derivative, *p*-C_6H_4Br·CO·CBr:CH·OH, m.p. 112° [100% enolic; red $FeCl_3$ colour; reduced by HI to (II)], which is resinified by hot KOAc–AcOH. HCl–EtOH hydrolyses (II) to (I) and HCO_2Et. 2 : 4 : 6-$C_6H_2Me_3$·CO·C(OH):CHPh (III) and Br–Et_2O give *α-bromo-α-phenyl-γ-mesitylpropane-βγ-dione*, an oil [24% enolic; reduced to (III) by HI], which with hot KOAc–AcOH gives *α-acetoxy-α-phenyl-γ-mesityl-Δ$^{\alpha}$-propen-β-ol-γ-one* (IV), m.p. 71° (100% enolic; unchanged by hot HCl– or H_2SO_4–EtOH; cleaved by alkaline H_2O_2 to EtOAc, BzOH, and $C_6H_2Me_3$·CO_2H), converted by hot AcCl into *αβ-diacetoxy-α-phenyl-γ-mesityl-Δ$^{\alpha}$-propen-γ-one*, m.p. 131° (no $FeCl_3$ colour; decolorises $KMnO_4$ and Br). Both OAc-compounds are converted by cold, conc. H_2SO_4 into *γ-keto-α-phenyl-γ-mesityl-Δ$^{\alpha}$-propene-αβ-diol* (V), m.p. 79—80° (greenish-blue $FeCl_3$ colour; 37% ene-diol). When kept in air or Et_2O or treated with H_2SO_4–EtOH, (V) gives *α-phenyl-γ-mesitylpropane-αβγ-trione*, m.p. 94°, *α-phenyl-β-mesitylglyoxal* (VI), m.p. 134°, H_2O_2, and CO_2. (VI) is also formed from (V) by Br–$CHCl_3$ or $FeCl_3$–EtOH, and from (IV) by Br–$CHCl_3$. Alkaline H_2O_2 oxidises (VI) to BzOH and $C_6H_2Me_3$·CO_2H. R. S. C.

Deformation of valency angles. Structure and absorption of derivatives of oximes. (Mme.) Ramart-Lucas and J. Hoch (Bull. Soc. chim., 1938, [v], **5**, 987—1010).—Measurements of the absorption of derivatives of oximes (*O* and *N* compounds) which cannot behave as tautomerides, and the structures of which have been determined in part by optical and in part by chemical methods, confirm the view that oximes exist not only in the "oxime" and "*iso*-oxime" forms but also in a peculiar form ("transparent" form) in which the union between the functional group and the remainder of the mol. is nil. The spectra of derivatives of CHPh:N·OH, 3 : 4-CH_2O_2:C_6H_3·CH:N·OH, CPhEt:N·OH, CPh_2:N·OH, *p*-OMe·C_6H_4C(N·OH)·C_6H_4Me-*p'* and of $CAlk_3$·CPh:N·OH are recorded. *O*-CH_2Ph derivatives are obtained by the action of NH_2·O·CH_2Ph on aldehydes or ketones or on ketimines or from the oxime, NaOEt, and CH_2PhCl in EtOH. CH_2Ph·NH·OH reacts readily with aldehydes but appears indifferent to ketones or their acetals although the change occurs with ketimines. The following are new or amended: *O*-, m.p. 55°, and N-*benzyl*-3 : 4-*methylenedioxybenzaldoxime*, m.p. 121°; *propiophenoneoxime* CH_2Ph *ether*, b.p. 195°/22 mm.; *O*-benzylbenzophenoneoxime, m.p. 61°, and *N*-benzhydrylbenzaldoxime, m.p. 166° (hydrolysed by hot dil. HCl to PhCHO and CHPh·NH·OH), formed from CPh_2:N·OH, NaOEt, and CH_2PhCl [thus CPh_2:NO·CH_2Ph (not isolated) → $CHPh_2$·NO:CHPh]; O-*benzyl*-4-*methoxy*-4'-*methylbenzophenoneoximes* (*cis*- and *trans*-isomerides), m.p. 71° and 115°, respectively; O-*benzyl*-3 : 4-*methylenedioxybenzophenoneoxime*, m.p. 84°; *Ph Bu$^{\gamma}$ ketoxime* CH_2Ph *ether*, m.p. 41°; *Ph* β-*methyl*-β-*hexyl ketoxime* CH_2Ph *ether*, b.p. 200°/15 mm., reduced (Na and EtOH) to *α-amino-α-phenyl-ββ-dimethylhexane*, b.p. 145—146°/12 mm. (corresponding *phenylcarbamide*, m.p. 140°), and CH_2Ph·OH; *Ph α-phenyl-β-methyl-β-propyl ketoxime* CH_2Ph *ether*, m.p. 82°; 2 : 2-*dimethylindanoneoxime* CH_2Ph *ether*, b.p. 200°/13 mm.; *indanoneoxime* CH_2Ph *ether*, b.p. 171—173°/1 mm., m.p. 29°, and an *isomeride*, m.p. 142—143°; 3 : 4-*methylenedioxybenzophenone*, m.p. 56°; p-*tolyl* p-*anisyl ketimine*, m.p. 61°; 3 : 4-*methylenedioxybenzophenoneimine*, b.p. 210—211°/11 mm. H. W.

Action of mixed organo-magnesium compounds on *N*-acyl-*N'*-phenylhydrazines. P. Grammaticakis (Compt. rend., 1938, **207**, 239—241; cf. A., 1937, II, 248, 287).—Prolonged heating of *N*-formyl-*N'*-phenylhydrazine with a large excess of MgPhBr at 116—120° affords mainly $COPh_2$ together with small amounts of CPh_2:N·NHPh (I) and CPh_2:NPh (II). NHAc·NHPh similarly treated affords mainly 2-phenylindole and small amounts of CPhMe:N·NHPh and COPhMe. NHBz·NHPh similarly affords (I), (II), NH:CPh_2, and $COPh_2$. In every case some NH_2Ph and NHPh·NH_2 are formed. The formation of these products can be explained by assuming that the *N*-acyl-*N'*-phenylhydrazines react as OH·CR:N·NHPh. J. L. D.

Nickel (Ni^{II}) salts of acyloinoximes and of oximinoketones. L. Malatesta (Gazzetta, 1938, **68**, 319—323).—Ni dibenzoinoxime (A., 1935, 981) in KOH–EtOH with $Ni(OAc)_2$ gives the *complex* $K[NiH(C_{14}H_{11}O_2N)_2]$, diamagnetic. Similarly *Ni piperoin-* and *anisoin-oxime*, paramagnetic, give diamagnetic *K* complexes. The *Ni* derivatives of furoin- and salicylald-oxime (*K* complex), of oximinobenzoylacetone and -acetophenone (*K* complex), and of α-benzildioxime are prepared, and χ and μ tabulated; all these, including K compounds, are paramagnetic. Structures are discussed. E. W. W.

Quinols. I. Hyposantonylquinol and tetrahydronaphthalenequinol. Y. Asahina and T. Momose (Ber., 1938, **71**, [*B*], 1421—1428).—Gradual addition of conc. HNO_3–conc. H_2SO_4 to hyposantonin in AcOH at 20—30° gives 2-*nitrohyposantanin* (I) (*A*; R = NO_2), m.p. 183°, $[\alpha]_D^{24}$ —67·6° in $CHCl_3$, also obtained similarly from *iso*-hyposantonin. Its constitution is established by its conversion (Zn dust and NH_4Cl in boiling 50% PhOH) through 2-*aminohyposantonin* (II), m.p. 193°, $[\alpha]_D^{24}$ —165·7° in $CHCl_3$ [*hydrochloride*, m.p. 118—119°



(*A*.)

(decomp.)], into *l*-desmotroposantonin, m.p. 198°, $[\alpha]_D^{28}$ −140·0° in abs. EtOH (acetate, m.p. 154°). Reduction (Pd–C in EtOH) of (I) yields *aminopyrosantonous acid*, m.p. 246° [*hydrochloride*, m.p. 212—213° (decomp.), $[\alpha]_D^{23}$ +62·5° in HCl], also obtained by hydrogenation of (II) and converted by HCl and $NaNO_2$ into *d*-santonous acid, m.p. 182—183°, $[\alpha]_D^{28}$ +75·0° in abs. EtOH (*Me* ester, m.p. 86°). Conc. H_2SO_4–conc. HNO_3 at 35—40° convert (I) into *dinitrohyposantonin*, m.p. 209°, $[\alpha]_D^{22}$ −62·0° in $CHCl_3$, whence (Pd–C in EtOH at 25°) *diaminohyposantonous acid*, m.p. 218—219°, $[\alpha]_D^{25}$ +79·1° in 1% HCl. Attempts reduce to (I) in neutral solution to 2-hydroxylaminosantonin were unsuccessful but (II) is transformed by Caro's acid into 2-*nitrosohyposantonin*, m.p. 146° (decomp.), $[\alpha]_D^{18}$ −185·8° in $CHCl_3$, which when warmed with Na_2SO_3 gives a solution which strongly reduces Fehling's solution and when directly subjected to Bamberger's reaction affords *hyposantonylquinol* (structure : A., 1938, II, 284), m.p. 222—223°, $[\alpha]_D^{24}$ +324·8° in abs. EtOH (*oxime*, m.p. 188°; *mono*-, m.p. 204°, and *di*-, m.p. 200—201°, *-acetate*), which is an anthelmintic and possibly the physiologically active derivative of santonin. 6-Nitro-1 : 2 : 3 : 4-tetrahydronaphthalene when treated with Zn dust and NH_4Cl in EtOH and then digested with dil. H_2SO_4 at 60—70° gives 10-*hydroxy*-2-*keto*-2 : 5 : 6 : 7 : 8 : 10-*hexahydronaphthalene*, m.p. 124—125°, which like its *acetate*, m.p. 81°, is a powerful anthelmintic. It is converted by Ac_2O–H_2SO_4 into the *diacetate*, m.p. 188°, of 5 : 8-dihydroxy-1 : 2 : 3 : 4-tetrahydronaphthalene, m.p. 179—180°. H. W.

New synthetic route to polycyclic hydroaromatic compounds. Synthesis of 2 : 3-benz*dicyclo*-[0 : 3 : 3]-Δ²-octene [and of 8-ketohexahydropentanthrylene ketone]. N. N. Chatterjee (J. Indian Chem. Soc., 1938, **15**, 211—216).—OH·CHPh·CN with CN·CHNa·CO_2Et, followed by $CH_2Cl{\cdot}CH_2{\cdot}CO_2Et$ yields *Et*$_2$ αβ-*dicyano*-α-*phenyl*-n-*butane*-βδ-*dicarboxylate*, m.p. 81°, b.p. 218—222°/5 mm., hydrolysed and decarboxylated to α-*phenyl*-n-*butane*-αβδ-*tricarboxylic acid*, m.p. 185° (decomp.), the *Et*$_3$ ester, b.p. 187—194°/5 mm., of which with Na in C_6H_6 gives *Et*$_2$ 2-*phenyl*cyclo*pentanone*-3 : 5-*dicarboxylate*, b.p. 184—192°/5 mm., hydrolysed and decarboxylated to 2-*phenyl*cyclo*pentanone*-3-*carboxylic acid* (I), m.p. 114—115°. This is reduced (Zn–Hg + HCl) to 2-*phenyl*cyclo*pentane*-1-*carboxylic acid*, b.p. 185—190°/10 mm., the chloride of which is cyclised ($AlCl_3$ in CS_2) to 4-*keto*-2 : 3-*benz*-dicyclo-[0 : 3 : 3]-Δ²-*octene*, $C_6H_4{<}\begin{matrix}CO—CH{\cdot}CH_2\\ CH{\cdot}CH_2\end{matrix}{>}CH_2$ (II), b.p. 127—132°/10 mm. (*semicarbazone*, m.p. 170°), reduced (Zn–Hg + HCl) to the *hydrocarbon* [(II); CO = CH_2], b.p. 118—124°/9 mm. The *Et* ester, m.p. 60° (*semicarbazone*, m.p. 173°), of (I) with Zn and $CH_2Br{\cdot}CO_2Et$ in C_6H_6 gives *Et*$_2$ 2-*phenyl*cyclo*pentanol*-3-*carboxylate*-1-*acetate*, b.p. 190—197°/6 mm., dehydrated ($SOCl_2$–Et_2O–C_5H_5N) to the Δ¹-cyclo*pentene ester*, b.p. 184°/5 mm., reduced (H_2, PtO_2, EtOH) to the *Et*$_2$ ester, b.p. 175—177°/5 mm., of 2-*phenyl*cyclo*pentane*-3-*carboxylic*-1-*acetic acid*, m.p. 170—173°. The chloride of this is cyclised ($AlCl_3$ in CS_2) to 8-*ketohexahydropentanthrylene ketone* (?). A. Li.

Adreno-genital syndrome. I. Isolation of 3(α)-hydroxyætiocholan-17-one, 3(β)-hydroxyætio*allo*cholan-17-one (*iso*androsterone), and a new triol from the urine of a woman with an adrenal hyperplasia. G. C. Butler and G. F. Marrian (J. Biol. Chem., 1938, **124**, 237—247, and Nature, 1938, **142**, 400; cf. A., 1937, III, 361).—The unhydrolysed urine of a woman with an adrenal hyperplasia and symptoms of virilism contained, in the ketonic portion of the neutral Et_2O-sol. fraction, 3(α)-hydroxyætiocholan-17-one [(β) is used to denote that the $C_{(3)}$–OH group is in cholesterol-like relation to $C_{(10)}$-Me, and (α) to denote epimeric configuration as in the bile acids and androsterone], not digitonin-precipitable, and 3(β)-hydroxyætio*allo*cholan-17-one (*iso*androsterone), digitonin-precipitable. These compounds (cf. A., 1934, 1221) have not previously been isolated directly from natural sources. The non-ketonic portion contains pregnane-3(α) : 17 : 20-triol (?) [Ac derivative, new m.p. 150—151° (cf. A., 1937, III, 361)], not digitonin-precipitable, and a *triol*, $C_{21}H_{36}O_3$, m.p. 210—212°, precipitable, which is probably a *pregnane*- [or allo*pregnane*-]3(β) : 17 : 20-*triol*; with $Pb(OAc)_4$ it gives an aldehyde or ketone, and a product, m.p. 144—146°. E. W. W.

Enol ethers of steroid ketones. E. Schwenk, G. Fleischer, and B. Whitman (J. Amer. Chem. Soc., 1938, **60**, 1702—1703).—With $CH(OEt)_3$, a little HCO_2H, and a drop of H_2SO_4 at 50° cholestenone, and testosterone benzoate and propionate give the enol *Et ethers*, m.p. 83·5—85° (clear at 95°), [α] −96° in C_5H_5N, m.p. 181—192° (softens at 175°), [α] −67·5° in C_5H_5N, and (I), m.p. 143—150°, [α] −140° in $CHCl_3$, respectively. In $CHCl_3$ (not C_5H_5N) the ethers are rapidly hydrolysed to the ketone, probably by adventitious traces of HCl. KOH–EtOH hydrolyses the ester grouping of (I) without affecting the OEt. Since [α] are negative, the ethylenic linkings are in different rings (*A* and *B*). R. S. C.

Reduction of Δ⁵-unsaturated 3-keto-derivatives of the *cyclo*pentanohydrophenanthrene series.—See B., 1938, 982.

Synthesis of 3 : 4-methylenedioxyphenylglyoxal. S. Kawai and K. Ashino (Bull. Chem. Soc. Japan, 1938, **13**, 480—481).—Homopiperonal and SeO_2 in hot EtOH give 3 : 4-*methylenedioxyphenylglyoxal*, an oil (*phenylhydrazone*, m.p. 140°; *quinoxaline* derivative, m.p. 167·5°), isolated as *Et semiacetal*, m.p. 107°. R. S. C.

Modified Gattermann reaction. Synthesis of hydroxyaldehydophenyl ketones. H. A. Shah and R. C. Shah (Nature, 1938, **142**, 163).—Polyhydric phenolic ketones give aldehydes in high yield by a modified Gattermann reaction (A., 1937, II, 21), the CHO entering the 2-position in the resorcinol nucleus when possible. Resacetophenone, orsacetophenone, 2-acetylresorcinol, phloracetophenone, and 2 : 4-dihydroxybenzophenone give 2 : 4-dihydroxy-3-, 2 : 4-dihydroxy-6-methyl-3-, 2 : 6-dihydroxy-5-, 2 : 4 : 6-trihydroxy-3-aldehydoacetophenone, and 2 : 4-dihydroxy-3-aldehydobenzophenone, respectively. The entry of CHO into the 3-position of, *e.g.*, 2 : 4 : 1-$(OH_2)C_6H_3{\cdot}COMe$ may be due to chelation between

OH and Ac stabilising the double linkings in the C_6H_6 ring. L. S. T.

Synthesis of αβ-diferulyl- [αβ-di-(4-hydroxy-3-methoxycinnamoyl)-]ethane (a homologue of curcumin). W. Lampe and J. Swiderski (Rocz. Chem., 1938, **18**, 120—124).—Sodio-*O*-carbomethoxyferulylacetone and I in Et_2O (12 hr. at room temp.) yield αβ-*di*(*carbomethoxyferulyl*)-αβ-*diacetylethane*, m.p. 220°, which with boiling AcOH (6 hr.) gives αβ-*di*-(*carbomethoxyferulyl*)*ethane*, m.p. 159—160°. This and 10% KOH at 50° (1·5 hr.) in H_2 give αβ-*diferulylethane* (I), m.p. 190—191°, together with its enolic *modification*, m.p. 179—180°. (I) dyes cotton a pale yellow, and does not give the curcumin reaction with H_3BO_3. The *Cu* salt, m.p. 158° (decomp.), of Et *O*-carbomethoxyferulylacetate is described. R. T.

Synthesis of 3-benzoyl-2-phenyl*cyclo*pentanone. R. C. Fuson, R. Johnson, and W. Cole (J. Amer. Chem. Soc., 1938, **60**, 1594—1595).—3-Benzoyl-2-phenyl*cyclo*pentanone (I) (A., 1934, 1005) is synthesised. The crude additive product from *cyclo*pentene, BzCl, and $AlCl_3$ in CS_2 at −5°, with $NPhEt_2$ at 180° gives 1-*benzoyl*cyclo*pentene*, b.p. 119—122°/3 mm., which with NaOMe and *p*-$C_6H_4Cl{\cdot}CHO$ gives 1-*benzoyl*-3-p-*chlorobenzylidene*-cyclo*pentene*, m.p. 118°. MgPhBr converts this into 1-*benzoyl*-2-*phenyl*-3-p-*chlorobenzylidene*cyclo*pentane*, m.p. 171° (corr.) (*oxime*, m.p. 115—120°), converted by NaOH–MeOH, best with a little *p*-$C_6H_4Cl{\cdot}CHO$, into an *isomeride*, m.p. 178° (corr.). Ozonisation of either form in AcOH gives (I) (*oxime*, m.p. 222—224°). 3-Benzoyl-2-phenyl-5-*p*-chlorobenzylidene-*cyclo*pentanone is prepared by heating (I) with *p*-$C_6H_4Cl{\cdot}CHO$ and NaOH–MeOH. R. S. C.

Preparation of polyhydroxy-derivatives in the steroid group; addition of hydrogen peroxide to αβ-unsaturated ketones. A. Butenandt and H. Wolz (Ber., 1938, **71**, [*B*], 1483—1487).—αβ-Dihydroxyketones are obtained from unsaturated ketones and H_2O_2 in Et_2O or C_6H_6 containing a little OsO_4 at room temp. Thus cholestenone gives *cholestane*-4 : 5-*diol*-3-*one*, m.p. 206—208°, $[\alpha]_D^{22}$ +43·8° in $CHCl_3$ (4-*monoacetate*, m.p. 225—227°). Δ^1-Cholestenone yields *cholestane*-1 : 2-*diol*-3-*one*, m.p. 186—188°, whilst *cholestane*-4 : 5-*diol*-3 : 6-*dione*, m.p. 243—245° after gradual decomp. at >200°, $[\alpha]_D^{21}$ −15·6° in $CHCl_3$ (4-*monoacetate*, m.p. 224—226°), is obtained from Δ^4-cholestene-3 : 6-dione. Progesterone affords *pregnane*-4 : 5-*diol*-3 : 20-*dione*, m.p. 249—250° (decomp.), $[\alpha]_D^{21}$ +104·5° in $CHCl_3$ (4-*monoacetate*, m.p. 223—225°), and testosterone acetate yields *androstane*-4 : 5 : 17-*triol*-3-*one* 17-*monoacetate*, m.p. 185—188°, $[\alpha]_D^{21}$ +35·7° in $CHCl_3$ [corresponding 4 : 17-*diacetate*, m.p. 220—222° (decomp.)]. Addition of 2 OH to the double linking vicinal to CO almost nullifies the physiological activity. H. W.

Sterols. XXXVI. Ketones from mares' pregnancy urine. R. E. Marker, E. J. Lawson, E. L. Wittle, and H. M. Crooks (J. Amer. Chem. Soc., 1938, **60**, 1559—1561; cf., A., 1938, II, 362).—The ketones, separated by Girard's reagent from the non-phenolic portion of mares' pregnancy urine, give mixed semicarbazone fractions, each containing at least one ketone and OH-ketone. They yield Heard's ketone, m.p. 252° (A., 1938, II, 146) (mol. wt. 672; probably composed of two sterols united by their O; semicarbazone, m.p. 300°), *allo*pregnanedione, m.p. 196—200°, pregnanedione, m.p. 118°, *allo*pregnan-3(β)-ol-20-one (I), m.p. 193°, *uran*-11-*ol*-3-*one* (II), m.p. 165° [gelatinous *semicarbazone*, m.p. 250° (decomp.)], and a *ketone*, m.p. 115—120° (no digitonide). The structure of (II) follows from its giving the Zimmermann reaction (CO at position 3), not giving a H succinate (inert OH at $C_{(11)}$), and oxidation to uranedione, m.p. 175—176°. Isolation of (I) supports the proposed scheme of reduction of progesterone. Other ketones were present in mares' pregnancy urine, but were not purified. R. S. C.

Carotenoids of invertebrates. E. Lederer (Bull. Soc. Chim. biol., 1938, **20**, 567—610).—Astacine (I) has been obtained from the ascidians *Dendrodoa grossularia*, van Beneden, and *Halocynthia papillosa* which also contains a xanthophyll, *cynthiaxanthine*, m.p. 188—190° (shows absorption bands in CS_2 at 517, 483, and 451 mμ.). The genital organs of *Pecten maximus* contain a xanthophyll termed *pectenoxanthine*, $C_{40}H_{54}O_3$, which contains 11 double linkings, 2 OH, and one CO and shows absorption bands in CS_2 at 518, 586, and 452 mμ. *Calanus finmarchicus* contains (I). The genital glands of *Strongylocentrotus lividus* contain *echinenone*, $C_{40}H_{58}O$, m.p. 192—193°, which is a ketone and behaves like provitamin-*A* and shows a strong absorption band in CS_2 at 488 mμ.; it contains half of the mol. of β-carotene. *Pentaxanthine*, $C_{40}H_{56}O_5$, m.p. 209—210°, which is obtained from the mesentery of *S. lividus*, is the only xanthophyll known which contains 5 O; it has 11 double linkings, 3 OH, and probably 2 CO and shows absorption bands in CS_2 at 506, 474, and 444 mμ. The carotenoids of the lower animals are derived from the plant carotenoids. P. G. M.

Sterols. XXXIX. Reduction of uranetrione. R. E. Marker, E. L. Wittle, and T. S. Oakwood (J. Amer. Chem. Soc., 1938, **60**, 1567—1569).—PtO_2-hydrogenation of uranetrione in EtOH–Et_2O at 25°/3 atm. proceeds homogeneously at $C_{(11)}$ and $C_{(20)}$, the products being a substance giving a digitonide and *urane*-3(α) : 11(β) : 20(β)-*triol* (I), m.p. 255° (*triacetate*, m.p. 192°, indifferent to H_2–PtO_2 in AcOH at 85° and CrO_3–AcOH at 25°; no digitonide). In AcOH at 85°/3 atm. (I), urane-3 : 11-diol (II), m.p. 215° (*loc. cit.*), and other products are obtained. Partial hydrogenation in EtOH gives an *uranoldione*, $C_{21}H_{32}O_3$, m.p. 225° (digitonide, proving a β-OH at $C_{(3)}$; *acetate*, m.p. 250°). $C_{(3)}$ is thus the first point of reduction. Formation of urane- and pregnanedione (A., 1938, II, 277) involves partial elimination of CO at $C_{(20)}$ [to give (II)] and at $C_{(11)}$ [with inversion at $C_{(9)}$ to form pregnanediol]. The uranetriol previously (*loc. cit.*) isolated is the 3(α) : 11(β) : 20(α)-triol. (II) is only slightly epimerised by Na-xylene. R. S. C.

Mechanism of the pyrocatechol–tyrosinase reactions. H. Wagreich and J. M. Nelson (J. Amer. Chem. Soc., 1938, **60**, 1545—1548).—In the presence of tyrosinase (I) at p_H 6·2 pyrocatechol (II)

absorbs 2 O. After absorption of 1 atom 98% of *o*-benzoquinone (III) is present. If (II) is oxidised to (III) by $Ce(SO_4)_2$ at p_H 4·4 or $K_3Fe(CN)_6$ at p_H 7·7, no O_2 is subsequently absorbed in absence of (I); in presence of (I) the rate of absorption of O_2 is the greater the longer is the time elapsing before addition of the (I), but the total amount absorbed is always approx. the same. Beyond a certain limit, nevertheless, a longer time interval does not increase the rate of absorption. This indicates that the (III) formed decomposes to a new oxidisable substance, which comes eventually into equilibrium with it. If (III) is formed by means of $Ce(SO_4)_2$ at p_H 4·8 or 4·5 and is then allowed mostly to decompose, addition of (I) leads to re-formation of (III) in amount indicating that 1 mol. of (II) is formed by each 2 mols. of (III) decomposed. Therefore, the following reactions are postulated: (*a*) slow, (III) + H_2O → 1 : 2 : 4-$C_6H_3(OH)_3$ (IV); (*b*) fast, (III) + (IV) → (II) + 2-hydroxy-*p*- or 4-hydroxy-*o*-benzoquinone (V); (*c*) fast, polymerisation of (V). Reaction (*c*) is indicated also by formation of humic material from aq. solutions of (III). Reactions (*a*) and (*b*) probably occur only when dil. solutions of (III) are rapidly oxidised at p_H 4—6, as the disappearance of (III) is a first-order reaction only in dil. solution and is accelerated by addition of (II). R. S. C.

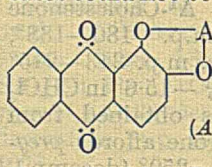
Mechanism of the pyrocatechol–tyrosinase reaction. II. Hydrogen peroxide question. C. R. Dawson and B. J. Ludwig (J. Amer. Chem. Soc., 1938, **60**, 1617—1621; cf. A., 1938, III, 338).—Tyrosinase (I), obtained from *Psalliota campestris*, has no peroxidase and negligible catalase activity. At p_H 4·2—6·6 in presence of (I) pyrocatechol (II) rapidly absorbs O_2 to give a substance absorbing 2 I and, therefore, either 1 mol. of *o*-benzoquinone (III) or an equiv. mixture of (III) + H_2O_2; between p_H 4·2 and 6·6 the stability of (III) is independant of the p_H, but in more alkaline solution decomp. is faster. Addition of H_2O_2 has no effect on the oxidation of (II) under the influence of (I) at p_H 4·1, at which p_H H_2O_2 is without effect on (III). Addition of catalase has no effect on the oxidation of (II) induced by (I) at p_H 4·1—6·7. It is concluded that H_2O_2 plays no part in the oxidation of (II) to (III). R. S. C.

Potentiometric and magnetometric study of the duroquinone system. L. Michaelis, M. P. Schubert, R. K. Reber, J. A. Kuck, and S. Granick (J. Amer. Chem. Soc., 1938, **60**, 1678—1683).—Potentiometric, reductive titration and the magnetic susceptibility during reduction of duroquinone indicate formation of a brown, paramagnetic, free semiquinone, $O{:}C_6Me_4{:}O^-$, the amount of which present in the equilibrium mixture depends on the p_H and is a max. (about 50%) at p_H 13. No quinhydrone is formed, owing to steric hindrance by the Me. Quinhydrones are formulated $C_6H_4\langle^{O—H—O}_{O—H—O}\rangle C_6H_4$, etc. R. S. C.

Silicon as reducing agent in organic chemistry. A. Rollett and H. Gantz (Monatsh., 1938, **72**, 63—64).—Si + aq. NaOH at 100° (bath) is a weak and slow-acting reducing agent. It does not attack $NO_2{\cdot}C_6H_4{\cdot}OH$ or $NO_2{\cdot}C_6H_4{\cdot}CO_2H$, but it reduces indigotin, anthraquinone, 1 : 5-dinitroanthraquinone (low yield of 1 : 5-nitroamino-compound), and also azo-dyes (fission at N:N). A. T. P.

Constitution and reactivity. XXI. Substantivity of derivatives of 1- and 2-aminoanthraquinone. K. Lauer and L. S. Yen (J. pr. Chem., 1938, [ii], **151**, 49—60).—Examination of the behaviour towards cotton cellulose of 1- and 2-acylaminoanthraquinones (acyl = Ac, $CH_2Cl{\cdot}CO$, $CCl_3{\cdot}CO$, Pr^{c}CO, Bz, *o*-, *m*- and *p*-$NH_2{\cdot}C_6H_4{\cdot}CO$, *o*-$CO_2H{\cdot}C_6H_4{\cdot}CO$, *p*-$C_6H_4Me{\cdot}SO_2$, and $CHPh{:}CH{\cdot}CO$) shows that substantivity is conditioned by keto–enolic tautomerism of the acylamino-group. The position of the equilibrium influences the rapidity of the completion of the dyeing but not the substantivity. The quantity of utilised dye alters with change in the acyl residue. The latter behaves as a substituent which affects the final union by its residual valencies; these can have a positive or negative action on substantivity according to the spatial position and polar character. H. W.

Alizarates. II. R. Haller (Helv. Chim. Acta, 1938, **21**, 844—853; cf. B., 1938, 637).—Alizarin-red which has not been subjected to the second treatment with oil and to steaming is decidedly altered by $FeCl_3$, $FeSO_4$, Sn$^{\cdot\cdot}$, $UO_2^{\cdot\cdot}$, Cr$^{\cdot\cdot\cdot}$, and Cu$^{\cdot\cdot}$ whereas finished alizarin-red remains unaffected. The effect does not depend on the presence of excess of alizarin (I). The same reactivity is shown by Ca and Al alizarate separately. The reaction is definitely ionic. Samples treated with a 20% solution of Turkey-red oil and then steamed have been impregnated with solutions of Al$^{\cdot\cdot\cdot}$, Fe$^{\cdot\cdot\cdot}$, Cr$^{\cdot\cdot\cdot}$, $UO_2^{\cdot\cdot}$, Cu$^{\cdot\cdot}$, Zn$^{\cdot\cdot}$, Ni$^{\cdot\cdot}$, Co$^{\cdot\cdot}$, Ca$^{\cdot\cdot}$, and Sn$^{\cdot\cdot}$. The properties of the lakes and their behaviour towards MeOH are recorded. When treated with boiling solutions of other metallic salts, it is found that Fe$^{\cdot\cdot\cdot}$ affects the colour of all other metallic mordants. Al$^{\cdot\cdot\cdot}$ is without influence. Cu$^{\cdot\cdot}$ has little influence on the unsteamed pigments, which are very greatly altered by $UO_2^{\cdot\cdot}$. Sn$^{\cdot\cdot}$ changes the colours due to Cu$^{\cdot\cdot}$, Co$^{\cdot\cdot}$, Ni$^{\cdot\cdot}$, and Zn$^{\cdot\cdot}$. Cr$^{\cdot\cdot\cdot}$ has no effect on the Al$^{\cdot\cdot\cdot}$ or Sn$^{\cdot\cdot}$ lakes; its effect in other cases could not be examined by reason of the similarity of colour. Anthrapurpurin and flavopurpurin behave similarly to (I). To Al alizarate the constitution (*A*) (R = H) is ascribed, its reaction with cold NaOH giving the salt (*A*; R = Na) from which it is regenerated by acidification. Boiling NaOH causes the production of (I) and of $Al(ONa)_3$. Dyeing animal fibres with alizarin-red does not necessitate the presence of Ca although this is frequently advocated. It is possible to dispense with the use of Turkey-red oil and hence also with the steaming. H. W.



(*A*.)

Halochromy phenomena in perylene, its quinones and substitution products.—See A., 1938, I, 385.

Pyrogenesis of alkali menthoxides. M. Brambilla (Annali Chim. Appl., 1938, **28**, 209—217).—Heating to 300—550° dehydrogenates Li, Na, and K menthoxides successively to the corresponding

menthone derivatives and thymoxides. The rate of decomp. of the menthoxides decreases with decrease in at. wt. of the metal, the reverse being true for their rate of formation from menthol and the metal.

F. O. H.

Synthesis of carane. P. C. Guha and D. K. Sankaran (Current Sci., 1938, **6**, 606).—Et Δ^1-tetrahydro-*p*-toluate with CMe_2N_2 at 0° for 2 weeks yields the *dicyclo*-(0 : 1 : 4)-heptane derivative, $CHMe{\cdot}CH_2{\cdot}CH\!<\!\begin{matrix}CH_2{-}CH_2\\ CH_2{-}C(CO_2Et)\end{matrix}\!>\!CMe_2$, b.p. 150—160°/6 mm., which on hydrolysis (5% alcoholic KOH) yields the corresponding carboxylic acid, m.p. 104—105°. Distillation (ZnO–BaO, reduced pressure) gives carane.

L. S. T.

Wagner–Meerwein rearrangement. Kinetic reinvestigation of the isomerisation of camphene hydrochloride. P. D. Bartlett and I. Pöckel (J. Amer. Chem. Soc., 1938, **60**, 1585—1590).—Rearrangement of camphene hydrochloride (I) to *iso*bornyl chloride is catalysed by the HCl inevitably present as dissociation product of (I). Kinetic experiments in $PhNO_2$ and recognition of this dissociation lead to equations accounting quantitatively for previous results (cf. A., 1937, II, 288). The effect of HCl explains the slow rate of reaction in basic solvents (Et_2O, $COMe_2$). Cl' is not a catalyst. *o*-Cresol is a strong and AcOH a weak catalyst.

R. S. C.

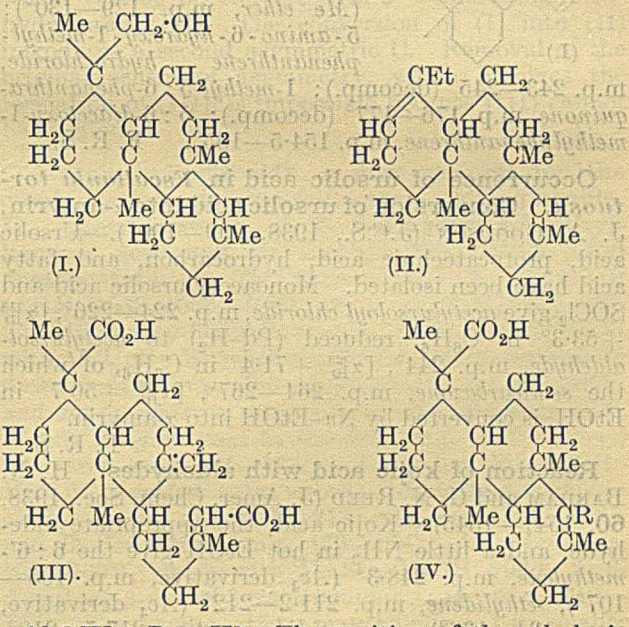
Salts of 3-bromo-*d*-camphor-10-sulphonic acid with organic bases. (Signa.) A. Federigi and (Signa.) E. Ortensi (Boll. Chim. farm., 1938, **77**, 397—400).—$(CH_2)_6N_4$, m.p. 146—147°, $[\alpha]_D^{18}$ +57·75° (all rotations in H_2O), *antipyrine*, m.p. 142—144°, $[\alpha]_D^{18}$ +54·27°, *pyramidone*, m.p. 150—152°, $[\alpha]_D^{18}$ +46·79°, and *piperazine* 3-*bromo*-d-*camphor*-10-*sulphonate*, m.p. 244° (decomp.), $[\alpha]_D^{18}$ +70·70°, are described.

E. W. W.

Fenchene series. VIII. Reaction mechanism of the dehydration of fenchyl alcohol. G. Komppa and G. A. N. Nyman (Annalen, 1938, **535**, 252—266; cf. A., 1938, II, 149).—Dehydration of fenchyl alcohol is shown by the following and published reactions to yield primarily α-fenchene (I), methylsantene (II), and *cyclo*fenchene; any β- (IV), γ- (V), or δ-fenchene formed arises by secondary rearrangement of (III). Use of *o*-$C_6H_4(CO)_2O$ leads to (I) with some (III), (II), (IV), and (?) (V). (III) is converted only at 190—200° by *o*-$C_6H_4(CO)_2O$ into (IV), (V), and *iso*fenchyl phthalate. Tschugaev's method gives (I) and (II) only. H_3PO_4 gives (III), (II), and (V) [(I) and (IV) are proved to be absent]; it converts (III) almost only into (II). $KHSO_4$ converts (III) into (V) and (IV). The products are identified mainly by oxidation.

R. S. C.

Diterpenes. XXXVII. Position of the carboxyl group in ring *A* of agathendiacid. L. Ruzicka and H. Jacobs (Rec. trav. chim., 1938, **57**, 509—519; cf. A., 1938, II, 287).—Ag *iso*noragathate and MeI give difficultly separable *Me* esters, m.p. 109—110°, $[\alpha]_D$ +27·2° in EtOH, and m.p. 92—93°, $[\alpha]_D$ −23·2° in EtOH. The mixed esters are reduced by Na–MeOH, –EtOH, or –*n*-$C_5H_{11}{\cdot}OH$ only with difficulty; in *n*-$C_5H_{11}{\cdot}OH$ mainly the amyl ester is obtained. Rapid addition of a little EtOH to the mixed esters and Na in xylene at 120° gives, however, a fair yield of *iso*noragathenol (I), b.p. 160—161°/0·1 mm., m.p. 120—121°; slow addition of the EtOH gives the *pinacol*, m.p. 222—226°. With 2-$C_{10}H_7{\cdot}SO_3H$ at 150—160° (I) gives the *hydrocarbon* (II), b.p. 118—122°/0·2 mm., dehydrogenated by Se at 330—340° to 7-methyl-1-ethylphenanthrene. This proves the formulæ of (I), (II), agathendiacid (III), *iso*agathendiacid [(IV); R = CO_2H], and *iso*noragathic



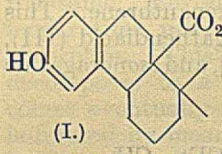
acid [(IV); R = H]. The position of the ethylenic linkings is open to doubt. By similar methods Et abietate gives 95% of abietinol, b.p. 163—167°/0·1 mm., and thence readily a *hydrocarbon*, $C_{20}H_{30}$, b.p. 127—129°/0·7 mm., and homoretene, new m.p. 81—82°. M.p. are corr.

R. S. C.

Recent progress in the chemistry of the terpenes. R. Dulou (Chim. et Ind., 1938, **40**, 3—18).—A review.

Podocarpic acid. I. I. R. Sherwood and W. F. Short (J.C.S., 1938, 1006—1013).—Podocarpic acid, (I), $C_{17}H_{22}O_3$, m.p. 193°, $[\alpha]_{578}$ +144°, has been shown to be tricyclic and to contain a phenolic nucleus. (I) forms an Ac derivative, m.p. 173—176° (cf. Oudemans, J. pr. Chem., 1874, **9**, 385), and with Me_2SO_4–NaOH gives Me podocarpate (II), m.p. 208° (lit. 174°) (*Bz* derivative, m.p. 143·5°); *Et*, m.p. 161°, and *p*-*nitrobenzyl podocarpate*, m.p. 204°, are similarly prepared. MeI–Na and (II) or (I) and Me_2SO_4–NaOH–EtOH yield *Me* O-*methylpodocarpate*, m.p. 128°, hydrolysed with difficulty to O-*methylpodocarpic acid*, m.p. 158°. Distillation of (I) with Zn affords 1-methylphenanthrene (*styphnate*, m.p. 152—153°). Dehydrogenation (Se) of (I) gives this hydrocarbon and a *phenol*, $C_{15}H_{12}O$, m.p. 161° (*picrate*, m.p. 182°; *acetate*, m.p. 118—119°; *benzoate*, m.p. 147°; *glycollic ether*, m.p. 191°), the *Me ether*, m.p. 87—87·5° (*picrate*, m.p. 140—141·5°), of which is oxidised to a *quinone*, m.p. 189° (*quinoxaline* derivative, m.p. 166°) [*acetoxy*-, m.p. 182·5—183·5°, and *hydroxy-quinone*, m.p. 264—

265° (decomp.), by oxidation of the acetate]. The phenol is 6-hydroxy-1-methylphenanthrene and with NaOAc–NH_4Cl–AcOH gives the corresponding *NHAc*-compound, m.p. 197·5—198° (*amine*, m.p. 151°; *iodomethylphenanthrene*, m.p. 144·5—145°). Distillation of Ca podocarpate yields *p*-cresol and carpene. The annexed provisional formula for (I) is suggested.



(I.)

The following are also described: 5-*bromo*-6-*hydroxy*-1-*methylphenanthrene*, m.p. 124° (*Me ether*, m.p. 129—130°); 5-*amino*-6-*hydroxy*-1-*methylphenanthrene hydrochloride*, m.p. 243—245° (decomp.); 1-*methyl*-5 : 6-*phenanthraquinone*, m.p. 176—177° (decomp.); 5 : 6-*diacetoxy*-1-*methylphenanthrene*, m.p. 154·5—155°. F. R. S.

Occurrence of ursolic acid in *Escallonia tortuosa*. Conversion of ursolic acid into α-amyrin. J. A. Goodson (J.C.S., 1938, 999—1001).—Ursolic acid, protocatechuic acid, hydrocarbon, and fatty acid have been isolated. Monoacetylursolic acid and $SOCl_2$ give *acetylursoloyl chloride*, m.p. 224—226°, $[\alpha]_D^{18}$ +53·3° in C_6H_6, reduced (Pd–H_2) to *acetylursolaldehyde*, m.p. 244°, $[\alpha]_D^{23}$ +71·4° in C_6H_6, of which the *semicarbazone*, m.p. 264—267°, $[\alpha]_D^{23}$ +50·7° in EtOH, is converted by Na–EtOH into α-amyrin. F. R. S.

Reaction of kojic acid with aldehydes. H. N. Barham and G. N. Reed (J. Amer. Chem. Soc., 1938, **60**, 1541—1545).—Kojic acid, the appropriate aldehyde, and a little NH_3 in hot EtOH give the 6 : 6′-*methylene*, m.p. 248·3° (*Ac*$_4$ derivative, m.p. 105—107°), *-ethylidene*, m.p. 211·2—212° (*Ac*$_4$ derivative, m.p. 134—136°), -n-*propylidene*, m.p. 217·5—218°, -n-*butylidene*, m.p. 192·4—193°, -n-*amylidene*, m.p. 185·6—187·2°, -n-*hexylidene*, m.p. 144—147°, -n-*heptylidene*, m.p. 152·6—153·6°, *-benzylidene* (I), m.p. 242·4° (decomp.) (*Ac*$_4$ derivative, m.p. 166—168°), *-γ-phenylpropylidene*, m.p. 182—183·5°, *-cinnamylidene*, m.p. 175—176°, -2-*furfurylidene*, m.p. 210—211°, and *-allylidene*, m.p. >250°, derivatives. CH_2O, but not other aldehydes, react similarly in H_2O. Resins are also formed during condensation in EtOH, and to a larger extent in H_2O, probably by further reaction similar to that involved in phenol–aldehyde resin formation. The structures ascribed to the products follow from analyses and from formation of unstable compounds with PhN_2Cl (PhN_2 attached to the phenolic OH). Kojic acid and PhN_2Cl give a stable product. (I) is also obtained [m.p. 250—256° (decomp.)] by $CHPhCl_2$ in $PhNO_2$ at 100—150°. M.p. are corr. R. S. C.

Saponins and sapogenins. VI. Surface films of chlorogenin and [its] derivatives. C. R. Noller. **VII. Structure of the side-chain of chlorogenin.** F. M. McMillan and C. R. Noller (J. Amer. Chem. Soc., 1938, **60**, 1629—1630, 1630—1633; cf. A., 1937, II, 346).—VI. The surface films of chlorogenin (I) and its diacetate are highly compressible; that of the derived diketone collapses at about 6 dynes per cm. These facts confirm location of the 2 OH of (I) in different rings and the relationship of (I) and gitogenin.

VII. *Chlorogenin diacetate*, m.p. 154—155°, and CrO_3 in AcOH at 32—33° (not 25° or 40°) give *chlorogenoic acid diacetate* (II), $C_{31}H_{46}O_8$, $+H_2O$, m.p. 114—116°, and anhyd., m.p. 210—211° (no semicarbazone; *Me* ester, m.p. 163°), hydrolysed to *chlorogenoic acid*, $C_{27}H_{42}O_6$, m.p. 169—170° (sinters at 161°). At, *e.g.*, 40° a small amount of a *diacetoxylactone*, (?) $C_{26}H_{38}O_6$, + MeOH, or $C_{27}H_{44}O_7$, m.p. 249—252°, is obtained; hydrolysis gives the $(OH)_2$-*lactone*, $C_{22}H_{34}O_4$, + MeOH, or $C_{23}H_{40}O_5$, m.p. 255—256°. Further oxidation of (II), *e.g.*, by $KMnO_4$, gives only a trace of an *acid*, $C_{27}H_{42}O_6$, m.p. 221—222°. With conc. HCl–AcOH (I) gives a very small amount of a ketone, yielding an impure semicarbazone, m.p. 114—118°. It is concluded that the side-chain of (I) resembles that of other steroid sapogenins. R. S. C.

Constituents of pyrethrum flowers. XII. Nature of the side-chain of pyrethrolone. F. B. LaForge and H. L. Haller (J. Org. Chem., 1938, **2**, 546—559; cf. A., 1938, II, 239).—The following reactions indicate, although not conclusively, that the ethylenic linkings in the side-chain of pyrethrolone (I) are not conjugated. Al–Hg (prep. described) in Et_2O reduces the OH of (I), yielding *pyrethrone* (II), b.p. 85—87°/0·35 mm. [*semicarbazone*, m.p. 216—218° (decomp.); *oxime*, m.p. 67° (*Bz* derivative, m.p. 94°); p-*nitrophenylhydrazone*, m.p. 139°], reduced by H_2–PtO_2 in EtOH to the H_4-ketone (dihydrojasmone) (III) and by Zn dust in HBr–AcOH to *dihydropyrethrone*, b.p. 115—118°/11 mm. [*semicarbazone*, m.p. 202°, hydrogenated (PtO_2) in EtOH to the semicarbazone of (III)]. Br adds to (II), but loss of HBr is so rapid that the reaction appears as substitution. There is no sign of 1 : 4-addition. Adding 1 mol. of Br in AcOH or EtOH gives 1 mol. of HBr and reducing the product with Zn dust regenerates (II). 2 mols. of Br similarly give 2 mols. of HBr and an oily product, reduced by Zn to (II) and other substances. Adding 2 mols. of Br to (I) gives 2 HBr and a product which regenerates (I). 1 : 2-Naphthaquinone does not react with (I) or (II), and $(CH{\cdot}CO)_2O$ gives resins. (II) absorbs 2 O from BzO_2H, but the product is unstable, and the Br-derivative of (I) does not react. When (II) is oxidised with $KMnO_4$, only $H_2C_2O_4$ is obtained. O_3 and (I) in CCl_4 at 0° give 23% of MeCHO; tetrahydropyrethrolone gives MeCHO and (?) CH_2O; (II) gives 15% of MeCHO. Heating (II) with Na in Et_2O gives a Na compound, converted by CO_2 into an amorphous acid. Attempts to add 1 H_2 to (II) give only (III) and unchanged (II). R. S. C.

Identification and constituents of the poisonous plants huang-t'eng and tsai-chung-yao. P. F. Mei and T. Q. Chou (Chinese Med. J., 1938, **54**, 37—39; cf. A., 1936, 1572).—The plants are probably identical with *Tripterygium Wilfordii*, Hook. They yield tripterin (changed to a *compound*, $C_{25}H_{34}O_4$, m.p. 219°, containing $COMe_2$ by recrystallisation from $COMe_2$; compound reconverted into tripetrin by recrystallisation from Et_2O) and approx. 1·5% of dulcitol. W. McC.

Onocerin. J. Zimmermann (Helv. Chim. Acta, 1938, **21**, 853—859).—Crude onocerin (I), isolated from the roots of *Ononis spinosa*, has m.p. (indef.) 205—226° whereas that derived by hydrolysis of the

diacetate (II), m.p. 224°, $[\alpha]_D$ +29·4° in $CHCl_3$, has m.p. 202—203°. Oxidation (CrO_3 in AcOH) of (I) affords onocerindiketone, m.p. 185° (*dioxime*, m.p. 236°). Similar oxidation of (II) yields the *diketone diacetate*, $C_{34}H_{48}O_6$, m.p. 302—303° (*dioxime*, m.p. 330°). Hydrogenation (Pt in warm AcOH) of (II) yields *tetrahydro-onocerin diacetate* (III), m.p. 218°, $[\alpha]_D$ +57·1° in $CHCl_3$, which does not give a colour with $C(NO_2)_4$; it is hydrolysed to *tetrahydro-onocerin*, m.p. 255°, oxidised to the corresponding *diketone*, m.p. 209—211° (*dioxime*, $C_{30}H_{50}O_2N_2$, m.p. 253—254°). The mother-liquors from (III) contain a substance hydrolysed to a *diol*, m.p. 187° (*diacetate*, m.p. 170°, $[\alpha]_D$ +55·2° in $CHCl_3$), which is oxidised to a *diketone*, m.p. 154° (*dioxime*, $C_{30}H_{50}O_2N_2$, m.p. 248°). Crude (I) is converted by boiling 90% HCO_2H into the *diformate*, $C_{32}H_{46}O_4$, m.p. 226° (vac.), $[\alpha]_D$ +104° in $CHCl_3$, hydrolysed to a *diol* (IV), m.p. 230° (vac.) [corresponding *diacetate*, m.p. 260° (vac.), $[\alpha]_D$ +106° in $CHCl_3$, also obtained from (II) and HCO_2H]. (IV) is oxidised to a *diketone*, m.p. 170° (*oxime*, $C_{30}H_{46}O_2N_2$, m.p. 244°). It is therefore probable that (I) is not a pentacyclic triterpene, into which, however, it is converted by boiling HCO_2H. H. W.

Functional groups of adermin. R. Kuhn and G. Wendt (Ber., 1938, **71**, [*B*], 1534—1535).—Vitamin-B_6 hydrochloride is converted by CH_2N_2 in MeOH into *adermin Me ether*, m.p. 89·5—90°, which does not give a colour reaction with $FeCl_3$ or couple with $SO_3H{\cdot}C_6H_4{\cdot}N_2^+$. It is transformed by Ac_2O in C_5H_5N into *diacetyladermin Me ether* (I), m.p. 53—54°. All three O of adermin belong to OH, of which one is phenolic and the others are alcoholic. Active H cannot be detected in (I) at an increased temp. The N of the vitamin is ring-*tert*. H. W.

Rottlerin. IV. K. S. Narang, J. N. Ray, and B. S. Roy (Current Sci., 1938, **6**, 606—608).—A defence of the $C_{31}H_{30}O_8$ formula for rottlerin and a criticism of the views of Robertson *et al.* (A., 1938, II, 199). L. S. T.

Heparin. T. Astrup and H. B. Jensen (J. Biol. Chem., 1938, **124**, 309—312).—Crude heparin purified by repeated centrifuging in N-NaOH and N-NaOH–NaCl and treatment with AcOH and fuller's earth etc. gives with $Ba(OAc)_2$–$Ba(OH)_2$ a Ba salt which with Na_2SO_4 gives, after repeated pptn. by NaCl in $COMe_2$ and in EtOH, the *Na* salt, $C_{26}H_{36}O_{41}N_2S_4Na_8$ (vac.-dried) [corresponding with $C_{26}H_{78}O_{58}N_2S_4$ (air-dried heparin); cf. A., 1936, 1535], $[\alpha]_D^{24}$ +43·7° (in H_2O?). In boiling 0·1N-HCl, this is inactivated in 3 min.; from the product a *Ba* salt, $C_{38}H_{52}O_{52}N_2S_2Ba_3$, is obtained, corresponding with an inactivated heparin, $C_{19}H_{29}O_{26}NS$, in which 1 hexosamine and 3 SO_3H groups have been lost. As $BaSO_4$ equiv. to only 1 SO_3H is found, 2 SO_3H may be bound to the hexosamine. E. W. W.

Mechanism of the formation of γ-acetopropyl [δ-keto-*n*-amyl] alcohol during hydrogenation-hydration of 2-methylfuran. Consecutivity of hydrogenation of the ethylenic linkings of 2-methylfuran. K. Toptschiev (Compt. rend. Acad. Sci. U.R.S.S., 1938, **19**, 497—498).—Hydrogenation-hydration of 2-methylfuran gives the 4 : 5-H_2-derivative, which hydrates to 2-hydroxy-2-methyl-furan; by ring-fission this gives $COMe{\cdot}[CH_2]_3{\cdot}OH$, which is the only product isolated (Russ. Pat. 48,104, 1937). R. S. C.

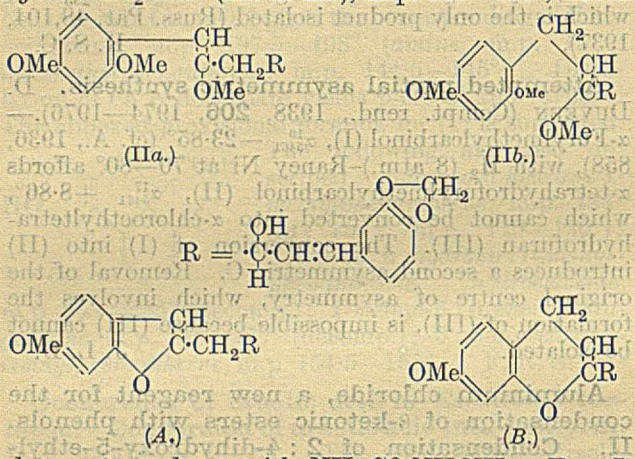
Attempted partial asymmetric synthesis. D. Duveen (Compt. rend., 1938, **206**, 1974—1976).—α-Furylmethylcarbinol (I), α_{5461}^{19} −23·85° (cf. A., 1936, 858), with H_2 (8 atm.)–Raney Ni at 70—80° affords α-tetrahydrofurylmethylcarbinol (II), α_{5461}^{17} +8·86°, which cannot be converted into α-chloroethyltetrahydrofuran (III). The conversion of (I) into (II) introduces a second asymmetric C. Removal of the original centre of asymmetry, which involves the formation of (III), is impossible because (III) cannot be isolated. J. L. D.

Aluminium chloride, a new reagent for the condensation of β-ketonic esters with phenols. II. Condensation of 2 : 4-dihydroxy-5-ethylbenzoic acid and its methyl ester with ethyl acetoacetate. S. M. Sethna and R. C. Shah (J.C.S., 1938, 1066—1069; cf. A., 1938, II, 152).—Me 2 : 4-dihydroxy-5-ethylbenzoate and $CH_2Ac{\cdot}CO_2Et$ with $AlCl_3$ give *Me 5-hydroxy-4-methyl-8-ethylcoumarin-6-carboxylate*, m.p. 186—187° (*Ac*, m.p. 183—185°, and *Bz* derivatives, m.p. 154—156°; *Me ether*, m.p. 87—88°), hydrolysed to the *acid*, m.p. 242° (efferv.) (*Ph* ester, m.p. 134—135°). The ester with AcOH–HCl in a sealed tube affords *5-hydroxy-4-methyl-8-ethylcoumarin*, m.p. 212—213° (*Ac*, m.p. 112—114°, and *Bz* derivatives, m.p. 173—174°; *Me ether*, m.p. 107—109°), which with Me_2SO_4–NaOH yields 2 : 6-*dimethoxy-β-methyl-3-ethylcinnamic acid*, m.p. 119—121°. The condensations may be effected in smaller yield with H_2SO_4. F. R. S.

Natural coumarins. XXXVII. Skimmin. E. Späth and O. Neufeld (Rec. trav. chim., 1938, **60**, 535—540; cf. A., 1938, II, 152).—Skimmin, $C_{15}H_{16}O_8$, $+H_2O$, m.p. 219—221° (decomp.), $[\alpha]_D^{18}$ −79·8° in C_5H_5N (tetra-acetate, m.p. 183—184°, $[\alpha]_D^{16}$ −62·7° in C_5H_5N), is proved to be umbelliferone β-glucoside by identification of the umbelliferone and glucose formed by hydrolysis, and by synthesis (m.p. 221—222°) from umbelliferone and acetobromoglucose. R. S. C.

Egonol. I. Constitution of egonol and a new permanganate oxidation process, "the benzene method." S. Kawai and T. Miyoshi (Ber., 1938, **71**, [*B*], 1457—1464).—Extraction of the fruits of *Styrax japonicum*, Sieb. and Zucc., with Et_2O gives "egonoki" oil, hydrolysed by KOH–H_2O–EtOH to egonol (I), $C_{20}H_{18}O_5$, m.p. 117·5—118°, b.p. 228—230°/0·15 mm., which contains 1 OMe, 1 OH [*acetate*, m.p. 107—107·5°, re-converted into (I) by hydrolysis; *p-nitrophenylurethane*, m.p. 208·5—209°], and CH_2O_2 (since it gives piperonylic acid when oxidised); the fifth O is in an ether bridge. (I) is optically inactive but evidence is adduced in favour of the view that this is due to racemisation during hydrolysis and that the natural material is optically active. (I) does not react with *o*-$C_6H_4(CO)_2O$ in C_6H_6 and is unaffected by Me_2SO_4 and alkali; OH is therefore *sec.* or *tert.* Very mild oxidation of (I) with CrO_3 in AcOH gives quantitatively only a polymeride of high m.p. KOH–

EtOH under pressure transforms (I) into *egonol hydrate Me_2 ether* (II*a* or II*b*), m.p. 125—126°, which



does not condense with $NH_2·CO·NH·NH_2$. For (I) the structure *A* or *B* is adduced.

Good results are obtained by oxidising with aq. $KMnO_4$ the well-agitated, emulsified C_6H_6 solution of (I) in H_2O. H. W.

Synthesis of α-tocopherol. P. Karrer, H. Fritzsche, B. H. Ringier, and H. Salomon (Helv. Chim. Acta, 1938, **21**, 820—825).—Synthetic α-tocopherol (I), obtained from trimethyquinol (II) and phytyl bromide, is converted by 3-bromocamphorsulphonyl chloride in C_5H_5N into a *bromocamphorsulphonate*, m.p. 48—50°, $[\alpha]_D^{20}$ +29·93°±2°, identical with that derived from natural (I). Allyl bromide, (II), and anhyd. $ZnCl_2$ in boiling light petroleum give 5-*hydroxy*-2 : 4 : 6 : 7-*tetramethylcoumaran* or 6-*hydroxy*-5 : 7 : 8-*trimethylchroman*, m.p. 126—127°. The *allophanate* of the product from geranyl bromide and (II) has m.p. 158°. Dimethylquinol reacts readily with αβ-unsaturated alkyl halides, usually giving mixtures of compounds. Neotocopherol, allyl bromide, and $ZnCl_2$ give *allylneotocopherol* (*allophanate*, m.p. 165°). H. W.

Vitamin-*E*. Synthesis of α-tocopherol. F. Bergel, A. Jacob, A. R. Todd, and T. S. Work (Nature, 1938, **142**, 36).—Racemic α-tocopherol has been synthesised by heating phytol and ψ-cumoquinol in presence of $ZnCl_2$ (cf. A., 1938, II, 290). 6-Hydroxychromans, 5-hydroxycoumarans, and α- and β-tocopherol are almost identical as regards absorption spectrum, reducing properties, and the effect of esterification on the absorption spectrum. Recent degradation evidence favours a chroman structure for the tocopherols. L. S. T.

Vitamin-*E*. I. Structure and synthesis of α-tocopherol. L. I. Smith, H. E. Ungnade, and W. W. Prichard (Science, 1938, **88**, 37—38).—α-Tocopherol (I) has been synthesised from trimethylquinol (II) and phytyl bromide without the aid of a catalyst, and from (II) and phytadiene. 6-Hydroxypentamethylchroman has been synthesised (*a*) from (II) and γγ-dimethylallyl bromide, (*b*) from (II) and isoprene, and (*c*) from 6-hydroxy-5 : 7 : 8-trimethyl-3 : 4-dihydrocoumarin and MgMeI. These syntheses indicate that Fernholz's structure for (I) (A., 1938, II, 186) is correct (cf. *ibid.*, 290). L. S. T.

Vitamin-*E*. III. Permanganate oxidation of α-tocopherol. O. H. Emerson (Science, 1938, **88**, 40).—Oxidation of α-tocopherol (I) in $COMe_2$ with neutral $KMnO_4$ affords a good yield of the $C_{21}H_{40}O_2$ lactone which was isolated as the benzylthiuronium salt of its OH-acid. Admixture with the corresponding salt obtained by the CrO_3 oxidation of (I) produced no depression of the m.p. Further support for the chroman structure of (I) is thus afforded. L. S. T.

Vitamin-*E*.—See A., 1938, III, 680.

Unsaponifiable matter of wheat germ oil. β-Tocopherol. A. Ichiba (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1938, **34**, 627—628; cf. A., 1938, III, 358).—β-Tocopherol allophanate has $[\alpha]_D$ +6·37° in $CHCl_3$. Pyrolysis gives a sublimate, m.p. 165°. α-Tocopherol allophanate has not been obtained, possibly owing to change during working up. R. S. C.

Flavones from the dibromides of *o*-hydroxyphenyl styryl ketones. Modified synthesis of apigenin and luteolin. W. A. Hutchins and T. S. Wheeler (Current Sci., 1938, **6**, 605).—The dibromides of certain *o*-hydroxyphenyl styryl ketones give better yields of the flavones by treatment with KCN–EtOH (cf. A., 1938, II, 18). *o*-Hydroxyphenyl α-bromo-β-ethoxy-β-alkoxyphenylethyl ketones give flavones with KCN–EtOH. 2-Hydroxy-4 : 6-dimethoxyphenyl *p*-methoxystyryl ketone is brominated to 5-*bromo*-2-*hydroxy*-4 : 6-*dimethoxyphenyl* αβ-*dibromo*-β-*p*-*anisylethyl ketone* which, when heated, gives 6-*bromo*-5 : 7 : 4′-*trimethoxyflavone*; with HI this gives apigenin. Luteolin is synthesised by heating 5-*bromo*-2-*hydroxy*-4 : 6-*dimethoxyphenyl* αβ-*dibromo*-β-3 : 4-*dimethoxyphenylethyl ketone* with KCN–EtOH and treating the *bromoflavone* formed with HI. L. S. T.

Nobiletin. I. K. F. Tseng. **II.** R. Robinson and K. F. Tseng (J.C.S., 1938, 1003—1004, 1004—1006).—I. An oil extracted by cold MeOH from *Citrus nobilis*, Lour, affords *nobiletin* (I), $C_{15}H_4O_2(OMe)_6$, m.p. 134°, hydrolysed (EtOH–KOH) to veratric acid.

II. Hydrolysis of (I) with EtOH–KOH yields acetoveratrone, isolated as the oxime, and demethylation (HI) gives 5 : 6 : 7 : 8 : 3′ : 4′-*hexahydroxyflavone*, m.p. 310—314° (decomp.) (Ac_6, m.p. 226—228°, and Bz_6 derivatives, m.p. 235—236°), which is methylated (CH_2N_2) to 5-*hydroxy*-6 : 7 : 8 : 3′ : 4′-*pentamethoxyflavone*, m.p. 145°. (I) is probably 5 : 6 : 7 : 8 : 3′ : 4′-hexamethoxyflavone. F. R. S.

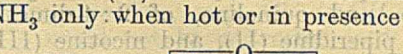
Colouring matter of red cabbage. III. I. Chmielewska, I. Smardzewska, and J. Kulesza (Rocz. Chem., 1938, **18**, 176—184).—Rubrobrassin chloride (I) (A., 1937, II, 71) is hydrolysed by HCl in MeOH to cyanidin chloride and glucose, leaving a OMe originally present unaccounted for. Similar treatment of 3 : 3′- and 5 : 7-dimethylcyanidin does not result in elimination of Me, whence it is supposed that the aglucone of (I) does not contain OMe, but that the disaccharide removed by hydrolysis consists of glucose and an unknown methylhexose. Carbomethoxyvanillyl chloride and Et sodio-αγ-dimethoxyacetoacetate interact in Et_2O, the solvent is distilled off, and the residue is boiled with 2·5% KOH for 2·5

hr., to yield 4-*hydroxy*-3-*methoxyphenyl methoxymethyl ketone* (II), b.p. 180°/22 mm., m.p. 62—63°. 3 : 4-*Dihydroxyphenyl methoxymethyl ketone*, m.p. 118° (decomp.), is prepared analogously from dicarbomethoxyprotocatechuyl chloride. The product of acetylation of (II) condensed with 4 : 6-dihydroxy-2-benzoyloxybenzaldehyde in EtOH–EtOAc, by saturating with HCl at 0°, yields 5-*benzoyl*-3 : 3′-*dimethylcyanidin chloride*. This is hydrolysed with 2N-NaOH to 3 : 3′-*dimethylcyanidin* (*chloride*, $+H_2O$), which is not attacked by boiling HCl–MeOH. 6-Hydroxy-2 : 4-dimethoxybenzaldehyde and 3 : 4-diacetoxyphenyl acetoxymethyl ketone in anhyd. HCO_2H when treated with HCl at 0° yield 5 : 7-*dimethylcyanidin chloride*. R. T.

New natural colouring matter of the naphthalene group. J. R. Price and R. Robinson (Nature, 1938, **142**, 147—148).—*Dunnione* (I), $C_{15}H_{14}O_3$, orange-red needles from H_2O or light petroleum, m.p. 98—99°, occurs as a deposit on the leaves and inflorescences of *Streptocarpus Dunnii*, Mast. (I) is a β-naphthaquinone derivative, and its behaviour towards alkalis indicates that the O is a member of an easily-ruptured chroman or coumaran ring. Acidification of the alkaline solution obtained under certain conditions does not regenerate (I), but forms a new *substance* which is probably an α-naphthaquinone derivative. The formation of MeCHO by oxidation with alkaline H_2O_2 and the 1·6 mols. of AcOH produced on oxidation with CrO_3 indicate that (I) is 2 : 3 : 3-trimethyl-6 : 7-benzocoumaran-4 : 5-quinone or the isomeride with the CMe_2 directly attached to O. L. S. T.

Derivatives of 1 : 4-dioxan. VII. F. P. A. Tellegen [with, in part, C. Vermande, C. Kuylaas, J. Ehrenburg, P. Maltha, and J. van Dalen] (Rec. trav. chim., 1938, **57**, 667—672; cf. A., 1938, II, 110).—2 : 3-Dichlorodioxan with $CH_3Br{\cdot}CH_2{\cdot}OH$ (I) or $CHPh_2{\cdot}CH_2{\cdot}OH$ (II) in hot C_6H_6 gives 2 : 3-*di*-β-*bromo*- (III), m.p. 41—43°, and 2 : 3-*di*-ββ-*diphenyl-ethyldioxan*, m.p. 121·5—122·5°, the rate of reaction being (II) < (I) < $CH_2Cl{\cdot}CH_2{\cdot}OH$. In boiling PhMe, PhOH (or NaOPh in $COMe_2$) and *p*-$NO_2{\cdot}C_6H_4{\cdot}OH$ give 2 : 3-*diphenoxy*-, m.p. 119—121°, and 2 : 3-*di*-p-*nitrophenoxy-dioxan*, m.p. 220—222° (reduced by $SnCl_2$ or Na_2S to *p*-$NH_2{\cdot}C_6H_4{\cdot}OH$), respectively. NaI in $COMe_2$ converts (III) into 2 : 3-*di*-β-*iodoethoxydioxan*, m.p. 51—52°. (II) is obtained from $CHPh_2{\cdot}OMe$ by successive action of Na and $(CH_2O)_3$. $CHPh_2{\cdot}CHO$ is unaffected by $Al(OEt)_3$ or H_2–Pd-C, and with H_2–Pt gives only a little $CHPh_2{\cdot}OH$. The halogeno-ethers do not react with Mg. Heating $CHCl_2{\cdot}CH(OEt)_2$ with $(CH_2{\cdot}OH)_2$ and H_2SO_4 with removal of the Et_2O formed gives 54% of 2-dichloromethyl-1 : 3-dioxa*cyclo*pentane, b.p. 188—191°/760 mm., 94°/20 mm. (cf. Meldrum *et al.*, A., 1936, 708), converted by Bz_2O–H_2SO_4 into $CHCl_2{\cdot}CHO$ and $(CH_2{\cdot}OBz)_2$. R. S. C.

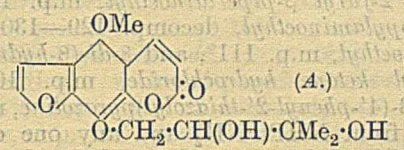
Sesamin. II. W. D. Cohen (Rec. trav. chim., 1938, **57**, 653—658; cf. A., 1929, 298).—Sesamin and Br–AcOH give the Br_2-derivative [(I); R = 2 : 5 : 6-$C_6H_2Br{\cdot}O_2CH_2$], m.p. 180·5—181°, $[\alpha]_D$ −9·6° in $CHCl_3$, converted by HNO_3 into 1 : 2 : 5 : 4-$CH_2O_2{\cdot}C_6H_2Br{\cdot}NO_2$ and an oily *substance* (?) (II). The structure of (II) is based on the reduction of $AgNO_3$–NH_3 only when hot or in presence of KOH,


(I.)

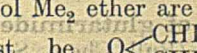

(II.)

on the very slow reaction with fuchsin–SO_2, on the inertness towards Fehling's solution, and on formation in dil. HCl of (? βγ-)*dihydroxyadipdialdehydedi*-2 : 4-*dinitrophenylhydrazone*. R. S. C.

Chemical constituents of Umbelliferæ. VI. Constituents of the root of *Angelica glabra*, Makino. T. Noguchi and M. Kawanami (Ber., 1938, **71**, [*B*], 1428—1430).—Aminobergapten is converted by diazotisation into 8-*hydroxy*-5-*methoxypsoralen*, m.p. 212° (decomp.), identical with the phenol obtained by the action of AcOH–H_2SO_4 on Byak-angelicin (I). The Et ether of this phenol is identical with 5-*methoxy*-8-*ethoxypsoralen*, m.p. 140—141°. (I) is therefore *A*.


(*A*.)

H. W.

Synthesis of eudesmin and pinoresinol dimethyl ether from *l*-asarinin and *d*-sesamin. T. Kaku and H. Ri (Keijo J. Med., 1938, **9**, 5—20).—*l*-Asarinin (I) or *d*-sesamin with KOH–MeOH, followed by CH_2N_2, may be converted into epi*eudesmin*, m.p. 133—134°, $[\alpha]_D^{16}$ −144·8° in $CHCl_3$ (normal form, eudesmin, m.p. 107—108°, $[\alpha]_D^{20}$ −64·2° in $CHCl_3$), or epi*pinoresinol Me*$_2$ *ether*, m.p. 133—134°, $[\alpha]_D$ +145·5° in $CHCl_3$ (normal form, pinoresinol Me_2 ether, m.p. 107—108° $[\alpha]_D^{16}$ +64·3° in $CHCl_3$). The following derivatives are described: r-epi*eudesmin*, m.p. 121—122°; *dinitro*epi*eudesmin*, m.p. 159—161°, $[\alpha]_D^{27}$ −73·9° in $CHCl_3$, and m.p. 222—225°; dinitroeudesmin, m.p. 212°, $[\alpha]_D^{22·5}$ +125·5° in $CHCl_3$; *mononitroeudesmin*, m.p. 168—170°, $[\alpha]_D^{22·5}$ +141·8° in $CHCl_3$; *dinitro*epi*pinoresinol Me*$_2$ *ether*, m.p. 159—161°, $[\alpha]_D^{27}$ +73·7° in $CHCl_3$; r-*dinitro*epi*eudesmin*, m.p. 219—220°; dinitropinoresinol Me_2 ether, m.p. 212—213°, $[\alpha]_D^{24}$ −124·6° in $CHCl_3$; mononitrospinoresinol Me_2 ether, m.p. 169—171°, $[\alpha]_D^{19}$ −143·2° in $CHCl_3$; r-dinitroeudesmin, m.p. 240—241°; *dibromo*epi*eudesmin*, m.p. 160—161°, $[\alpha]_D^{27}$ −106·3° in $CHCl_3$; dibromoeudesmin, m.p. 173° $[\alpha]_D^{27}$ +69·3°; *dibromo*epi*pinoresinol Me*$_2$ *ether*, m.p. 160—161°, $[\alpha]_D^{27}$ +107·1° in $CHCl_3$; dibromospinoresinol Me_2 ether, m.p. 173°, $[\alpha]_D^{21}$ −68·5° in $CHCl_3$; *r-dibromo*epi*eudesmin*, m.p. 157—158°, and r-dibromoeudesmin, m.p. 177—178°. The conclusion is reached that eudesmin and pinoresinol Me_2 ether are optical antipodes and that (I) must be  (R = 3 : 4-$C_6H_3{\cdot}O_2CH_2$). F. R. S.

Acid properties of pyrrole. M. Deželić and B. Belia (Annalen, 1938, **535**, 291—300).—Measurements of η indicate by max. the existence of 2 : 1, 1 : 1,

or 1 : 2 compounds of pyrrole with $CH_2Ph{\cdot}NH_2$ (I), β-picoline, and quinoline, of 2 : 4-dimethylpyrrole with (I), piperidine (II), and nicotine (III), and of 2 : 4-dimethyl-3-ethylpyrrole with (II) and (III). Evolution of heat on mixing indicates reaction of pyrrole with NEt_3. Acids, EtOH, and PrCHO do not form compounds. The acidity of pyrrole thus proved is connected with the aromatic nature of the ring, for which an electronic structure is given. R. S. C.

Heterocyclic ketones. II. β-Amino-ketones containing thiophen, thiazole, and furan nuclei, and their behaviour towards phenylhydrazine. G. A. Levvy and H. B. Nisbet (J.C.S., 1938, 1053—1056).—The syntheses of β-amino-ketones of the type $R{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}NR_2,HCl$ from 2-acetylthiophen, 2-acetyl-4-phenylthiazole, and 2-acetylfuran by the Mannich reaction are described: 2-*thienyl* β-*piperidinomethyl*, m.p. 199°, and β-*dimethylaminoethyl ketone hydrochloride*, m.p. 172°; 4-*phenyl*-2-*thiazolyl* β-*piperidinoethyl*, m.p. 193—195° (decomp.), β-*dimethylaminoethyl*, m.p. 174°, β-*diethylaminoethyl*, m.p. 142°, and β-*di*-n-*propylaminoethyl ketone hydrochloride*; 2-*furyl* β-*piperidinoethyl*, m.p. 185—186°, β-*di*-n-*propylaminoethyl*, decomp. 129—130°, β-*di*-n-*butylaminoethyl*, m.p. 111°, and β-*di*-(β-*hydroxyethyl*)-*aminoethyl ketone hydrochloride*, m.p. 100—101°; 1-*phenyl*-3-(4′-*phenyl*-2′-*thiazolyl*)*pyrazoline*, m.p. 198°, obtained from $NHPh{\cdot}NH_2$ and any one of the 4-phenyl-2-thiazolyl compounds; and the *phenylhydrazone* of 2-acetyl-4-phenylthiazole, m.p. 141° (N-*Ac* derivative, m.p. 209°). F. R. S.

Pyridine and quinoline series. I. Historical. II. Synthesis of 4-hydroxymethylpiperidine from citric acid. III. Theory of the hydrogenation of nuclear carboxylic acids of the pyridine series to carbinols. P. Rabe [with, in part, O. Spreckelsen, L. Wilhelm, and H. Hüter] (J. pr. Chem., 1938, [ii], **151**, 65—81).—I. The relationship of C_5H_5N and quinoline to the cinchona alkaloids is discussed.

II. 2 : 6-Dichloropyridine-4-carboxylic acid (I) is reduced (Sn and 30% HCl) to 2 : 6-dichloro-4-hydroxymethylpyridine, m.p. 133° (benzoate, m.p. 121°), which is converted (H_2–Pd sponge in KOH–MeOH containing $BaCO_3$ at room temp.) into 4-hydroxymethylpyridine, m.p. (indef.) 47—50° [hydrochloride, m.p. 175° (decomp.); non-cryst. benzoate and its *picrate*, m.p. 186°], whence (H_2–Pt sponge–1% H_2SO_4) the very hygroscopic 4-*hydroxymethylpiperidine*, b.p. 118—120°/10 mm., m.p. 56—62°.

III. Treatment of pyridine-3- or -4-carboxylic acid with Sn and 30% HCl gives the corresponding carbinol in comparatively poor yield. Electrolysis of (I) at a Pb cathode in aq. or alcoholic H_2SO_4 or treatment of it with H_2 (Pd sponge in 10% H_2SO_4 or AcOH) does not cause replacement of halogen. This is effected by H_2 (Pd) in a basic medium. H. W.

Electrolytic reduction of glutarimide and its derivatives. B. Sakurai (Bull. Chem. Soc. Japan, 1938, **13**, 482—488).—Glutarimide and its *N*-Me, *N*-Et, and *N*-Ph derivatives are electrolytically reduced at a Pb cathode, best in 20—30, 50, 50, and 80—90% H_2SO_4, respectively, to the piperidones in good yield. Further reduction in 50% H_2SO_4 at a special Pb or Zn–Hg cathode gives the piperidine derivatives. N-*Ethyl*-, b.p. 250—260°, and N-*phenylglutarimide*, m.p. 145°, *piperidone platinichloride*, m.p. 176° (decomp.), N-*ethyl*-, b.p. 105—106° [*platinichloride*, m.p. 164° (decomp.)], and N-*phenyl-piperidone*, m.p. 98° [*platinichloride*, m.p. 176° (decomp.)], *N*-ethyl- [*platinichloride*, m.p. 202° (decomp.)] and *N*-phenyl-piperidine (*platinichloride*, $+2H_2O$) are described. R. S. C.

Tautomerism of homologues of pyridine. Syntheses in the pyridine series. V. Condensation reactions. A. E. Tschitschibabin (Rec. trav. chim., 1938, **57**, 582—585; cf. A., 1938, II, 245).—Na derivatives of α- (I) and γ-picoline (II) and quinaldine (III) react with RHal as do Grignard reagents. Thus, addition of $COPh_2$ in (III) to $NaNH_2$ in (III) gives 2-α-*hydroxy*-αα-*diphenylethylquinoline*, m.p. 160—162° (*hydrochloride*). (I) gives similarly a good yield of 2-α-*hydroxy*-αα-*diphenylethylpyridine*, m.p. 142° (*hydrochloride*). Aliphatic ketones, however, give mainly condensation products derived from the ketone, and camphor gives also a very poor yield of *tert.* alcohol. PhCHO gives a little 2-α-hydroxy-α-phenylethylpyridine, the main products being those of the Cannizzaro reaction. MeOBz and EtOBz with (I) and $NaNH_2$ give mainly BzOH and NH_2Bz with some 2-phenacylpyridine (IV), m.p. 56°. PhCN, (I), and $NaNH_2$ give cyaphenin and the imine [hydrolysed to (IV)], but (II) gives only 4-*phenacylpyridine*, m.p. 100—105°. R. S. C.

Formation of 3 : 5-di-iodo-2(4)-hydroxypyridine from 2-halogenopyridines. Z. Rodewald (Rocz. Chem., 1938, **18**, 96—102).—2-Bromo- or 2 : 6-dibromo-pyridine heated at 185° (20 hr.) with conc. HI yields a mixture of 3 : 5-di-iodo-2- (I) and -4-hydroxypyridine (II). The process is represented: C_5H_4NBr or $C_5H_3NBr_2 + HI \rightarrow C_5H_5N \rightarrow (+ I)$ 3 : 5-di-iodopyridine → 3 : 4 : 5- and 2 : 3 : 5-tri-iodopyridine → $(+H_2O)$ (I) and (II). Since C_5H_5N and HI under similar conditions give only NH_3 and C_5H_{12}, it is supposed that the iodination of C_5H_5N is catalysed by some unknown intermediate product. R. T.

Influences of alkyl groups in carbonyl compounds. E. E. Ayling (J.C.S., 1938, 1014—1023).—The effect of the nature of R in CORR′ is that expected from electronic considerations when R takes part in the reaction. For *k* of RCO_2H, the *m*-nitration of ROBz, the prototropy of COPhR, and the Hantzsch reaction with aliphatic aldehydes (new, comparable data are provided) anomalies occur when R = Pr^{α}, becoming less marked with higher members; this is due to the terminal Me in $COPr^{\alpha}$ approaching closest to the CO and thus exerting the max. field effect (attraction of the unshared electrons of the O by Me). The following new data are recorded: b.p. of RCHO, R = Pr^{α} 75·5°/755·5 mm., Bu^{α} 103°/767 mm., Bu^{β} 93°/764 mm., CHPh:CH 134°/19 mm., $CH_2Ph{\cdot}CH_2$ 101·5°/10·5 mm., and CH_2Ph 82°/10 mm.; *Et*$_2$ 2 : 6-*dimethyl*-4-n-*butyl*- (I), m.p. 97°, -4-β-*phenylethyl*- (II), m.p. 112°, -4-n-*propyl*-, m.p. 125·5°, -4-*iso*butyl-, m.p. 97°, -4-*n*-amyl-, m.p. 56°, and -4-benzyl- (III), m.p. 119°, and 2 : 4 : 6-*trimethyl*-, m.p. 130°, -1 : 4-*dihydropyridine*-3 : 5-*dicarboxylate*. (III) or the corre-

sponding Pr^{β} ester (IV) with hot N-HNO_3 gives Et_2 2 : 6-dimethylpyridine-3 : 5-dicarboxylate, but (I) and (II) give *Et*$_2$ 2 : 6-*dimethyl*-4-n-*butyl*-, b.p. 198—199°/16 mm., and -4-β-*phenylethyl-pyridine*-3 : 5-*dicarboxylate* (V), m.p. 34°, b.p. 246—247°/18 mm. (*nitrate*, m.p. 128°), respectively. With S at 170° or 200° (II), (III), and (IV) give *Et*$_2$ 2 : 6-*dimethyl*-4-iso*propyl*-, b.p. 183°/11 mm., and -4-*benzyl-pyridine*-3 : 5-*dicarboxylate*, b.p. 225°/12 mm., m.p. 46° (*hydrochloride*, m.p. 89°), and (V). R. S. C.

Pyridine derivatives.—See B., 1938, 902.

Syntheses of pyrrole and indole derivatives by use of magnesyl derivatives. Q. Mingoia (Boll. Chim. farm., 1938, **77**, 337—358).—A review. E. W. W.

Preparation of isatin-β-oxime. V. Hovorka and V. Sýkora (Chem. Listy, 1938, **32**, 241—243).—The β-oxime is prepared from isatin and NH_2OH,HCl in boiling aq. solution. R. T.

Synthesis of 6 : 7-dimethoxyquinoline. S. Sugasawa, K. Kakemi, and T. Tsuda (Proc. Imp. Acad. Tokyo, 1938, **14**, 67—68).—2-Keto-6 : 7-dimethoxy-1 : 2 : 3 : 4-tetrahydroquinoline with P_2S_5 and K_2S in xylene yields 2-*thion*-6 : 7-*dimethoxy*-1 : 2 : 3 : 4-*tetrahydroquinoline*, m.p. 151°, which is reduced at a Pb cathode in EtOH–H_2SO_4 to 6 : 7-*dimethoxy*-1 : 2 : 3 : 4-*tetrahydroquinoline*, an oil (*hydrochloride*, m.p. 196°; *NO*-, m.p. 137°, and *Bz* derivative, m.p. 102°), oxidised by Pd and cinnamic acid to 6 : 7-*dimethoxyquinoline*, an oil [*hydrochloride*, m.p. 232° (decomp.); *picrate*, m.p. 251—252° (decomp.)]. J. D. R.

Reaction between hydrazine hydrate and 4-chloroquinoline derivatives. O. G. Backeberg and C. A. Friedmann (J.C.S., 1938, 972—977).—The compound, obtained by Koenigs *et al.* (A., 1935, 989) by heating N_2H_4 and 4-chloroquinaldine at 150° in a sealed tube is 3 : 4-*diaminoquinaldine* (I), m.p. 122° (*platinichloride*, decomp. >300°), the Ac_2 derivative, m.p. 193°, being converted by EtOH–HCl into 2 : 2′-*dimethylquin*(3 : 4 : 5′ : 4′)*iminazole*, m.p. 100° (*picrate*, m.p. 200°; *platinichloride*, decomp. >300°). HCO_2H and (I) yield 2-*methylquin*-(3 : 4 : 5′ : 4′)*iminazole*, m.p. 97° (*picrate*, m.p. 210°). (I) is also obtained by the method of Marckwald and Chain (A., 1900, i, 521). 4-Chloro-6-, -5 (or -7)-, and -8-methyl-, -5 : 7-, and -6 : 8-dimethyl-quinaldine all react similarly with N_2H_4 in a sealed tube. The following are described: 4-*hydrazino*-8-*methyl*-, m.p. 199°; 3 : 4-*diamino*-8-, m.p. 122° (*picrate*, m.p. 202°), and -6-*methyl*-, m.p. 153° [*picrate*, m.p. 208° (decomp.)]; 4-*hydroxy*-5(or 7)-*methyl*-, m.p. 273°, 4-*chloro*-5(or 7)-*methyl*-, m.p. 78° (*picrate*, m.p. 193°), 3 : 4-*diamino*-5(or 7)-*methyl*-, m.p. 150° [*picrate*, m.p. 212° (decomp.)], 3 : 4-*diamino*-6 : 8-*dimethyl*-, m.p. 140° (*picrate*, m.p. 183°), 4-*hydroxy*-5 : 7-*dimethyl*-, m.p. 288° (decomp.) (*picrate*, m.p. 207°), 4-*chloro*-5 : 7-*dimethyl*-, m.p. 73° (*picrate*, m.p. 226°), and 3 : 4-*diamino*-5 : 7-*dimethyl*-*quinaldine*, m.p. 150° (*picrate*, m.p. 214°), and 3 : 4-*diaminoquinoline*, m.p. 129° (*picrate*, m.p. 197°), and 4-*anilino*-3-*methylquinaldine*, m.p. 219°. 4 : 4′-*Azo*-5 : 7 : 5′ : 7′-*tetramethylquinaldine*, m.p. 250° (decomp.), is also obtained from N_2H_4 and 4-chloro-5 : 7-dimethylquinaldine. 3 : 4-*Dichloroquinaldine*, m.p. 67° (4-*OH*-compound, m.p. 340°), could not be converted into the corresponding $(NH_2)_2$-compound, and nitration of 4-aminoquinaldine gives 4-*nitroaminonitroquinaldine*, decomp. 200°, and *dinitro*-4-*aminoquinaldine*, m.p. 276°, reduced (Na_2S) to 4-*aminonitroaminoquinaldine*, m.p. 220° (decomp.). F. R. S.

Reaction between phenylhydrazine and 4-chloroquinoline derivatives, and the preparation of the corresponding 4-benzeneazo- and 4-amino-compounds. O. G. Backeberg (J.C.S., 1938, 1083—1087).—$NHPh{\cdot}NH_2$ and 4-chloroquinolines react to form (i) the corresponding 4-phenylhydrazino-compound, if the reaction is carried out at 200° in an inert solvent, and (ii) the corresponding 4-amino-3-anilino-compound, if the reaction is in a sealed tube at 200°. The 4-phenylhydrazino-compounds are unstable in air, and are readily oxidised ($FeCl_3$) to the 4-benzeneazo-compounds, which can be reduced (Zn–HCl) to the 4-NH_2-derivatives. The following are described: 4-*phenylhydrazino*-, m.p. 188° [*hydrochloride*, m.p. 284° (decomp.)], and 4-*benzeneazo-quinaldine*, m.p. 100°; 4-*amino*-3-*anilino*-, m.p. 142° [*hydrochloride*, m.p. 218° (decomp.)], not identical with 4-p-*aminoanilino-quinaldine*, m.p. 173°; 1′-*phenyl*-2 : 2′-*dimethylquin*(3 : 4 : 5′ : 4′)-*iminazole*, m.p. 124° (*platinichloride*, decomp. >300°); 4-*acetamido*-3-*anilinoquinaldine*, m.p. 117°; 4-*phenylhydrazino*-, m.p. 205°, 4-*benzeneazo*-, m.p. 104°, and 128°, 4-*amino*-, m.p. 205°, and 4-*amino*-3-*anilino*-, m.p. 100°, -6-*methylquinaldine*; 4-*benzeneazo*-, m.p. 76°, 4-*amino*-, m.p. 161°, and 4-*amino*-3-*anilino*-, m.p. 137°, 5(or 7)-*methylquinaldine*; 4-*benzeneazo*-, m.p. 104°, 4-*amino*-, m.p. 141°, and 4-*amino*-3-*anilino*-, m.p. 101°, -8-*methylquinaldine*; 4-*benzeneazo*-, m.p. 126°, 4-*amino*-, m.p. 166°, and 4-*amino*-3-*anilino*-, m.p. 127°, -5 : 7-*dimethylquinaldine*; 4-*benzeneazo*-, m.p. 117°, 4-*amino*-, m.p. 165°, and 4-*amino*-3-*anilino*-, m.p. 105°, -6 : 8-*dimethylquinaldine*; 4-*benzeneazo*-, m.p. 105—109°, and 4-*amino*-6-*ethoxyquinaldine*, m.p. 197°; 4-*benzeneazo*-, m.p. 117°, and 4-*amino*-8-*ethoxyquinaldine*, m.p. 222°; 4-*benzeneazoquinoline*, m.p. 70° and 89°; 4-*amino*-3-*anilinoquinoline*, m.p. 134°; and 4-*benzeneazo*-, m.p. 133°, and 4-*amino*-3-*methylquinaldine*, m.p. 189°. F. R. S.

Synthesis of 2 : 4-diarylaminoquinoline derivatives. II. K. Dziewoński and W. Dymek [with M. Głowacka, M. Kitliński, and J. Kuźma] (Rocz. Chem., 1938, **18**, 145—157).—Di-*p*-tolylacetamidine and PhNCS at 220° (4 hr.) yield 4-*anilino*-2-p-*toluidino*-6-*methylquinoline*, m.p. 79° [*hydrochloride*, m.p. 274°; *nitrate*, m.p. 231°; *picrate*, m.p. 253°; *NO*-derivative, m.p. 153° (decomp.)], hydrolysed by NaOH–EtOH to 2-p-*toluidino*-4-*hydroxy*-6-*methylquinoline*, m.p. 300—305°, and this further to 2 : 4-*dihydroxy*-6-*methylquinoline*, m.p. >350°. NHPhAc and $CO(NHPh)_2$ (I) heated at 260° for 5 hr. yield 2 : 4-dianilinoquinoline [*nitrate*, m.p. 212° (decomp.); *sulphate*, m.p. 312°; NO_2-derivative, m.p. 213—215°; *Br*-derivative (II), m.p. 194—196° (*hydrobromide*, m.p. 282°)]. 2-Anilino-4-hydroxyquinoline (III), PCl_5, and $POCl_3$ (3 hr. at the b.p.) afford 4-*chloro*-2-*anilinoquinoline*, m.p. 161°. (III) in 15% KOH and Me_2SO_4 (30 min.

at the b.p.) yield 2-*anilino*-4-*methoxyquinoline*, m.p. 118—120°. (II) is hydrolysed by EtOH–NaOH (6 hr. at 220°) to 2(4)-*anilino*-*dihydroxyquinoline*, m.p. 318—320°. EtCO·NHPh, NH_2Ph, and (I) (3 hr. at 290°) yield 2 : 4-*dianilino*-3-*methylquinoline*, m.p. 190° [*hydrochloride*, m.p. 282—283°; *picrate*, m.p. 243° (decomp.); 2(4)-*NO*-derivative, m.p. 110° (decomp.); 2(4)-N-*Ac* derivative, m.p. 177°], from which a mixture of 4-*anilino*-2-, m.p. 260—262°, and 2-*anilino*-4-*hydroxy*-3-*methylquinoline*, m.p. 264—266°, is obtained by hydrolysis with EtOH–NaOH (220°; 8 hr.). $CH_2Ph·CO·NHPh$ and (I) (280°; 3 hr.) afford 2 : 4-*dianilino*-3-*phenylquinoline*, m.p. 180—181° (*picrate*, m.p. 230—231°), hydrolysed as above to 4-*anilino*-2-, m.p. 295°, and 2-*anilino*-4-*hydroxy*-3-*phenylquinoline*, m.p. 236—238°, and by prolonged hydrolysis to 2 : 4-*dihydroxy*-3-*phenylquinoline*, m.p. 320—323°. *s*-Di-*p*-tolylcarbamide and NHPhAc (280°; 3 hr.) yield 2-*anilino*-4-p-*toluidino*-6-*methylquinoline*, m.p. 90—100° (*hydrochloride*, m.p. 250°). R. T.

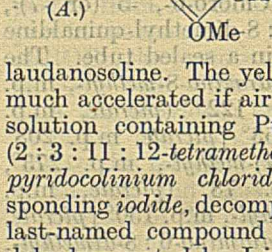
Derivatives of 2-phenylquinoline-4-carboxylic acid. A. Lespagnol and (Mlle.) Bar (Bull. Sci. Pharmacol., 1938, **45**, 200—203).—2-Phenylquinoline-4-carboxyl chloride hydrochloride, m.p. 135°, is obtained cryst. by the action of boiling $SOCl_2$ on the acid and separation from the cold liquid. Interaction of it in C_5H_5N with 2 : 1 : 3-$OH·C_6H_3Me·CO_2H$ gives 2-*phenylcinchonoyl*-m-*toluic acid*, m.p. 180°, transformed by NH_3 into 2-phenylquinoline-4-carboxylamide, m.p. 195°. *Piperazine* 2-*phenylquinoline*-4-*carboxylate* has m.p. 203°. H. W.

Condensation of pyruvic acid with aromatic amines and aldehydes. IV. C. Leśkiewiczówna and S. Weil (Rocz. Chem., 1938, **18**, 174—175).—*o*-Anisidine and $AcCO_2H$ in EtOH (at the b.p.) condense with veratraldehyde, anisaldehyde, or 3-nitrovanillin, giving 8-*methoxy*-2-(3′ : 4′-*dimethoxyphenyl*)-, $+H_2O$, m.p. 105—106°, -2-p-*methoxyphenyl*-, m.p. 203—204°, or -2-(2′-*nitro*-4′-*hydroxy*-3′-*methoxyphenyl*)-*quinoline*-4-*carboxylic acid*, m.p. 170—173° (decomp.). R. T.

Relationships between physicochemical properties and pharmacological action of alkoxyquinoline compounds.—See A., 1938, III, 688.

Isomerisation phenomena of 2-aminoindan-1 : 3-dione derivatives. G. Wanag and U. Walbe (Ber., 1938, **71**, [*B*], 1448—1456).—2-Anilino-2-phenylindan-1 : 3-dione is converted by NaOMe in boiling MeOH into 1 : 4-*diketo*-2 : 3-*diphenyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline, m.p. 156° (vac.), which passes when heated at 110° in an open vessel into phthalanil, m.p. 204°, and is transformed by acid into 1 : 4-*diketo*-3-*phenyl*isochroman, $C_6H_4<^{CO·CHPh}_{CO·O}$, m.p. 148° (*phenylhydrazone*, m.p. 161°; p-*nitrophenylhydrazone*, m.p. 166—167°), which is reduced (Clemmensen) to dibenzyl-2-carboxylic acid and by Sn and 2N–HCl to 4-*hydroxy*-1-*ketophenyl*isochroman, m.p. 162° (decomp.) when rapidly heated or m.p. 143—144° after softening at about 130° when slowly heated; this does not give CO-derivatives but is transformed by Ac_2O in C_5H_5N into the *compound*, $C_{15}H_{10}O_2$, m.p. 90°. 1 : 4-*Diketo*-3-*phenyl*-2-p-*anisyl*-, m.p. 181°, and -2-p-*tolyl*-, m.p. 183°, -1 : 2 : 3 : 4-*tetrahydro*isoquinoline are obtained analogously. 2-Bromo-2-phenylindan-1 : 3-dione and $CH_2Ph·NH_2$ in Et_2O yield 2-*benzylamino*-2-*phenylindan*-1 : 3-*dione*, m.p. 109° (unstable *hydrochloride*; *NO*-derivative, m.p. 125°), transformed by NaOMe in boiling MeOH into 2-*benzylamino*-1 : 4-*diketo*-3-*phenyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline, m.p. 132° (vac.) after softening, 2-iso*Butylamino*-1 : 4-*diketo*-3-*phenyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline has m.p. 118° (vac.). 2-*Amino*-2-*phenylindan*-1 : 3-*dione*, m.p. 99° (*Ac* derivative, m.p. 246°), gives 1 : 4-*diketo*-3-*phenyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline, m.p. 257° after softening at 220°, transformed by NaOMe and MeI in boiling MeOH into the *Me* derivative, m.p. 240° after softening at 234°. 2-Anilino-2-methylindan-1 : 3-dione is converted into 1 : 4-*diketo*-2-*phenyl*-3-*methyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline, m.p. 160—161° (vac.). 2-Bromo-2-methylindan-1 : 3-dione yields 2-p-*toluidino*-2-*methylindan*-1 : 3-*dione*, m.p. 163° (*nitroso*-2-p-*toluidino*-2-*methylindan*-1 : 3-*dione*, m.p. 183°), which gives 1 : 4-*diketo*-2-p-*tolyl*-3-*methyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline, m.p. 157—158° (vac.). 2-p-*Anisidino*-2-*methylindan*-1 : 3-*dione*, m.p. 131°, affords 1 : 4-*diketo*-2-p-*anisyl*-3-*methyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline, m.p. 162—163° (vac.). H. W.

Synthesis of dibenzopyridocoline derivatives. I. Synthesis of 5 : 18-9 : 14-(2 : 3 : 11 : 12-tetramethoxy)dibenzo-6 : 7 : 15 : 6-tetrahydropyridocoline. S. Sugasawa and K. Kakemi (Proc. Imp. Acad. Tokyo, 1938, **14**, 214—217).—The K derivative of 2-keto-6 : 7-dimethoxy-1 : 2 : 3 : 4-tetrahydroquinoline is converted by β-3 : 4-dimethoxyphenylethyl bromide and Cu powder in boiling xylene into 2-*keto*-6 : 7-*dimethoxy*-1-β-3′ : 4′-*dimethoxyphenylethyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*. This is transformed by $POCl_3$ in boiling PhMe into 5 : 18-9 : 14-(2 : 3 : 11 : 12-*tetramethoxy*)*dibenzo*-6 : 7 : 15 : 16-*tetrahydro*-8 : 17-*dehydropyridocolinium chloride*, decomp. 228° after changing colour at 220°, which is hydrogenated (PtO_2–Pt-black in EtOH) to 5 : 18-9 : 14-(2 : 3 : 11 : 12-*tetramethoxy*)*dibenzo*-6 : 7 : 15 : 16-*tetrahydropyridocoline* (*A*), m.p. 153—154° (*methiodide*, decomp. 237—238°; *hydrochloride*, decomp. 236—237°), identical with that derived from homolaudanosoline. The yellowing of the free base in air is much accelerated if air is passed through the alcoholic solution containing Pt-black, whereby 5 : 18-9 : 14-(2 : 3 : 11 : 12-*tetramethoxy*)*dibenzo*-8 : 17-*dehydropyridocolinium chloride*, decomp. 231—232° (corresponding *iodide*, decomp. 279—280°), is produced; the last-named compound also results when the base is dehydrogenated by I in EtOH. H. W.



(*A*.)

Dyes derived from thiohydantoin. III. G. P. Pendse (J. Indian Chem. Soc., 1938, **15**, 229—231).—Thiohydantoin condenses (position 5) with the following compounds in hot Ac_2O, yielding *dyes* having the m.p. given: phenanthraquinone, 146°; tetramethyldiaminobenzophenone, 166°; acenaphthenequinone, >260°; isatin, >260°; fluorenone, 102°; alizarin,

157°; benzil, 93°; dibenzylideneacetone, 113°; *p*-benzoquinone, 136°; anthraquinone, 167°. A. Li.

Simplified method of preparing histidine. L. E. Gilson (J. Biol. Chem., 1938, **124**, 281—285).—The method of Hanke and Koessler (A., 1920, i, 756) is simplified. Hæmoglobin hydrolysed by HCl is treated with NaOH, followed, after filtration, by H_2S or Na_2S. AcOH is added, followed by a relatively small amount of $HgCl_2$. Na_2CO_3 then ppts. the $HgCl_2$ salt of histidine, decomposed in aq. suspension by H_2S, giving the monohydrochloride of histidine, which is isolated as the dihydrochloride from a mixture of conc. HCl with 5 vols. of 80% dioxan. Full details are given. E. W. W.

Condensation of phenylmethylpyrazolone derivatives with aromatic aldehydes. (A) J. Janicka, C. Hiszpańska, and S. Weil. (B) W. Dmowska and S. Weil (Rocz. Chem., 1938, **18**, 158—160, 170—173).—(A) 1-Aryl-3-methylpyrazol-5-one condenses with aldehydes, in EtOH–NaOH solution, to yield 4-m-*nitro*-, m.p. 176—177°, and 4-(3′ : 4′-*dimethoxybenzylidene*)-1-o-*tolyl*-3-*methylpyrazol*-5-*one*, m.p. 222—223°, 4-p-*dimethylaminobenzylidene*-, m.p. 180°, 4-p-*methoxybenzylidene*-, m.p. 142°, 4-(4′-*hydroxy*-3′-*methoxybenzylidene*)-, m.p. 187°, and 4-(2′-*nitro*-4′-*hydroxy*-3′-*methoxybenzylidene*)-1-p-*tolyl*-3-*methylpyrazol*-5-*one*, m.p. 209°, and 4-(2′-*nitro*-4′-*hydroxy*-3′-*methoxybenzylidene*)-1-*phenyl*-3-*methylpyrazol*-5-*one*, m.p. 192°.

(B) 4-p-*Dimethylamino*-, m.p. 196°, and 4-p-*nitrobenzylidene*-1-*phenyl*-3-*methylpyrazol*-5-*one*, m.p. 209—210°, are prepared as above. With *m*-NO_2·C_6H_4·CHO the product of condensation is 4 : 4′-m-*nitrobenzylidene*-*di*-(1-*phenyl*-3-*methylpyrazol*-5-*one*) (I), m.p. 227—228°. This crystallises as a dihydrate from aq. EtOH, and the dihydrate loses H_2O at 100°, to yield an isomeric, presumably enolic, form of (I), m.p. 164—165°. R. T.

2-Undecyl- and 2-heptadecyl-glyoxaline.—See B., 1938, 889.

Hydroxy-acids and their derivatives. VII. 2 : 5-Dialkylpiperazines. H. Ōeda (Bull. Chem. Soc. Japan, 1938, **13**, 465—470).—The products obtained by hydrogenation of α-NH_2-amides and believed (A., 1937, II, 235, 456) to be (·CHR·CH_2·NH_2)$_2$ are identified as 2 : 5-dialkylpiperazines. Leucine anhydride and Na–EtOH give 2 : 5-*diisobutylpiperazine*, m.p. 80—83° [*hydrochloride*, m.p. >330°; (*PhSO*$_2$)$_2$ derivative, m.p. 211—213° (corr.); identical with the product from OH·$CHBu^{\beta}$·CO·NH_2], and a base (*hydrochloride*, m.p. 160—162°).

NH_2·CH(CH_2Ph)·CO_2Et, b.p. 135—136°/8 mm., and Na–EtOH give 2 : 5-*dibenzylpiperazine*, m.p. 166—167° (corr.) [*Bz*$_2$ derivative, m.p. 281—283° (corr.); identical with the product from OH·CPhMe·CO·NH_2], with *l*-, m.p. 92—94° (corr.), $[\alpha]_D^{23}$ −24·4° in EtOH [*Bz* derivative, m.p. 169—171° (corr.)], and dl-β-*amino*-γ-*phenylpropyl alcohol*, m.p. 71—73° (corr.) [*Bz* derivative, m.p. 148—149° (corr.)]. R. S. C.

Pyrimidines. CLVIII. Oxidation of mercaptopyrimidines with chlorine water. T. B. Johnson and J. M. Sprague (J. Amer. Chem. Soc., 1938, **60**, 1622—1624).—2-Alkylthiolpyrimidines and 4-hydroxy-2-alkylthiolpyrimidines differ in their reaction with Cl_2 in H_2O or MeOH (cf. A., 1938, II, 30). Thus, passing Cl_2 into 4-amino-2-ethylthiol-5- or -6-methylpyrimidine and a little HCl in aq. MeOH gives 4-*chloroamino*-2-*ethylsulphonyl*-5- (I), m.p. 125—126°, and -6-*methylpyrimidine*, m.p. 133—134°, respectively. $NaHSO_3$ reduces (I) to 4-amino-2-ethylsulphonyl-5-methylpyrimidine, m.p. 136—137°. Similarly, 4-chloro-2-ethylthiol-6-methylpyrimidine gives 4-*chloro*-2-*ethylsulphonyl*-6-*methylpyrimidine*, b.p. 189—191°/3·5 mm., converted by cold NH_3–EtOH or hot aq. NH_3 into 4-*chloro*-2-*amino*-6-*methylpyrimidine*, m.p. 182—183°. 4-Hydroxy-2-ethylthiol-5-methylpyrimidine in MeOH gives 5-*chloro*-2 : 4-*diketo*-6-*methoxy*-5-*methylhexahydropyrimidine*, m.p. 220—221°, reduced by HI to "thymine." 4-Hydroxy-2-ethylthiol-6-methylpyrimidine gives 5 : 5-*dichloro*-2 : 4-*diketo*-6-*methoxy*-6-*methyltetrahydropyrimidine*, m.p. 274—275° (decomp.), reduced by Sn–HCl to 5-chloro-6-methyluracil, and 6-hydroxy-2-methyl- or -ethyl-thiolpyrimidine gives 5 : 5-dichloro-2 : 4-diketo-6-methoxytetrahydropyrimidine, m.p. 225—226°. R. S. C.

Attempted synthesis of methylenediquinazolone derivatives. A. Kassur and S. Weil (Rocz. Chem., 1938, **18**, 163—169).—CH_2(CO·NH_2)$_2$ or NH_2·CO·CH_2·CO·NHPh and *o*-NH_2·C_6H_4·CO_2H (I) (4—5 hr. at 150—155°) yield CH_2(CO·NHPh)$_2$ (II). Et malon-*p*-anisidide (III) and (I) (4—5 hr. at 160°) afford CH_2(CO·NH·C_6H_4·OMe)$_2$ (IV). Et malon-*p*-toluidide and (I) (5 hr. at 160°) give the *substance*, $C_6H_4<\begin{matrix}CO\cdot NR'\\N=CR\end{matrix}$ (R = CH_2·CO·NH·C_6H_4Me; R′ = *p*-C_6H_4·CO_2H), m.p. 218—219°. In presence of $POCl_3$ (I) condenses with NHPhAc, to yield 3-phenyl-2-methylquinazol-4-one, with phenacetin to give 3-*p*-phenetyl-2-methylquinazol-4-one, and with (IV) to give "*methylenedi*-(p-*methoxyphenyl*)*quinazolone*," m.p. >310°. PhCHO and (II) in EtOH and Na (24 hr. at the b.p.) give a condensation *product*, m.p. 242—243°, of 1 mol. of PhCHO with 2 mols. of (II). *o*-OH·C_6H_4CHO condenses with malon-*o*-toluidide or (III) in presence of piperidine, to give coumarin-3-carboxy-*o*-toluidide or -p-*anisidide*, m.p. 214°. R. T.

Formation of 2- and 3-3′-pyridylpyrrole by the thermal decomposition of 1-3′-pyridylpyrrole. J. P. Wibaut and H. P. L. Gitsels (Rec. trav. chim., 1938, **57**, 755—760).—Passage of 1-3′-pyridylpyrrole through a tube at 710—720° gives 3-, m.p. 137·5°, b.p. 160°/0·2 mm. [*monopicrate*, m.p. 199°; *picrolonate*, m.p. 254—255° (decomp.); 1-*Me* derivative (*picrate*, m.p. 194·5—195·5°)], and 2-3′-*pyridylpyrrole* (I), m.p. 100—100·8° [*picrate*, m.p. 202—203°; *picrolonate*, m.p. 250° (decomp.); K–MeI in PhMe gives β-nicotyrine]. The product, m.p. 72°, of Pictet *et al.* (A., 1895, i, 627), supposed to be (I), was thus a mixture, and the structural significance of their synthesis of nicotine disappears. R. S. C.

Reaction of certain diazosulphonates derived from β-naphthol-1-sulphonic acid. XVIII. 1 : 4-Diketo-3-(aminoaryl)tetrahydrophthalazines and related compounds. F. M. Rowe, M. A.

LÉCUTIER, and A. T. PETERS (J.C.S., 1938, 1079—1083).—The methods by which 1 : 4-diketo-3-(nitroaryl)tetrahydrophthalazines and 4-keto-1-methoxy-3-(nitroaryl)-3 : 4-dihydrophthalazines have been obtained are reviewed. 4-*Keto*-1-*methoxy*-3-(4′-*aminophenyl*)-3 : 4-*dihydrophthalazine*, m.p. 197°, obtained by reduction ($Na_2S_2O_4$) of the NO_2-compound, is deaminated to the 3-Ph derivative, and 1 : 4-*diketo*-3-(4′-*aminophenyl*)*tetrahydrophthalazine* (+H_2O), m.p. 247—248° (N-*Ac* derivative, m.p. 299—300°), and the 3′-*aminophenyl* compound, m.p. 233—234° [N-*Ac* derivative (+H_2O), m.p. 153—154°], are similarly prepared. Reduction of the NO_2-compounds with $SnCl_2$–HCl affords 4-*keto*-1-*methoxy*-3-(3′-*aminophenyl*)-3 : 4-*dihydrophthalazine*, m.p. 181° (*Ac* derivative, m.p. 246—247°), and the 2′-*aminophenyl* compound, m.p. 234—235° (*Ac* derivative, m.p. 219—220°), and 1 : 4-*diketo*-3-(2′-*aminophenyl*)*tetrahydrophthalazine* (+C_5H_5N), m.p. 430° (decomp.) (Ac_2 derivative, m.p. 224—225°), converted by heating into 2′ : 4-*anhydro*-1 : 4-*diketo*-3-(2′-*aminophenyl*)*tetrahydrophthalazine*, m.p. >430° (decomp.) (O-*Ac* derivative, m.p. 222—223°). 4-*Keto*-1-*methoxy*-3-(4′-*chloro*-2′-*nitrophenyl*)-3 : 4-*dihydrophthalazine*, m.p. 225—228°, is reduced (Fe–AcOH) to the -NH_2-compound, m.p. 217—219° (*Ac* derivative, m.p. 272—274°). 1 : 4-*Diketo*-3-(4′-*chloro*-2′-*aminophenyl*)-*tetrahydrophthalazine*, m.p. >440° (Ac_2 derivative, m.p. 245—246°), obtained by reduction ($SnCl_2$) of the -NO_2-compound, m.p. 286—287°, gives the 2′ : 4-*anhydro*-derivative, m.p. >440° (O-*Ac* derivative, m.p. >440°), on heating. F. R. S.

Amino-alcohols derived from carbazole. L. RUBERG and L. SMALL (J. Amer. Chem. Soc., 1938, **60**, 1591—1593).—2-Acetyl-9-methylcarbazole (prep. in 77% yield from 1 : 9-diacetylcarbazole, Me_2SO_4, and KOH in aq. $COMe_2$) (1 mol.), $(CH_2O)_3$ (2·5 mols.), and the appropriate amine hydrochloride (1·2 mol.) in *iso*-C_5H_{11}·OH give 2-β-*dimethylamino*-, m.p. 111·5—113·5° (*hydrochloride*, m.p. 191·5—193°), -*diethylamino*-, m.p. 70·5—72·5° (sinters at 69°) [*hydrochloride*, m.p. 163·5—166° (sinters at 160°)], and -1′ : 2′ : 3′ : 4′-*tetrahydroisoquinolino*-*propionyl*-9-*methylcarbazole*, m.p. 123—125° [*hydrochloride*, m.p. 211—213° (sinters at 209°)], hydrogenated (PtO_2) to 9-*methyl*-2-γ-*dimethylamino*-, m.p. 96·5—99° [*hydrochloride*, m.p. 195—196·2°; p-*nitrobenzoate hydrochloride*, m.p. 165—166·5° (softens at 164°)], -*diethylamino*- (I), m.p. 75·2—76° (sinters at 73°) [*picrate*, m.p. 136—138·5°; p-*nitrobenzoate hydrochloride*, m.p. 179—180·5° (sinters at 177°); decomposed by HCl–EtOH], and -1′ : 2′ : 3′ : 4′-*tetrahydroisoquinolino*-α-*hydroxy*-n-*propylcarbazole*, m.p. 151·5—153° [decomposed by HCl–EtOH; *styphnate*, m.p. 171—175° (decomp.; sinters at >135°); p-*nitrobenzoate hydrochloride*, m.p. 159·5—161° (sinters at 153°)]. Use of impure material in the prep. of (I) leads to a *substance*, m.p. 133—135° (*oxime*, m.p. 172—173°). 1-*Keto*-9-*methyl*-1 : 2 : 3 : 4-*tetrahydrocarbazole*, m.p. 101·5—103·5°, with $(CH_2O)_3$ and $NHMe_2$,HCl gives 1-*keto*-9-*methyl*-2-*dimethylaminomethyl*-1 : 2 : 3 : 4-*tetrahydrocarbazole*, m.p. 74—75° (sinters at 72·5°) [*hydrochloride*, m.p. about 190° (decomp.; sinters at about 180°)], hydrogenated to 1-*hydroxy*-9-*methyl*-2-*dimethylaminomethyl*-1 : 2 : 3 : 4-*tetrahydrocarbazole*, m.p. 123·5—125°, which is dehydrated by HCl–EtOH to (?) 9-*methyl*-2-*dimethylaminomethyl*-3 : 4-*dihydrocarbazole hydrochloride*, m.p. 192—194° (decomp.; sinters at about 180°). (I) approaches codeine in analgesic action, but has a convulsant effect; it shows the Straub tail-reaction of morphine in mice. R. S. C.

Alkaline degradation of tetrahydroxybutylquinoxaline and new quinoxaline derivatives. K. MAURER and B. BOETTGER (Ber., 1938, **71**, [*B*], 1383—1391).—Tetrahydroxybutylquinoxaline is transformed by NaOMe in warm MeOH–C_5H_5N mainly into the red amorphous 1 : 2-*dihydroquinoxalylglycollaldehyde* (I), m.p. 138—144° (decomp.), the constitution of which is established by its conversion by NHPh·NH_2 into *quinoxalylglyoxalphenylosazone* (II), $C_{22}H_{18}N_6$, m.p. 243°, and by Ac_2O–C_5H_5N into *quinoxalylglycollaldehyde acetate*, m.p. 117°, which immediately reduces cold Fehling's solution. Alkaline oxidation of (I) affords quinoxaline-2-carboxylic acid (III), m.p. 210°. Short treatment of (I) with boiling NH_2Ph gives 1 : 2-*dihydroquinoxalylglycollaldehydeanil* (IV), m.p. 188°, converted by excess of NHPh·NH_2 in hot EtOH into (II) and by boiling Ac_2O into the *acetate* (V), $C_{18}H_{15}O_2N_3$, m.p. 134°; it is oxidised by O_2 in presence of alkali to (III) and PhNC. Dehydrogenation of (IV) by H_2O_2 in PhMe gives *quinoxalylglycollaldehydeanil*, m.p. 208°, converted by NHPh·NH_2 into (II) and by Ac_2O in boiling C_5H_5N into (V). The constitution of (IV) is further established by its gradual transformation into the *pyrazine* derivative (VI), m.p. 253°. 1 : 2-*Dihydroquinoxalylglycollaldehyde*-p-*tolil*, m.p. 150°, is readily transformed into the corresponding *dehydro*-compound, m.p. 190°, and affords a *pyrazine* derivative, $C_{34}H_{26}N_6$, m.p. 267°. The *xylil*, m.p. 106°, its *dehydro*-compound, m.p. 187°, and the *pyrazine* derivative, m.p. 276°, are described. (III) (improved prep.) gives a Fe^{II} and an *aniline*, m.p. 156°, salt. *Quinoxaline*-2-*carboxyl chloride*, m.p. 115°, from (III) and $SOCl_2$, yields the corresponding *anilide*, m.p. 180°, p-*toluidide*, m.p. 150°, m-4-*xylidide*, m.p. 132°, and *Et* ester, m.p. 85°. *Tetrahydroquinoxaline*-2-*carboxanilide* has m.p. 154°. H. W.

Flavinduline derivatives. VIII. K. YAMADA and N. HASEBE (J. Soc. Chem. Ind. Japan, 1938, **41**, 160—161B).—The solubility, colour reactions, dyeing properties, and fastness of the *dyes* (*A*; R = Cl + 0·5$ZnCl_2$, m.p. 209—211°; R = Br, m.p. 220—222°; R = I, m.p. 128—130°) derived from *p*-benzoquinone (I) and *o*-NH_2·C_6H_4·NHEt are described. The similar dyes from phenanthraquinone [*chloride* (+0·5

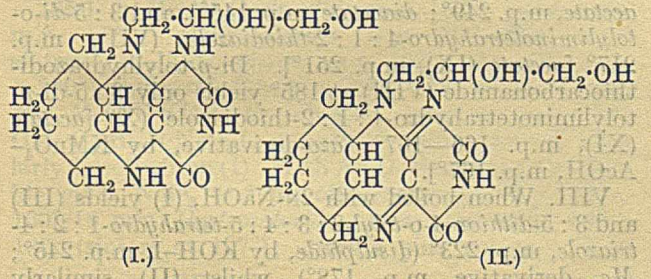
$ZnCl_2$), m.p. 206—208°; *bromide*, m.p. 218—220°; *iodide*, m.p. 154—156°] have been prepared. H. W.

Pyrimidines.—See B., 1938, 889.

Triazines. II. Lactim–lactam isomerism in substituted tetrahydrotriazines. (Miss) E. Bloch and H. Sobotka (J. Amer. Chem. Soc., 1938, **60**, 1656—1658; cf. A., 1938, II, 70).—Benzoylbiuret (modified prep.), m.p. 214—216°, is converted by KOH into 4 : 6-diketo-2-phenyl-3 : 4 : 5 : 6-tetrahydrobiuret, m.p. 297—300°. This is dimethylated by CH_2N_2 in dry Et_2O partly at the two *sec.* N and partly at the N in position 3 and the enolic form of the CO at 6, giving 4 : 6-*diketo*-2-*phenyl*-3 : 5-*dimethyl*-3 : 4 : 5 : 6-*tetrahydrotriazine* (I), m.p. 132°, and 4-*keto*-6-*methoxy*-2-*phenyl*-3-*methyl*-3 : 4-*dihydrotriazine* (II), m.p. 183°. With 25% NaOH (I) gives BzOH, NH_3, and >1 mol. of NH_2Me; with Br it gives a cryst. Br_4-derivative, unstable in air, Et_2O, or aq. alkali or in presence of Ag salts. With 2N-NaOH or aq. or alcoholic HCl (II) gives 4 : 6-*diketo*-2-*phenyl*-3-*methyl*-3 : 4 : 5 : 6-*tetrahydrotriazine*, m.p. 278—280°, which could not be converted into (I), but with CH_2N_2 gives 80% of (II). M.p. are corr. R. S. C.

Absorption of light and tautomerism of uric acid and cyanuric acid. E. Agallidis, H. Fromherz, and A. Hartmann (Ber., 1938, **71**, [*B*], 1391—1398).—It is not possible to maintain the arguments advanced by Biltz (cf. A., 1937, II, 78) against the author's conception, based on measurements of the absorption of light, that uric acid and its salts invariably exist in the keto- (lactam) -form even in alkaline solution. It is shown in the case of cyanuric acid (I), which exists in a keto-form in acid and a OH-form in alkaline solution, that a keto–enolic equilibrium of this type can be very readily detected by its light absorption curve. In the practically saturated aq. solution of (I), 5·6% of the OH-form is present. H. W.

Octahydroflavins. P. Karrer and R. Ostwald (Rec. trav. chim., 1938, **57**, 500—502).—In presence of PtO_2 9-$\beta\gamma$-dihydroxy-*n*-propyl*iso*alloxazine in H_2O absorbs 4 H_2 to give the H_8-derivatives (I), decomp. 255—260° (yellowish-green fluorescence in ultra-violet light), oxidised in alkaline solution to the H_6-



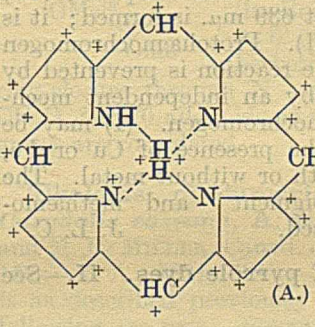
(I.) (II.)

derivative (II), decomp. about 263° (violet-blue fluorescence in ultra-violet light). 9-Hydroxyethyl- and 9-*d*-arabityl-*iso*alloxazine, but not lactoflavin, give similar H_8-derivatives; the effect of Me in positions 6 and 7 is evident. R. S. C.

Lactoflavinphosphoric acid-adeninenucleotide from liver and the co-enzyme of *d*-alaninedehydrogenase. P. Karrer, P. Frei, B. H. Ringier, and H. Bendas (Helv. Chim. Acta, 1938, **21**, 826—828).—A prep. of lactoflavinphosphoric acid-adeninenucleotide (I) from liver was able to activate *d*-alaninedehydrogenase, but the property was lost after further purification of (I). H. W.

Photoluminescent properties of synthetic flavin.—See A., 1938, I, 435.

Porphyrins and their metallic salts. V. Absorption and fluorescence of porphyrins in different solvents and the detailed structure of the porphin ring. F. Haurowitz [with F. Kraus and G. Appel] (Ber., 1938, **71**, [*B*], 1404—1412).—The absorption spectra of dimethylmesoporphyrin (I) and tetramethylhæmatoporphyrin in 31 media and certain acids and the fluorescence have been measured. Replacement of hexane by polar solvents causes a displacement of band I (in red) towards shorter λ and of the max. of band IV (in blue) towards longer λ. In the non-polar solvents CCl_4 and CS_2 all the visible absorption bands are displaced towards the red. Displacement of the absorption max. by polar solvents is not accompanied by marked spreading or depression thereof. Only in the alcohols, MeOH to C_5H_{11}·OH, do the bands become less defined so that the max. of the weak band 1*a* can no longer be accurately measured. Apparently, therefore, the chromophoric groups of the porphyrins are not immediately accessible to the solvent mols. and solvation does not occur. In mineral acids salt formation and true solvation of the chromophoric basic N-containing groups must be assumed. The fluorescence of the porphyrins is extinguished by MeI and $CHBr_3$ and greatly weakened by $C_2H_4Br_2$. In spite of their numerous double linkings porphyrins behave as aromatic and not as unsaturated olefinic compounds. They are not hydrogenated by $Na_2S_2O_4$ or by H_2–Pd–asbestos in alkaline solution. Their perbromides are readily converted by loss of Br into the initial materials. The absorption spectrum of mesoporphyrin ester hydrochloride in $CHCl_3$ is not considerably affected by $SbCl_3$. (I) is unchanged by molten maleic anhydride. The intimate structure of the porphyrin ring is, therefore, best expressed by *A*. H. W.



(A.)

Behaviour of chlorophyll derivatives towards chlorophyllase. H. Fischer and R. Lambrecht (Z. physiol. Chem., 1938, **253**, 253—260).—Chlorophyllase (I) catalyses the esterification of phæophorbide-*a* and -*b* and of the corresponding *meso*-compounds with MeOH and EtOH but does not cause ring-cleavage or enable Mg to enter into complex combination. It does not catalyse the esterification of pyrophæophorbide-*a*, of phæoporphyrin-a_5, of other porphyrins, or of hæmin but it removes Me from the Me_3 ester of purpurin-7 [yielding the corresponding Me_2 ester (+0·5H_2O), m.p. 225°] and from the Me_3

ester of *meso*purpurin-7 and hydrolyses the Me ester of *meso*purpurin-18. (I) also causes other changes in the constitution of the *meso*-compounds. Chlorins of the chlorophyll and the bacteriochlorophyll series are not affected by (I). The $\cdot[CH_2]_2\cdot CO_2H$, the CO_2H at 10, and the H at $C_{(5)}$ and $C_{(6)}$ in chlorophyll and its derivatives have a decisive effect on the action of (I). W. McC.

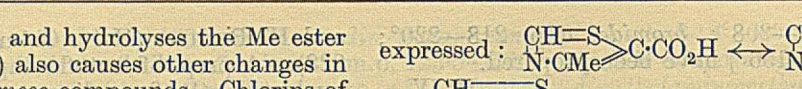
(A) **Coupled oxidation of ascorbic acid and hæmochromogens.** (B) **Chemical mechanism of the oxidation of protohæmatin to verdohæmatin.** R. Lemberg, B. Cortis-Jones, and M. Norrie (Biochem. J., 1938, **32**, 149—170, 171—186; cf. A., 1937, III, 364).—(A) The coupled oxidation of C_5H_5N-hæmochromogen and ascorbic acid (I) by atm. O_2 results in the oxidation of 0·2 mg. of hæmatin (II) and 1 mg. of (I). Verdohæmochromogen (III) is the only oxidation product of (II) and catalyses the oxidation of (I), from which the main oxidation product is dehydroascorbic acid. Oxidation of (II) is more affected by temp. variation than that of (I). The oxidation of (I) $\propto$ the O_2 tension whilst that of (II) is little affected. NaCN inhibits the reaction to an extent depending on the (I) concn. Glutathione preserves (I) by back-reduction of its oxidation product, (I) acting as H-carrier between (II) and glutathione.

(B) In the formation of (III) from C_5H_5N-hæmochromogen an intermediate hæmatin compound (IV) with an absorption band at 639 mμ. is formed; it is oxidised by atm. O_2 to (III). Protohæmochromogen yields (IV) with H_2O_2; the reaction is prevented by catalase. (I) is oxidised by an independent mechanism involving $Fe^{\cdots}$ hæmochromogen. (I) may be replaced by cysteine in the presence of Cu or Fe, but not by glutathione with or without metal. The mechanism of "green pigment" and methæmoglobin formation is discussed. J. L. C.

Absorption spectra of pyrrole dyes. II.—See A., 1938, I, 432.

Fluorescence of the chlorins.—See A., 1938, I, 434.

Preparation of 3-keto-8-carboxy-2-methyl-3 : 4-dihydro-1 : 4-benzoxazine. H. W. Coles and W. G. Christiansen (J. Amer. Chem. Soc., 1938, **60**, 1627—1628).—3 : 2 : 1-$NH_2\cdot C_6H_3(OH)\cdot CO_2H$ and $CHMeBr\cdot COBr$ in C_6H_6 give 3-*α-bromopropionamidosalicylic acid*, m.p. 188° (corr.) (sinters at 178°), converted by 10% NaOH at 60° into 3-*keto*-2-*methyl*-3 : 4-*dihydro*-1 : 4-*benzoxazine*-8-*carboxylic acid*, m.p. 285° (corr.), which has no antipyretic or hypnotic action. R. S. C.

Structure of thiazole. H. Erlenmeyer and H. M. Weber (Helv. Chim. Acta, 1938, **21**, 863—866).—4-Methylthiazole-5-carboxylic acid (I) suspended in D_2O is neutralised by NaOD; after 3 hr. at room temp. the solution is acidified with D_2SO_4, when 4 H of (I) are found to have been replaced by 4 D. An analogous behaviour is not shown by *o*-$C_6H_4Me\cdot CO_2H$. A tautomeric equilibrium which is not expressed by the usual formula is thus necessitated for (I). This and the aromatic character of S are expressed:  H. W.

Properties of isosteric and structurally similar compounds. VII. Preparation of 3-hydroxybenzthiazole. H. Erlenmeyer, H. Ueberwasser, and H. M. Weber (Helv. Chim. Acta, 1938, **21**, 709—711).—Boiling *o*-$OMe\cdot C_6H_4\cdot NH\cdot CHO$ is transformed by S into 3-*methoxy*-1-*thiolbenzthiazole*, m.p. 208°, oxidised by NaOCl to 3-*methoxybenzthiazole*-1-*sulphonic acid* (*Na* and *K* salts). This is converted by Na–Hg and 50% H_2SO_4 into 3-*methoxybenzthiazole*, m.p. 103°, transformed by boiling conc. HI or 48% HBr into 3-*hydroxybenzthiazole*, m.p. 143°. H. W.

Constitution of the so-called dithiourazole of Martin Freund. Ring-closure of hydrazodithiodicarbonamide and its mono- and di-substituted derivatives. VII. Action of heat. VIII. Action of sodium hydroxide. IX. Action of hydrochloric acid. X. Action of acetic anhydride. P. C. Guha and D. R. Mehta. **XI. Isomeric changes of some triazoles and thiodiazoles.** P. C. Guha and S. L. Janniah (J. Indian Inst. Sci., 1938, **21**, **A**, 41—59, 60—64; cf. A., 1933, 726).—VII. Hydrazodithiodicarbonamide at 210—215° yields 3-imino-5-thiontetrahydro-1 : 2 : 4-triazole. Similarly phenyl-, *o*-tolyl- (I), and *p*-tolyl-hydrazodithiocarbonamide (II) at 180—185° yield respectively 3-imino-5-thion-4-phenyltetrahydro-1 : 2 : 4-triazole, 3-*imino*-5-*thion*-4-*o*-, (III), m.p. 231° (*acetate*, m.p. 205°; *Me* derivative, by Me_2SO_4–NaOH, m.p. 142°), and -4-*p*-*tolyltetrahydro*-1 : 2 : 4-*triazole*, m.p. 277° (IV) (*acetate*, m.p. 160°; *Me* derivative, m.p. 142°). Diphenylhydrazodithiocarbonamide at 180° yields 5-anilo-3-thion- and 3 : 5-diphenylimino-tetrahydro-4 : 2 : 1-thiodiazole, whilst above 200° an alkali-sol. *product*, m.p. 206°, and alkali-insol. *product*, m.p. 232—233° (*acetate*, m.p. 174°), are formed. Similarly, di-*o*-tolylhydrazodithiodicarbonamide (V) at 170° yields 3-*thion*-5-*imino*-5-*o*-*tolyltetrahydro*-4 : 1 : 2-*thiodiazole*, (VI), m.p. 213—214° [*disulphide*, by oxidation with I, m.p. 200°; *Me* derivative, by MeI–MeOH–KOH, m.p. 158° (*acetate*, m.p. 123°); *CH_2Ph* derivative, by CH_2PhCl in EtOH–KOH, m.p. 112—113°; *acetate*, m.p. 249°; *diacetate*, m.p. 145°], and 3 : 5-*di*-*o*-*tolyliminotetrahydro*-4 : 1 : 2-*thiodiazole* (VII), m.p. 217° [*acetate* (IX), m.p. 251°]. Di-*p*-tolylhydrazodithiocarbonamide (VIII) at 185° yields only 3 : 5-di-*p*-tolyliminotetrahydro-4 : 1 : 2-thiodiazole (X) [*acetate* (XI), m.p. 166—167°; *azo*-derivative, by $KMnO_4$–AcOH, m.p. 167°].

VIII. When boiled with 2N-NaOH, (I) yields (III) and 3 : 5-*dithion*-4-*o*-*tolyl*-2 ; 3 : 4 : 5-*tetrahydro*-1 : 2 : 4-*triazole*, m.p. 223° (*disulphide*, by KOH–I, m.p. 245°; *Me_2* derivative, m.p. 178°), whilst (II), similarly treated, yields (IV) and 3 : 5-*dithion*-4-*p*-*tolyl*-2 : 3 : 4 : 5-*tetrahydro*-1 : 2 : 4-*triazole*, m.p. 213° [*disulphide*, m.p. 227° (decomp.); *Me_2* derivative, m.p. 140°].

IX. When heated with conc. HCl for 30 min. (V) yields (VI) and (VII) whilst (VIII) yields 5-*p*-tolylimino-3-thiontetrahydro-4 : 1 : 2-thiodiazole.

X. When heated with Ac_2O, (I) yields the *acetate*,

m.p. 265°, of 5-o-*tolyliminotetrahydro*-4 : 1 : 2-*thiodiazole*, m.p. 206—207°, whilst (II) yields the *acetate*, m.p. 298°, of 5-p-*tolyliminotetrahydro*-4 : 1 : 2-*thiodiazole*, m.p. 188°. With (V), Ac_2O yields (IX), which is hydrolysed (HCl) to 2 : 3 *dihydro*-3-o-*tolylamino*-3 : 5-endo-o-*tolylimino*-4 : 1 : 2-*thiodiazole*, m.p. 223°; similar treatment of (VIII) yields (XI), hydrolysed to (X).

XI. With Ac_2O, 3 : 5-dithiol-4 : 1 : 2-thiodiazole yields *di*-(3-*thiol*-2 : 4 : 5-*thiodiazole*) *sulphide*, m.p. 180° (*dibenzyl* derivative, m.p. 107°), whilst 3 : 5-dithiol-4 : 2 : 1-triazole yields the *diacetate*, m.p. 330°, which is hydrolysed (HCl) to a *substance*, $C_2H_3N_3S_2$, m.p. 228°, probably either 5-imino-3-thiol-4 : 1 : 2-thiodiazole or 3-thiol-3 : 5-*endo*thio-2 : 3-dihydro-1 : 2 : 4-triazole. 3 : 5-Dithiol-4-phenyl-1 : 3 : 4-triazole when heated with HCl yields 3-thion-5-anilotetrahydro-4 : 1 : 2-thiodiazole. J. D. R.

New heterocyclic syntheses. II. Reactions with halogeno-oximes. C. Musante (Gazzetta, 1938, **68**, 331—342).—$NH{:}CPh{\cdot}NH_2$,HCl (I) in MeOH–NaOMe with $CPhCl{:}N{\cdot}OH$ (II) yields 3 : 5-diphenyl-1 : 2 : 4-oxadiazole. With KCNO in aq. EtOH, (II) gives 3-phenyl-1 : 2 : 4-oxadiazol-5-one. With NH_4CNS in aq. EtOH, 2-*imino*-4-*phenyl*-1 : 3 : 5-*oxathiazole* (III), m.p. 82—84°, is formed, which is readily (*e.g.*, by steam-distillation) converted into 4-*phenyl*-1 : 3 : 5-*oxathiazol*-2-*one ureide* (IV), m.p. 165—166°, and PhNCS, which is also obtained, with N_2 and CO_2, from (III) and HNO_2, or from (IV) and boiling aq. HCl. With (I) and MeOH–NaOMe, $CO_2Et{\cdot}CCl{:}N{\cdot}OH$ gives the *Et* ester, m.p. 110—111°, of 5-*phenyl*-1 : 2 : 4-*oxadiazole*-3-*carboxylic* acid (cf. A., 1912, i, 724), m.p. 119—120° (decomp. to benzoylcyanamide). Using excess of (I), a product, m.p. 172° is obtained. Structures and mechanisms are discussed. E. W. W.

8-Methyl-2 : 2′-diethyloxa-thia- [-selena-]carbocyanine iodide.—See B., 1938, 984.

Calycanthidine, a new simple indole alkaloid. G. Barger, (Miss) A. Jacob, and J. Madinaveitia (Rec. trav. chim., 1938, **57**, 548—554).—The seeds (45 kg.) of *Calycanthus floridus* yield, besides calycanthine (probably contains 2 tryptophan nuclei), *calycanthidine* (I) (12 g.), $C_{13}H_{16}N_2$, m.p. 142°, $[\alpha]_D^{20}$ −285·1° in MeOH (*hydriodide*, m.p. 182°; *perchlorate*, m.p. 158°; *platinichloride*, m.p. 198—200° after sintering at 175°; *picrate*, m.p. 192°; *chromate*, m.p. >300°), the *methiodide*, m.p. 180—215°, of which with MeI–MeOH–KOH or $-K_2CO_3$ gives a *salt* (II), $OMe{\cdot}C_{12}H_{23}N{\cdot}NMe_3I$, m.p. 221°, also obtained similarly directly from (I). With Ag_2O–MeOH the methiodide gives NMe_3 and an oily *compound*, b.p. 120—160°/14 mm. [*hydrochloride*, amorphous, m.p. 135—137° (sinters at 107°); gives a pink colour with *p*-$NMe_2{\cdot}C_6H_4{\cdot}CHO$; unaffected by H_2–PtO_2]. With Ehrlich's reagent (I) gives a pale yellow colour, converted reversibly by heat into a claret colour. (I) contains NMe and possibly CMe. (I) and (II) may have the formulæ shown. However, (I) and dil. HCl–HNO_2 give in the cold a neutral, yellow ppt. (resinified by an excess of HNO_2), given by dl-N-*methyltetrahydroharman* (III) only when heated (then unaffected by an excess of HNO_2), and determination of CMe in (I) gives a very low, in (III) a fair, result. Further, (III) with MeI–K_2CO_3–MeOH gives a normal *methiodide*, m.p. 228—229°. (III), obtained from *N*-methyltryptamine and MeCHO in 0·25N-H_2SO_4 at 50—100°, has m.p. 112° and could not be resolved by way of the l-*malate*, m.p. 239°, $[\alpha]_D^{20}$ −2·2° in MeOH, or d-*camphorsulphonate*, m.p. 229°, $[\alpha]_D^{20}$ +24·2° in MeOH. Conversely, attempts to racemise (I) failed. R. S. C.

***iso*Quinoline and other alkaloids.** G. Barger (Congr. Int. Quim. pura apl., 1934, **9**, IV, 97—122; Chem. Zentr., 1936, ii, 2727).—The investigation of the metabolism of higher plants by comparing the structures of plant constituents (alkaloids) is recalled with reference to the *iso*quinoline group. It is shown that (with the accompanying numbering) benzyl*iso*quinolines may be obtained by ring-closure through 6 : β′ : N, the aporphines by a second ring-closure through 6 : 2′ (leading to 3′ : 4′ derivatives) or 6 : 6′ (4′ : 5′-derivatives), and the berberine group by a second ring-closure through N and an additional C (from CH_2O ?). 70 alkaloids as well as those of the indole group are considered. A. H. C.

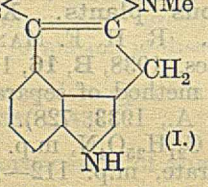
Alkaloids of fumariaceous plants. XVII. *Corydalis caseana*, A. Gray. R. H. F. Manske and M. R. Miller (Canad. J. Res., 1938, **B**, **16**, 153—157; cf. A., 1931, 764).—The method of separation is as described previously (cf. A., 1933, 728). The following are new: *caseanine*, $C_{21}H_{25}O_4N$, m.p. 142° (+H_2O, m.p. 115—116°; picrate, m.p. 112—113°, identical with aurotensine Me_2 ether picrate); a dimethoxy-phenolic *compound*, $C_{19}H_{21}O_4N$, m.p. 257° (previous darkening); *casealutine*, $C_{20}H_{23}O_4N$, m.p. 230° (converted by CH_2N_2 into caseanine), and *isomerides*, m.p. 218° after sintering some degrees lower, and 145° (*OMe*-derivative, m.p. 186°), respectively. J. L. D.

Alkaloids of *Lycopodium clavatum*, L. O. Achmatowicz and W. Uziębło (Rocz. Chem., 1938, **18**, 88—95).—*L. clavatum* plants contain 0·12% dry wt. of alkaloids, of which 40% are crystallisable, and consist of 83% of *lycopodine*, $C_{16}H_{25}ON$, m.p. 115—116°, $[\alpha]_D^{20}$ −9·01° in $COMe_2$ (*methiodide*, m.p. 335—337°; *methochloride*, m.p. 238—240°), 12% of *clavatine*, $C_{16}H_{25}O_2N$, m.p. 212—213°, $[\alpha]_D^{20}$ −365·7° in $COMe_2$ (*methiodide*, m.p. 317—318°), and 3% of *clavotoxine*, $C_{17}H_{27}O_2N$, m.p. 185—186°. The alkaloids do not contain NMe or OMe. They give characteristic colour reactions with the usual alkaloid reagents. All are physiologically active, stimulating the respiratory centre of mammals, and paralysing the central and peripheral nervous systems of frogs. R. T.

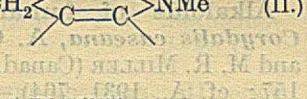
***Lycoris* alkaloids. XIII. *N*-Isomerism of lycorine methiodide.** H. KONDO, H. KATSURA, and S. UYEO (Ber., 1938, **71**, [*B*], 1529—1533).—Treatment of lycorine with MeI gives the α-methiodide (I), m.p. 247° (decomp.), $[\alpha]_D^{20}$ −46·11° in H_2O, and the β-methiodide (II), m.p. 281° (decomp.) [*monohydrate*, m.p. 198° (decomp.), $[\alpha]_D^{20}$ +122·9° in H_2O ≡ $[\alpha]_D^{20}$ +128·1° for the anhyd. material]. The Hofmann degradation of either compound leads to the same methine base, m.p. 98·5° [*hydrochloride*, m.p. 214—215° (decomp.)]. The Emde degradation of *lycorine α-methochloride*, $C_{16}H_{17}O_4N$,MeCl,$2H_2O$, leads to a *methine* base, $C_{17}H_{17}O_2N$, m.p. 71—71·5° [*picrate*, m.p. 197—198° (decomp.)], also obtained from *lycorine β-methochloride*, m.p. 305° (decomp.). The stereoisomerism of (I) and (II) is therefore due to co-ordinatively quadrivalent N. H. W.

Acidimetric titration of ergometrine. F. REIMERS (Quart. J. Pharm., 1938, **11**, 252—259).—The presence of ergotoxine, ergotinine, and ergotamine in ergometrine (I) can be shown by pptn. of the former with picric acid. Ergometrine can be determined by titration with 0·1N-HCl (macro-method) or 0·02N-HCl (micro-method) using bromophenol-blue as indicator. In the micro-method the error is +0·2%. K_{acid} and K_{base} for (I) at approx. 22° are $10^{-6\cdot80}$ and $10^{-7\cdot28}$ respectively. J. N. A.

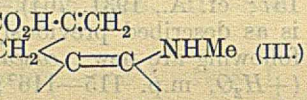
Position of the carboxyl group in lysergic acid. W. A. JACOBS and L. C. CRAIG (J. Amer. Chem. Soc., 1938, **60**, 1701—1702).—At 300°/25 mm. dihydrolysergic acid (I) partly sublimes unchanged and partly yields a neutral *substance* (II), $C_{16}H_{16}ON_2$, m.p. 305—307° (decomp.), $[\alpha]_D^{25}$ −219° in C_5H_5N (obtained in



(I.)



(II.)



(III.)

33% yield at 350°), hydrogenated to the H_2-derivative, m.p. 336° (decomp.). Thus (I) and (II) have the formulæ shown, (I) being a β-NH_2-acid (in accordance with unpublished data on dissociation const.) and yielding (II) by way of (III). R. S. C.

Chemistry and biochemistry of the alkaloids related to tryptophan. G. BARGER (Bull. Soc. Chim. biol., 1938, **20**, 685—704).—A lecture.

Conversion of colchicine into colchiceine. E. BOYLAND and E. H. MAWSON (Biochem. J., 1938, **32**, 1204—1206).—The colorimetric determination of colchiceine (I), based on the development of a green colour with $FeCl_3$ in $CHCl_3$, is described. Colchicine is hydrolysed to (I) (93%) by heating for 1 hr. at 100° with 0·1N-HCl. P. G. M.

α-Phenylcinchononitrile. T. LIPIEC and S. WEIL (Rocz. Chem., 1938, **18**, 161—162).—α-Phenylcinchonoyl chloride in ligroin and $Hg(CN)_2$ (6 hr. at the b.p.) yield α-phenylcinchononitrile, which when hydrolysed (cold dil. HCl) gives α-phenylcinchonic acid, and is converted by Na in C_5H_{11}·OH into 2-phenyl-1 : 2 : 3 : 4-tetrahydrocinchonic acid. R. T.

Degradation of quaternary ammonium salts of strychnine alkaloids. O. ACHMATOWICZ (Congr. int. Quim. pura apl., 1934, **9**, IV, 230—232; Chem. Zentr., 1936, ii, 2728; cf. A., 1934, 788).—Following the suggestion (A., 1932, 527) that strychnine and brucine contain the group ·N·CH_2·C(·CH)·CH·, exhaustive methylation of dihydrostrychnidine *A* (I) and dihydrobrucidine (II) has been effected. The following new *bases* were obtained from (I): $C_{20}H_{30}O_2N_2$, m.p. 159° (the OH-compound corresponding with methoxymethyltetrahydrostrychnine, which is obtained on methylating with Me_2SO_4) [O-*Ac* derivative, m.p. 254°, decomp. by heating into (I) and MeOAc]; $C_{21}H_{28}ON_2$, m.p. 142°, 196°. The last two de-bases contain C·C and NMe as they are degraded by H_2 and Pd–C (cf. A., 1933, 406). Methylstrychnidinium chloride gives a de-base, $C_{21}H_{27}ON$(NMe), m.p. 176°, and methylbrucinium and methylstrychninium chlorides are degraded similarly, the latter to two bases, $C_{21}H_{23}O_2N$(NMe), m.p. 145°, and $C_{21}H_{25}O_2N$(NMe), m.p. 201°, both yielding the above base, m.p. 176°, on electrolytic reduction, as does the base of m.p. 142° on catalytic reduction. Dihydrobrucidine behaves analogously. Structural formulæ are advanced. A. H. C.

***Strychnos* alkaloids. XCIX. Hydrogenation of *apo*nucidine and its derivatives.** H. LEUCHS (Ber., 1938, **71**, [*B*], 1525—1528).—*apo*Nucidine (I) is hydrogenated (Adams) and then acetylated to N-*acetyldihydroaponucidine* [*perchlorate*, m.p. about 260° (decomp.) after blackening]. N-Acetyl*apo*nucidine [*perchlorate*, m.p. about 262° (decomp.), $[\alpha]_D^{23}$ −64° in H_2O] is transformed by the successive action of Me_2SO_4 in C_6H_6 and 0·5N-$HClO_4$ into N-*acetyl*a*ponucidine methoperchlorate*, m.p. 240—245°, $[\alpha]_D^{20}$ −46° in H_2O; this is hydrogenated (PtO_2) and separated by NH_3–$CHCl_3$ into a compound which gives a *methiodide*, $C_{18}H_{30}O_2N_2$,MeI, m.p. 295—298° (decomp.), and a *substance*, $C_{17}H_{26}O_2N_2$ (*methoperchlorate*, m.p. 215—220°, decomp. about 260°). (I), Bz_2O, and NaOBz at 95—115° afford N-*benzoyl*a*ponucidine*, m.p. about 160°, decomp. 230—240°, $[\alpha]_D^{23}$ −49·2° in H_2O, which gives analogously N-*benzoyl*a*ponucidine methoperchlorate*, m.p. about 247° (decomp.) after softening at 210°, $[\alpha]_D^{22}$ −13° in H_2O. N-*Methyl*a*ponucidine methiodide*, m.p. about 302° (vac.; decomp.), is hydrogenated (PtO_2) to the *compound*, $C_{16}H_{26}ON_2$,MeI,HI, m.p. 312—317° (vac.; decomp.). N-*Methyl*a*ponucidine dimethoperchlorate*, m.p. >300°, is hydrogenated (PtO_2) to the *compound*, $C_{16}H_{26}ON_2$, $2MeClO_4$, m.p. 280—282° (vac.; decomp.). H. W.

Synthesis of *apo*morphine dimethyl ether. J. M. GULLAND (Chem. and Ind., 1938, 774).—Examination of the papers of Avenarius and Pschorr (Ber., 1929, **62**, 321) and of Gulland *et al.* (J.C.S., 1929, 1791) shows that unequivocal statements attributing a synthesis of *apo*morphine Me_2 ether to the former authors are unjustified. H. W.

Menisine, isomeric with tetrandrine. T. Q. CHOU (Chinese J. Physiol., 1938, **13**, 167—171; cf.

A., 1935, 1433).—The methochloride of menisine (I) or tetrandrine (II) with boiling aq. 10% NaOH affords a product from which C_6H_6 extracts an optically inactive methine *base*, $C_{40}H_{46}O_6N_2$, m.p. 171° (*methiodide*, m.p. 257°), and a *methiodide*, m.p. 217°; the C_6H_6-insol. portion gives a *base*, $C_{42}H_{54}O_{11}N_2$, m.p. 248° (decomp.), $[\alpha]_D^{18}$ +625° in MeOH [*methiodide*, m.p. 258° (decomp.)]. The above methiodides when converted into methochlorides and boiled with aq. 10% NaOH afford NMe_3 and a *substance*, $C_{36}H_{32}O_6$, m.p. 221°. (I) at 150° in 3 hr. affords (II) completely. J. L. D.

New aromatic arsenical derivatives. II. Acids and arsenical derivatives of benzophenone. E. V. Zappi and J. F. Salellas (Anal. Asoc. Quím. Argentina, 1938, **26**, 21—29; cf. A., 1937, II, 172).—Diazotised $CO(C_6H_4{\cdot}NH_2\text{-}p)_2$ by the usual method yields *benzophenone*-4 : 4′-*diarsinic acid*, blackens when heated (*semicarbazone*, infusible), also obtained by oxidation of $CH_2(C_6H_4{\cdot}AsO_3H_2\text{-}p)_2$ with CrO_3 or $KMnO_4$; with NaH_2PO_2 in dil. H_2SO_4 it gives 4′ : 4‴-*arsenobisdibenzophenone*-4 : 4″-*arsinic acid*, no m.p., $CH_2(o\text{-}NO_2{\cdot}C_6H_3{\cdot}AsO_3H_2\text{-}p)_2$, which with alkaline $KMnO_4$ gives 2 : 2′-*dinitrobenzophenone*-4 : 4′-*diarsinic acid*, no m.p. F. R. G.

Configuration of heterocyclic compounds. IX. Optical resolution of 8-chloro-10-phenylphenoxarsine-2-carboxylic acid. (Miss) M. S. Lesslie (J.C.S., 1938, 1001—1003).—5-*Chloro*-2-p-*tolyloxyphenylarsinic acid*, m.p. 199—200°, prepared from 4-chloro-2-aminophenyl *p*-tolyl ether, with conc. H_2SO_4 gives 8-*chloro*-2-*methylphenoxarsinic acid*, m.p. 289—291°, converted by HCl–SO_2 into 8 : 10-*dichloro*-2-*methylphenoxarsine*, m.p. 171—172°. This compound and MgPhBr yield 8-*chloro*-10-*phenyl*-2-*methylphenoxarsine*, m.p. 75—76°, oxidised ($KMnO_4$) to dl-8-*chloro*-10-*phenylphenoxarsine*-2-*carboxylic acid*, m.p. 220—221°. This acid has been resolved through d-α-*phenylethylamine* l-, m.p. 236—237°, $[\alpha]_{5791}^{20}$ −71·7° in MeOH, and l-α-*phenylethylamine* d-8-*chloro*-10-*phenylphenoxarsine*-2-*carboxylate*, $[\alpha]_{5791}^{20}$ +71·3° in MeOH, into l-, m.p. 202—203°, $[\alpha]_{5791}^{20}$ −68·7° in $COMe_2$, and d-8-*chloro*-10-*phenylphenoxarsine*-2-*carboxylic acid*, m.p. 202—203°, $[\alpha]_{5791}^{20}$ +69·0° in $COMe_2$. The acid shows high optical stability. F. R. S.

Organo-derivatives of arsenic, antimony, mercury, and gold.—See B., 1938, 982—983.

Dissociation of hydrogen ions from the sulphates of amino-phenylboric acids.—See A., 1938, I, 457.

Mercury derivatives of aromatic compounds with an unsaturated side-chain. R. Priester (Rec. trav. chim., 1938, **57**, 811—818).—The data of Manchot (A., 1919, i, 145; 1920, i, 519, 720, 780, 905) are extended and, in part, corr. Safrole (I) and $Hg(OAc)_2$ in H_2O give the oily additive compound, converted by aq. NaCl into the compound, (I),HgCl·OH, new m.p. 140—141°, reconverted into (I) by 2N-HCl at 60°. Eugenol (II) gives the *compound*, (II),HgR·OH (R = OAc), m.p. 120·5—121·5°, converted into the basic compounds, in which R = Cl, m.p. 103—104°, Br, m.p. 125—126°, and I, m.p. 136°. With 2 mols. of $Hg(OAc)_2$ (II) gives the additive compound 1 : 2 : 5 : 4-(OH)(OMe)C_6H_3(,HgCl·OH)·CH_2·CH:CH_2,HgCl·OH [regenerates (II)], which at 100° loses H_2O, yielding the compound 1 : 2 : 5 : 4-(OH)(OMe)C_6H_2(HgCl)·C_3H_5,HgCl·OH [does not regenerate (II)]. Eugenol Me ether (III) and $Hg(OAc)_2$ give a poor yield of the *compound*, (III),Hg(OH)·OAc, m.p. 69—70°, converted by NaCl into the basic chloride, m.p. 114—115°. R. S. C.

Osmotic pressure, mol. wt., and stability of gliadin.—See A., 1938, I, 456.

Filling of micro-combustion tubes.—See A., 1938, I, 478.

Qualitative micro-method for the identification of alkyl groups united to oxygen or nitrogen. Micro-Zeisel method. I. M. Furter (Helv. Chim. Acta, 1938, **21**, 872—879).—The substance is heated with HI (*d* 1·7) in presence of Pt tetrahedra and the vapours are passed through a P suspension, $Na_2S_2O_3$, and $CdSO_4$ solution. After being dried by $CaCl_2$ they pass into a constricted tube containing a well-cooled suspension of 3 : 5-$(NO_2)_2C_6H_3{\cdot}CO_2Ag$ in anhyd. Et_2O. When the action is over the tube is sealed at the constriction and heated at 100°. The alkyl group is identified by determination of the m.p. of the alkyl dinitrobenzoate thus produced supplemented by observations on its mol. compound with α-$C_{10}H_7{\cdot}NH_2$. H. W.

Characterisation of the acetyl group in medicinal chemicals by the formation of "lanthanum-blue." A. D. Del Boca and A. Remezzana (An. Farm. Bioquim., 1935, **6**, 111—116; Chem. Zentr., 1936, ii, 2167).—The Ac group in a series of medicinals (heroin, aconitine, aspirin, tannigen, NHPhAc, exalgin, phenacetin, but not with salophen) is indicated by the La-blue reaction of the product obtained by distilling with dil. H_2SO_4 (often in presence of $FeCl_3$). A. H. C.

Improved Kurt Meyer titration. S. R. Cooper and R. P. Barnes (Ind. Eng. Chem. [Anal.], 1938, **10**, 379).—Di*iso*butylene is preferable to β-$C_{10}H_7{\cdot}OH$ for absorbing the excess of Br in the indirect Kurt Meyer titration of CH_2Bz_2. Abs. MeOH is preferable to EtOH as a solvent for the Br. The method detailed gives results agreeing to within 1% as against 7% for the original method. The mean val. obtained for the % of enol form in CH_2Bz_2 is 95·66. L. S. T.

Sulphuric acid analysis of gaseous olefines. M. P. Matuszak (Ind. Eng. Chem. [Anal.], 1938, **10**, 354—360).—Data indicating the influence of the following factors on the analytical results obtained in the determination of gaseous olefines by absorption in H_2SO_4 are given: reversibility of absorption; solubility of gaseous hydrocarbons in H_2SO_4; effect of acid-sol. absorption products on solubility of hydrocarbons; solubility of hydrocarbons in pptd. polymeric products and liberation of unabsorbed gas by strong adsorbents. Apparatus and technique to overcome these difficulties are described with a view of making the determination accurate for low and high concns. of gaseous olefines. F. N. W.

Determination of small quantities of methyl bromide in air. R. L. Busbey and N. L. Drake (Ind. Eng. Chem., [Anal.], 1938, **10**, 390—392).—The air containing MeBr is passed through 25 c.c. of a 2% EtOH–KOH solution at 68° for 1 hr. in a specially designed apparatus, the mixture diluted with 225 c.c. of H_2O, and the EtOH removed by distillation. To the residual liquid (150 c.c.) are added 20 c.c. of aq. NaOCl solution (7 g. Cl per 100 c.c. of 12% aq. NaOH), 5 g. of NaCl, and 10 g. of boric acid, and after heating (100°; 0·25 hr.), 20 c.c. of 10% aq. HCO_2Na solution are added to the mixture to destroy excess of HOCl. After boiling for 5 min. and cooling, solid KI, a few drops of 5% aq. NH_4 molybdate, and 50 c.c. of 2N aq. HCl are added and the liberated I is titrated with 0·1N-$Na_2S_2O_3$. The average error reported on analyses of 13 samples ranging from 0·048 to 0·0065 g. is −1·7%. F. N. W.

Determination of ethyl acetate. E. Butschowitz and A. Vlk (Ann. Chim. Analyt., 1938, [iii], **20**, 175—177).—The EtOAc is weighed in a sealed bulb and saponified by KOH. A. Li.

Extension of the resorcinol–sulphuric acid reaction to the succinate ion. G. Denigès (Bull. Trav. Soc. Pharm. Bordeaux, 1936, **74**, 12—17; Chem. Zentr., 1936, ii, 827).—0·02—0·04 g. of the acid, anhydride, or succinate is heated to boiling with 2 c.c. of H_2SO_4 and 4 drops of NaBr–NaOBr solution, Br is removed in an air stream, the solution is allowed to cool for 1 min., and 1 drop of the reagent (2 g. of resorcinol, 0·5 c.c. of H_2SO_4, H_2O to 100 c.c.) is added. A wine-red colour, with a characteristic absorption band at 5275 A., results. H. J. E.

Möhler–Denigès reagent for tartaric acid. C. H. Liberalli (Rev. Quim. Farm., 1935, **1**, 12—15; Chem. Zentr., 1936, ii, 2184).—MnO_4' or Cr_2O_7'' in small quantity do not interfere with the resorcinol test for tartaric acid (I). Gluconic, lactic, and pyroracemic acids in presence of Br′ or I′, or citric acid in presence of Br′, I′, or MoO_4'', give colorations similar to that obtained with (I). A. J. E. W.

Determination of amino-acids. W. H. Stein, C. Niemann, and M. Bergmann (J. Amer. Chem. Soc., 1938, **60**, 1703—1704).—When NH_2-acids in H_2O are treated with precipitants, the amount remaining in solution is often quantitatively governed by the solubility product of the ppt. Some NH_2-acids can thus be determined by weighing the amount of ppt. produced by varying amounts (excess) of precipitant. Glycine, *l*-alanine, and *l*-leucine are thus determined with dioxpyridic acid, *l*-proline with rhodanilic acid, and tyrosine with dioxanilic acid. R. S. C.

Separation of the chrysanthemumcarboxylic acids. A. A. Pantsios (Ind. Eng. Chem., [Anal.], 1938, **10**, 386—387).—As steam-distillation of chrysanthemum-monocarboxylic acid (I) causes decomp., acid methods of pyrethrin I analysis are inaccurate. It is possible to separate the two chrysanthemum acids by the selective extraction of (I) with light petroleum, although the method is not sufficiently accurate for the analysis of pyrethrum flowers. F. N. W.

Determination of pyridine. C. Belcot (Ann. Chim. Analyt., [iii], **20**, 173—175).—Small quantities of C_5H_5N are determined by pptg. with KCNS and $CuSO_4$, and determining excess of Cu iodometrically, but for large quantities the method of Schultze (A., 1888, 539) is sufficiently accurate. A. Li.

Fröhde's reagent: a reagent for morphine and for other phenolic compounds. C. C. Fulton (J. Lab. clin. Med., 1938, **53**, 625—630).—Fröhde's reagent provides a sensitive and sp. test for morphine, the main colour sequence being intense purplish-red, changing to weak brown or even fading out completely, and then developing as strong bright green. T. H. H.

Identification of ecgonine. F. Amelink (Pharm. Weekblad, 1938, **75**, 861—864).—Characteristic microcryst. ppts. are obtained with ecgonine solutions and $PtCl_4$–NaI, $AuCl_3$–NaBr, $HgCl_2$, and Dragendorff's reagent. The sensitivity in all cases is 0·1—0·2%. S. C.

Potentiometric and conductometric analysis of cinchonidine salt solutions. H. L. Pedersen (Dansk Tidsskr. Farm., 1938, **12**, 161—187).—0·01N-Cinchonidine salts may be titrated potentiometrically in excess of HCl against 0·1N-NaOH with an accuracy of 0·25%. The p_H of cinchonidine dihydrochloride (I) solutions has been measured over the range 0·02—0·005N. The titration of cinchonidine tetrasulphate has been investigated. Conductometric titration of 0·01N-(I) against N-NaOH gives vals. 2% > against N-$AgNO_3$. The solubilities of (I) and cinchonidine disulphate have been measured conductometrically. M. H. M. A.

Identification of alkaloids. K. E. Jackson (Ind. Eng. Chem., [Anal.], 1938, **10**, 380—381).—A systematic summary of known methods for the identification of 42 common alkaloids. F. N. W.

Determination of alkaloids by a combined precipitation–acidimetric process. R. Dietzel and W. Paul (Süddeuts. Apoth.-Ztg., 1936, **76**, 474—477; Chem. Zentr., 1936, ii, 1577).—50—100 mg. of base are dissolved in 15 c.c. of 0·1N-HCl, mixed slowly with 30 c.c. of a solution of 1 g. of I and 1·5 g. of KI in 100 c.c. of H_2O, made up to 50 c.c., and shaken for 5 min. The solution is filtered, decolorised with $Na_2S_2O_3$, and the amount of acid fixed as X,HI,I_x (X = base) determined by titrating HCl remaining in the filtrate against 0·1N-alkali using phenolphthalein. K_2HgI_4 may replace KI_3. The procedure is valid for morphine, atropine, strychnine, brucine, narcotine, papaverine, cocaine, hyoscyamine, veratrine, codeine, aconitine, and for colchicine on flocculating the complex with NaCl but not for nicotine, quinine, piperine, berberine, *apo*morphine, or purines. A. H. C.

Determination of mercury in inorganic and organic compounds and pharmaceutical preparations.—See A., 1938, I, 473.