BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

MARCH, 1938.

Valencies of carbon.—See A., I, 122.

Simplified method of writing electronic formulæ.—See A., I, 122.

Aliphatic substitution and the Walden inversion. E. D. HUGHES (Trans. Faraday Soc., 1938, **34**, 202—221).—Published work is summarised and discussed. E. S. H.

Ozonation of hydrocarbons (hexane, heptane, and octanes).—See A., I, 148.

Reaction of pure hydrocarbons in presence of aluminium chloride. G. EGLOFF, E. WILSON, G. HULLA, and P. M. VAN ARSDELL (Universal Oil Products Co., Chicago, Booklet No. 212, 1937, 74 pp.).—The reactions of various hydrocarbons are reviewed. R. B. C.

Reaction mechanism for nitrating paraffin hydrocarbons. R. F. MCCLEARY and E. F. DEGERING (Ind. Eng. Chem., 1938, **30**, 64—67).—A mechanism is suggested to account for all the observed products of vapour-phase nitration of paraffin hydrocarbons. Evidence is given in support of the view that free radical formation is an essential intermediate step in the reaction, oxidation of the hydrocarbon or some induced dissociation leading to the formation of these radicals, which in turn react with the HNO_3 affording nitroparaffins. The observed oxidation products may be accounted for by assuming direct oxidation of either the parent hydrocarbon or olefine shown to be formed during the reaction. F. N. W.

Nitration of *n*-pentane. H. B. HASS and J. A. PATTERSON (Ind. Eng. Chem., 1938, **30**, 6769).—Vapour-phase nitration of *n*-pentane by the method previously described (A., 1936, 587) affords nitromethane (1·1) and -ethane (7·19), α-nitro-propane (13·85) and -butane (12·5), and α- (21·6), β- (20·8), and γ-nitropentane (23·0%). These findings agree with the views of McCleary and Degering (preceding abstract). F. N. W.

Polymerisation of propylene by dilute phosphoric acid. L. A. MONROE and E. R. GILLILAND (Ind. Eng. Chem., 1938, **30**, 58—63).—Stepwise polymerisation of $CHMe{:}CH_2$ with 10—50% H_3PO_4 at 260—235°/170—410 atm. shows that the first product is the dimeride, which with more $CHMe{:}CH_2$ forms the trimeride and thence the tetrameride. With temp. <300° and $[H_3PO_4]$ <30%, the composition of the product (100—35% dimeride) depends solely on the extent of polymerisation of the feed; above these limits the dimeride content of the mixed polymerides is decreased with increased yield of more complex compounds. The mechanism of the reaction is discussed in view of the fact that the observed rate of polymerisation ∝ the square of the gas-phase $CHMe{:}CH_2$ concn., and to the first power of the acid concn. F. N. W.

Reactions of isoprene and dimethylbutadiene. G. DUPONT and C. PAQUOT (Compt. rend., 1937, **205**, 805—807; cf. A., 1937, II, 27).—Isoprene (I) in EtOH with H_2–Raney Ni in an atm. of H_2 at 0° gives a mixture of equal amounts of $CMeEt{:}CH_2$ and γ-methyl-Δ^{β}-butene (II), but no $CHPr^{\beta}{:}CH_2$ as determined by the Raman spectrum. 3 H is absorbed at "complete" hydrogenation, when the Raman spectrum indicates the presence of (II) only. βγ-Dimethylbutadiene (III) similarly absorbs 2 H to give 67% of βγ-dimethyl-Δ^{α}-butene and 33% of βγ-dimethyl-Δ^{β}-butene. (I) with CBz:CBz in a sealed tube at 120—130° affords 1 : 2-*dibenzoyl*-4-*methyl*-$\Delta^{1:4}$-cyclo*hexadiene*, m.p. 58—59°. (III) similarly affords 1 : 2-*dibenzoyl*-4 : 5-*dimethyl*-$\Delta^{1:4}$-cyclo*hexadiene*, m.p. 106—107°. J. L. D.

Mechanism of polymerisation. II. Dimerisation of βγ-dimethylbutadiene in presence of an acid catalyst. E. H. FARMER and R. C. PITKETHLY (J.C.S., 1938, 11—19).—With 0·1% H_2SO_4 in AcOH, $(CH_2{:}CHMe\cdot)_2$ (I) yields 1 : 3 : 4-*trimethyl*-1-iso*propenyl*-Δ^3-cyclo*hexene* (II), b.p. 85°/15 mm., 202—203°/761 mm., the structure of which is proved by the following synthesis. (I) with $CH_2{:}CMe\cdot CO_2Me$ yields *Me* 1 : 3 : 4-*trimethyl*-Δ^3-*tetrahydrobenzoate* (III). b.p. 106°/19 mm., hydrolysed by NaOH–EtOH to 1 .3 : 4-*trimethyl*-Δ^3-*tetrahydrobenzoic acid*, m.p. 56° (*anilide*, m.p. 94·5°); and converted by O_3 in EtOAc into *Me* α-*acetonyl*-γ-*acetyl*-α-*methylpropionate* (*disemicarbazone*, m.p. 200°). (III) with MgMeI in Et_2O yields 1-*acetyl*-1 : 3 : 4-*trimethyl*-Δ^3-cyclo*hexene* (*semicarbazone*, m.p. 151°), 1 : 3 : 4-*trimethyl*-Δ^3-cyclo*hexenyldimethylcarbinol* (IV), b.p. 105—108°, and a *liquid* [probably the Me ether of (IV)], b.p. 68—71°. Dehydration of (IV) with $KHSO_4$ yields (II), which with Pt–H_2 in EtOH gives a H_2-*compound* (not homogeneous), and this with Br in CS_2 gives the solid (m.p. 57°) and liquid stereoisomerides of 1 : 2-*dibromo*-1 : 2 : 4-*trimethyl*-4-iso*propyl*cyclo*hexane*. Hydrogenation of (II) with HI–P or Pt–H_2 in AcOH (poor yields) gives 1 : 2 : 4-*trimethyl*-4-iso*propyl*cyclo*hexane*, b.p. 177°, whilst with Se at 300° an oil, b.p. 160—170° (probably 3 : 4-dimethylcumene), is formed which is oxidised ($KMnO_4$–Na_2CO_3) to trimellitic acid. Ozonolysis of (II) affords CH_2O in 70% yield, and oxidation ($KMnO_4$) gives a dicarbonyl *compound*, $C_{12}H_{20}O_2$ (*disemicarbazone*, m.p. 251°), which is considered to originate from a dicyclic dimeride present as impurity in (II). Polymerisation

of (I) with 1·0% H_2SO_4 in AcOH yields a *dimeride*, m.p. 66°, and *trimeric* βγ-*dimethylbutadiene*. (I) with CHMe:CH·CO_2Et affords *Et* 2 : 4 : 5-*trimethyl*-Δ^4-*tetrahydrobenzoate*, b.p. 127—130°/28 mm., hydrolysed (KOH–EtOH) to the *acid*, m.p. 137° (*anilide*, m.p. 162°). J. D. R.

Formation and structure of polymerides of the insoluble cross-linked type. R. G. W. Norrish and E. F. Brookman (Proc. Roy. Soc., 1937, **A**, **163**, 205—220).—A series of cross-linking agents are described together with the properties of their co-polymerides with monovinyl compounds. Support is given to Staudinger's view (the formation of three-dimensional macro-mols.) of the structure of these polymerides and a general formula is given. It is suggested that the electronic properties of the group X in the divinyl compound $(CH_2{:}CH)_2X$ determines the cross-linking properties in the same way that the electronic properties of R in the monovinyl compound $CH_2{:}CH{\cdot}R$ determines the ease of polymerisation of those compounds. G. D. P.

Formation of benzene in the radiochemical polymerisation of acetylene. II. Quantity of benzene formed. C. Rosenblum (Bull. Soc. chim. Belg., 1937, **46**, 503—518; cf. A., 1937, II, 236).—Polymerisation of C_2H_2 under the influence of α- and β-rays from Rn gives 20% conversion into C_6H_6, the formation of which is attributed to the rearrangement of an active linear trimeride. The diminution of the C_6H_6 : cuprene ratio as the reaction proceeds is due to a secondary polymerisation of the C_6H_6. J. D. R.

Hydration of acetylenes. II. Δ^β-Pentinene. Reactivity in homologous series. E. L. R. Mowat and J. C. Smith (J.C.S., 1938, 19—22).—Δ^β-Pentinene with 80% H_2SO_4 at 0° yields about 50% each of COMePr$^\alpha$ and $COEt_2$, the proportions of the ketones being determined by the m.p. of the mixture of semicarbazones and *p*-nitrophenylhydrazones. Together with the results of the hydration of Δ^θ-undecynoic acid (A., 1937, II, 440) this indicates that in the hydration of CMe:CR, the acetylenes display increasing reactivity with increasing length of alkyl chain due to the increase in negativity of C attached to alkyl. J. D. R.

Interaction of alkyl iodides with sodium guaiacoxide in ethyl alcohol.—See A., I, 86.

Rate and mechanism of hydrolysis and alcoholysis of *tert.*-butyl chloride. Application to the transition state theory of solvent effects.—See A., I, 86.

Classification of complexes of magnesium chloride with organic compounds containing oxygen according to nature of oxygen linking. M. L. Quinet (Compt. rend., 1937, **205**, 675—677; cf. A., 1935, 179; 1937, I, 256).—The no. of org. mols. combining with 1 mol. of $MgCl_2$ depends on the nature of O linking in the org. mol., viz., 6 for OH-compounds (analogous to $MgCl_2,6H_2O$), and 3 for CO-compounds. Ethers do not combine with $MgCl_2$. Complexes of $MgCl_2$ with H_2O and alcohols do not react with aldehydes and ketones, whilst those with aldehydes and ketones are immediately decomposed by H_2O and alcohols, thus providing a method of prep. of complexes of $MgCl_2$ with higher alcohols. Decomp. by heat gives in all cases MgO. Alcohols give intermediately oxychlorides $MgCl_2,3Mg(OR)_2$. Ketones give the 1 : 1 mol. compounds. Thus $MgCl_2,3COMe_2$ at 100° gives $MgCl_2,COMe_2$ and at 200° $Mg(OEt)_2$, whilst at 56° dehydration occurs with formation of phorone and $MgCl_2,2H_2O$. E. G. B.

Decomposition of methyl alcohol over rhenium.—See A., I, 88.

Effect of alkali on copper methyl alcohol catalysts.—See A., I, 149.

Catalytic esterification of alcohols of the series $C_nH_{2n+1}{\cdot}OH$ without the participation of organic acids. M. M. Koton (J. Gen. Chem. Russ., 1937, **7**, 2188—2194).—The yields of esters obtained by passing EtOH, PrOH, or BuOH over Cu catalysts at 275° fall in the series Cu filings > Cu–Zr > pptd. Cu > Cu–Ce, whilst in the case of *iso*-$C_5H_{11}{\cdot}OH$ the series pptd. Cu > Cu filings > Cu–Zr > Cu–Ce obtains. The yields of ester, acid, and aldehyde obtained with the above catalysts and alcohols are tabulated. R. T.

Catalytic properties of cerium oxide.—See A., I, 88.

Spectrographic and chemical study of aliphatic terpenes. II. Alcohols and aliphatic aldehydes. G. Dupont, V. Desreux, and R. Dulou (Bull. Soc. chim., 1937, [v], **4**, 2016—2026; cf. A., 1937, II, 200).—Raman spectral data indicate that geraniol (from Java citronella oil) does not contain α-geraniol, but that the terminal double linking observed is due to the presence of linalol. The Raman spectrum of pure β-geraniol has been determined. The product of catalytic hydrogenation over Ni (citronellol, not dehydrogeraniol) confirms the absence of α-geraniol in the original. The Raman spectra of geraniol and nerol are almost identical. The specimen of linalol examined consisted almost entirely of the β form; on catalytic hydrogenation (Ni or Pt) it yielded dihydrolinalol. Spectral data show that citral contains no α form, whilst citronellal is a mixture of β with α. On catalytic hydrogenation citral contains no α form, whilst citronellal is a mixture of β with α. On catalytic hydrogenation citral yields citronellal and then citronellol. E. S. H.

Linolenyl alcohol. Preparation and properties. O. Turpeinen (J. Amer. Chem. Soc., 1938, **60**, 56—57).—Me linolenate and Na–BuOH give a 70—72% yield of *linolenyl alcohol*, m.p. −5° to −2° (*p-nitrophenylurethane*, m.p. 91—92°), which tends to "dry" in air and with PtO_2 in AcOH absorbs 2 H_2 to yield *n*-$C_{18}H_{37}{\cdot}OH$. R. S. C.

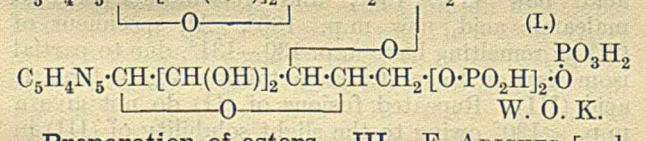
Photochemistry of alkyl nitrites.—See A., I, 90.

Alkylation of reactive methylene groups with alkyl sulphates. E. Bowden (J. Amer. Chem. Soc., 1938, **60**, 131).—Numerous compounds with reactive CH_2 are alkylated in satisfactory yield by Et_2SO_4 and NaOEt or $NaNH_2$. Examples are $CH_2Ac{\cdot}CO_2Et$, camphor, $CH_2Ph{\cdot}CO_2Et$, BuCN, COPhMe, COMeBu, etc. R. S. C.

Steric correspondence of the biological glycerol-α-phosphoric acid and β-phosphoglyceric acid. W. KIESSLING and P. SCHUSTER (Ber., 1938, **71**, [*B*], 123—128).—The biological (—)-glyceryl-α-phosphoric acid (I) (as Ba salt) is oxidised by Br in alkaline solution to (+)-β-phosphoglyceric acid (II), $[\alpha]_D^{20}$ +13·6°. The compound cannot be fermented and is not esterified with glucose through phosphopyruvic acid to $AcCO_2H$ and hexose monophosphate. Its Ba H salt is identical with that of the natural acid. Independent evidence of the steric correspondence of (I) and (II) is furnished by the hydrolysis by N-HCl at 126° of (II) to Ba glycerate, $[\alpha]_D^{20}$ —10°, whilst for the hydrolysate of the biological (—)-β-phosphoglyceric acid the val. $[\alpha]_D^{20}$ +12° is determined. H. W.

Synthesis of phosphatides. I. Synthesis of dipalmityl-β-kephalin and dipalmityl-β-lecithin. I. KABASHIMA (Ber., 1938, **71**, [*B*], 76—80).—β-Glycerylphosphoric acid is separated from technical Na glycerophosphate as the compound of its Ba salt with $Ba(NO_3)_2$ and converted by palmityl chloride into αα′-dipalmitylglyceryl-β-phosphoric acid, the Ag salt (I) of which is transformed by β-bromoethylamine picrate in $CHCl_3$–$COMe_2$ at 85—90° into dipalmityl-β-kephalin. *Dipalmityl-β-lecithin*, m.p. 181°, is obtained analogously from (I) and *trimethyl-β-bromoethylammonium picrate*, m.p. 158—159°. NMe_3 and $C_2H_4Br_2$ at 125—130° give *trimethyl-β-bromoethylammonium bromide*, m.p. 223° (decomp.). H. W.

Dinucleotidepyrophosphoric acid of yeast. W. KIESSLING and O. MEYERHOF (Naturwiss., 1938, **26**, 13—14).—The CCl_3·CO_2H extract of fresh beer yeast contains a substance which on esterification with phosphopyruvic acid in presence of rabbit-muscle extract yields the pyrophosphoric acid derivative of diadenosine-5′ : 5′-diphosphoric acid, to which on the basis of its composition and properties formula (I) is assigned. (I), $[\alpha]_{5446}^{20}$ —39·2° in N-H_2SO_4 (calc. on the basis of adenylic acid content), yields a *Ag* salt, $C_{20}H_{24}O_{19}N_{10}P_4Ag_4$, and on alkaline hydrolysis yields adenosinepyrophosphoric acid (1 mol.) and adenylic acid (1 mol.). Apparently the greater part of the adenosine-5′-phosphoric acid of yeast exists as the dinucleotide which, like adenylic acid, acts as a phosphorylating enzyme.



(I.)

W. O. K.

Preparation of esters. III. F. ADICKES [and, in part, M. MEISENHEIMER and G. HINDERER] (J. pr. Chem., 1938, [ii], **150**, 81—94; cf. A., 1936, 1251).—*αβ-Dichloroisobutyryl chloride*, b.p. 156—162°/740 mm., from $Pr^{\beta}COCl$ and Cl_2 at 40—50°, gives with EtOH *Et αβ-dichloroisobutyrate*, b.p. 188—189°/735 mm. $COBu^{\gamma}$·$CHNa$·CO_2Et and EtI give *Et β-keto-γ-methyl-α-ethylisovalerate*, b.p. 109°/16 mm., converted by Br in boiling CCl_4 into the *α-Br*-ester, b.p. 131°/16 mm. $CHMe(CO_2Et)_2$ and S_2Cl_2 give *Et*$_2$ *α-chloro(methylmalonate)*, b.p. 102—103°/12 mm. Irradiating CH_2Ph·$COCl$ and Br and pouring the product into EtOH gives 5% of *Et αα-dibromo-α-phenylacetate*, b.p. 170°/15 mm. *Me* 2 : 2′-*diphenylenebenzylpyruvate*, m.p. 117—119°, is obtained with 9-benzylfluorene from $(C_6H_4)_2C{:}C(ONa)$·CO_2Me and CH_2PhCl in hot Et_2O. *p*-C_6H_4Me·SO_2Na and the appropriate Cl-ester in EtOH give *Et* p-*toluenesulphonyl-phenyl-*, m.p. 113·5—114°, and *-diphenyl-acetate*, m.p. 126—127°, *Et*$_2$ p-*toluenesulphonylmalonate*, m.p. 39—40°, and Et α-*p*-toluenesulphonyl*iso*butyrate, m.p. 79—80°. $CHPh(CO_2Me)_2$ with S_2Cl_2 or Cl_2 gives *Me*$_2$ *α-chloro(phenylmalonate)*, m.p. 57—57·5°. The prep. of Et 2 : 4 : 6-trinitrobenzoate, phenylcyanoacetate, mandelate, benzilate, α-chlorodiphenylacetate, Et_2, forms, m.p. 74—76° and 89—90°, and Me_2 2 : 2′-diphenylenepyruvate, *forms*, m.p. 127—128° and 117·5°, is improved. MeCHO and *p*-C_6H_4Me·SH in AcOH give *acetaldehyde di-*p*-tolyl mercaptal*, oxidised by $KMnO_4$ to *ethylidene* p-*tolyl sulphoxide* p-*tolyl sulphone*, m.p. 112—113°, and a substance (? the disulphone), m.p. 108—109°. 9-Fluorenyl *p*-tolyl sulphone does not react with CH_2N_2. R. S. C.

Action of ammonia on esters. H. E. FRENCH and G. G. WRIGHTSMAN (J. Amer. Chem. Soc., 1938, **60**, 50—51).—The rate of reaction of 13 simple alkyl acetates with aq. NH_3 is reported. The rate decreases with increase in mol. wt. and with introduction of side-chains, the more so the closer is the side-chain to the O. *tert.*-Alkyl esters react more slowly than *sec.*-alkyl esters. Hydrolysis always occurs as well as formation of the amide and is depressed by similar influences, but to a smaller extent. R. S. C.

Isotopic exchange reactions of organic compounds. II. Survey of the monocarboxylic acid series. III. Kinetics of the isomerisation and isotope exchange of vinylacetic acid. D. J. G. IVES (J.C.S., 1938, 81—91, 91—97).—The partition of D and H between monocarboxylic acids and dil. D_2O at 100° in presence of 1·05 mol. of NaOH is studied by the method described previously (A., 1935, 1350) modified and improved for the determination of *d*, to an accuracy of a few p.p.m., with small samples. With AcOH, exchange of C·H for C·D occurs in alkaline but not in neutral solution. Phenylacetic, acrylic, crotonic, and sorbic acids undergo alkali-catalysed exchange reactions, but propionic, *iso*butyric, benzoic, *p*-toluic, α- and β-phenylpropionic, and cinnamic acids do not. No exchange accompanies the acid hydrolysis or saponification of EtOAc. These results are discussed in relation to the mechanism of exchange reactions with reference to evidence available from chemical reactions and to theories of structure.

III. It is shown that the exchange reaction of vinylacetic acid proceeds faster than the isomerisation to crotonic acid, the respective velocity coeffs. being 0·009 and 0·0058 min.$^{-1}$, indicating that the isomerisation is a bimol. reaction. A kinetic proof is given that the D : H ratio in the α-position of the βγ-isomeride in equilibrium with the solvent is unchanged during the formation of the intermediate ions postulated by the prototropic theory of three-C tautomerism. On the basis of the constancy of the D : H ratio in the α-position, the relative rates of removal from, and addition to, the vinylacetic acid

mols. of protons and deuterons are found to be 3·15 and 3·55, giving a val. of 0·89 for the exchange equilibrium const. J. D. R.

Action of concentrated sulphuric acid on oleic acid. A. STEGER, J. VAN LOON, (FRL.) B. R. N. VELLENGA, and B. PENNEKAMP (Rec. trav. chim., 1938, **57**, 25—32).—Oleic acid when treated with conc. H_2SO_4 and the resulting sulphuric ester hydrolysed with H_2O yields a mixture of hydroxystearic acids, which on distillation gives a mixture of solid (66%) and liquid acids (34%). The solid acids with O_3 in $CHCl_3$ yield sebacic, azelaic, and suberic acids, and must be a mixture of Δ^{η}-, Δ^{θ}-, and Δ^{ι}-elaidic acids. Similarly, the liquid acids are shown to be a mixture of Δ^{η}-, Δ^{θ}-, and Δ^{ι}-oleic acids. Ozonisation of a technical product rich in "*iso*oleic acid" also shows the presence of the three isomeric elaidic acids above. E. I.

Fatty acids. III. Properties of linoleic acids prepared by debromination and by low-temperature crystallisation. Quantitative determination. J. B. BROWN and J. FRANKEL (J. Amer. Chem. Soc., 1938, **60**, 54—56; cf. A., 1937, II, 84).—380 g. of 93·5% pure α-linoleic acid (I) are obtained by crystallisation from 2 kg. of the unsaturated acids of maize oil. The acid is identified with that prepared by debromination. Under standard conditions (I) gives 0·906 times its wt. of solid tetrabromide (theory 2·14), a proportion which can be used for determining (I). R. S. C.

Action of oxalic acid on a cobaltic chloropentammine.—See A., I, 156.

Additive compound of oxalyl chloride and dioxan. G. A. VARVOGLIS (Ber., 1938, **71**, [*B*], 32—34).—Addition of $(COCl)_2$ in light petroleum to dioxan (I) in the same solvent at −5° to −7° gives the additive *compound*, $C_4H_8O_2,C_2O_2Cl_2$, m.p. 67—68° (slight decomp.), which can be kept for months in a sealed tube in absence of air, but loses (I) when exposed to air, after which the $(COCl)_2$ is hydrolysed by atm. moisture. In freezing C_6H_6 the compound appears extensively solvolysed. $(COCl)_2$ does not give analogous compounds with Et_2O or di*iso*amyl ether and (I) does not appear to react with AcCl, BzCl, $CH_2(COCl)_2$, fumaryl, succinyl, *s*- or *as*-phthalyl, or terephthalyl chloride. H. W.

Addition of malonic enolates to αβ-unsaturated ketones. A. MICHAEL (J. Org. Chem., 1937, **2**, 303—307; cf. A., 1931, 67, 603; 1932, 252; 1933, 608).—The anomalous αδ-addition of malonic enolates to αβ-acetylenic esters found by Kon *et al.* (A., 1932, 601, 1127; 1937, II, 48) is discussed in relation to energy and chemical affinity. The reaction course is governed by the max. possible neutralisation of Na in the resulting enolates. Thus Na in the αδ-additive products $(CO_2Et)_2CR{\cdot}CR'{:}C{:}C(ONa){\cdot}OEt$ (I) is better neutralised than in the corresponding αβ-products $CO_2Et{\cdot}CHR{\cdot}CHR'{\cdot}C(CO_2Et){:}C(ONa){\cdot}OEt$ from αβ-ethylenic esters. The anomalous γ-alkylation of (I) with R = H with EtI whilst (I) with R = Me gives $(CO_2Et)_2CMe{\cdot}CR'{:}CEt{\cdot}CO_2Et$ is due to the γ-Me of (I) with R = Me being more strongly attached than the γ-H when R = H. The contention of Kon *et al.* (*loc. cit.*) and of Holden and Lapworth (A., 1931, 1271) that in $CHMe(CO_2Et)_2$ (II) additions to αβ-unsaturated esters, the αβ-Me_2 ester (III) is in all cases formed by rearrangement of the βγ-Me_2 ester (IV) first formed and that unless NaOEt is present the latter is formed, is refuted. Thus (II) with $CHR{:}CH{\cdot}CO_2Et$ (V) in presence of NaOEt gives $CO_2Et{\cdot}CH_2{\cdot}CHR{\cdot}CMe(CO_2Et)_2$ (VI), whilst $CO_2Et{\cdot}CMe{:}C(ONa){\cdot}OEt$ with (V) gives $CO_2Et{\cdot}CHMe{\cdot}CHMe{\cdot}CHR{\cdot}C(CO_2Et){:}C(ONa){\cdot}OEt$ and not the Na enolate of (VI). An explanation of the alleged formation of (III) from (IV) based on formation of an intermediate C_4-ring by elimination of EtOH, followed by fission and addition of EtOH, is untenable since such rings are stable to EtOH. Additive reactions of enolates cannot therefore be explained on the basis of valency alone. E. G. B.

Single- and double-shelled malonato-complexes and double-shelled succinato-complexes.—See A., I, 92.

Maleic acid production. Vapour-phase oxidation of crotonaldehyde using vanadium pentoxide catalysts. W. L. FAITH and A. M. SCHAIBLE (J. Amer. Chem. Soc., 1938, **69**, 52—54).—Increasing the ratio of air to $CHMe{:}CH{\cdot}CHO$ increases the amount of maleic anhydride formed in presence of V_2O_5 at 250—600°. V_2O_5 on Al gives higher yields than does V_2O_5 on pumice owing to the greater thermal conductivity of the former. For V_2O_5 on pumice the optimum temp. is 350° (31·8% yield with a 325 : 1 air–aldehyde mixture); for V_2O_5 on Al it is 450° (44·5% yield with a 520 : 1 mixture). R. S. C.

Non-reaction of acetylketen and maleic anhydride and some notes on maleic acid. C. D. HURD, A. S. ROE, and J. W. WILLIAMS (J. Org. Chem., 1937, **2**, 314—318; cf. A., 1936, 967).—$CHAc{:}CO$ does not react with furan or with maleic anhydride (I), but with (I) a slight separation of maleic acid (II) occurs, also observed with (I) and $CH_2Ac{\cdot}CO_2Et$. The acid has m.p. 137° (lit. m.p. 130—131°) (cf. A., 1907, i, 1063; 1908, i, 735). Its nature is shown by its mixed m.p. with the product, m.p. 136°, obtained from (I) and H_2O, and by the prep. in full yield from all specimens by action of Ac_2O and the appropriate amine of *N*-*p*-tolylmaleamic acid, new m.p. 195°, and *N*-4-methoxyphenylmaleamic acid, new m.p. 186°. All specimens of (II) on remelting have m.p. 130—131°, due to partial isomerisation to mixtures containing 3% of fumaric acid (III). Repeated fusions of (II) do not give a m.p. <130° owing to the slight solubility of (III) in the fused mixtures. E. G. B.

Double-shelled citrato-complexes of various cobaltic and chromic ammines in the dissolved state.—See A., I, 92.

Calcium borogluconate. H. T. MACPHERSON and J. STEWART (Biochem. J., 1938, **32**, 76—78).—Ca borogluconate is formed from 1 mol. of Ca gluconate and 2 mols. of H_3BO_3 by loss of H_2O. In H_2O, it behaves as a mixture of these substances. The product of Dryerre and Greig (A., 1935, 775) is a mixture of Ca mono- and di-borogluconates. J. N. A.

Stability of the free formyl radical. M. Burton (J. Amer. Chem. Soc., 1938, **60**, 212).—Published evidence supports the existence and stability of HCO. R. S. C.

Formylation of carbon atoms by the method of amide condensation. G. V. Tschelincev and B. M. Dubinin (J. Gen. Chem. Russ., 1937, **7**, 2309—2313).—$HCO{\cdot}NPh_2$, NaOEt, and $COMe_2$, COPhMe, or camphor yield respectively $CH_2Ac{\cdot}CHO$, $CH_2Bz{\cdot}CHO$, or formylcamphor. R. T.

Depolymerisation process in formaldehyde solutions.—See A., I, 147.

Chemistry of chloral and chloral hydrate. N. W. Hirwe (J. Univ. Bombay, 1937, **6**, Part II, 182—198).—A review.

Synthesis of $\Delta^{\alpha\epsilon}$-octadienal. G. Goethals (Bull. Acad. roy. Belg., 1937, [v], **23**, 721—738).—Me Δ^{β}-pentenoate is reduced with MeOH and Na at 60° to a 3 : 1 mixture, b.p. 53—54°/20 mm., of Δ^{γ}-*pentenol* [*chloride* (I), b.p. 107—107·6°/755 mm.; *iodide* (II), b.p. 53·6°/20 mm.], *n*-pentanol, and smaller amounts of methoxyamyl alcohol and β- or γ-methoxyvaleric acid. The Grignard reagent from a mixture of (I) and (II) when treated with acraldehyde affords $\Delta^{\alpha\zeta}$-*octadienol*, b.p. 72·5—75·5/10 mm., converted by PBr_3 and C_5H_5N into a mixture of primary and sec.-*bromides*, b.p. 72—83°/10 mm. The latter is treated with AgOBz, the *benzoates* are separated by fractional distillation, and the purity is checked by the Raman spectra. On hydrolysis with KOH–MeOH, the purified ester gives $\Delta^{\beta\zeta}$-*octadienol*, b.p. 88—90·5°/10 mm., containing about 12% of octenol, which with $K_2Cr_2O_7$–H_2SO_4 affords trans-$\Delta^{\beta\zeta}$-*octadienal*, b.p. 77—79°/10 mm. (*semicarbazone*, m.p. 169·3—170°). The aldehyde resinifies on keeping and has a somewhat irritating, much less pleasant odour than the nonadienal. The optical properties of the above compounds, including the Raman spectra, are discussed. S. C.

Two alkoxyacetaldehydes. Their preparation and properties. N. L. Drake, H. M. Duvall, T. L. Jacobs, H. T. Thompson, and H. M. Sonnichsen (J. Amer. Chem. Soc., 1938, **60**, 73—76).—Passage of $OMe{\cdot}[CH_2]_2{\cdot}OH$ over Cu at 425° gives the max. yield of $OMe{\cdot}CH_2{\cdot}CHO$, b.p. 92°/770 mm., which yields a p-*nitro*-, m.p. 115—115·5°, and 2 : 4-*dinitrophenylhydrazone*, m.p. 124—125°, and an azeotropic mixture, b.p. 88·5°/770 mm., with 12·8% of H_2O; no semicarbazone could be isolated. $OEt{\cdot}[CH_2]_2{\cdot}OH$ and Cu at 300° give 43% of *ethoxyacetaldehyde*, b.p. 105—106° (p-*nitro*-, m.p. 113—114°, and 2 : 4-*dinitro-phenylhydrazone*, m.p. 116—117°), which gives an azeotropic mixture, b.p. 90—91°, with 21·8% of H_2O. Both aldehydes polymerise to liquid *trimerides*, depolymerised by distillation with a trace of p-$C_6H_4Me{\cdot}SO_3H$ in very poor and 40—50% yield, respectively. The OMe-aldehyde gives also a *tetrameride*, m.p. 142—142·5°. $OBu{\cdot}[CH_2]_2{\cdot}OH$ gives less readily *butoxyacetaldehyde*, b.p. 130—135°. R. S. C.

Preparation of ketones from higher fatty acids. V, VI. K. Kino (J. Soc. Chem. Ind. Japan, 1937, **40**, 437—438B; cf. A., 1937, II, 483).—V. The frothing of 40 g. of fatty acid (usually stearic) with 1·8 g. of Mg at 330—340° is completely prevented by 5—10 g. of Cr soap and diminished by 10 g. of Ca soap. 10 g. of Ba soap stops both frothing and formation of ketone. Zn, Ni, Mg, Cu, Al, and Pb soaps are without effect.

VI. Mn, Zn, and Mg soaps decompose slowly at 250—260°, 300—310°, and 280—290°, and rapidly at >300°, >330—340°, and 330—340°, respectively. R. S. C.

Amine catalysis of the dealdolisation of diacetone alcohol. F. H. Westheimer and H. Cohen (J. Amer. Chem. Soc., 1938, **60**, 90—94).—The rate of dissociation of $OH{\cdot}CMe_2{\cdot}CH_2{\cdot}COMe$ (I) in NH_2Me–NH_3MeCl, $NHMe_2$–NH_2Me_2Cl, NMe_3–$NHMe_3Cl$, and NEt_3–$NHEt_3Cl$ to $COMe_2$ at 18° is pseudo-unimol., being independent of the concn. of (I). With NH_2Me or $NHMe_2$ it is dependent on the [OH′] and on the concn. of mol. amine, but with NMe_3 or NEt_3 is independent of the latter. The reaction is thus not one of general base catalysis, and the slow step is probably $O^-{\cdot}CMe_2{\cdot}CH_2{\cdot}COMe \rightarrow COMe_2 + COMe{\cdot}CH_2^-$. With NH_2Me and $NHMe_2$, however, some intermediate, possibly a ketimine, involving the H attached to N, must be formed. R. S. C.

Absorption spectra of carbohydrates in sulphuric acid.—See A., I, 59.

Active form of monosaccharides. III. Mechanism of addition of hydrocyanic acid. IV. Reactivity of glucose-6-phosphate. A. V. Stepanov and B. N. Stepanenko (Biochimia, 1937, **2**, 875—893, 917—925).—III. The catalytic effect of addition of bases to solutions of sugars (glucose, galactose, fructose) and HCN is at a max. when the entire HCN is neutralised. The reaction of cyanohydrin formation is represented: $>C{:}O + NH_4^{\cdot} \rightleftharpoons {:}C{\cdot}ONH_4 \overset{CN'}{\rightleftharpoons} {:}C(ONH_4){\cdot}CN \overset{H_2O}{\longrightarrow} {:}C(OH){\cdot}CN + NH_3 + H_2O$. The reaction proceeds in 10% but not in 80% MeOH, in which ionisation of NH_4CN is suppressed. The velocity of reaction in presence of C_5H_5N or piperidine ∝ dissociation consts. of the cyanides formed, but is smaller with NMe_3 than with NH_3, showing that not only the dissociation const. of the salt, but also the nature of the cation, influences the reaction.

IV. Cyanohydrin formation is more rapid with Ba glucose-6-phosphate than with glucose, in presence or absence of NH_3. R. T.

Reaction of monosaccharides with phenylhydrazine in presence of sodium hydrogen sulphite. A. D. Braun (Biochimia, 1937, **2**, 801—807).—Fructose in aq. $NaHSO_3$ yields a cryst. phenylhydrazide with $NHPh{\cdot}NH_2$ at 10°; under these conditions aldoses (glucose, mannose, galactose, arabinose) do not react. Production of fructose by heating glucose with dil. AcOH is confirmed. R. T.

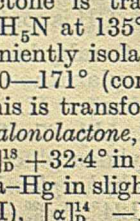
Syntheses with 5 : 6-anhydro*iso*propylideneglucose. V. 6-Diphenylamino-*d*-chinovose [6-*d*-glucosyldiphenylamine]. H. Ohle and M. Andrée (Ber., 1938, **71**, [*B*], 27—31; cf. A., 1936, 1491).—Anhydro*iso*propylideneglucose and $NHPh_2$ at 135—137° give 6-*diphenylamino*isopropylidene-*chinofuranose* (I), m.p. 124°, $[\alpha]_D^{20}$ −73·3° in $CHCl_3$,

—46·7° in AcOH, better obtained at 100° in the absence of air. It gives a *diacetate*, m.p. 124°, $[\alpha]_D^{20}$ —6·1° in $CHCl_3$, which dissolves slowly and without yielding a cryst. product in Br–AcOH, and a 3 : 5-*di*-p-*toluenesulphonate*, m.p. 145°, $[\alpha]_D^{20}$ —49·1° in $CHCl_3$. Hydrolysis of (I) in PrOH is absence of air gives 6-*diphenylamino*-β-d-*chinovose*, which separates from MeOH as the *monohydrate* (II), m.p. 90—91°, decomp. >100°, $[\alpha]_D^{20}$ —37·2° (no mutarotation) in $COMe_2$. Slight and slow mutarotation is observed in C_5H_5N or MeOH with or without NaOH. In 5N-HCl the sugar has $[\alpha]_D^{20}$ +111·2°. The absence of mutarotation is not due to the rapidity with which equilibrium is established but to the great stability of the β-variety. Treatment of (II) with Ac_2O in C_5H_5N at 0° gives 6-*diphenylamino*-β-d-*chinopyranose tetra-acetate* (III), m.p. 190—191°, $[\alpha]_D^{20}$ +7·18° in $CHCl_3$, $[\alpha]_D^{21\cdot5}$ —5·0° in $COMe_2$, readily transformed by HBr–AcOH into 6-*diphenylamino*-α-d-*chinopyranosyl* 1-*bromide triacetate* (IV), m.p. 147—148°, $[\alpha]_D^{20}$ +102·2° in $CHCl_3$, re-converted by AgOAc in AcOH into (III). (IV) and Ag_2CO_3 in MeOH at 20° yield 6-*diphenyl-amino*-β-*methyl*-d-*chinopyranoside* 2 : 3 : 4-*triacetate*, m.p. 128—129°, $[\alpha]_D^{21}$ —53·1° in MeOH, $[\alpha]_D^{20}$ —46·4° in $COMe_2$, —55·9° in $CHCl_3$, hydrolysed by NaOMe in MeOH to 6-*diphenylamino*-β-*methyl*-d-*chinopyranoside*, m.p. 208°, $[\alpha]_D^{17}$ —29·0° in $COMe_2$. H. W.

Reaction for distinguishing fructose from glucose. E. V. Zmačinski (Compt. rend. Acad. Sci. U.R.S.S., 1937, **17**, 415—416).—When warmed with a small quantity of S, glycerol, and aq. $Pb(OAc)_2$, fructose, but not glucose, gives a black colour. J. D. R.

Acetals of galactose and of dibenzylidene-glucose. M. L. Wolfrom, L. J. Tanghe, R. W. George, and S. W. Waisbrot (J. Amer. Chem. Soc., 1938, **60**, 132—134).—Dibenzylideneglucose Et_2 mercaptal 6-benzoate, $CdCO_3$, and $HgCl_2$ in EtOH at 70—80° give *dibenzylidene*-d-*glucose* Et_2 *acetal* 6-*benzoate* (I), m.p. 141—143°, $[\alpha]_D^{26}$ +14° in $CHCl_3$. Dibenzylideneglucose Et_2 mercaptal gives similarly *dibenzylidene*-d-*glucose* Et_2 *acetal*, m.p. 133—135°, $[\alpha]_D^{25}$ +16° in $CHCl_3$, also obtained from (I) by hot 0·5N-NaOEt and converted into (I) by BzCl–C_5H_5N. The Me_2 *acetal* 6-*benzoate*, m.p. 156—159° after softening at 142°, $[\alpha]_D^{24}$ +14° in $CHCl_3$, is similarly prepared, and the appropriate galactose mercaptals afford d-*galactose* Et_2, m.p. 79°, $[\alpha]_D^{30}$ +17·5° in $CHCl_3$, and Me_2 *acetal penta-acetate*, m.p. 128—129°, $[\alpha]_D^{20}$ +16° in $CHCl_3$, hydrolysed by 0·7M-$Ba(OMe)_2$ at 0° to d-*galactose* Et_2, m.p. 127—128°, $[\alpha]_D^{20}$ +15° in H_2O, and Me_2 *acetal*, m.p. 122—123°, $[\alpha]_D^{28}$ +16° in H_2O. R. S. C.

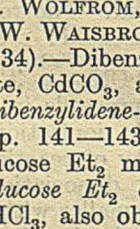
***l*-Talose.** C. Glatthaar and T. Reichstein (Helv. Chem. Acta, 1938, **21**, 3—6).—*l*-Galactono-lactone is transformed by H_2O and C_5H_5N at 135° into *l*-talonic acid, conveniently isolated as the *K* salt, m.p. 170—171° (corr.), $[\alpha]_D^{14}$ —1·2° in H_2O. This is transformed by dil. H_2SO_4 into *l-talonolactone*, m.p. 134—136° (corr.), $[\alpha]_D^{18}$ +32·4° in H_2O, which is reduced by Na–Hg in slightly acid solution to non-cryst. l-*talose* (I), $[\alpha]_D^{14}$ —16·9° in H_2O (*o-nitro-phenylhydrazone*, m.p. 144—146°, $[\alpha]_D^{16}$ —77·4° in MeOH).


(I.)

H. W.

Complete acetylation and methylation of α-*d*-tagatose. Y. Khouvine and Y. Tomoda (Compt. rend., 1937, **205**, 1414—1415).—Treatment of α-*d*-tagatose with Ac_2O and $ZnCl_2$ at 0° or 50° does not give a cryst. product, whereas with Ac_2O and C_5H_5N at —5°, 0°, or 20—30°, α-d-*tagatopyranose penta-acetate*, m.p. (block) 132°, $[\alpha]_{578}^{20}$ +20° in $CHCl_3$, —25° in MeOH, results. It does not add H in presence of Raney Ni and its ultra-violet spectrum has not the characteristic ketonic band. Tagatose tetra-acetate could not be obtained cryst. Methylation of α-*d*-methyltagatoside by NaOH and Me_2SO_4 gives only incompletely methylated syrups, whereas very frequently repeated treatments with MeI and Ag_2O leads to α-*pentamethyltagatopyranoside* (I), b.p. 40°/10^{-4} mm., $[\alpha]_{578}^{20}$ +21·4° in MeOH. The cyclic structure is established by the Raman spectrum and refractive index. Hydrolysis of (I) with 0·72% HCl at 100° gives *tetramethyltagatose*, b.p. 52°/10^{-4} mm., $[\alpha]_{578}$ —3·4° in MeOH. H. W.

Guloheptonic acids; α-*d*-α-guloheptose. H. S. Isbell (J. Res. Nat. Bur. Stand, 1937, **19**, 639—650).—Treatment of the compound, *d*-gulose,$CaCl_2$,H_2O, with NaCN followed by $Ca(OH)_2$ gives ppts. of the basic Ca salts of the epimeric guloheptonic acids. Decomp. of the mixture with aq. H_2SO_4 and concn. of the resulting solution affords d-α-*guloheptonic acid* (I), $C_7H_{14}O_8$, m.p. 128°, $[\alpha]_D^{20}$ —12·6°. d-α-*Guloheptono*-γ-*lactone* (II), $C_7H_{12}O_7$, m.p. 145°, $[\alpha]_D^{20}$ +25·5°, and the *phenylhydrazide*, m.p. 156°, $[\alpha]_D^{20}$ +29·3°, *Pb*, $[\alpha]_D^{20}$ —6·6°, and *Ba*, $[\alpha]_D^{20}$ —1·4°, salts of (I) are described. The mother-liquors from (I) yield d-β-*guloheptonic acid*, m.p. 135°, $[\alpha]_D^{20}$ +12·8° (*Pb*, $[\alpha]_D^{20}$ +16·7°, and *Ba*, $[\alpha]_D^{20}$ +1·5°, salts). Reduction of (II) with Na–Hg yields α-d-α-*guloheptose* (III), $C_7H_{14}O_7$, m.p. 127°, $[\alpha]_D^{20}$ —45·7° to —16·9° (equilibrium) in H_2O. Observations of mutarotation at 20·1° and 0·3° show a fast change accompanied by a smaller slow change; hence the equilibrium solution contains at least three modifications of the sugar in dynamic equilibrium. The proportions of the constituents involved in the rapid reaction vary with the temp. so that a change in temp. results in rapid mutarotation. The temp. coeff. for the rapid mutarotation reaction corresponds with those for the rapid reactions which cause the deviations in the mutarotations of galactose (IV), arabinose, talose, ribose, and *d*-β-glucoheptose, whereas the temp. coeffs. for the slow change agree with those for the slow reactions which cause the normal mutarotations of glucose, mannose, (IV), gulose, and talose. The structure, reactions, and properties of (III) resemble those of α-*d*-talose and provide additional evidence that the properties of the sugars are determined in large measure by the configuration of five C atoms comprising the pyranose ring. H. W.


(III.)

A holodiglucoside obtained from sophora-flavonoloside. J. Rabaté and J. Dussy (Compt. rend., 1937, **205**, 1431—1433; cf. A., 1936, 768).—

Hydrolysis of sophoraflavonoloside with boiling 0·2% H_2SO_4 gives campherol and *sophorose*, $C_{12}H_{22}O_{11}$, m.p. (block) 195—196°, $[\alpha]_D^{20}$ +37° to +22°. It contains 8 OH and one free ·CHO. It is hydrolysed by boiling 1·5% H_2SO_4 or by emulsin to glucose. It is not identical with gentiobiose or cellobiose. H. W.

Configurative relationship of γ-heptylamine to norleucine. P. A. Levene and M. Kuna (J. Biol. Chem., 1938, **122**, 291—295).—(+)-γ-Heptylamine is structurally correlated with (+)-β-hexylamine. (−)-γ-Amino-Δ^{α}-heptene (A., 1937, II, 437) with Ac_2O–C_5H_5N yields (−)-*acet*-Δ^{α}-*γ-heptenylamide*, b.p. 105—110°/1·5 mm., $[\alpha]_D^{25}$ −0·75°, ozonised to (+)-α-*acetamidohexaldehyde*, b.p. 130—135°/3 mm., $[\alpha]_D^{25}$ +5·7° in Et_2O, which is reduced (Adams) to (+)-β-*acetamidohexyl alcohol* (*acetylnorleucinol*), b.p. 150—165° (bath)/0·1 mm. (micro-distilling flask described), $[\alpha]_D^{25}$ +3·6° in EtOH, also obtained, b.p. 135—150° (bath)/0·1 mm., $[\alpha]_D^{25}$ +2·1° in EtOH, from (−)-norleucinol (A., 1937, II, 139), already structurally correlated with (+)-β-hexylamine and with (−)-α-aminohexoic acid. E. W. W.

Ammines of the Roussin's black salt series.—See A., I, 94.

Formation and decomposition of amino-acids by intermolecular transference of amino-groups. II. Equilibrium reaction between *l*(+)-glutamic and pyruvic acids, and between *l*(+)-alanine and α-ketoglutaric acid. A. E. Braunschtein and M. G. Kritzman (Biochimia, 1937, **2**, 859—874).—Equilibrium is attained in the reaction glutamic acid + pyruvic acid ⇌ alanine + α-ketoglutaric acid in 20—25 min. at 37°, in presence of muscle pulp, with addition of $CH_2Br{\cdot}CO_2Na$ and Na_2HAsO_3 to inhibit glycolysis and oxido-reduction reactions. The equilibrium mixture contains approx. equal amounts of the substrates. R. T.

Simple synthesis of *dl*-citrulline. A. C. Kurtz (J. Biol. Chem., 1938, **122**, 477—484).—α-Carbamidoarginine (A., 1936, 59) is converted by $Ba(OH)_2$ and H_2SO_4 into *dl*-ornithine monosulphate. This when boiled in H_2O with CuO yields *dl*-ornithinecopper sulphate, which with $CO(NH_2)_2$ yields the Cu derivative of *dl*-citrulline (I) [m.p. 220—221° (decomp.) confirmed; cf. A., 1932, 196], which is liberated by H_2S. It is suggested that (I) has the structure $\left[NH_2{\cdot}[CH_2]_3{\cdot}CH<\begin{matrix}NH_2\\CO{\cdot}O\end{matrix}>\right]_2Cu$, and that the α-$NH_2$ is thus protected by the co-ordinate linking. The $CuCl_2$ derivative of *dl*-lysine similarly gives a product which is apparently ε-carbamidolysine. E. W. W.

Synthesis of *r*-α-amino-β-hydroxy-*n*-butyric acid. E. Abderhalden and W. Stenger (Z. physiol. Chem., 1938, **251**, 171—182).—Repetition of the work of Abderhalden and Heyns (A., 1934, 638) except in that the hydrolysis of Me α-bromo-β-methoxybutyrate is interrupted as soon as dissolution of the ester is complete gives an acid which becomes partly cryst., m.p. 59°. Amination of the separated portions gives the same α-amino-β-hydroxybutyric acid (I), decomp. 237—239°; this product from either source gives the same *Bz*$_1$, m.p. 176°, and *Bz*$_2$, m.p. 174°, derivatives and the same *α-benzenesulphonamido-β-hydroxybutyric acid*, m.p. 162°. Reduction of the two acids by P and HI (*d* 2·0) at 150° gives the same α-aminobutyric acid; *α-benzenesulphonamidobutyric acid* has m.p. 145°, whereas the corresponding β-*compound* melts at 120°. Coupling of (I) with *dl*-α-bromo*iso*hexoyl chloride affords two dl-α-*bromo*iso-*hexoamido*-dl-β-*hydroxybutyric acids*, (II), m.p. 155°, and (III), m.p. 122°; the latter is attacked by trypsin whereas the former is not. Amination of (III) leads to α-dl-*leucylamino*-β-*hydroxybutyric acid*, decomp. 193°, which is hydrolysed by erepsin; the isomeric *compound*, decomp. 233°, remains unattacked. Hydrolysis of (III) yields an r-α-*amino*-β-*hydroxybutyric acid* (IV), decomp. 227—229° after darkening at 215°, whereas (II) gives an isomeric *acid* (V), decomp. 239—241° after darkening at 225°; the mixed m.p. is about 231° after becoming brown at 215°. The *Bz*$_1$ and *Bz*$_2$ derivatives of (IV) have m.p. 178° and 147—148°, respectively, whilst the corresponding derivatives of (V) melt at 176° and 174°, respectively. (V) appears identical with the dl-*allo*threonine of West and Carter (A., 1937, 328) but (IV) cannot be immediately identified with threonine. Injection of (IV) into the rabbit causes appearance in the urine of a dextrorotatory compound, presumably *l*(+)-threonine; its *Bz*$_1$ derivative, m.p. 151°, has $[\alpha]_D^{20}$ +25·1° in EtOH. H. W.

Synthesis of β-hydroxyleucine [α-amino-β-hydroxy*iso*butylacetic acid] and of β-hydroxynorleucine [α-amino-β-hydroxy-*n*-hexoic acid]. E. Abderhalden [with, in part, F. W. Ziesecke and A. Bahn] (Z. physiol. Chem., 1938, **251**, 164—170).—Addition of Br to *n*-hexoic acid and red P and treatment of the product with EtOH gives *Et α-bromohexoate*, b.p. 87—89°/vac., transformed by boiling NPhEt_2 into *Et* Δ^{α}-*hexenoate*, b.p. 59—63°/vac., which with $Hg(OAc)_2$ in NaOH affords *Et α-bromomercuri-β-methoxy*-n-*hexoate*, an oil. This is converted by Br in $CHCl_3$ into *Et α-bromo-β-methoxy*-n-*hexoate*, b.p. 108—110°/12 mm., whence *α-bromo-β-methoxy*-n-*hexoic acid*, transformed by NH_3 at 37° into *β-methoxynorleucine*, m.p. 231° (decomp.), demethylated by HBr (*d* 1·49) to r-α-*amino*-β-*hydroxy*-n-*hexoic acid* (I) (*β-hydroxynorleucine*), m.p. 245—246°, reduced by P and HI (*d* 2) at 140—150° to *dl*-norleucine. (I) gives a *phenylcarbamate*, $C_{13}H_{18}O_4N_2$, m.p. 160—163°, a *phenylhydantoin* derivative, $C_{13}H_{16}O_3N_2$, m.p. 157—159°, and *α-benzamido*-β-*hydroxy*-n-*hexoic acid*, m.p. 185—186°; a Bz_2 derivative could not be obtained. A similar series of changes starting from *iso*hexoic acid gives successively *Et α-bromo*iso*hexoate*, b.p. 62°/14 mm., *Et γ-methyl*-Δ^{α}-*pentenoate*, b.p. 56·5—60°/vac., *Et α-bromomercuri-β-methoxy-γ-methyl*-n-*valerate*, *Et α-bromo-β-methoxy-γ-methyl*-n-*valerate*, b.p. 104—108°/13 mm., *α-bromo-β-methoxy-γ-methyl*-n-*valeric acid*, and *α-amino-β-methoxy-γ-methyl*-n-*valeric acid* (*β-methoxyleucine*), m.p. 256—258°. The last-named compound is demethylated by boiling HBr (*d* 1·49) to *α-amino-β-hydroxy-γ-methyl*-n-*valeric acid* (II) (*β-hydroxyleucine*), m.p. 242—244°, which is reduced to leucine. (II) gives a *phenylcarbamate*, $C_{13}H_{18}O_4N_2$, m.p. 198°, a *phenylhydantoin*,

$C_{15}H_{16}O_3N_2$, m.p. 197—200°, and an ill-defined *Bz* derivative. H. W.

α-Sulphonyl- and αα-disulphonyl-amides. E. L. D'Ouville and R. Connor (J. Amer. Chem. Soc., 1938, **60**, 33—36).—*p*-$C_6H_4Me{\cdot}SO_2Na$ and the appropriate α-chloro- or α-bromo-amide in hot EtOH give α-p-*toluenesulphonyl-acet-*, m.p. 166—167°, *-propion-*, m.p. 168—168·5°, and -n-*butyr-amide* (I), m.p. 175—175·5°. $CH_2Cl{\cdot}CO{\cdot}NH_2$ or $CHCl_2{\cdot}CO{\cdot}NH_2$ and Na mercaptides in EtOH at $>0°$ (to avoid oxidation by the Cl) give α-*n*-butyl-, m.p. 57—58°, α-*benzyl-*, m.p. 97—98°, αα-*di*-n-*butyl-*, m.p. 104·5—105°, and αα-*di*-p-*tolyl-thiolacetamide*, m.p. 172·5—173·5°, oxidised by H_2O_2 to α-n-*butane-*, m.p. 119—119·5°, α-*toluene-*ω-, m.p. 178·5—179°, αα-*di*-n-*butane-*, m.p. 180·5—181·5°, and αα-*di*-p-*toluene-sulphonylacetamide*, m.p. 195—196° [hydrolysed by aq. NaOH to $CH_2(SO_2{\cdot}C_6H_4Me)_2$]. The appropriate alkyl bromide, alkanesulphonylacetamide, and NaOEt afford (I), α-p-*toluenesulphonyl*iso*hexoamide*, m.p. 151·5—152°, α-n-*butane-*, m.p. 125—125·5°, and α-*toluene-*ω-*sulphonyl*-n-*butyramide*, m.p. 196—198°. The $(RSO_2)_2$, but not the RSO_2, compounds dissolve in aq. Na_2CO_3. Some of the products are hypnotics. R. S. C.

Relationship between taste and constitution of dihydrazides of alkylmalonic acids and their derivatives. J. J. Blanksma and H. De Graff (Rec. trav. chim., 1938, **57**, 3—12).—By condensation of the appropriate hydrazide with aldehydes and ketones, the following are prepared. Malonodihydrazide (I) yields *malonodi*-iso*propylidene-*, m.p. 180°, -benzylidene-, *anisylidene-*, m.p. 221°, and *-piperonylidene-hydrazide*, m.p. 223°. Methylmalonodihydrazide (II) yields *methylmalonodi*-iso*propylidene-*, m.p. 178°, -benzylidene-, *-anisylidene-*, m.p. 241°, *-piperonylidene-hydrazide*, m.p. 247°. Ethylmalonodihydrazide (III) yields ethylmalonodi-*iso*propylidene-, -benzylidene-, *-anisylidene-*, and *piperonylidene-hydrazide*, m.p. 223°. *n*-Propylmalonodihydrazide (IV) (*Ac*$_2$ derivative, m.p. 245°) yields n-*propylmalonodi*-iso*propylidene-*, *-benzylidene-*, m.p. 245°, *-anisylidene-*, m.p. 244°, and *-piperonylidene-hydrazide*, m.p. 244°. iso*Propylmalonodihydrazide* (V), m.p. 214° (*Ac*$_2$ derivative, m.p. 254°), yields iso*propylmalonodi*-iso*propylidene-*, m.p. 204°, *-benzylidene-*, m.p. 261°, *-anisylidene-*, m.p. 278°, and *-piperonylidene-hydrazide*, m.p. 283°. n-*Butylmalonodihydrazide* (VI), m.p. 142°, yields n-*butylmalonodi*-iso*propylidene-*, m.p. 110°, *-benzylidene-*, m.p. 239°, *-anisylidene-*, m.p. 242°, and *piperonylidene-hydrazide*, m.p. 253°. Benzylmalonodihydrazide (VII) (*Ac*$_2$ derivative, m.p. 246°) yields *benzylmalonodi*-iso*propylidene-*, m.p. 168, *-benzylidene-*, m.p. 242°, *anisylidene-*, m.p. 248°, and *piperonylidene-hydrazide*, m.p. 244°. (I) to (VII) possess sweet tastes, the sweetness diminishing in numerical order. Acetylation decreases greatly or eliminates the sweet taste. Condensation of the hydrazino-residue with aldehydes and ketones causes disappearance of the sweet taste and produces bitterness. *Et*$_2$ *hydrazinomalonate*, m.p. 87°, and *hydrazinomalonodihydrazide*, m.p. 175°, are tasteless. E. I.

Coloured free radical derived from cyanogen. E. V. Zappi and R. Labriola (Bull. Soc. chim., 1938, **5**, [v], 27—29).—When solutions of CNI in Et_2O and of NaOEt are mixed in N_2 a yellow coloration appears, disappearing on admission of O_2 with formation of a white ppt. of NaI, NaCN, Na_2CO_3, and NH_4 salts; also present are MeCHO, $CO(NH_2)_2$, CHI_3, and $CN{\cdot}NH_2$. This reaction is not shown by Na, K, or Zn with CNI nor by NaOEt with MeCN, $CHPh_2{\cdot}CN$, CNCl, CNBr, or compounds containing positive I. A primary or *sec.* alcohol must be present. It is assumed that I·C:N reacts with NaOEt to give I·CNa:NNa, EtOH, and MeCHO. CNaI:NNa decomposes into NaI and the coloured radical :C:NNa (or C:NNa) which either passes into NaCN or with O_2 gives its peroxide $(CNNa)_2O_2$. This is either hydrolysed to $NH_2{\cdot}CO_2H$ and NaOH, passing into Na_2CO_3 and NH_3, or reacts with NH_3 to give $CO(NH_2)_2$ and NaOH. E. G. B.

Photolysis of azomethane.—See A., I, 153.

Phosphonic acids and their alkyl esters from αβ-unsaturated ketones. L. R. Drake and C. S. Marvel (J. Org. Chem., 1937, **2**, 387—399).—Ketones $CHR{:}CH{\cdot}CO{\cdot}R$ (R = alkyl or aryl) add PCl_3 in Ac_2O to give phosphonyl chlorides $\begin{matrix}CHR{\cdot}CH{:}CR\\PO(X)—O\end{matrix}$ (I) (X = Cl), hydrolysed to ketophosphonic acids $PO(OH)_2{\cdot}CHR{\cdot}CH_2{\cdot}CO{\cdot}R$ (II). (I) with long-chain aliphatic alcohols R′OH give cryst. alkali-insol. mono-esters $OR'{\cdot}PO(OH){\cdot}CHR{\cdot}CH_2{\cdot}CO{\cdot}R$ (III) in which the acidic properties of the OH are masked by the R′. Mesityl oxide (IV) with PCl_3 in Ac_2O gives, after hydrolysis of the reaction mixture, δ-methylpentan-β-one-δ-phosphonic acid (V), m.p. 62—63°, or with the appropriate alcohol the *Bu*, b.p. 82—100/2×10^{-4} mm., and n-*decyl*, b.p. 104—145°/1×10^{-4} mm., esters of (V). With tetradecanol (VI) and hexadecanol, the corresponding alkyl chloride and $\begin{matrix}CMe_2{\cdot}CH{:}CMe\\PO(OH)—O\end{matrix}$ are obtained. This indicates that (III) are formed through (I) (X = OR′), giving with the liberated HCl, $R'O{\cdot}PO(Cl){\cdot}CHR{\cdot}CH_2{\cdot}CO{\cdot}R$, which with more R′OH gives (III). Heating of (III) may lead to (I) (X = OH) (VII) and R′Cl. Alternatively (VII) may be the first product, passing into (III) by addition of R′OH. The following *αγ-diphenylpropan-α-one-γ-phosphonates* are described. n-*Decyl*, m.p. 107—108° (reduction with H_2—Pt gives *αγ-diphenylpropane-γ-phosphonic acid*, m.p. 168—171°); n-*dodecyl*, m.p. 110—113°; n-*tetradecyl*, m.p. 112—114°; n-*hexadecyl*, m.p. 108—110°; n-*octadecyl*, m.p. 105—109°; n-*octadec-ι-enyl*, m.p. 89—90°. $(CHBz{:})_2$ with PCl_3 gives, after hydrolysis, *αδ-diphenylbutane-αδ-dione-β-phosphonic acid*, m.p. 183—185° (decomp.). With decanol (VIII) or (VI), the cyclic *compound*, m.p. 197—198°, corresponding with (VII), is produced. *PBuCl*$_2$, b.p. 157—150°/750 mm., reacts like PCl_3 and with (IV) and $CHPh{:}CHBz$ (IX) yields respectively the *Bu* derivative of (V) (*K* salt) and n-*butyl-αγ-diphenylpropan-α-one-γ-phosphonic acid*, m.p. 191—193°. $PCl(OPh)_2$ in the same way adds to (IV) yielding the *Ph*$_2$ ester of (V), b.p. 136—150°/8×10^{-4} mm., and to $CHAc{:}CH_2$ (X) yielding *Ph*$_2$ *butan-β-one-δ-phosphonate*, b.p. 95—112°/3×10^{-4} mm. No phosphonic acid can be isolated from (X) and PCl_3, but with (VIII) the

reaction mixture yields *di*-n-*decyl butan*-β-*one*-δ-*phosphonate*, b.p. 120—170°/1 × 10^{-4} mm. PCl_3 does not add to CHPh:CH·CO_2Ph nor $AsCl_3$ to (IX).

Phosphonic acids CHEtR·CH(PO_3H_2)·CH_2·CO·R′ are prepared from PCl_3 and ketones CHEtR·CH:CH·CO·R′. The following are described: Δ^{γ}-ε-*ethylnonen*-β-*one*, b.p. 163—167°/2 mm.; Δ^{θ}-κ-*ethyltetradecen*-η-*one*, b.p. 130—134°/3—4 mm.; Δ^{δ}-γ-*ethyldodecen*-ζ-*one*, b.p. 97—103°/2 mm.; ε-*ethylnonan*-β-*one*-δ-, m.p. 66—69°, ε-*ethylheptan*-β-*one*-δ-, dark brown oil, γ-*ethylundecan*-ζ-*one*-δ-, m.p. 60—65°, and ι-*ethyltridecan*-ζ-*one*-θ-, dark brown oil (*Na* salt), -*phosphonic acid*; γ-*ethyldodecan*-ζ-*one*-δ-, dark oil, and Δ^{δ}-γι-*diethylundecen*-ζ-*one*-θ-, yellow oil, -*phosphonic anhydride*. E. G. B.

Organo-boron compounds. [I.] Study of reaction mechanisms. Primary aliphatic boronic acids. H. R. Snyder, J. A. Kuck, and J. R. Johnson. **II. Reducing action of some organo-boric acids.** J. R. Johnson, M. G. Van Campen, jun., and O. Grummitt. **III. Reactions of tri-*n*-butylborine.** J. R. Johnson, H. R. Snyder, and M. G. Van Campen, jun. **IV. Reaction of tri-*n*-butylborine with peroxides and with oxygen. Mechanism of autoxidation.** J. R. Johnson and M. G. Van Campen, jun. (J. Amer. Chem. Soc., 1938, **60**, 105—111, 111—115, 115—121, 121—124).—I. Org. B compounds are investigated because they may resemble the hypothetical active forms of C compounds owing to the open sextet of electrons of the B. Alkane-boronic acids, Alk·$B(OH)_2$, are best prepared from pure Me_3BO_3 and the Grignard reagent in Et_2O under pure N_2 at −75°. Thus are obtained *n*-butane- (I), m.p. 92—94° [*Na* salt (II), +0·5H_2O, over P_2O_5 gives the *salt*, $Na_2(BuBO)_2O$], n-*hexane*-, m.p. 88—90°, n-*pentane*-, m.p. 93—94°, *n*-propane-, m.p. 106—107°, *iso*butane-, m.p. 106—112°, and impure n-*tetradecane*-α-*boronic acid*, m.p. indefinite. These m.p. are obtained only by drying over 65% H_2SO_4 in N_2; the acids frequently separate as hydrates and, when dried as usual, pass into oxides, RBO. These acids resemble the aromatic boronic acids only in being oxidised by H_2O_2 to the alcohol and H_3BO_3 and in thermal decomp.; when heated, (II) gives C_4H_{10}. The acids are inert to aq. Hg, Cd, Zn, and Cu halides, conc. aq. alkalis, and 40% HBr or HI at 100°. They readily autoxidise, yielding first OR·$B(OH)_2$ and then by hydrolysis ROH and H_3BO_3. With ammoniacal $AgNO_3$ they give 1 atom of Ag and the hydrocarbon, R_2; thus (I) gives 70—80% of *n*-C_8H_{18}. They are extremely weak acids and cannot be titrated with alkali even in presence of mannitol. They readily lose H_2O over P_2O_5 or H_2SO_4, when heated alone in vac., or when treated with $SOCl_2$, yielding trimeric oxides; n-*butyl*-, b.p. 138°/18 mm., and n-*hexyl-boron oxide*, b.p. 178—182°/24 mm., are thus obtained. These add H_2O exothermally to regenerate the acid; the former gives a ppt. with dry NH_3 in Et_2O and reacts exothermally with EtOH, MeOH, NHPh·NH_2, and bases, and with $MgBu^aBr$ at −65° gives much $BBu(OH)_2$ and some BBu^a_3. B is determined in the acids by fusion with Na_2O_2 in a Parr bomb and in other compounds by oxidation with alkaline H_2O_2 and subsequent fusion at 130—150°; in both cases the H_3BO_3 formed is finally titrated. The stability of the oxides is explained by resonance and an electronic explanation is suggested for the resemblance of the acids to aldehydes. *sec.*- and *tert.*-Alkane- and *cyclo*alkane-boronic acids differ from those described above.

II. Marked differences in the behaviour of aliphatic and aromatic boronic acids are noted. Aromatic boronic acids are mainly hydrolysed by ammoniacal $AgNO_3$, only a trace of Ag being pptd. Toluene-α-boronic acid, m.p. 104°, is very readily autoxidised, even in presence of H_2O, which inhibits oxidation of $BBu(OH)_2$; it is stable to hot H_2O or 5% HCl, but with hot 5% NaOH gives quantitatively PhMe and H_3BO_3; with ammoniacal $AgNO_3$ it gives Bz_2 and Ag. *iso*Butane-β-boronic acid, m.p. 103—105° (decomp.), with $SOCl_2$ gives *B Bu$^{\gamma}$ oxide*, b.p. 66—68°/5 mm., m.p. 20°, and is also unusually readily autoxidised; with ammoniacal $AgNO_3$ it gives Ag and Bu$^{\gamma}$OH with only traces of C_2Me_6 and a little *iso*-C_4H_8 and *iso*-C_4H_{10}. *Furan*-2-*boronic acid*, dimorphic, m.p. 110° (decomp.) and 121—122°, can be titrated in presence of mannitol; it is stable in air; with aq. or ammoniacal $AgNO_3$ it gives the Ag salt, which decomposes, when warmed, to yield furan and no Ag; with aq. $HgCl_2$ it gives 2-chloromercurifuran, with $CuCl_2$ or $CuBr_2$ it gives the Cu^{I} halide and 2-halogenofuran, and with I gives 2-iodofuran. Thiophen-2-boronic acid, m.p. 134—135°, resembles the furan-acid in being titratable and in its reactions with $AgNO_3$, $HgCl_2$, $CuBr_2$, and I; with Br it gives 2-bromothiophen and with warm N-HCl or boiling 20% NaOH yields thiophen. The instability of the alkyl compounds to Ag_2O solutions may be due to the non-formation of Ag salts, and the formation of hydrocarbons, R_2, may occur by way of AgAlk.

III. Alkylborines can react only by the open sextet of the B functioning as an electron-acceptor to give complexes, X–Y→BR_3, or by the alkyl group forming a H-bridge, *e.g.*, X–Y→H·CH_2·BR_2. Addition reactions are discovered and interpreted by the former reaction mechanism. *Tri*-n-*butylborine*, b.p. 108—110°/20 mm., is obtained in 80% yield from MgBuBr and BF_3 or in 50% yield from Me_3BO_3 and an excess of MgBuBr. It oxidises rapidly and exothermally in air and ignites when poured on to cotton. It does not react with bases, *p*-C_6H_4Me·SO_2H, or *p*-C_6H_4Me·SH, but gives a red colour with picric acid. Quaternary boriates, $M^+[BR_4]^-$, could not be isolated, but their existence is proved. Thus, BBu^a_3 reacts exothermally with 2 mols. of MgPhBr in Et_2O with formation of two layers, the lower of which contains $[BPhBu^a_3]^-[MgPh(Et_2O)_n]^+$, since with H_2O it gives slowly C_6H_6 and BBu_3 and with PhNCO gives incompletely NHPhBz; BBu^a_3 reacts exothermally with 1 mol. of $MgPh_2$ in Et_2O to give two layers, the lower of which contains the complex boriate. In Et_2O BBu_3 also reacts exothermally with LiPh, $LiBu^a$, and $MgBu^aBr$ without separation into layers, but not with $ZnBu^a_2$. Failure hitherto to report such reactions is due to use of hydrocarbon solvents, since solvation with Et_2O appears to be essential for their occurrence. With 48% aq. HBr BBu_3 gives 1 mol. each of *n*-C_4H_8 and BBu_2Br; the bromide is at once hydrolysed to di-*n*-butylborinic acid, which is isolated

by dehydration (distillation in vac. in N_2) to *di-n-butylboron oxide*, $(BBu_2)_2O$, b.p. 136°/12 mm. This oxide is rapidly oxidised and ignites in air if in a thin film; it is unaffected by cold aq. alkali; when heated with BuOH with continuous removal of H_2O it gives *Bu^a di-n-butylborinate*, $BBu^a_2{\cdot}OBu^a$, b.p. 110—111°/19 mm., which reacts incompletely with MgPhBr to yield a little $BPh(OH)_2$. With anhyd. HBr at 55—60° BBu_3 gives 1 mol. each of C_4H_{10} and *B Bu$^a_2$ bromide*, b.p. 44°/4 mm., stable to Ag and amalgams, but readily hydrolysed to $BBu_2{\cdot}OH$ by H_2O. BBu_3 is stable to I or Br in CCl_4, but with Br alone a complex reaction occurs: fission gives BuBr and BBu_2Br, and then *B Bu^a dibromide*, BBu^aBr_2, b.p. 65°/23 mm.; simultaneously some substitution in the Bu occurs, liberating HBr, which in part reacts with BBu_3 to give C_4H_{10} and BBu_2Br. With Bu$^\gamma$OCl (3 mols.), even at −80°, BBu_3 gives 33% of Bu^{a}Cl, indicating the reaction, $BBu^a_3 + Bu^\gamma OCl \rightarrow BBu^a_2{\cdot}OBu^\gamma + Bu^aCl$, but some substitution also occurs and elimination of HCl leads to some *butenyl di-n-butylborinate*, b.p. 70—71°/4 mm., and probably some $B(C_4H_7)_3$. It is assumed that, when HBr reacts with BBu_3, co-ordination of the Br and B increases the mobility of a Bu, which then undergoes an irreversible $\alpha \rightarrow \gamma$ shift to yield C_4H_{10}. Similarly, the O of BuOCl co-ordinates with the B and Bu^{a}Cl is split off by the $\alpha \rightarrow \gamma$ shift. Failure of BBu_3 to lose >1 Bu to Br and the stability of BBu_2Br to HBr (experimentally proved) are attributed to a resonance effect, $BBu_2{-}Br \rightleftharpoons \bar{B}Bu_2{=}\overset{+}{B}r$, by which unshared electrons of the Br partly satisfy the acceptor activity of the B and thus diminish its affinity for an external donor mol. so that co-ordination does not now supply sufficient energy to the Bu to enable the $\alpha \rightarrow \gamma$ shift to occur. Bromination by Br may be due to activation of CH_2 by the neighbouring B or of Br mols. by BBu_3.

IV. Bz_2O_2 and BzO_2H in $CHCl_3$ react readily with BBu^a_3, *e.g.*, $BBu_3 + 3BzO_2H \rightarrow B(OBu)_3 + 3BzOH$, and subsequent treatment with cold alkali gives 3BuOH and H_3BO_3 (almost quantitatively with BzO_2H). In presence of H_2O BBu_3 absorbs 0·5 O_2 to give 92% of $BBu^a_2{\cdot}OBu^a$, b.p. 120—121°/24 mm. (see above), the reaction being interpreted thus: $BBu_3 + O_2 \rightarrow Bu_3B{\leftarrow}O{:}O$; $BBu_3O_2 + BBu_3 \rightarrow 2BBu_2{\cdot}OBu$. In dry air 1 O_2 is absorbed and the product obtained is pure *Bu$^a_2$ n-butane-α-boronate*, $BBu(OBu)_2$, b.p. 110—111°/24 mm.; this is similarly interpreted, the intermediate $BBu_2{\cdot}OBu$ co-ordinating with O_2 when H_2O is absent. The inability of $BBu_2{\cdot}OBu$ to oxidise further in H_2O is due to the B·O linking and may be connected with the ability of the boronic acids to form hydrates. Ease of cleavage of alkyl decreases in the following series: $BR_3 > BR_2X > BRX_2$, X being Br, OH, or OAlk; this is explained by the resonance theory elaborated above for the reaction with Br. BzO_2H and H_2O_2 remove all three, Br and dry O_2 remove two, and HBr and moist O_2 remove one alkyl from the B. R. S. C.

Compounds of bivalent platinum with α-alanine. A. A. Grünberg and L. M. Volschtein (Bull. Acad. Sci. U.R.S.S., 1937, 885—905; cf. A., 1937, II, 330).—The compound of $[PtAn_2]$ (HAn = alanine) reported by Ley and Ficken (A., 1912, i, 243) is a non-electrolyte with a *trans*-configuration. The *compound* [PtAnG] (HG = glycine), with a *trans*-configuration, has been obtained by the reaction $K[PtCl_2An] + HG \rightarrow [PtAnG] + KCl + HCl$. The *compounds* $[PtCl_2,2HAn]$, $[PtCl_2,HAn,HG]$, $[Pt,2NH_3,2HAn]Cl_2$, $[Pt,2NH_3,HAn,HG]Cl_2$, $[Pt,2T,2HAn]Cl_2$ (T = $CS(NH_2)_2$), $[Pt,2T,HAn,HG]Cl_2$, $[Pt,2NH_3,An_2]$, $[Pt,2NH_3,An,G]$, $[Pt,2T,An_2]$, and $[Pt,2T,An,G]$ have been prepared. Compounds of the formula $M_2[PtAn_4]$ could not be obtained in the solid state owing to their high solubility, but the *compound* $[Pt,4HAn,Cl_2]Cl_2$ has been prepared. R. C.

Hydroxy-compounds of quadrivalent platinum.—See A., I, 94.

Vapour-phase reactions of *cyclo*propane with iodine and bromine. R. A. Ogg, jun., and W. J. Priest (J. Amer. Chem. Soc., 1938, **60**, 217—218).—*cyclo*Propane and I at 250°/300 mm. give mainly $CH_2(CH_2I)_2$; the reaction is unaffected by light and so I atoms play no part. In light at room temp. Br gives rapidly $CH_2(CH_2Br)_2$ and 2% of HBr; in the dark at 220° reaction is as fast as that with I, but much HBr is formed. Gaseous HCl, HBr, and HI react only slightly at 300°, but at room temp. HCl reacts slowly, doubtless by a complex mechanism. All reactions were effected in Pyrex glass. R. S. C.

Organic reactions with boron fluoride. XVIII. Reaction of ethers with benzene. M. J. O'Connor and F. J. Sowa (J. Amer. Chem. Soc., 1938, **60**, 125—127).—Reaction of ethers with C_6H_6 in presence of BF_3 occurs by intermediate olefine formation, since $(n\text{-}C_5H_{11})_2O$ gives $CHPhMePr^a$ (29·6% with 40·4% of polyamyl derivatives) and $(iso\text{-}C_5H_{11})_2O$ gives *tert.*-amylbenzene (12·4% with 32% of polyamyl derivatives). Pr^β_2O and $(CH_2Ph)_2O$ react vigorously with C_6H_6, forming $PhPr^\beta$ and CH_2Ph_2, respectively, also formed from $PhOPr^\beta$ and $CH_2Ph{\cdot}OEt$ (which react explosively), respectively. Et_2O and $(C_5H_{11})_2O$ react only at high temp. and pressure. Di- (mostly *p*- with very little *o*-) and poly-alkyl compounds are usually also formed. BF_3 causes reaction by co-ordination with the ethereal O and thus weakening the C·O linking. Some dehydration of the alcoholic fission product to an olefine and consequent further reaction with C_6H_6 occurs. R. S. C.

Synthesis of *o*- and *m*-propenyltoluene and *o*-allyltoluene. R. J. Levina and I. C. Grinberg (J. Gen. Chem. Russ., 1937, **7**, 2306—2308).—The b.p., *n*, and *d* of *o*-, *m*-, and *p*-C_6H_4MeBr, *o*-, *m*-, and *p*-tolylethylcarbinol, *o*-, m-, b.p. 94·5°/22 mm., and *p*-propenyltoluene, and *o*-, *m*-, and *p*-allyltoluene are tabulated. R. T.

Salts of nitro-compounds. II. Reaction of the silver salt of phenylnitromethane with diphenylbromomethane. G. B. Brown and R. L. Shriner (J. Org. Chem., 1937, **2**, 376—380; cf. A., 1937, II, 490).—$CHPhAg{\cdot}NO_2$ (I) with $CHPh_2Br$ (II) yields a mixture of $CHPh_2{\cdot}CHPh_2$ (III) and α-$(CHPh{\cdot}NO_2)_2$ (IV) by two simultaneous couplings. Thus (I) decomposes into (IV) and free Ag, which then couples two mols. of (II) yielding (III). (I) in

C_6H_6 yields on shaking β-$(CHPh{\cdot}NO_2)_2$ (V), also formed by action of NO_2 on stilbene or of I on $CHPhNa{\cdot}NO_2$. (IV) and (V) both yield triphenyl*iso*oxazole by action of alkali. E. G. B.

Mesitylene derivatives. III. Reaction of di-(2 : 4 : 6-trimethylphenyl)methyl chloride (dimesitylmethyl chloride) with molecular silver. W. T. Nauta and P. J. Wuis (Rec. trav. chim., 1938, **57**, 41—60; cf. A., 1937, II, 332).—Di-(2 : 4 : 6-trimethylphenyl)methyl chloride (I) in C_6H_6 with Ag in N_2 gives an orange colour which rapidly changes to a stable red-violet. The colour of this solution, which does not obey Beer's law on dilution, and is destroyed by O_2, is considered to be due to the *dimesitylmethyl* radical. Attempts to isolate *tetramesitylethane* (II) from the solution give mixtures, m.p. 140—190°, containing dimesitylmethane; (I) heated in N_2 or with C_5H_5N yields only resinous material, and no (II). (I) with Ag in C_6H_6 in O_2 (absorption of 3 O) yields 2 : 4 : 6-trimethyl-phenol (III) and -benzaldehyde, dimesityl ketone, and a *substance* $(C_{19}H_{23}O)_n$, m.p. 257° (decomp.), which with Zn–AcOH yields a little (III). The solution of (I) in C_6H_6 with Ag absorbs NO with formation of a blue-green colour, rapidly changing to yellow, and from this solution dimesitylcarbinol is isolated. E. I.

Magnetic investigation of ωω′-phenylpolyenes.—See A., I, 128.

Syntheses with *p-cyclo*hexylbenzyl chloride. D. Bodroux and R. Thomassin (Compt. rend., 1937, **205**, 1417—1418).—*p-cyclo*Hexylbenzyl chloride (I) reacts readily with Mg in presence of Et_2O and the product is transformed by O_2 and CO_2 into p-cyclo*hexylbenzyl alcohol*, m.p. 40° (yield 34%), and p-cyclo*hexylphenylacetic acid*, m.p. 78·5° (yield 55% if the gas is used and 60% if the solid is employed), respectively. *p-cyclo*Hexyltoluene and *di*-p-cyclo*hexyldibenzyl*, m.p. 148—149° [also from (I) and Na in boiling Et_2O], are formed as by-products. Oxidation of (I) by boiling dil. $Cu(NO_3)_2$ or, preferably, $Pb(NO_3)_2$ affords p-cyclo*hexylbenzaldehyde*, b.p. 158—160°/10 mm. (corresponding *anil*, m.p. 117—118°), with a considerable proportion of p-cyclo*hexylbenzoic acid*, m.p. 197—198°. H. W.

Configurational effects in the solvolytic reactions of α-phenylethyl chloride.—See A., I, 86.

2-Ethylnaphthalene. G. Lévy (Ann. Chim., 1938, [xi], **9**, 5—87).—2-$C_{10}H_7Ac$, obtained by addition of $AlCl_3$ to $C_{10}H_8$ and AcCl in $PhNO_2$ at −5° to 0°, is reduced by H_2 in presence of Ni–pumice at 200° to 2-$C_{10}H_7Et$ (I), b.p. 257—258° (corr.)/760 mm., m.p. −7° to −6·5°, purified through the picrate, m.p. 76·5—77°; it is accompanied by its H_4-derivative, which is readily dehydrogenated by S to (I). Clemmensen's method gives unsatisfactory results probably owing to polymerisation of 2-vinylnaphthalene formed intermediately. Reduction of 8-*keto*-2-*ethyl*-5 : 6 : 7 : 8-*tetrahydronaphthalene* (II) [*semicarbazone*, m.p. 197° (corr.)] by Zn–Hg and 5N-HCl gives 2-*ethyl*-5 : 6 : 7 : 8-*tetrahydronaphthalene* (III), b.p. 239—239·5° (corr.)/736 mm. 1-*Keto*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (IV), b.p. 109°/13 mm. [*semicarbazone*, m.p. 207·5° (corr.)], is converted similarly (with subsequent treatment with Raney Ni) into 2-*ethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (V), b.p. 235—235·5° (corr.)/731 mm. Hydrogenation of (I) in presence of Ni prepared at 360° leads exclusively to (III); in presence of Ni obtained at 280° 2-*ethyldecahydronaphthalene* (VI) appears to result in considerable amount with a mixture of (III) and (V). Reduction by Na in boiling *iso*amyl alcohol gives only 2-*ethyldihydronaphthalene*, b.p. 245° (corr.)/760 mm. (non-cryst. *dibromide*), whereas use of Ni prepared at 250° leads to (VI), b.p. 222° (corr.)/760 mm. Hydrogenation of (V) at 160° in presence of Ni obtained at 250° gives (VI), b.p. 92°/13 mm., 222° (corr.)/760 mm. (probably a mixture of isomerides).

Addition of 100% HNO_3 to (I) in AcOH at 3° to 10° gives preponderatingly a cryst. NO_2-derivative (VII), m.p. 49·5—50°, reduced to an *amine* (VIII), m.p. 25—28° (*Ac* derivative, m.p. 156·5°), and a non-characterised isomeric NO_2-compound, transformed into an *amine* (IX) (*Ac* compound, m.p. 148·5—149°). (VIII) is transformed by dil. acid under pressure or by diazotisation and subsequent treatment with steam into 2-*ethyl*-1-*naphthol* (X), m.p. 69·5—70° (*picrate*, m.p. 119·5°). (VII) is therefore 2-*nitro*-1-*ethylnaphthalene*. $CH_2Ph{\cdot}CH_2Br$ (prep. from $CH_2Ph{\cdot}CH_2{\cdot}OH$ described) and $CHNa(CO_2Et)_2$ yield *Et*$_2$ β-*phenylethylmalonate*, b.p. 156°/4 mm., which with EtBr gives *Et*$_2$ β-*phenyldiethylmalonate*, b.p. 151°/3 mm., whence successively β-*phenyldiethylmalonic acid*, m.p. 129°, and γ-*phenyl*-α-*ethyl*-n-*butyric acid*, b.p. 180°/16 mm., m.p. 104°. This is converted by cold $SOCl_2$ into γ-*phenyl*-α-*ethyl*-n-*butyryl chloride*, b.p. 142°/15 mm., cyclised by $AlCl_3$ in light petroleum to 1-keto-2-ethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (see above), dehydrogenated by Se at 300—360° to (X). (IX) is hydrolysed by dil. H_2SO_4 at 200° into an *ethylnaphthol* (XI), m.p. 56·5—57° [*picrate*, m.p. 131—131·5° (corr.)]. $CH_2Ph{\cdot}CHO$ and MgEtBr afford α-*phenylbutan*-β-*ol*, b.p. 106—107°/13 mm., readily converted into β-*bromo*-α-*phenylbutane*, b.p. 109—110°/? pressure, which does not appear to react with $CHNa(CO_2Et)_2$. Benzylethylmalonic acid is decarboxylated to α-*benzylbutyric acid*, b.p. 174°/15 mm., the iso*amyl* ester, b.p. 154°/15 mm., of which is reduced by Na in boiling *iso*amyl alcohol to β-*benzyl*-n-*butyl alcohol*, b.p. 142—144°/16 mm. β-*Benzyl*-n-*butyl bromide*, b.p. 131°/14 mm., is transformed into the corresponding *nitrile*, b.p. 142°/13 mm., hydrolysed by conc. HCl at 120—130° to β-*benzyl*-n-*valeric acid*, b.p. 175°/13 mm. The chloride of this is cyclised by $AlCl_3$ to 4-*keto*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. 145°/14 mm. [*semicarbazone*, m.p. 171·5° (corr.)], dehydrogenated by Se to the very unstable 2-*ethyl*-4-*naphthol*, b.p. 170°/11 mm., m.p. 50·5—51° [*picrate*, m.p. 145° (corr.).] Addition of $AlCl_3$ to a mixture of succinic anhydride, PhEt, and C_6H_6 yields β-*p*-ethylbenzoylpropionic acid, m.p. 102—103°, reduced (Clemmensen) to γ-*p*-ethylphenylbutyric acid (XII), m.p. 70°, the *chloride*, b.p. 143—145°/18 mm., of which is cyclised to 8-keto-2-ethyl-5 : 6 : 7 : 8-tetrahydronaphthalene, b.p. 152—154°/

18 mm. (see above); dehydrogenation of this gives (XI). Alternatively, a mixture of PhEt, trioxymethylene, and $ZnCl_2$ is transformed by HCl into p-*ethylbenzyl chloride*, b.p. 102—103°/19 mm., which with HCN or $Et_2C_2O_4$ gives *Et*$_2$ p-*ethylbenzylmalonate*, b.p. 175—178°/3 mm. The corresponding *acid*, m.p. 144—145°, is decarboxylated to β-p-*ethylphenylpropionic acid*, m.p. 73°, the *amyl ether*, b.p. 169—171°/12 mm., of which is reduced to γ-p-*ethylphenylpropyl alcohol*, b.p. 140°/12 mm. (*phenylurethane*, m.p. 56°). This is transformed through the *bromide* and *cyanide*, b.p. 154—155°/15 mm., into (XII).

Sulphonation of (I) gives 2 : 6-$C_{10}H_6Et{\cdot}SO_3H$ (very sparingly sol. *Ba* salt), the *Na* salt (XIII) of which is transformed by PCl_5 into 2-*ethylnaphthalene*-6-*sulphonyl chloride*, m.p. 69—69·5°, whence the corresponding *amide*, m.p. 190—191° (corr.). Fusion of (XIII) with NaOH at 270—300° affords 2-*ethyl*-6-*naphthol* (XIV), m.p. 97—98° [*picrate*, m.p. 106—107°; *Me ether* (XV), m.p. 58°]. p-*Methoxybenzyl chloride* (XVI), b.p. 120°/18 mm., is condensed with difficulty with $CEtNa(CO_2Et)_2$ to *Et*$_2$ p-*methoxybenzylethylmalonate*, b.p. 161°/2 mm.; the corresponding *acid*, m.p. 131·5—132·5°, is decarboxylated to α-p-*methoxybenzyl*-n-*butyric acid*, b.p. 195°/13 mm., the *amyl* ester, b.p. 188—189°/13 mm., of which is reduced to β-p-*methoxybenzyl*-n-*butyl alcohol*, b.p. 165°/15 mm. Bromination of the alcohol gives only resins and it is therefore converted by $SOCl_2$ and $NPhMe_2$ into β-p-*methoxybenzyl*-n-*butyl chloride*, b.p. 160°/13 mm. This is transformed through the *iodide*, b.p. 165°/13 mm., into the *nitrile*, b.p. 172—175°/13 mm., hydrolysed to γ-p-*methoxybenzyl*-n-*valeric acid*, b.p. 205°/13 mm., the *chloride*, b.p. 175°/13 mm., of which is cyclised to 4-*keto*-6-*methoxy*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. 180°/13 mm. [*semicarbazone*, m.p. 171—172° (corr.)]. Reduction of the ketone yields 6-*methoxy*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. 148—153°/13 mm., readily dehydrogenated by S at 260° giving (XV), demethylated by boiling HI to (XIV).

(XVI) is converted by an excess of NaCN in dry $COMe_2$ into *p*-anisylacetonitrile, hydrolysed to the acid, m.p. 88°, the *amyl* ester, b.p. 134°/13 mm., of which is reduced to β-*p*-anisylethyl alcohol, m.p. 28°. The corresponding chloride is condensed with $CEtNa(CO_2Et)_2$ to *Et*$_2$ β-p-*anisylethylethylmalonate*, b.p. 200°/5 mm., hydrolysed to β-p-*anisylethylethylmalonic acid*, m.p. 122°. This is decarboxylated to α-p-*anisylethyl*-n-*butyric acid*, b.p. 212°/19 mm., the *chloride*, b.p. 177°/19 mm., of which is cyclised to 1-*keto*-7-*methoxy*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. 175°/17 mm., m.p. 46—46·5°. Reduction of the ketone (Clemmensen) yields 7-*methoxy*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, dehydrogenated to 7-*methoxy*-2-*ethylnaphthalene*, m.p. 51—52°.

H. W.

Compound decomposing easily in the pure state under the catalytic influence of the container. S. C. J. Olivier and J. Wit (Rec. trav. chim., 1938, **57**, 90—94).—Crude 2-$C_{10}H_7{\cdot}CH_2Br$ (I) may be distilled without decomp. (155—180°/14 mm.), but on redistillation the pure (I) decomposes into HBr and a *substance*, $(C_{11}H_8)_n$, probably polymeric di-2-naphthylethylene. The decomp. is most rapid in soft glass, slowest in Pyrex, and is accelerated by pumice. The prep. from (I) of 2-$C_{10}H_7{\cdot}CH_2{\cdot}CN$ (100%) and 2-$C_{10}H_7{\cdot}CH_2{\cdot}CO_2H$ (>90%) is described.

E. I.

Dissociable anthracene oxides. Photo-oxidation of anthracene. C. Dufraisse and M. Gérard (Bull. Soc. chim., 1937, [v], **4**, 2052—2063; cf. A., 1935, 969, 1488; 1936, 1110).—When irradiated in CS_2 or $CHCl_3$ anthracene gives a photo-oxide, and when in C_6H_6 or Et_2O a polymeride. In CS_2 + Et_2O both processes are inhibited. The possible mechanism of photo-oxidation through an intermediate dimeride is discussed on a steric basis; the intervention of a 9 : 10-diradical is considered unlikely.

E. W. W.

Dissociable anthracene oxides. Question of monatomic *meso*-bridges. 9-Phenyl-9 : 10-dihydro*meso*thioanthracene and 2 : 5-diphenyl-3 : 4-benzthiophen. C. Dufraisse and D. Daniel (Bull. Soc. chim., 1937, [v], **4**, 2063—2070).—Bistrzycki's "9-phenyl-9 : 10-dihydro*meso*thioanthracene" (A., 1922, i, 268; cf. also A., 1924, i, 1333) is actually 2 : 5-*diphenyl*-3 : 4-*benzthiophen* (I), m.p. 118—119°, since it can be obtained from 2 : 5-diphenyl-3 : 4-benzfuran (II) (A., 1932, 1257) and P_2S_5, and since absorption spectra of (I) and (II) show only normal differences between a thiophen and a furan. The pyrogenic formation of 9-phenylanthracene from (I) (Zn) is also observed with (II) and with *o*-$C_6H_4Bz_2$; at >400°, anthracene is formed.

E. W. W.

Phenanthrene derivatives. VIII. Hexarylethanes containing the phenanthrene nucleus. W. E. Bachmann and M. C. Kloetzel (J. Org. Chem., 1937, **2**, 356—375).—The dissociation of hexa-arylethanes in solution is due to weakness of the C·C linking and to stability of the triarylmethyl radicals produced, and is accounted for by a combination of steric hindrance and resonance (cf. Bent *et al.*, A., 1936, 291, 1341). The dissociation-promoting effect of the phenanthrene nucleus has been studied by determining the dissociation of *s*-diphenanthryltetra-arylethanes (I). Equilibrium solutions of (I) and the corresponding phenanthryldiaryl radicals (II) are prepared by shaking the appropriate phenanthryldiarylchloromethane in C_6H_6 or $PhNO_2$ with Ag in N_2. The radicals rapidly absorb O_2 to form the corresponding peroxides. Solutions of 1- (III), 2- (IV), and 3- (V) *-phenanthryldiphenylmethyl* are relatively stable in the dark, whereas those of 9-*phenanthryl-diphenylmethyl* (VI) and *-diphenylenemethyl* (VII) decompose spontaneously. The apparent mol. wts. of the ethanes corresponding with (III), (IV), and (V) and also of *s*-di-α- and -β-naphthyl- and *s*-di-*p*-diphenylyl-tetraphenylethanes are determined cryoscopically in the filtered solutions. (VI) and (VII) are too unstable to permit mol. wt. determinations. The dissociations calc. from the mol. wts. show that the dissociation-promoting effect of 1- and 2-$C_{14}H_9$ ranks with that of α-$C_{10}H_7$ and is > that of *p*-diphenylyl and 3-$C_{14}H_9$, while that of the latter two groups is > that of β-$C_{10}H_7$.

Benzoylation of phenanthrene gives a mixture of

1- (VIII) and 9-benzoylphenanthrene. (VIII) with MgPhBr gives *diphenyl-1-phenanthrylcarbinol*, m.p. 163—164° [*Me*, m.p. 193—199°, and *Et*, m.p. 151—152°, *ether*; *diphenyl-1-phenanthryl-methane*, m.p. 175—176°, and *-acetic acid*, m.p. 230—232° (decomp.)], which with hot AcCl gives the corresponding *chloromethane* (IX), m.p. 212° (decomp.) (*compounds* with $SnCl_4$, $FeCl_3$, and $ZnCl_2$). On shaking with Ag in C_6H_6 and evaporating, (IX) yields s-*di-1-phenanthryltetraphenylethane* as a red oil. *Di(diphenyl-1-phenanthrylmethyl) peroxide* has m.p. 175—176° (decomp.). *Diphenyl-2-phenanthrylcarbinol* [*Me*, m.p. 105—106° and 111—112° (dimorphic), and *Et*, m.p. 116—117°, *ether*; *diphenyl-2-phenanthryl-methane*, m.p. 151—152°, and *-acetic acid*, m.p. 232—233°] from Me 2-phenanthroate and MgPhBr, with hot AcCl gives the corresponding *chloromethane*, m.p. 160—161° (*compounds* with $HgCl_2$, $SnCl_4$, $FeCl_3$, and $ZnCl_2$), yielding s-*tetraphenyl-di-2-phenanthrylethane* as a red oil. *Diphenyl-3-phenanthrylcarbinol*, m.p. 100—102° (Me, m.p. 147—148°, and *Et*, m.p. 155—156°, *ether*; *diphenyl-3-phenanthryl-methane*, m.p. 122—123°, and *-acetic acid*, m.p. 215—216°), is prepared from Me 3-phenanthroate and MgPhBr. (The compound previously described as this is the Me ether; cf. Bachmann, A., 1935, 622.) Hot AcCl gives the corresponding *chloromethane*, m.p. 132·5—133·5° (*compounds* with $SnCl_4$, $FeCl_3$, and $ZnCl_2$), yielding s-*tetraphenyldi-3-phenanthrylethane*, m.p. 150—152° (decomp.) in N_2. *Diphenyl-9-phenanthrylcarbinol* (X) (*Me*, m.p. 165°, and *Et*, m.p. 139—140°, *ether*; *diphenyl-9-phenanthrylacetic acid*, m.p. 257—259° (decomp.)], from 9-$C_{14}H_9$·MgBr and COPhMe, gives with hot AcCl 9-phenyl-1 : 2 : 3 : 4-dibenzofluorene (*acetate*, m.p. 254—255°; corresponding *fluorenol*, m.p. 181°; 9-*Cl*-derivative, m.p. 172—174°; *peroxide*, m.p. 209—211°), and with cold AcCl the corresponding *chloromethane* (XI), m.p. 182—183° (decomp.), yielding a very unstable solution of s-*tetraphenyldi-9-phenanthrylethane*. With Ag in presence of O_2, (XI) yields *di(diphenyl-9-phenanthrylmethyl) peroxide*, m.p. 184—186° (decomp.), also obtained from (XI) and Na_2O_2. The spontaneous decomp. of (VI) [also obtained from 9-$C_{14}H_9$·CPh_2Na and $(CMe_2Br)_2$] gives a *product*, m.p. 275—280° (decomp.) in N_2, probably a dimeride, analagous to $CHPh_2$·C_6H_4·CPh_3 formed from CPh_3. Diphenylene-9-phenanthrylcarbinol (*acetate*, m.p. 113—115°; *Me*, m.p. 231—232°, and *Et*, m.p. 173—174°, *ether*; *diphenylene-9-phenanthryl-methane*, m.p. 192—193°), from 9-$C_{14}H_9$·MgBr and fluorenone, gives with hot AcCl and AcBr, respectively, the corresponding *chloro-* (XII), m.p. 211—212° (*compounds* with $HgCl_2$ and $SnCl_4$), and *bromo-* (XIII), m.p. 230° (decomp.), *-methanes*. (XII) with Ag in PhBr gives a solution of s-*didiphenylenedi-9-phenanthrylethane*, decomp. on standing. (XIII) with Ag in presence of O_2 gives *di(diphenylene-9-phenanthrylmethyl) peroxide*, m.p. 208—210° (decomp.).

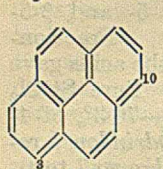
E. G. B.

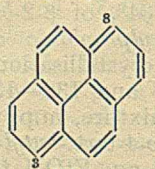
20-*tert*.-Butylcholanthrene. L. F. Fieser and D. K. Snow (J. Amer. Chem. Soc., 1938, **60**, 176—177).—*p*-$C_6H_4BrBu^{\gamma}$, b.p. 228—236°, with $(CH_2O)_3$, $ZnCl_2$–$AlCl_3$, and HCl at 60—70° give a difficultly separable mixture, b.p. 120—140°/5 mm., of 4-*bromo*-2- and -3-*chloromethyl*tert.-*butylbenzene*, converted by $CHNa(CO_2Et)_2$ into mixed esters, b.p. 190—200°/6 mm., hydrolysis of which affords a mixture, m.p. 132—134°, of β-2-*bromo*-5- and β-5-*bromo*-2-tert.-*butylphenylpropionic acid*. Fractionation of the esters and crystallisation of the acids gave acids, m.p. 151—152° and 138—139°. Pure $SOCl_2$ and $AlCl_3$ lead to a mixture, m.p. 69·3—70·3°, of 4-*bromo*-7- and -7-*bromo*-4-tert.-*butyl*-1-*hydrindone*, reduced by Zn–Hg–HCl–aq. EtOH to 4-*bromo*-7-tert.-*butylhydrindene*, b.p. 149—150°/6 mm. The Grignard reagent therefrom with α-$C_{10}H_7$·CN affords 46% of crude 4-α-*naphthoyl*-7-tert.-*butylhydrindene*, pyrolysed at 390—400° in 8% yield to 20-tert.-*butylcholanthrene*, m.p. 204—205° (corr.) (*picrate*, m.p. 149—150°), which is only slowly, if at all, carcinogenic. 10-Ethyl-1 : 2-benzanthracene and 20-ethylcholanthrene produce tumours more slowly than do the Me homologues.

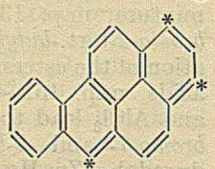
R. S. C.

1′-Methyl- and 1′ : 10-dimethyl-1 : 2-benzanthracene. L. F. Fieser and A. M. Seligman (J. Amer. Chem. Soc., 1938, **60**, 170—176).—*p*-C_6H_4Br·CO·$[CH_2]_2$·CO_2H [best (74% yield) prepared from PhBr, $(CH_2$·$CO)_2O$, and $AlCl_3$ at 100°; oxidised to *p*-C_6H_4Br·CO_2H], m.p. 148—149°, is reduced by mossy Zn–Hg in aq. HCl–AcOH–PhMe in 75% yield to γ-p-*bromophenylbutyric acid*, m.p. 71—72°, b.p. 175—176°/3 mm. (with some Ph·$[CH_2]_3$·CO_2H), the *chloride*, b.p. 147—148°/4 mm., of which with $AlCl_3$ in CS_2 gives 7-*bromo*-1-*keto*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. 142—143°/3 mm., m.p. 76—77°, converted by MgMeCl into 6-*bromo*-4-*methyl*-1 : 2-*dihydronaphthalene*, b.p. 113—114°/2·5 mm. Dehydrogenation by S or Se causes loss of Br, but addition of Br in CCl_4 at −10° and removal of HBr, finally at 200°, gives 59% of nearly pure 7-*bromo*-1-*methylnaphthalene*, b.p. 124—125°/3 mm. (*picrate*, m.p. 92·5—93·5°). 1 : 7-$C_{10}H_6Me$·MgBr and *o*-$C_6H_4(CO)_2O$ in C_6H_6 give 30% of 7-o-*carboxybenzoyl*-1-*methylnaphthalene* (I), m.p. (+Et_2O) 120—126° after softening at 118° and (anhyd.) 153—153·5°, reduced by Zn and aq. NaOH to o-8′-*methyl*-2′-*naphthylmethylbenzoic acid* (98%), m.p. 143—144°, which with $ZnCl_2$–AcOH–Ac_2O gives 1-*methyl*-1 : 2-*benzanthranyl* 9-*acetate* (II), m.p. 173—174°. Zn–$CuSO_4$–NaOH–H_2O–PhMe then affords 1′-*methyl*-1 : 2-*benzanthracene* (III), m.p. 138·5—139·2 (*di-*, m.p. 120—121°, and *mono-picrate*, m.p. 129·5—130·5°). Interaction of (II) and $MgBu^{\alpha}Br$ leads only to 1′-*methyl*-1 : 2-*benzanthraquinone*, m.p. 189—189·5°. With MgMeCl in Et_2O–C_6H_6 (I) gives an oily lactone, reduced by Zn–Hg–AcOH–HCl to o-α-8′-*methyl*-2′-*naphthylethylbenzoic acid* (70%), m.p. 183·5—184·5°, cyclised by $ZnCl_2$ to 1′ : 10-*dimethyl*-1 : 2-*benzanthranyl* 9-*acetate*, m.p. 190—191°, which is reduced by Zn–Hg–NaOH–PhMe to 1′ : 10-*dimethyl*-1 : 2-*benzanthracene* (19%) (IV), m.p. 122·5—123·5° or 124—125° (*picrate*, m.p. 147—148°), with a little of its 9 : 10-H_2-derivative, m.p. 113—114° (*picrate*, m.p. 126—127°), also obtained from (IV) by Na–Et_2O–C_6H_6. No tumours were obtained by injecting (II) or (IV) into mice, but (IV) causes ulceration. The reactivity of benzpyrene mainly at positions 3 or 10 and to a smaller extent at position 8 indicates the bond structure (V) with a little (VI), whence (VII) becomes probable for 3 : 4-benzpyrene; reactivity at positions

marked * is then explained, as also is the pharmacological inactivity of (III) and (IV). The stabilising


(V.)


(VI.)


(VII.)

effect of OH in benzpyrene is discussed. M.p. are corr. R. S. C.

Synthesis and reactions of fluorocyclene. K. Dziewoński and L. Gizler (Bull. Acad. Polonaise, 1937, **A**, 441—454).—The best yield of fluorocyclene (*peri*-tetranaphthylene*cyclo*octadiene) (I) (A., 1925, i, 649) is obtained by heating acenaphthene with PbO_2 at 220—280°, or at 180—220° under pressure. At 345—395°/10 mm., (I) decomposes to acenaphthylene, biacene, and decacyclene. With Na in C_5H_{11}·OH–xylene, (I) gives *tetrahydro-*, $C_{48}H_{32}$, m.p. 348—349°, *octahydro-*, m.p. 336—337°, and *docecahydro-fluorocyclene*, m.p. 326°; the structure of these is discussed. E. W. W.

Reduction of aromatic nitro-compounds. III. Reduction of nitro-compounds and their derived products in presence of acids. V. O. Lukaschevitsch (J. Gen. Chem. Russ., 1937, **7**, 2209—2225).—β-Arylhydroxylamines are obtained in 60—70% yield by reducing the corresponding NO_2-compounds with Zn, Cd, or Pb, in AcOH. Reduction with Zn or $SnCl_2$ in conc. HCl gives anilines, with about 10% of chloroanilines, which are not formed with Fe or Cu. This difference is ascribed to the catalytic action of the systems Fe^{II}–Fe^{III} or Cu^{I}–Cu^{II} on arylhydroxylamines or arylhydrazines, which are rapidly reduced to amines under the conditions of the experiment, without formation of chloranils, as with Sn, Zn, or Hg. The products of reduction of azobenzenes vary according to the metal and concn. of acid; the velocity of reduction of NO_2-, azoxy-, azo-, aminoazo-, and hydrazo-compounds depends similarly on these and other factors. Hydrazo-compounds are not obligatory intermediates in reduction of NO_2-compounds to amines. R. T.

Reduction of nitro-compounds by iron.—See B., 1938, 136.

Catalytic gas-phase reduction of nitrobenzene to aniline.—See A., I, 150.

Separation of *m*-2-, *m*-4-, and *p*-xylidines.—See B., 1938, 136.

Bromocupric complexes.—See A., I, 91.

Study of the tertiary amine oxide double linking by means of absorption spectra and rotatory dispersion.—See A., I, 64.

Preparation of symmetrical and asymmetric aminopropanediol and their derivatives. H. P. Den Otter (Rec. trav. chim., 1938, **57**, 13—24).—NH_2·$CH(CH_2$·$OH)_2$ (I) with 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$ in EtOH yields β-(2 : 4-*dinitrophenylamino*)*propane-αγ-diol*, m.p. 133°, nitrated (fuming HNO_3) to β-(2 : 4 : 6-*trinitrophenylnitroamino*)*propane-αγ-diol dinitrate* (II), m.p. 142—143° (decomp.). Similarly are obtained β-2 : 4 : 6-*trinitrophenyl-*, m.p. 150°, β-2 : 4-*dinitronaphthyl-*, m.p. 199°, and β-5-*chloro*-2 : 4-*dinitrophenyl-aminopropane-αγ-diol* (III), m.p. 126—127°, which are nitrated to (II), β-2 : 4-*dinitronaphthyl-*, m.p. 117°, and β-3-*chloro*-2 : 4 : 6-*trinitrophenyl-nitroaminopropane-αγ-diol dinitrate*, decomp. 40°, respectively. (III) and (I) in EtOH yield 4 : 6-*dinitro*-1 : 3-*bis*-(ββ′-*dihydroxy*isopropylamino)*benzene*, m.p. 174°, nitrated to 2 : 4 : 6-*trinitro*-1 : 3-*bis*-(ββ′-*dihydroxy*-isopropylnitroamino)*benzene tetranitrate*, decomp. 50—60°. From α-aminopropane-βγ-diol (IV) are prepared α-2 : 4-*dinitrophenyl-* (V), m.p. 95°, α-2 : 4 : 6-*trinitrophenyl-* (VI), m.p. 136°, α-2 : 4-*dinitronaphthyl-* (VII), m.p. 189°, and α-5-*chloro*-2 : 4-*dinitrophenyl-aminopropane-βγ-diol* (VIII), m.p. 90°. Nitration of (V) and (VI) yields α-2 : 4 : 6-*trinitrophenyl-*, m.p. 80° (decomp.), and of (VII) and (VIII), α-2 : 4-*dinitronaphthyl-*, m.p. 80° (decomp.), and α-3-*chloro*-2 : 4 : 6-*trinitrophenyl-nitroaminopropane-βγ-diol dinitrate*, m.p. about 50°, respectively. (IV) and (VIII) in EtOH yield 4 : 6-*dinitro*-1 : 3-*bis*-(βγ-*dihydroxypropylamino*)*benzene*, m.p. 163°, nitrated to 2 : 4 : 6-*trinitro*-1 : 3-*bis*-(βγ-*dihydroxypropylnitroamino*)*benzene tetranitrate*, m.p. 73° (decomp.). *d*-Glucosamine similarly yields αβγδ-*tetrahydroxy*-ε-2 : 4 : 6-*trinitrophenyl-*, m.p. 183°, -ε-2 : 4-*dinitronaphthyl-*, m.p. 218° (decomp.), and -ε-5-*chloro*-2 : 4-*dinitrophenyl-aminohexaldehyde*, m.p. 190°. Methods of prep. of (I) and (IV) are given. E. I.

Nitrosoacylarylamines. I. Decomposition of nitrosoacetanilide in solution. E. C. Butterworth and D. H. Hey (J.C.S., 1938, 116—119).—Earlier work (A., 1934, 764; 1935, 78, 828; cf. Waters, A., 1937, II, 97) indicates that the decomp. of NAcPh·NO (I) in C_6H_6 (yielding Ph_2 and N_2) and in other solvents is a free-radical reaction, *i.e.*, (I) → Ph· + N_2 + OAc· and OAc· → Me· + CO_2. The effect of concn. on the decomp. in C_6H_6 has been studied at 20° with 2—20% solutions. With increasing concn. of (I) the yield of N_2 rises but that of Ph_2 falls, owing to the formation of ter- and polyphenyls. Yields of N_2 and Ph_2 are practically independent of the scale of the reaction (cf. *loc. cit.*). The decomp. of 2% solutions of (I) in C_6H_6 at 10°, 20°, 30°, and 40° shows that with rising temp. the rate of evolution of N_2 increases but the yield of N_2 is unaffected. The best yield of Ph_2 is at 20°. The energy of activation of the reaction is about 22,000 g.-cal. Evolution of N_2 at 20° from 2% solutions of (I) in $CHCl_3$, CCl_4, C_2HCl_3, $C_2H_2Cl_4$, $C_6H_4Cl_2$ (technical), tetralin, decalin, Bu_2O, EtOAc, and *o*-C_6H_4Me·NEt_2 varies widely, indicating reactions between solvent and solute. Rates of evolution of N_2 show that the reactions are unimol. The velocity coeff. is not appreciably affected by the nature of the solvent. Reactions in CCl_4 and C_2HCl_3 yield some PhN_2Cl, and in EtOAc, some Me·CHO. E. G. B.

***N*-Aryl-*N*′-dialkylaminoalkylcarbamides as local anæsthetics.** H. Wenker (J. Amer. Chem. Soc., 1938, **60**, 158—159).—The appropriate carbimide and amine yield N-*phenyl*-N′-β-*piperidino-*, m.p. 149°, and -N′-β-*di*-n-*butylamino-* (I), m.p. 113°, N-o-*anisyl*-N′-β-*piperidino-*, m.p. 135°, and -N′-β-*di*-n-*butylamino-* (II), m.p. ≮94°, and N-p-*ethoxy-*

phenyl-N′-β-*piperidino*-iso*propylcarbamide*, m.p. 124°, and N-*phenyl*-N′-β-*piperidino*iso*propylthiocarbamide*, m.p. 123°. The hydrochlorides of (I) and (II) are local anæsthetics. Piperidine and $NHBu^{\alpha}_2$ with propylene oxide give *N*-β-hydroxy-*n*-propylpiperidine and β-*hydroxy*-n-*propyldibutylamine*, b.p. 130°/15 mm., converted by $SOCl_2$ into the *hydrochlorides*, m.p. 204° and an oil, respectively, of N-β-*chloro*-n-*propylpiperidine* and β-*chloro*-n-*propyldibutylamine*, which with NH_3–MeOH at 60° give N-β-*amino*-n-*propylpiperidine*, b.p. 193—194°, and β-*amino*-n-*propyldibutylamine*, b.p. 132°/15 mm. R. S. C.

Anthranyl- and 1 : 2 : 5 : 6-dibenzanthranylcarbimides. I. H. J. Creech and W. R. Franks (J. Amer. Chem. Soc., 1938, **60**, 127—128).—By the use of a large excess of $COCl_2$ 9-aminoanthracene, if rigidly purified, gives 80% of 9-*anthranylcarbimide*, m.p. 75·5—76·5°, which affords *Me*, m.p. 265—266°, and *Et* 9-*anthranylcarbamate*, m.p. 236·5—237°, and β-9-*anthranylcarbamidoethyl alcohol*, m.p. 263—264°. 1 : 2 : 5 : 6-*Dibenzanthranylcarbimide* (prep. in 75% yield), m.p. 181—181·5°, gives *Me*, m.p. 264—265°, and *Et* 1 : 2 : 5 : 6-*dibenzanthranyl*-9-*carbamate*, m.p. 224—224·5°, and β-1 : 2 : 5 : 6-*dibenzanthranyl*-9-*carbamidoethyl alcohol*, m.p. 308—309°. Carbamides are obtained, but are difficult to purify. Experiments are usually carried out in N_2. R. S. C.

Reaction of dienes with diazo-compounds. B. Arbusov and S. Rafikov (J. Gen. Chem. Russ., 1937, **7**, 2195—2201).—*p*-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ in aq. HCl and $(CH_2{:}CH{\cdot})_2$ at 0° yield $NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2$ and α-(p-*nitrobenzeneazo*)*butadiene*, m.p. 118—119°, converted by reduction ($SnCl_2$ in HCl) into *p*-$C_6H_4(NH_2)_2$ and pyrroline. The product obtained similarly with $(CHMe{:}CH{\cdot})_2$ is β-(p-*nitrobenzeneazo*)-$\Delta^{\beta\beta}$-*hexadiene*, m.p. 172—173°, reduced to 2 : 5-dimethylpyrroline. R. T.

Azo-dyes and their intermediate products. XIX. Tolane and deoxybenzoin dyes. P. Ruggli and F. Lang (Helv. Chem. Acta, 1938, **21**, 38—50; cf. A., 1936, 1373).—Chlorination of 4 : 4′-dinitrostilbene (I) in strongly illuminated, boiling AcOH gives a mixture of products from which 4 : 4′-dinitrotolane (II) is obtained in reasonable yield. Better results are obtained in hot $PhNO_2$, whereby the dichloride, m.p. 282—286°, is readily isolated. The best process consists in adding Br in $PhNO_2$ to (I) in hot $PhNO_2$ and conversion of the dibromide, m.p. 283°, into (II) by KOH–MeOH. Hydrogenation (≡12 H; Ni in EtOAc–EtOH–H_2O) of homogeneous (II) gives 4 : 4′-diaminotolane (III) in good yield accompanied by a small proportion of *cis*-4 : 4′-diaminostilbene. (III) gives Ac_2, m.p. 281°, Bz_2, m.p. 332°, and $(CHPh{:})_2$, m.p. 207°, derivatives. Diazotisation of (III) followed by coupling with 2 mols. of naphthionic acid gives *tolane-red* (IV), $[C{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_5(NH_2){\cdot}SO_3Na]_2$, whilst with 1 : 4-$OH{\cdot}C_{10}H_6{\cdot}SO_3H$ *tolane-violet*, $[C{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_5(OH){\cdot}SO_3Na]_2$, is produced. Both are substantive dyes to cotton, which is dyed by the latter only in presence of Na_2SO_4. Both are colloidal. Attempts to establish the constitution of (IV) by reductive fission were unsuccessful since from the strongly acid solution (V) (below) is isolated. The acetylenic linking persists after tetrazotisation since treatment of the solution with EtOH leads to tolane free from CH_2PhBz. Treatment of (III) with dil. HCl at 100° and then at the b.p. of the solution gives 4 : 4′-diaminodeoxybenzoin (V), m.p. 145° [*oxime*, m.p. 146°; $(CHPh{:})_2$ derivative, m.p. 181°], in 50% yield. Treatment of (V) with 2 mols. of HNO_2 and of the product with naphthionic acid gives the red *dye*, $NH_2{\cdot}C_6H_4{\cdot}C(N{\cdot}OH){\cdot}CO{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_5(NH_2){\cdot}SO_3Na$, in which free NH_2 can be detected by after-diazotisation on the fibre and development with *H*-acid or, preparatively, by diazotisation and coupling with 6 : 2-$C_{10}H_6Br{\cdot}OH$. Condensation of *p*-$NO_2{\cdot}C_6H_4{\cdot}CHO$ with *p*-$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO_2H$ in presence of piperidine gives essentially *trans*-4 : 4′-dinitrostilbene-7-carboxylic acid (cf. Cullinane, A., 1923, i, 606). *p*-$NO_2{\cdot}C_6H_4{\cdot}CHO$, *p*-$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO_2Na$, Ac_2O, and $ZnCl_2$ give *cis*-4 : 4′-dinitrostilbene-7-carboxylic acid, m.p. 265—267°, decarboxylated by Cu powder in quinoline at 210° to cis-4 : 4′-*dinitrostilbene*, m.p. 185—186°, isomerised by I in $PhNO_2$ at 210° to the corresponding *trans*-compound, m.p. 286—287°, and reduced (Ni in EtOAc–EtOH–H_2O) to the *cis*-4 : 4′-$(NH_2)_2$-compound. H. W.

Union of aryl nuclei. I. Extensions of the Gomberg reaction. W. S. M. Grieve and D. H. Hey [with, in part, J. L. Dunn and E. R. B. Jackson] (J.C.S., 1938, 108—113).—Methods of synthesis of unsymmetrical diaryls from diazo-compounds are reviewed. Attempts have been made to increase the yield from the normal Gomberg reaction (cf. A., 1924, i, 1295; 1926, 944) using PhN_2Cl and C_6H_6, the NaOH being (i) added to the mixture of PhN_2Cl and C_6H_6, or (ii) mixed with C_6H_6 and the PhN_2Cl added to the mixture. Method (i) has been used in presence of $MgSO_4$ (cf. Gomberg and Bachmann, A., 1927, 245), $CuSO_4$, and CH_2O, with aq. NH_3 and NaOAc in place of NaOH, and in N_2. Method (ii) has been used with addition of lissapol *A*, with $Ca(OH)_2$ for NaOH, and at 30° and 50°. In no case was the yield of Ph_2 markedly affected. No diaryl is formed from PhN_2Cl or *o*-$CO_2H{\cdot}C_6H_4{\cdot}N_2Cl$ (I) and aq. NaOBz, or from (I) and C_6H_6, whereas reaction of MeOBz with PhN_2Cl (cf. *idem*, A., 1924, i, 1295) or of *o*-$CO_2Me{\cdot}C_6H_4{\cdot}N_2Cl$ (II) with C_6H_6 is normal. These results indicate that two phases are essential and that reaction takes place in the non-aq. medium and is probably non-ionic. The use of solid reactants (in solution) in the Gomberg reaction requires the solvent to be neutral, H_2O-immiscible, and inert towards diazo-compounds. $CHCl_3$ and CCl_4 give low yields of diaryl, some reaction with the solvent occurring; thus PhN_2Cl with CCl_4 gives some PhCl. This is in accord with the view (cf. A., 1935, 78; 1934, 764; Waters, A., 1937, II, 97) that these reactions involve formation of free radicals, which react also with the solvent. (II) with $C_{10}H_8$ in CCl_4, PhN_2Cl with Ph_2 in $CHCl_3$ or CCl_4, *p*-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ with Ph_2 in $CHCl_3$, and *p*-$OMe{\cdot}C_6H_4{\cdot}N_2Cl$ with $COPh_2$ in CCl_4, give respectively *Me* o-*α-naphthylbenzoate*, m.p. 87—88° (the free acid gives *ms*-benzanthrone on ring-closure), *p*-$C_6H_4Ph_2$, 4′-nitro-*p*-diphenylbenzene, and 4-methoxy-4′-ben-

zoyldiphenyl (also obtained from BzCl, 4-methoxydiphenyl, and $AlCl_3$). Diazotised α- and β-$C_{10}H_7{\cdot}NH_2$ with C_6H_6 give respectively 1- and 2-$C_{10}H_7Ph$ in small yield. E. G. B.

Introduction of deuterium into the aromatic nucleus. II. Orientation of certain substituents. A. P. Best and C. L. Wilson (J.C.S., 1938, 28—29).—Bromination of deuterated PhOH and NH_2Ph gives the corresponding 2 : 4 : 6-Br_3-derivatives, free from D, showing that the deuteration had been exclusively *ortho–para*, in agreement with the hypothesis that nuclear deuteration in aromatic compounds is an electrophilic substitution (cf. A., 1936, 1322). E. G. B.

Thermal and catalytic decomposition of phenoxides. VIII. Influence of the methoxy-group. Preparation and properties of the sodium, potassium, and silver salts of halogenated *p*-methoxyphenols. IX. Influence of the *o*-methoxy-group. X. Influence of the methyl group. Preparation and properties of the sodium and potassium salts of *o*- and *p*-cresols. XI. Preparation and properties of silver phenoxides. W. H. Hunter and F. F. Ratman (J. Gen. Chem. Russ., 1937, **7**, 2202—2205, 2206—2208, 2226—2229, 2230—2234).—VIII. Attempted iodination in aq. KOH of *p*-OH·C_6H_4·OMe (I) led to the production of amorphous polymerisation products only. (I) and Br in AcOH give 2 : 5-dibromo-4-methoxyphenol, the Na salt of which is highly unstable, and could not be obtained pure. Bromination in absence of AcOH gives 2 : 3 : 5 : 6-tetrabromo-4-methoxyphenol (K, + 1, 2, and $3H_2O$, Na, and Ag *salts*). The OMe in *p*-position confers instability, and Br *meta* to OH stability, to the salts.

IX. The Ag salts of trichloro- or tribromo-pyrogallol Me_2 ether are decomposed by hot H_2O with liberation of Ag. In boiling C_6H_6 the products are AgCl(Br) and amorphous polymerides, ≯5% of the OMe being eliminated during the process. Introduction of OMe *ortho* to OH does not affect the process of polymeride formation, but favours decomp. of Ag salts with liberation of Ag.

X. The Na and K salts of 3 : 5-di-iodo- and -bromo-*o*- and -*p*-cresol are described, and their relative stability under the above conditions is determined.

XI. The Ag salts of 3 : 5-di-iodo- and -bromo-*o*- and -*p*-cresol are described, and evidence is adduced that the coloured forms of such salts possess a quinonoid structure; the intensity of the coloration and the stability of the salts fall in the order I > Br > Cl for mono-, di-, and tetra- and in the reverse order for tri-halogen derivatives. R. T.

Nitration of acyl derivatives of 4 : 5-dibromo- and 4 : 5 : 6-tribromo-guaiacol. L. C. Raiford and R. E. Silker (J. Org. Chem., 1937, **2**, 346—355).—4 : 5-Dibromo- (I) and 4 : 5 : 6-tribromo- (II) -guaiacol cannot be nitrated by HNO_2 or fuming HNO_3, although a reaction occurs in the latter case, probably complete oxidation. The *Ac* derivative, m.p. 101—102°, of (I) gives with fuming HNO_3 4-*bromo*-5-*nitro*-2-*methoxy*- (III), m.p. 160—161°, and 4 : 5-*dibromo*-3-*nitro*-2-*methoxy*- (IV), m.p. 91·5—92·5°, -*phenyl acetate*. (III) is hydrolysed to 4-*bromo*-5-*nitroguaiacol* (V), m.p. 118—119°, this structure being preferred to the alternative 5 : 4-structure since OMe has greater *o*–*p*-directing influence than OAc. Meldola and Streatfeild's bromonitroguaiacol (J.C.S. 1898, **73**, 689) is probably (V), which is methylated to 4-bromo-5-nitroveratrol. The structure of (IV) is shown by its hydrolysis to 4 : 5-*dibromo*-3-*nitroguaiacol* (VI), m.p. 164—165°, which is methylated to 4 : 5-dibromo-3-nitroveratrol. The *Bz* derivative, m.p. 110·5—111·5°, of (I) with fuming HNO_3 yields only 4 : 5-*dibromo*-3-*nitro*-2-*methoxyphenyl benzoate*, m.p. 116—117°, giving (VI) on hydrolysis. Similarly the *Ac*, m.p. 119—120°, and *Bz*, m.p. 148—149°, derivatives of (II) give with fuming HNO_3 4 : 5 : 6-*tribromo*-3-*nitro*-2-*methoxyphenyl acetate* (VII), m.p. 98—99°, and *benzoate* (VIII), m.p. 140—141° [together with 3—4% of the m-*nitrobenzoate* (IX), m.p. 202—203°], respectively. On hydrolysis (VII), (VIII), and (IX) all give 4 : 5 : 6-*tribromo*-3-*nitroguaiacol*, m.p. 101—102° (O-CO_2Me, m.p. 105—108°, and O-CO_2Et, m.p. 93—94°, derivatives). These results support the view that acylation of a OH in a C_6H_6 derivative suppresses its directive influence. 4 : 5 : 6-Tribromo-3-nitroveratrole has m.p. (new) 122—123°. E. G. B.

Complex compounds of picric acid and other nitrophenols with cuprammonium salts. N. P. Agafoschin (J. Gen. Chem. Russ., 1937, **7**, 2235—2239).—The compounds
$[2 : 4 : 6\text{-}(NO_2)_3C_6H_2{\cdot}O{\cdot}]_2Cu(NH_3)_4$ and
$[2 : 4\text{-}(NO_2)_2C_6H_3{\cdot}O{\cdot}]_2Cu(NH_3)_4$ are obtained by adding aq. picric acid or 2 : 4-$(NO_2)_2C_6H_3{\cdot}OH$, respectively to aq. cuprammonium hydroxide. Pure products were not obtained analogously with *o*-nitro-phenol or -cresol. R. T.

Polyalkylphenols.—See B., 1938, 139.

Condensation of tertiary aryl-substituted carbinols with phenol in the presence of aluminium chloride. L. H. Welsh [with N. L. Drake] (J. Amer. Chem. Soc., 1938, **60**, 59—62).—In presence of $AlCl_3$ $CPhMe_2{\cdot}OH$ and PhOH give 68—72% of p-α-*phenylisopropylphenol* (I), b.p. 213—214°/25 mm., m.p. 73° (corr.) (*diphenylurethane*, m.p. 126°; gives p-α-*phenylisopropylphenoxyacetic acid*, m.p. 117°), and some 3-phenyl-1 : 1 : 3-trimethylhydrindene (formed by polymerisation of $CPhMe{:}CH_2$). The structure of (I) is proved by its methylation to, and prep. by HBr from, p-α-*phenylisopropylanisole*, b.p. 198—199°/25 mm., which is obtained from *p*-OMe·C_6H_4·MgBr and $CPhMe_2Cl$. $CPh_2Me{\cdot}OH$ gives 80% of *p*-$CPh_2Me{\cdot}C_6H_4{\cdot}OH$ with $CPh_2{:}CH_2$ and a resinous (?) polymeride. $CPh_3{\cdot}OH$ gives 95% of *p*-$CPh_3{\cdot}C_6H_4{\cdot}OH$. Dehydration of the carbinols, when possible, to the ethylene is indicated by the isolation of the ethylenes or their polymerisation products, and by the fact that $CH_2Ph{\cdot}CPh_2{\cdot}OH$ and C_6H_6 give $(CHPh_2)_2$ and not $CH_2Ph{\cdot}CPh_3$. R. S. C.

***N*-Aralkylaminophenols.**—See B., 1938, 139.

Electrolytic substitution in naphthols. II. Electrolytic introduction of the nitroso-group into naphtholsulphonic acids. K. Emi (Rep. Imp. Ind. Res. Inst., Osaka, 1935, **16**, No. 9, 1—28; cf. B., 1935, 1036).—The yield of nitroso-

naphtholsulphonic acid is > that of $NO{\cdot}C_{10}H_6{\cdot}OH$. $OH{\cdot}C_{10}H_5(SO_3H)_2$ gives a better yield than $OH{\cdot}C_{10}H_6{\cdot}SO_3H$. Introduction of SO_3H increases the yield of the NO-compound. When 1 : 4-$OH{\cdot}C_{10}H_6{\cdot}SO_3H$ is electrolysed in aq. NaOAc–$NaNO_2$, 1 : 2 : 4-$OH{\cdot}C_{10}H_5(NO_2)_2$ is produced in addition to the NO-compound. CH. ABS. (*e*)

Isomerisation during Grignard synthesis. Isomeride of amber musk. B. M. DUBININ (J. Gen. Chem. Russ., 1937, **7**, 2183—2187).—5-Bromo-3-methoxytoluene, Mg, and $Bu^{\gamma}I$ in Et_2O do not react until most of the Et_2O has distilled off; the residue is heated under reflux for 30 min., when 3-methoxy-4-*tert.*-butyltoluene (I) is obtained in 40% yield. The product obtained by using MeI in place of $Bu^{\gamma}I$ is 5-methoxy-*m*-xylene. Migration of the Bu^{γ} group is ascribed to formation of $CMe_2{:}CH_2$, which condenses with 3-methoxytoluene to yield (I). R. T.

Synthesis of mono-ethers of 2 : 4-di(hydroxymethyl)anisole. M. ANGLADE (Compt. rend., 1937, **205**, 1158—1160; cf. A., 1936, 1247).—2 : 4-Di(methoxymethyl)anisole with AcCl–$ZnCl_2$ in light petroleum (cf. A., 1933, 710) gives 4-chloromethyl-2-methoxymethylanisole (I), which with AcOH–NaOAc followed by aq. EtOH–KOH at room temp. affords 4-*hydroxymethyl*-2-*methoxymethylanisole*, b.p. 141°/5 mm. (*phenylcarbamate*, m.p. 73·5°). The *OEt*-analogue has b.p. 142°/4 mm. (*phenylcarbamate*, m.p. 58·5°). (I) and its OEt-analogue with $(CH_2)_6N_4$ afford 4-methoxy-3-methoxymethyl- and -3-ethoxymethylbenzaldehyde (cf. A., 1937, II, 422), respectively, thus proving the structures of the OH-derivatives. J. L. D.

Pyrolysis of alkylallyl and alkylcrotyl ethers of phenol and *o*-cresol. C. D. HURD and M. P. PUTERBAUGH (J. Org. Chem., 1937, **2**, 381—386).—Pyrolysis of ethers $OPh{\cdot}CH_2{\cdot}CH{:}CHR$ (R = Et, Pr, or Bu) gives mixtures of *o*-alkenylphenols, $OH{\cdot}C_6H_4{\cdot}CHR{\cdot}CH{:}CH_2$ and $OH{\cdot}C_6H_4{\cdot}CHR'{\cdot}CH{:}CHR''$ (cf. Lauer and Filbert, A., 1936, 1244). Small amounts of PhOH are also formed. The corresponding *o*-tolyl ethers similarly give 6-alkenyl-2-methylphenols and *o*-cresol. Phenyl and *o*-tolyl α-alkylcrotyl ethers on pyrolysis give mainly alkali-insol. products; PhOH and *o*-cresol are also formed. The following are described. Δ^{β}-*Octen*-δ-*ol*, b.p. 74°/8 mm. (from $CHMe{:}CH{\cdot}CHO$ and $MgBu^{\alpha}Br$); δ-*chloro*-Δ^{β}-*octene*, b.p. 69—70°/9 mm.; o-*pentenyl*-, b.p. 110—112°/7 mm., o-*hexenyl*-, b.p. 120—122°/6—7 mm., o-*heptenyl*-, b.p. 125—127°/6 mm., 6-*pentenyl*-2-*methyl*, b.p. 107—110°/3 mm., 6-*hexenyl*-2-*methyl*-, b.p. 112—115°/3 mm., and 6-*heptenyl*-2-*methyl*-, b.p. 120—121°/4 mm., -*phenol*; *Ph* γ-*ethyl*-, b.p. 91—95°/4 mm., γ-n-*propyl*-, b.p. 105—107°/4 mm., and γ-n-*butyl*-, b.p. 102—103°/3 mm., -*allyl ethers*; *Ph* α-*ethyl*-, b.p. 89—91°/5 mm., α-n-*propyl*-, b.p. 103—104°/4 mm., and α-n-*butyl*-, b.p. 107—108°/4 mm., -*crotyl ethers*; o-*tolyl* γ-*ethyl*-, b.p. 106—108°/3 mm., γ-n-*propyl*-, b.p. 115—117°/6 mm., and γ-n-*butyl*-, b.p. 105—108°/3 mm., -*allyl ethers*; o-*tolyl* α-*ethyl*-, b.p. 100—102°/6 mm., α-n-*propyl*-, b.p. 96—98°/4 mm., and α-n-*butyl*-, b.p. 118—119°/4 mm., -*crotyl ethers*.

The following new physical data, *inter alia*, are recorded: pyrocatechol monoallyl, b.p. 103—104·5°/8 mm., and diallyl, b.p. 112—115°/8 mm., ether; 3-, b.p. 132—138°/9 mm., and 4-allyl-, b.p. 141—144°/7 mm., 3 : 6-di-, b.p. 132—137°/6 mm., and tri-, b.p. 175—180°/10 mm., -allyl-pyrocatechol; allylpyrocatechol diallyl, b.p. 140—155°/12 mm., and resorcinol monoallyl, b.p. 130—135°/7 mm., ether; 4-mono-, b.p. 143—150°/5—9 mm., and 4 : 6-di-, b.p. 178—183°/12 mm., -allylresorcinol. E. G. B.

Cleavage of diphenyl ethers by sodium in liquid ammonia. III. 4 : 4′-Disubstituted diphenyl ethers. F. C. WEBER and F. J. SOWA (J. Amer. Chem. Soc., 1938, **60**, 94—95; cf. A., 1937, II, 412).—By cleavage of $C_6H_4R{\cdot}O{\cdot}C_6H_4R'$ by Na the following effectiveness of *p*-substituents in strengthening the O·Ar linking is demonstrated: Me < Bu^{γ} < OMe < NH_2. This order is also that of increasing *o*–*p*-directing power. The following order of electronegativity of substituted Ph is deduced: *p*- > *o*- > *m*-NH_2 > *p*-OMe > *p*-Bu^{γ} > *p*- > *m*- > *o*-Me > H > *m*- > *o*-OMe > *m*- > *o*- > *p*-CO_2H. p-*Anisyl* p-*tolyl*, m.p. 49—50°, b.p. 193—198°/22 mm., and p-*hydroxyphenyl ether*, m.p. 64—65°, b.p. 183—193°/16 mm., and p-*tolyl* p-tert.-*butylphenyl ether*, b.p. 174—178°/4 mm., are prepared. R. S. C.

Action of nitrous acid on (phenyl-2-hydroxy-α-naphthylmethyl)amine. III. F. E. RAY and W. R. HAEFELE (J. Amer. Chem. Soc., 1938, **60**, 36—38; cf. A., 1935, 97).—$\frac{1}{2}{>}C_{10}H_6{<}^{CHPh-}_{O{\cdot}CHPh}{>}NH$ (I) and Na–Hg–CO_2 in EtOH at 60° give N-*benzyl*-N-(*phenyl*-2-*hydroxy*-α-*naphthylmethyl*)*amine*, m.p. 143° (*hydrochloride*, m.p. 176°; violet $FeCl_3$ colour). Similar reduction of the NO-derivative of (I) gives (?) the *substance* $CH{<}^{C_6H_4{\cdot}CH{\cdot}CHPh}_{CH—CH——O}{>}C_{10}H_6{<}^{1}_{2}$, m.p. 141° (no $FeCl_3$ colour; stable to HCl), probably by partial reduction to $CH_2Ph{\cdot}NH{\cdot}NH_2$, partial hydrolysis to β-$C_{10}H_7{\cdot}OH$, and union of the products. Passage of N_2O_3 into 2 : 1-$OH{\cdot}C_{10}H_6{\cdot}CHPh{\cdot}NH_2$ (II) in Et_2O–Ac_2O–AcOH gives a *substance*, $C_{21}H_{20}O_2N_2$, m.p. 125° [Liebermann reaction positive; no $FeCl_3$ colour; regenerates (II) with HCl; gives the CHI_3 and cacodyl oxide reactions], reduced by Na–Hg to a *substance*, $C_{34}H_{33}O_2N$, m.p. 137° [blue $FeCl_3$ colour; with HCl gives PhCHO and (II)]. R. S. C.

Hydroxydiphenyl sulphides.—See B., 1938, 139.

Quinol and its oxidation products in alkaline solutions. H. STAUDE (Z. wiss. Phot., 1938, **37**, 3—5).—Quinol solutions free from *p*-benzoquinone (I) can be prepared by steam-distillation at low pressure in pure N_2, crystallising the quinol, and dissolving it in alkali carbonate solution, all in an O_2-free atm.; a simpler method is to reduce any (I) by treating the solution (in O_2-free atm.) with Gladstone–Tribe Cu–Zn couple, and then add the solution to the alkali carbonate solution, also under N_2. Pure quinol is colourless. Absorption curves are given. The solutions keep indefinitely under N_2, but discolour rapidly in air. If little alkali is present, the (I) can be extracted with Et_2O, but not if more alkali is added. (I) (without air, *e.g.*, under PhMe) gives with NaOH a blue-green colour (hydroxy-

quinonate) which turns red with acid (hydroxyquinone), the reaction being reversible and the inversion point p_H 9·5. Other reactions are given. J. L.

Oxidation processes. XI. Autoxidation of duroquinol. T. H. James and A. Weissberger (J. Amer. Chem. Soc., 1938, **60**, 98—104; cf. A., 1937, I, 623).—Duroquinol (I) in alkali is oxidised quantitatively to duroquinone (II) and H_2O_2. The rate is dependent on $[OH']^2$, showing that the first step is formation of $O^-\cdot C_6Me_4\cdot O^-$. Two processes then occur, viz., (*a*) reaction of the ion with O_2, the rate being $\propto [O_2]$ and the concn. of (I), and (*b*) further reaction with (II) (if present), the rate being $\propto$ the concn. of (I) and (II) and independent of the $[O_2]$. The autoxidation is catalysed by $CuSO_4$, the rate of this reaction being $\propto [O_2]$. Na_2SO_3 is not an inhibitor. At high alkalinity relatively slow autoxidation of (II) occurs. R. S. C.

Additive compounds of dihydric phenols. Y. Garreau (Compt. rend., 1937, **205**, 1072—1074).—Addition of quinol to a solution of $(CH_2\cdot NH_2)_2$, SO_2, and the metallic hydroxide gives *compounds* $3C_6H_4(OH)_2,2(CH_2\cdot NH_2)_2,X,2H_2O$ in which X = Cu, Zn, and Cd and the *substance* $6C_6H_4(OH)_2,7(CH_2\cdot NH_2)_2,4NiSO_3,8H_2O$. Under analogous conditions resorcinol gives only the *compound* $C_6H_4(OH)_2,2(CH_2\cdot NH_2)_2,CuSO_3,H_2O$. H. W.

Antiseptics. IV. Alkylpyrocatechols. E. Miller, W. H. Hartung, H. J. Rock, and F. S. Crossley (J. Amer. Chem. Soc., 1938, **60**, 7—10; cf. A., 1933, 499).—Conditions are given for the prep. of o-$C_6H_4(O\cdot CO\cdot Alk)_2$ and their rearrangement by $AlCl_3$ in presence of o-$C_6H_4(OH)_2$ in CS_2 in good yield to 4-acylpyrocatechols with smaller amounts of the 3-isomerides. Isolation of the acyl chloride or the ester is unnecessary. The same products are obtained from acylguaiacols. Thus are prepared 4-*n*-butyryl-, m.p. 139°, 4-*n*-, m.p. (anhyd.) 93—94° (lit. 143—144°) or (+0·5H_2O or 0·5 dioxan) 100—101°, 4-iso-, m.p. 106·5—107·5°, and 3-iso-*valeryl*-, m.p. 93—95°, 4-*n*-, m.p. 93·8° [some 4 : 3 : 1-$OH\cdot C_6H_3(OMe)\cdot CO\cdot C_5H_{11}$ is also obtained from guaiacol], 4-iso-, m.p. 73—73·5°, and 3-iso-*hexoyl*-, b.p. 195—205°/(? 4 mm.), 4-n-*heptoyl*-, m.p. 78—79°, 4-, m.p. 95·5—96°, b.p. 225°/5 mm., and 3-n-*octoyl*-, m.p. 87—88°, and 3-*propionyl-pyrocatechol*, b.p. 182—187°/5 mm., m.p. 102·5—103·5°. Reduction by H_2–Pd or, less well, by Zn–Hg–HCl gives 4-n-*butyl*- (I), b.p. 143—147°/5 mm., 4-n-, b.p. 158—159°/7 mm., and -iso-*amyl*-, b.p. 155—160°/6 mm., m.p. 55·5—58·5°, 4-n- (II), b.p. 164—169°/5 mm., and -iso-*hexyl*-, b.p. 161—164°/5 mm., 4-n-*heptyl*- (III), b.p. 195—200°/12 mm., m.p. 40°, and 4-n-*octyl-pyrocatechol*, b.p. 178°/5 mm., m.p. 40°. PhOH coeffs. against *S. aureus* are (I) 29, (II) 129, and (III) 177, showing the effect of alkyl. R. S. C.

Organic reactions with boron fluoride. XVII. J. F. McKenna and F. J. Sowa (J. Amer. Chem. Soc., 1938, **60**, 124—125).—Fluorescein is prepared in almost quant. yield by use of BF_3 in C_6H_6, and phenolphthalein in 72% yield by BF_3 without solvent. Nitriles and alcohols react thus: $3ROH + R'CN + BF_3 \rightarrow BF_3,NH_3 + CR'(OR)_3 \rightarrow R'CO_2R + R_2O$, yields being moderate; this mechanism is confirmed by decomp. of $CH(OEt)_3$ into HCO_2Et–BF_3 and Et_2O,BF_3. In presence of BF_3, esters and NH_2Ph give anilides (2—10%) and alcohols. $Bu^{\beta}OH$ and $Bu^{\gamma}OH$ with PhOH and BF_3 give p-$C_6H_4Bu^{\gamma}\cdot OH$ as main product. R. S. C.

Preparation of glycerides of phenyl-substituted aliphatic acids and their reduction to alcohols. Preparation of phenylethyl alcohol. G. Darzens (Compt. rend., 1937, **205**, 682—684).—Glycerides of $CH_2Ph\cdot CO_2H$ (I) are prepared in good yields from (I), glycerol (II), and HCl first at 145—150°, and subsequently at 135—140°/15 mm. for 16—20 hr. Excess of (II) gives the *α-monoglyceride*, and excess of (I) the *triglyceride*, neither obtained cryst. (II) (1 mol.) with 2 mols. of (I) yields the *αγ-diglyceride*, m.p. 62·5°, of (I). On reduction (Na, amyl alcohol) the glycerides all give $Ph\cdot[CH_2]_2\cdot OH$ [prep. from (I) and (II) described]. Homologues of (I) behave similarly; $Ph\cdot[CH_2]_2\cdot CO_2H$ gives the *triglyceride*, reduced to $Ph\cdot[CH_2]_3\cdot OH$, also obtained by reduction of the *triglyceride*, m.p. 111°, of cinnamic acid. E. G. B.

Catalytic hydrogenation of β-ionone : dihydro-β-ionone, dihydro-β-ionol, and derivatives of α- and β-ionol. J. Kandel (Compt. rend., 1937, **205**, 994—996).—β-Ionone (I) is hydrogenated (H_2–Ni) at 150 kg. per sq. cm. at room temp. to dihydro-β-ionone (II); at 90°, a mixture of (II) and *dihydro-β-ionol*, b.p. 132·5°/14 mm., m.p. 39·5° (*allophanate*, m.p. 171·5°), is formed. Reduction of (I) with $Al(OPr^{\beta})_3$ yields *β-ionol* (III), b.p. 130·5°/14·5 mm., whilst dehydration of α-ionol and (III) (SiO_2 gel at 300°) yields respectively 3-βδδ-, b.p. 96—97°/16·5 mm., and 2-*αγγ-trimethylbutadienyl*cyclo*hexene*, b.p. 108—110°/15 mm. The *Me*, b.p. 115°/15·5 mm., and *Et ethers*, b.p. 120°/14 mm., *formate*, b.p. 127·5—128°/15 mm., *acetate*, b.p. 134°/15 mm., *propionate*, b.p. 144—145°/15 mm., *benzoate*, b.p. 168—169°/2 mm., p-*nitrobenzoate*, m.p. 88°, and *allophanate*, m.p. 151—152°, of α-ionol and the *acetate*, b.p. 136·5°/14·5 mm., *propionate*, b.p. 145—146°/15 mm., iso*butyrate*, b.p. 150°/15·5 mm., *benzoate*, b.p. 205—206°/15 mm., and p-*nitrobenzoate*, m.p. 85°, of (III) are described. J. D. R.

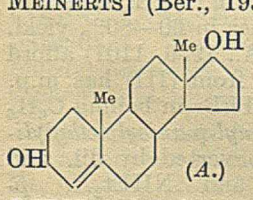
Menthadiene hydrocarbons obtained by dehydration of active and inactive 3-methyl-1-(α-hydroxy*iso*propyl)*cyclo*hexanols. M. Godchot and (Mlle.) G. Cauquil (Compt. rend., 1938, **206**, 88—90; cf. A., 1937, II, 241).—Me *l*-3-methyl*cyclo*hexanol-1-carboxylate (cf. *ibid.*, 62) with MgMeI affords l-3-*methyl*-1-(α-*hydroxy*isopropyl)cyclo*hexanol* (I), m.p. 52°. *Me* dl-3-*methyl*cyclo*hexanol*-1-*carboxylate*, b.p. 109—110°/15 mm., similarly affords dl-3-*methyl*-1-(α-*hydroxy*isopropyl)cyclo*hexanol* (II), m.p. 47°. (I) and (II) with aq. $H_2C_2O_4$ at 120° afford l-, $[\alpha]_{5780}$ −103·5°, and dl-1-*methyl*-3-iso*propenyl*-$\Delta^{2\text{ or }3}$-cyclo*hexene*, b.p. 184°/745 mm., respectively (together with ketonic material), which with H_2–Raney Ni give d-, b.p. 165°/760 mm., $[\alpha]_{5780}$ +22·48°, and dl-1-*methyl*-3-iso*propyl*-$\Delta^{2\text{ or }3}$-cyclo*hexene*, b.p. 165°/760 mm., respectively. These are reduced (H_2–PtO_2) to l-, b.p. 167°/760 mm., $[\alpha]_{5780}$ −1·36°, and dl-1-*methyl*-3-iso*propyl*cyclo*hexane*, b.p. 167°/760

mm., respectively. The Raman spectra of the hydrocarbons are determined. J. L. D.

Dehalogenation by silver [nitrate] of the iodohydrins of α-cyclanediols. M. Tiffeneau and B. Tchoubar (Compt. rend., 1937, **205**, 1411—1413).—Dehalogenation of 2-iodo-1-methyl*cyclo*hexanol with $AgNO_3$ (cf. A., 1933, 384) gives 2-methyl*cyclo*hexanone (I) with 10% of acetyl*cyclo*pentane (II); (I) is a secondary product formed by the action of nitric acid on the primary epoxide (III). Dehalogenation with Ag_2O gives (III) (80%), the corresponding glycol (IV) (10%), (II) (5%), and some (I) possibly arising from a small trace of *cis*-iodohydrin. The action of cold HNO_3 on (III) causes immediate isomerisation into (I) and hydration to (IV) without production of (II). 2-Iodo-1-ethyl*cyclo*hexanol, obtained by the action of HOI on Δ^1-ethyl*cyclo*hexene, is transformed by $AgNO_3$ mainly into the nitrate of the corresponding glycol and into the epoxide (V), which is isomerised by the liberated HNO_3 to 2-ethyl*cyclo*hexanone (VI) and hydrated to *trans*-2-ethyl*cyclo*hexane-1 : 2-diol (VII). Propionyl*cyclo*pentane is also formed in small proportion. This is not produced by the action of dil. HNO_3 on (V), which gives solely (VI) and (VII). 2-Iodo*cyclo*pentanol, from HOI and *cyclo*pentene, is almost exclusively transformed by $AgNO_3$ into the corresponding epoxide, which is hydrated by HNO_3 produced simultaneously to the glycol without isomerisation into *cyclo*pentanone or *cyclo*butylformaldehyde. 2-Iodo*cyclo*hexanol and 2-iodo-4-methyl*cyclo*hexanol are transformed in 30% yield into *cyclo*pentylformaldehyde and 3-methyl-*cyclo*pentylformaldehyde, respectively; the corresponding glycol (VIII) (20—40%) and its nitrate also result. (VIII) is formed by hydration by dil. HNO_3 of the initial epoxide, which is almost the sole product from the iodohydrin and Ag_2O. H. W.

Structure of β-sitosterol and its preparation from stigmasterol. S. Bernstein and E. S. Wallis (J. Org. Chem., 1937, **2**, 341—345).—Bengtsson's results (A., 1936, 69) indicate that β-sitosterol (I) should be identical with 22-dihydrostigmasterol (II). This is confirmed by prep. of (II) by side-chain hydrogenation (H_2–Pd) of stigmasteryl acetate, hydrolysis, and removal of small amounts of sterols hydrogenated in the 5 : 6 position by conversion of the product into the *p*-toluenesulphonates and hydrolysis (aq. $COMe_2$), when (II) alone is regenerated. Physical data for (II) and its derivatives approximate closely to those for (I) from cottonseed oil and its corresponding derivatives. Hydrogenation (H_2–PtO_2) of (I) gives stigmastanol. E. G. B.

Δ^4-Androstene-3 : 17-diol. A. Butenandt and A. Heusner [with, in part, D. von Dresler and U. Meinerts] (Ber., 1938, **71**, [*B*], 198—204).—Testosterone behaves like cholestenone (I) towards $Al(OPr^\beta)_3$ in boiling $Pr^\beta OH$ since it is reduced to a mixture of *n*- (II), m.p. 153—154°, $[\alpha]_D^{19}$ +48·52° in EtOH, and epi- (III), m.p. 202—206°, $[\alpha]_D^{22}$ +187·5° in C_5H_5N, -Δ^4-*androstenediol* (cf. *A*), separable by pptn.



(*A*.)

of (II) by digitonin from EtOH. The *diacetates* of (II) and (III) have m.p. 101—102° and 121°, respectively. (II) and (III) give a marked red colour with $CCl_3{\cdot}CO_2H$ and their physical properties in comparison with the Δ^4-unsaturated reduction products of (I) and the corresponding steroids show that displacement of the double linking from Δ^5 towards Δ^4 is accompanied by inversion of sign of optical rotation. Treatment of (II) with boiling 95% EtOH containing a little conc. HCl gives $\Delta^{3:5}$-*androstadien*-17-*ol*(+0·5H_2O) (IV), m.p. 146°, the *acetate*, m.p. 122—123°, $[\alpha]_D^{19}$ −147·4° in EtOH, of which is also obtained from (III) and Ac_2O at 100°. The physiological action of (II) and (III) is described. Dehydration of Δ^5-androstenediol by anhyd. $CuSO_4$ gives (IV), which is also obtained by reduction [$Al(OPr^\beta)_3$] of $\Delta^{3:5}$-androstadienone. H. W.

Sterols. XXVIII. Pregnanetriols from pregnancy urine. R. E. Marker, O. Kamm, H. M. Crooks, T. S. Oakwood, E. L. Wittle, and E. J. Lawson (J. Amer. Chem. Soc., 1938, **60**, 210—211; cf. A., 1938, II, 58).—Mares' pregnancy urine affords *pregnanetriol*-A (10 mg. per gallon), $C_{21}H_{36}O_3$, m.p. 295—300° (*triacetate*, m.p. 136°), and -B (6 mg. per gallon), m.p. 300—302°, $[\alpha]_D^{25}$ −41° in C_5H_5N (*triacetate*, m.p. 168°), best purified by way of the acetates: -*A* and -*B* may be related as are pregnanediol and *allo*pregnanediol. -*B* may be identical with the compound of Haslewood *et al.* (A., 1934, 1126). -*A* and -*B* give no ppt. with digitonin and contain an angular Me since they give no $C_{10}H_8$ derivative with Pt-black at 300°. One OH in -*A* is at $C_{(20)}$, probably as CHMe·OH, since the CHI_3 reaction is positive; a second OH is probably at $C_{(3)}$; the third, probably not *tert.* as it can be acetylated, is probably in the same position as the unreactive nuclear OH of the cortical hormone derivative of Reichstein (A., 1936, 1383). R. S. C.

Normal long-chain acids terminating in *cyclo*hexyl or *cyclo*pentyl. II. *cyclo*Pentylvaleric acid and its derivatives. M. M. Katznelson and M. S. Kondakova (Compt. rend. Acad. Sci. U.R.S.S., 1937, **17**, 367—370).—Mg *cyclo*pentyl bromide and furfuraldehyde yield cyclo*pentylfurylcarbinol*, b.p. 114—116°/8 mm., converted by EtOH–HCl into the *Et* ester, b.p. 140—147°/9 mm., of δ-cyclo*pentyl-lævulic acid*, m.p. 65°. Reduction (Clemmensen) of this ester gives the *-valeric acid*, m.p. 11°, b.p. 150—153°/9 mm. (*Me* ester, b.p. 118—119°/12 mm.; *chloride*, b.p. 124°/12 mm.; *amide*, m.p. 138°; *anilide*, m.p. 81—81·5°; *Cd* salt). A. Li.

***cyclo*Pentyl- and *cyclo*hexyl-succinic acids and resolution of *cyclo*pentylsuccinic acid.** S. K. Ranganathan (Current Sci., 1937, **6**, 277—278).—Et sodio-α-carbethoxysuccinate condenses with *cyclo*pentyl and *cyclo*hexyl bromides to give respectively Et α-carbethoxy-α-*cyclo*pentyl-, b.p. 166°/45 mm., and -α-*cyclo*hexyl-succinate, b.p. 168°/45 mm. Hydrolysis and decarboxylation yields *cyclo*pentyl- (I), m.p. 117° (anhydride, b.p. 176°/30 mm.; *Et* ester, b.p. 142°/6 mm.), and *cyclo*hexyl-succinic acid, m.p. 143°. (I) has been resolved through the brucine salt into the *d*-, m.p. 135°, $[\alpha]_D^{26}$ +17·81°, and *l*-acids, m.p. 135°, $[\alpha]_D^{26}$ −16·94° (in $COMe_2$). F. R. S.

Alkoxyalkyl esters of alicyclic carboxylic acids.—See B., 1938, 140.

***m*-Xylylacetic acid and its derivatives.** J. V. Harispe (Bull. Inst. Pin, 1937, 155—173, 195—216).—An account of work reviewed previously (A., 1936, 992, 1506). H. W.

Rôle of the acetyl derivative as an intermediary stage in the biological synthesis of amino- from keto-acids. V. du Vigneaud and O. J. Irish (J. Biol. Chem., 1938, **122**, 349—370).—Biological conversion of (−)- into (+)-α-amino-γ-phenylbutyric acid in the dog is demonstrated, and the hypothesis of Knoop (A., 1911, ii, 514) of oxidation via the Ac derivative to the CO-acid and subsequent asymmetric synthesis of the NHAc-acid (by reaction with $AcCO_2H$ and NH_3) is confirmed. The results with the *dl*-acid are confirmed. When the (−)- or (+)-acid is fed to dogs, (+)-α-acetamido-γ-phenylbutyric acid (with some hydroxy-acid and hippuric acid), which corresponds with the (+)-NH_2-acid (I), is excreted. Feeding of *dl*-α-acetamido-γ-phenylbutyric acid leads to excretion of excess of the (−)-form, showing biological hydrolysis of the (+)-isomeride. (I) is shown to correspond with the naturally occurring NH_2-acids by Lutz and Jirgensons' method (A., 1930, 460), and should therefore be renamed l-(+)-α-*amino-γ-phenylbutyric acid*. Preliminary metabolic experiments with *dl*-acetylphenylalanine showed that a larger amount of the (−)-Ac derivative is excreted, confirming the results of Knoop and Blanco (A., 1925, i, 1208), but not their conclusion that the original hypothesis (above) should be abandoned, since the (−)-Ac derivative corresponds with (+)-, not (−)-phenylalanine. The above results reinstate the $AcCO_2H$–acetylation theory for the synthesis *in vivo* of NH_2-acids, which is discussed.

$CH_2Ph{\cdot}CH_2{\cdot}CH(CO_2H)_2$ is brominated and converted by NH_3 into dl-α-*amino-γ-phenylbutyric acid*, m.p. 305—306°, of which the *formyl* derivative, m.p. 130—131° [*brucine* salt, m.p. 160—162°, $[\alpha]_D^{30}$ −23·2° in MeOH, of the (−)-form], is resolved and hydrolysed to (−)-, m.p. 323—325°, $[\alpha]_D^{30}$ −47·0° in N-HCl, and (+)-α-*amino-γ-phenylbutyric acid*, m.p. 326—328°, $[\alpha]_D^{30}$ +48·8° in N-HCl [*Ac* derivative, m.p. 179—180°, $[\alpha]_D^{26}$ +26·7° in EtOH, also obtained biologically (see above)]. M.p. are corr. E. W. W.

Hexadeuterobenzene as solvent for optically active substances. H. Erlenmeyer and H. Schenkel (Helv. Chim. Acta, 1938, **21**, 114).—Me (+)-mandelate has $[\alpha]_D^{20}$ +174·78±0·13° $[\alpha]_{5105\cdot6}^{20}$ +252·88±0·13° in C_6H_6 and $[\alpha]_D^{20}$ +173·44±0·26° and $[\alpha]_{5105\cdot6}^{20}$ +251·32±0·26° in C_6D_6. H. W.

2-Chloro-4 : 5- and -5 : 6-diaminobenzoic acid. H. Goldstein and A. Studer (Helv. Chim. Acta, 1938, **21**, 51—56).—Reduction of 4 : 5 : 2-$(NO_2)_2C_6H_2Cl{\cdot}CO_2H$ with $SnCl_2$ and conc. HCl gives 2-*chloro*-4 : 5-*diaminobenzoic acid*, m.p. 219° [*dihydrochloride* (I); Ac_2 derivative, m.p. about 242° (decomp.)], slowly converted by boiling glacial AcOH into 6-*chloro*-2-*methylbenziminazole*-5-*carboxylic acid*, m.p. about 324° (decomp.). Treatment of (I) with HNO_2 leads to 6-*chlorobenztriazole*-5-*carboxylic acid*, m.p. about 320° (decomp.). With Ac_2 and benzil, (I) gives 7-*chloro*-2 : 3-*dimethyl*-, m.p. 260°, and 7-*chloro*-2 : 3-*diphenyl-quinoxaline*-6-*carboxylic acid*, m.p. 247° (decomp.), respectively. 5 : 2-$NO_2{\cdot}C_6H_3Cl{\cdot}CO_2H$ is reduced by $SnCl_2$ and conc. HCl to 5 : 2-$NH_2{\cdot}C_6H_3Cl{\cdot}CO_2H$, the Ac derivative, m.p. 216·5°, of which is converted by HNO_3 (*d* 1·52) at 50—60° into 2-*chloro*-6-*nitro*-5-*acetamidobenzoic acid*, m.p. 236° (decomp.). This is hydrolysed by 10% KOH to 2-*chloro*-6-*nitro*-5-*aminobenzoic acid*, m.p. 202°, reduced ($SnCl_2$ and conc. HCl) to 2-*chloro*-5 : 6-*diaminobenzoic acid* (II) [*dihydrochloride*; Ac_2 derivative, m.p. about 242° (decomp.)]. The constitution of (II) rests on the established presence of 2 NH_2 in the *ortho*-position to one another and on its difference from the known 2-chloro-4 : 5- or -3 : 5-diamino-acids. (II) is condensed with Ac_2 and benzil to 6-*chloro*-2 : 3-*dimethyl*-, m.p. 278° (decomp.), and with benzil to 6-*chloro*-2 : 3-*diphenyl-quinoxaline*-5-*carboxylic acid*, m.p. 248°, respectively. M.p. are corr. H. W.

Synthesis of sympathomimetically active local anæsthetics. K. H. Slotta and R. Kethur (Ber., 1938, **71**, [*B*], 59—63).—*m*-$NH_2{\cdot}C_6H_4{\cdot}CHO$ is transformed (diazo-method) into *m*-$CN{\cdot}C_6H_4{\cdot}CHO$, which with $MeNO_2$ in presence of KOH gives ω-nitro-*m*-cyanostyrene in 42·5% yield. This is converted by HCl in MeOH–Et_2O into the *hydrochloride*, m.p. 151°, of the methyliminoether of ω-nitrostyrene-*m*-carboxylic acid from which little (I) (below) could be obtained. *p*-$CHO{\cdot}C_6H_4{\cdot}CO_2Me$ condenses with $MeNO_2$ in presence of KOH to *Me* p-ω-*nitrovinylbenzoate*, m.p. 178°, obtained in smaller yield by use of NH_3MeCl as condensing agent. It is reduced electrolytically at a Pb electrode to *Me* p-β-*aminoethylbenzoate hydrochloride*, m.p. 208—211°. Similarly *p*-$CHO{\cdot}C_6H_4{\cdot}CO_2Et$ affords successively *Et* p-ω-*nitrovinylbenzoate*, m.p. 112°, and *Et* p-β-*aminoethylbenzoate hydrochloride*, m.p. 178°, which, like the Me ester, is a powerful anæsthetic. *m*-$CHO{\cdot}C_6H_4{\cdot}CO_2Me$ similarly gives *Me* m-ω-*nitrovinylbenzoate* (I), m.p. 119°, in 69·7% yield, electrolytically reduced to *Me* m-β-*aminoethylbenzoate hydrochloride*, m.p. 142°; the corresponding *Et* esters have m.p. 109° and 114°, respectively. The *m*-derivatives are not anæsthetics. H. W.

Action of mixed organo-magnesium compounds on hydroxy- or alkoxy-aromatic amides. P. Couturier (Compt. rend., 1937, **205**, 800—802; cf. A., 1927, 875).—2 : 4-$(OAc)_2C_6H_3{\cdot}COCl$ with $NHEt_2$ affords 2 : 4-*diacetoxybenzdiethylamide*, m.p. 79°, hydrolysed (dil. NaOH) to β-*resorcyldiethylamide* (I), m.p. 142°, which with MgEtBr (5 mols.) in boiling C_6H_6 gives a 10% yield of 2 : 4-$(OH)_2C_6H_3{\cdot}COEt$; (I) is intermediate in reactivity between an *o*- and *p*-OH-compound. Similarly o- (II), b.p. 170°/17 mm., and *p*-methoxy- (III), 3 : 4-dimethoxy-, and 3 : 4 : 5-trimethoxy-benzdiethylamide with MgEtBr afford the corresponding propiophenones in 60—80% yield. In addition (II) and (III) (cf. A., 1936, 1107) afford basic products [*picrate* of that from (III) has m.p. 115° (decomp.)]. (III) with MgPhBr in boiling C_6H_6 affords no ketone but (*diphenyl*-p-*anisylmethyl*)*diethylamine*, b.p. 117°/3 mm. converted by dil. acid into diphenyl-*p*-anisylcarbinol and $NHEt_2$. *p*-$OMe{\cdot}C_6H_4{\cdot}CO{\cdot}NH_2$ and 3 : 4 : 5-$(OMe)_3C_6H_2{\cdot}CO{\cdot}NH_2$

react similarly with MgEtBr to give propiophenones (70%) together with p-*methoxy-*, m.p. 45° and 3 : 4 : 5-*trimethoxy-propiophenoneimine*, m.p. 48°, which are easily hydrolysed (HCl) and when heated under pressure give NH_3. J. L. D.

γ-Chloropropyl imidobenzoate [α-iminobenzyl γ-chloropropyl ether] hydrochloride. J. B. Cloke and F. A. Keniston (J. Amer. Chem. Soc., 1938, **60**, 129—131).—PhCN, $Cl{\cdot}[CH_2]_3{\cdot}OH$, and HCl in Et_2O at 0° give *α-iminobenzyl γ-chloropropyl ether hydrochloride* (I), m.p. 116·2°; some dihydrochloride [converted when kept over soda-lime and CaO in a vac. into (I)] is also formed. With H_2O (I) gives only $Cl{\cdot}[CH_2]_3{\cdot}OBz$, b.p. 154—156°/22 mm., the hydrolysis being unimol., $k = 0{\cdot}00784$ at 28°; the γ-Cl accelerates the reaction as compared with that of $OPr^{\alpha}{\cdot}CPh{:}NH_2Cl$. When heated, (I) gives NH_2Bz and $[CH_2]_3Cl_2$. The free imine rearranges to $Cl{\cdot}[CH_2]_3{\cdot}NHBz$ and μ-phenylpentoxazoline hydrochloride. R. S. C.

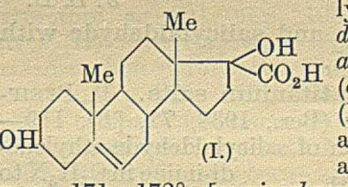
Electrosynthesis of methyl di*cyclo*hexyl-4 : 4′-dicarboxylate from methyl hydrogen *trans*-hexahydroterephthalate. F. Fichter and T. Holbro (Helv. Chim. Acta, 1938, **21**, 141—151).—The inability of Me H *trans*-hexahydrophthalate to undergo Kolbe's electrosynthesis is attributed to hindrance due to the proximity of the CO_2H groups since similar difficulties are not encountered with the corresponding terephthalate. p-$C_6H_4(CO_2Me)_2$ is hydrogenated (Pt-black in AcOH) to a mixture from which Me_2 *trans*-hexahydroterephthalate, m.p. 71°, separates. Hydrolysis of the residual ester mixture and treatment of the acids with conc. HCl at 120° gives the pure *trans*-acid, smoothly esterified by MeOH–H_2SO_4 and then partly hydrolysed to Me H *trans*-hexahydroterephthalate, m.p. 126°. Electrolysis of *K Me* trans-*hexahydroterephthalate* in MeOH with Pt anode and Cu cathode gives *Me_2 dodecahydrodiphenyl-4 : 4′-dicarboxylate* (I), m.p. 100—101°, accompanied by Me Δ^3-*cyclo*hexenecarboxylate containing a small proportion of Me hexahydrobenzoate. (I) is hydrolysed by KOH–MeOH–H_2O to a mixture (II) of acids, $C_{14}H_{22}O_4$, m.p. 245—250° after gradual darkening above 200° (corresponding *Ba* salt). Treatment of (II) with conc. HCl at 180° leads to trans-trans-*dodecahydrodiphenyl-4 : 4′-dicarboxylic acid*, m.p. about 345° (*Me_2* ester, m.p. 117°). H. W.

Action of organomagnesium compounds on *o*-*NN*-diethylphthalamic acid. N. Maxim and (Mlle.) A. Andreescu (Bull. Soc. chim., 1938, [v], **5**, 54—57; cf. A., 1928, 519).—Interaction of *o*-$NEt_2{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H$ (I) with Mg alkyl or aryl halides provides a general method of prep. of phthalides in good yield; *o*-$XMg{\cdot}O{\cdot}CO{\cdot}C_6H_4{\cdot}CR_2{\cdot}O{\cdot}MgX$ and $NHEt_2$ are first formed, the former being hydrolysed to *o*-$CO_2H{\cdot}C_6H_4{\cdot}CR_2{\cdot}OH$, which then loses H_2O yielding phthalides. Thus are prepared di-*n*-propyl-, di*iso*butyl-, di*iso*amyl-, b.p. 196°/12 mm., dibenzyl-, and diphenyl-phthalides. E. G. B.

5-Bromo- and 5-chloro-2-naphthoic acid. H. Goldstein and R. Matthey (Helv. Chim. Acta, 1938, **21**, 62—66).—5 : 2-$NH_2{\cdot}C_{10}H_6{\cdot}CN$ (I) is transformed by Sandmeyer's reaction into 5 : 2-$C_{10}H_6Br{\cdot}CN$, m.p. 154°, identical with the compound obtained by bromination of 2-$C_{10}H_7{\cdot}CN$, and hydrolysed by boiling H_2SO_4–AcOH–H_2O to 5-bromo-2-naphthoic acid (II), m.p. 270°, identical with the product of the direct bromination of 2-$C_{10}H_7{\cdot}CO_2H$. (II) gives a *Me* ester, m.p. 73°, a *chloride*, m.p. 83°, *amide*, m.p. 195°, and *anilide*, m.p. 202·5°. Similarly (I) is transformed into 5 : 2-$C_{10}H_6Cl{\cdot}CN$, identical with that obtained by the chlorination of 2-$C_{10}H_7{\cdot}CN$ and hydrolysed to 5-chloro-2-naphthoic acid (III), m.p. 270° (*Me* ester, m.p. 81°; *chloride*, m.p. 89°; *amide*, m.p. 190·5°; anilide, m.p. 202·5°). The m.p. of (II) and (III) are identical and nearly the same as that of their mixtures. The graph showing the relationship between m.p. and composition of mixtures of (II) and (III) is nearly a horizontal straight line. M.p. are corr. H. W.

Synthesis of 1-hydroxy-2-naphthonitrile. J. A. McRae and L. Marion (Canad. J. Res., 1937, **15**, **B**, 480—485).—$CH_2Ph{\cdot}CHO$ (I) and $CN{\cdot}CHNa{\cdot}CO_2Et$ in EtOH give αα′-dicyano-β-benzylglutaric acid, m.p. 168° (lit. 173°) [also formed from (I) and aq. $CN{\cdot}CH_2{\cdot}CO_2Na$], and (probably) Et α-cyano-β-benzylacrylate, b.p. 182°/15 mm. The latter when distilled at 2—4 mm. loses EtOH and forms 1-*hydroxy*-2-*naphthonitrile* (II), m.p. 179° (*Me ether*, m.p. 50—51°; 4-p-*nitrobenzeneazo*-derivative, m.p. 275°), also obtained from 1 : 2-$OH{\cdot}C_{10}H_6{\cdot}CH{:}N{\cdot}OH$ and aq. EtOH–KCN. (II) and BzCl in C_5H_5N give a *compound*, m.p. 159—160°. Contrary to Linstead and Williams (A., 1926, 1245), (I) is oxidised by AcOH–CrO_3 to BzOH. M.p. are corr. D. E. W.

Sex hormones. XXVIII. Preparation of Δ⁵-3-*trans*-17-dihydroxyætiocholenic acid from Δ⁵-*trans*dehydroandrosterone. L. Ruzicka and K. Hofmann (Helv. Chim. Acta, 1938, **21**, 88—93).—Treatment of Δ⁵-17-hydroxy-3-*trans*acetoxy-17-ethinylandrostene with Br in CCl_4 followed by ozonisation and treatment of the product with H_2O affords, after esterification, *Me* Δ⁵-17-*hydroxy*-3-trans*acetoxyætiocholenate*, m.p. 163—164°, hydrolysed to Δ⁵-3-trans-17-*dihydroxyætiocholenic acid* (I), m.p. 260—261° (decomp.) [*Me* ester (II), m.p. 190—191°], and *trans*-dehydroandrosterone acetate, m.p. 171—172° [*semicarbazone*, m.p. about 270° (decomp.)]. (I) is treated successively with Br and CrO_3 in AcOH at room temp. and then debrominated by Zn dust to Δ⁴-androstene-3 : 17-dione, m.p. 172—173°. (II) is transformed by cold Ac_2O–C_5H_5N into its *acetate*, m.p. 201—202°. Δ⁵-3-trans-17-*Diacetoxyætiocholenic acid*, m.p. 220—220·5°, and its *Me* ester, m.p. 145—145·5°, are described. M.p. are corr. H. W.



(I.)

Bile acids. LIII. M. Schenck (Z. physiol. Chem., 1938, **251**, 32—40; cf. A., 1937, II, 420).—The *iso*nitroketo-acid, $C_{24}H_{33}O_{10}N$, yields a *dioxime*, whilst the α-acid, $C_{24}H_{34}O_{10}N_2$, and the ketolactam-tricarboxylic acid, $C_{24}H_{35}O_8N$, yield *monoximes* with NH_2OH. Bi*iso*idanic acid appears to yield a *trioxime* and hence is probably a triketotricarboxylic

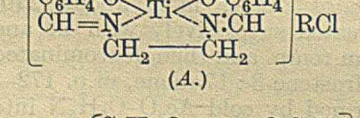
acid; oximation in alkaline solution gives the monoxime of the " benzilic acid rearrangement " product (cf. A., 1927, 1080). The β-acid, $C_{24}H_{34}O_{10}N_2$, yields no oxime with NH_2OH. The possible structures of the acids are discussed in the light of these results. W. McC.

Catalytic hydrogenation of cinnamaldehyde and of citronellal. [Nickel as catalyst of the Cannizzaro reaction.] M. Delépine and C. Hanegraaff (Bull. Soc. chim., 1937, [v], **4**, 2087—2093).—In addition to results previously recorded (A., 1937, II, 421), $CH_2Ph{\cdot}CH_2{\cdot}CHO$ gives, on keeping, a *trimeride*, m.p. 64°. Discrepancies between unsaturation of citronellal (I) and H_2 absorbed when Ni is used are due to a Cannizzaro reaction. With Ni in EtOH or Et_2O, (I) yields citronellol and Ni citronellate. Similarly Pr^aCHO and Ni in H_2O yield Bu^aOH and $(Pr^aCO_2)_2Ni$. The reaction can be represented: $5RCHO + Ni + 2H_2O \rightarrow (RCO_2)_2Ni + 3CH_2R{\cdot}OH$, the Cannizzaro reaction being accompanied by reduction by Ni. E. W. W.

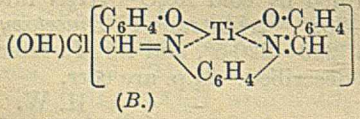
Reducing action of alkali benzyloxides on hydratropaldehyde and α-alkylcinnamaldehydes. P. Mastagli (Compt. rend., 1937, **205**, 802—805; cf. A., 1937, II, 102).—Hydratropaldehyde or its *p*-Me derivative, in boiling 2N-$CH_2Ph{\cdot}OH$–KOH (I) or –NaOH (II), affords the corresponding alcohol, H_2, and BzOH. β-Phenyl-, b.p. 116°/18 mm. (*allophanate*, m.p. 175°), and β-p-*tolyl-propyl alcohol*, b.p. 124°/17 mm. (*allophanate*, m.p. 157°), are described. αβ-Unsaturated aldehydes are converted into saturated alcohols by (I) but not by (II) at 100°. α-Ethylcinnamaldehyde with (II) at 100° gives β-ethylcinnamyl alcohol (*allophanate*, m.p. 147°) and NaOBz; at 200° the saturated alcohol is formed. The following are prepared similarly (m.p. of *allophanates* in parentheses): β-n-*butyl*-, b.p. 155°/15 mm. (155°); -*amyl*- (160°); -*hexyl*-, b.p. 176°/15 mm. (142°); -*octyl*-, b.p. 198°/15 mm. (138°); -*nonyl*-, b.p. 212°/17 mm. (132°); -*nonenyl*-, b.p. 212°/17 mm. (127°); and -*decyl-cinnamyl alcohol*, b.p. 221°/15 mm., m.p. 42° (137°). J. L. D.

Reaction of vanillin and salicylaldehyde with acetone.—See A., I, 147.

Internally complex titanium salts. P. Pfeiffer and H. Thielert (Ber., 1938, **71**, [*B*], 119—123).—Cautious addition of salicylaldehyde-ethylenedi-imine in C_5H_5N to $TiCl_4$ in C_5H_5N gives basic *Ti salicylaldehyde-ethylenedi-imine chloride* (I) (*A*; R = OH), which dissolves without decomp. in H_2O giving a solution in which Cl can be quantitatively pptd. by $AgNO_3$. The corresponding *nitrate*, decomp. 245°, and *perchlorate* result on addition of the requisite acid. With conc. H_2SO_4 (I) evolves HCl copiously, thus confirming the ionoid nature of Cl. The position of OH is uncertain and it is placed outside the complex radical for convenience. The production of an *acetate* (*A*; R = OAc) from (I) and Ac_2O throws no light on the problem. Similarly salicylaldehyde-*o*-phenylenedi-imine gives the *substance B*, whence the corresponding *perchlorate*. H. W.



(*A*.)



(*B*.)

Synthesis of *p-cyclo*hexylbenzaldehyde and *p-cyclo*hexylbenzoic acid. D. Bodroux and R. Thomassin (Compt. rend., 1937, **205**, 991—993).—*p-cyclo*Hexylbromobenzene (improved prep.) and Mg in Et_2O yield Mg *p-cyclo*hexylphenyl bromide (I), and a little 4 : 4′-*dicyclohexyldiphenyl*, m.p. 202—203°. Interaction of (I) and $CH(OEt)_3$ followed by hydrolysis (dil. HCl) yields *p-cyclo*hexylbenzaldehyde, whilst (I) with solid CO_2 in Et_2O gives *p-cyclo*hexylbenzoic acid (61% yield; with gaseous CO_2 the yield is very poor), oxidised ($KMnO_4$) to p-$C_6H_4(CO_2H)_2$. J. D. R.

Two stereoisomeric *dl*-dihydrocamphorones. R. Calas (Compt. rend., 1938, **206**, 59—61).—2-Methyl-5-*iso*propyl-Δ⁴-*cyclo*pentenone (I) with H_2–Raney Ni in neutral or alkaline solution gives trans- (II), b.p. 179·8°/766 mm. [*semicarbazone*, m.p. 209°; *oxime*, b.p. 117°/16 mm.; *carbanilidoxime*, a liquid and m.p. 139° (two forms)], and cis-2-*methyl*-5-iso*propyl*-cyclo*pentanone* (III), b.p. 179·7°/766 mm. [*semicarbazone*, m.p. 198°; *oxime*, b.p. 118—119°/15 mm.; *carbanilidoxime*, m.p. 78° and 142° (two forms)]; the configurations are deduced from the fact that (II) reacts with NH_2OH and is reduced (Na in Et_2O–H_2O) more readily than (III). (I) with H_2–Pt-black in neutral solution affords (II), whereas in AcOH, (III) is formed. The Raman spectra of (II) and (III) are identical. J. L. D.

Syntheses with β-chloroethyl and β-vinyl ketones. Preparation of Δ²-*cyclo*hexenones. J. Décombe (Compt. rend., 1937, **205**, 680—682; cf. A., 1936, 1094, 1490).—α-Substituted derivatives (I) of β-chloroethyl and β-vinyl ketones differ from the parent ketones in reduced mobility of halogen atom and in mol. refraction. Blaise–Maire condensation of $COEt{\cdot}CH_2{\cdot}CH_2Cl$ with $CH_2Ac{\cdot}CO_2Et$ to give 3-methyl-Δ²-*cyclo*hexenone (A., 1908, i, 390) can be generalised for (I). Thus (I) with β-ketonic esters yield diketo-esters (II), which on hydrolysis [$Ba(OH)_2$] give Δ²-*cyclo*hexenones (yield from β-ketonic esters, 35—55%) by way of the 6-CO_2Et derivatives. (II) could not be isolated pure since on distillation they partly cyclise to decarboxylated products. The following are described. 3 : 4-Dimethyl-, b.p. 92—95°/15 mm. [oxime, b.p. 132—135°/15 mm. (lit. m.p. 105—109°) (benzoate, m.p. 112—113°)], 3-*methyl*-6-*ethyl*-, b.p. 95—98°/12 mm. [*oxime*, b.p. 135—140°/15 mm. (p-*nitrobenzoate*, m.p. 193°)], 4-*methyl*-3-*ethyl*-, b.p. 99—104°/15 mm. [*oxime*, b.p. 143—148°/16 mm. (*benzoate*, m.p. 76°)], 2 : 4-*dimethyl*-3-*ethyl*-, b.p. 105—106°/15 mm. (*oxime*, m.p. 68°), 4-*methyl*-3 : 6-*diethyl*-, b.p. 122—127°/15 mm. (*oxime*, b.p. 152—154°/15 mm.), and 2 : 4 : 6-*trimethyl*-3-*ethyl*-, b.p. 118—121°/15 mm. [*oxime*, b.p. 150—152°/15 mm. (p-*nitrobenzoate*, m.p. 106°)], -Δ²-cyclo*hexenones*. E. G. B.

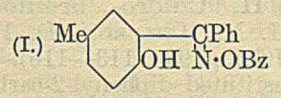
Mechanism of ketolisation by mixed amino-magnesium compounds. J. Colonge (Bull. Soc. chim., 1938, [v], **5**, 98—102; cf. A., 1934, 1359).—2 : 2 : 6 : 6-Tetramethyl*cyclo*hexanone (I) [prepared by successive methylation ($NaNH_2$–MeI or Me_2SO_4)

of 2-methyl*cyclo*hexanone], which cannot enolise, does not react with NPhMe·MgBr, and when COMeBu$^{\gamma}$ is added to the mixture, only COBu$^{\gamma}$·CH_2·CMeBu$^{\gamma}$·OH is formed; (I) is recovered unchanged. The non-condensation of (I) to a OH-ketone is due to steric hindrance; previous results (A., 1933, 698) can be similarly explained without postulating enolisation of the ketone by the Mg derivative. E. G. B.

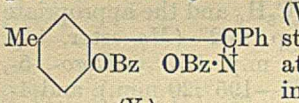
Prototropy in relation to the exchange of hydrogen isotopes. III. Comparison of the rates of racemisation and of hydrogen exchange in a ψ-acidic ketone. S. K. Hsü, C. K. Ingold, and C. L. Wilson (J.C.S., 1938, 78—81).—According to the ionisation theory of prototropy, the rate of isomerisation of ψ-acids is equal to the rate of ionisation, since equilibrium between a ψ-acid and its ions is established slowly relatively to that between the ions and the true acid. Since H exchange depends on H ionisation, comparison of rates of H exchange and of isomerisation provides a test for the above theory. The rate of isomerisation, *i.e.*, of enolisation, of a ψ-acidic ketone is measured by bromination or by racemisation, and the rate of H exchange by D uptake, all measurements being made in the same protium-free D solvent. *l*-COPh·CHMeEt, b.p. 64°/0·02 mm., with NaOD in 2 : 1 dioxan–D_2O at 35° shows equal rates of racemisation and of H exchange. From this and previous results it is concluded that bromination, racemisation, and H exchange of an enolisable ketone are all controlled by its ionisation. E. G. B.

Oximation of aldehydes and ketones. G. Vavon and P. Anziani [in part with P. Aubertein] (Bull. Soc. chim., 1937, [v], 4, 2026—2037).—Velocity (*v*) of oxime formation is a min. with equimol. amounts of NH_2OH,HCl and NaOH, except with phenolic aldehydes, which require excess of NaOH. Ratios of max. to min. *v* may be very great (600 for vanillin). Steric hindrance reduces *v*, *e.g.*, in substituted acetophenones. A mixture of NH_2OH,HCl and NH_2OH is a stable and effective reagent, permitting the prep. of *dimethylallyl*-, m.p. 126°, *methylethylallyl*-, m.p. 92° (98°?), *ethyldiallyl*-, m.p. 138°, and *diethylallyl-acetophenoneoxime*, m.p. 130°. Aldehydes with *o*-OH have much greater *v* than those with *m*- or *p*-OH; chelation is supposed. Oxime formation with terpene ketones is studied, and an improved prep. of fenchoneoxime, m.p. 164—165°, is described. E. W. W.

Chemical effects accompanying hydrogen bonding. I. Acyl derivatives of the 2-hydroxy-5-methylbenzophenoneoximes [phenyl 4-hydroxy-*m*-tolyl ketoximes]. A. H. Blatt (J. Amer. Chem. Soc., 1938, **60**, 205—210).—Differences in behaviour of *syn*- and *anti*-*o*-hydroxybenzophenoneoximes are ascribed to the presence or absence of OH·N linkings, because such differences are destroyed by acylation of the phenolic OH or by salt formation. In general H-linkings have less effect on chemical properties than have other linkings since the energy needed to break them is less. syn-*Ph* 4-*hydroxy*-m-*tolyl ketoxime benzoate* (I), m.p. 148—149°, is hydrolysed to the parent oxime by NaOH, rearranged to 1-phenyl-4-methylbenzoxazole (II) by Na_2CO_3, and converted by pyrolysis into 2-phenyl-4-methyl*iso*-benzoxazole. The corresponding anti-*oxime benzoate* (III), m.p. 174—175°, is hydrolysed to the *anti*-oxime by NaOH or Na_2CO_3, and pyrolysis gives (II) in very poor yield. These reactions resemble those of the acetates (A., 1936, 1511), except that the

(I.)  (IV.)

anti-oxime acetate gives a mixture of oxazole and *iso*-oxazole when pyrolysed; the latter product is considered to result from a change of configuration prior to pyrolysis. The *dibenzoate*, m.p. 147—148°, of the *syn*-oxime resembles the *anti*-monobenzoate in being hydrolysed without rearrangement by NaOH or Na_2CO_3; under mild conditions syn-*Ph* 4-*benzoyloxy*-m-*tolyl ketoxime* (*A*), m.p. 162—163°, is obtained. The *dibenzoate*, m.p. 132—133°, of the *anti*-oxime is unaffected by Na_2CO_3, but is hydrolysed by NaOH either to the oxime or to (III); formation of (III) proves the configuration (IV), since in the alternative (V) the BzO·N would be sterically protected from attack. Absence of H-bonding in (*A*) is shown by its giving 4 : 1 : 3-OBz·C_6H_3Me·NHBz and not the benzoxazole on Beckmann rearrangement.


(V.)

With AcCl at room temp. the *syn*-oxime gives (II); at the b.p. it gives the *syn*-acetate (free phenolic OH) or very slowly by rearrangement the anti-*diacetate*, m.p. 100°, which is obtained very readily (hot or cold) from the *anti*-oxime or its monoacetate, and is hydrolysed to the *anti*-oxime by acids or alkali. The oximes or their acetates all give 4 : 1 : 3-OAc·C_6H_3Me·NHBz when treated with Ac_2O–H_2SO_4. With $PhSO_2Cl$ in C_5H_5N or 20% aq. KOH the *anti*-oxime gives 4 : 1 : 3-OH·C_6H_3Me·CO·NHPh, but the *syn*-oxime affords (II) in C_5H_5N and the *iso*benzoxazole in 20% KOH, which shows the destruction of the H-linking by salt-formation. syn-*Ph* 4-*hydroxy*-m-*tolyl ketoxime* 2 : 4 : 6-*trimethylbenzoate* [structure as (I)], m.p. 108—109° or 149—150°, gives (II) with Na_2CO_3 or NaOH and the *iso*benzoxazole when pyrolysed. The anti-2 : 4 : 6-*trimethylbenzoate*, m.p. 176—177°, decomposes when pyrolysed, resists ordinary treatment with alkali, but furnishes (II) by long treatment with NaOH. Thus formation of (II) and hydrolysis occur by different mechanisms; the former is favoured by H-linkings and may be brought into prominence by preventing sterically the addition necessary for hydrolysis. R. S. C.

Substituted benzophenoneimines.—See B., 1938, 140.

Tautomerisation of an optically active azomethine. G. T. Borcherdt and H. Adkins (J. Amer. Chem. Soc., 1938, **60**, 3—6).—The rate of isomerisation of *l*-*p*-C_6H_4Cl·CPh:N·CHPhMe (I), $[\alpha]_{5873}^{28}$ −19·5°, $[\alpha]_{5461}^{26}$ −26·3° in EtOH, is determined (*a*) by decrease in α and (*b*) by hydrolysis of the mixture formed and determination of the resultant mixed ketones by the polarograph. The methods give identical results, $k_1 = 0{\cdot}00635$ hr.$^{-1}$, showing that the isomeric azomethines are in dynamic equilibrium

with each other. *p*-C_6H_4Cl·COPh, m.p. 75·5—76°, gives the dichloride, b.p. 139°/0·2 mm., which with *d*-CHPhMe·NH_2, $[\alpha]_{5873}^{25}$ +39·24°, gives (I). The *dl*-amine, b.p. 70°/10 mm., is prepared from CPhMe:N·OH by H_2–Raney Ni in EtOH at 125 atm. in 73% yield. R. S. C.

Union of aryl nuclei. II. Chloro-, bromo-, and nitro-fluorenones. I. M. Heilbron, D. H. Hey, and R. Wilkinson (J.C.S., 1938, 113—116).—Ring-closure of nuclear-substituted diphenyl-2-carboxylic acids provides a synthesis of the corresponding substituted fluorenones. Me diphenyl-2-carboxylates are prepared from diazotised *o*-NH_2·C_6H_4·CO_2Me (I) (or derivatives) and PhR (or C_6H_6). Use of PhR leads to a mixture of Me 2'- and 4'-substituted-diphenyl-2-carboxylates (cf. A., 1935, 78). Thus diazotised (I) with PhCl and PhBr gives respectively mixtures of Me 2'- and 4'-chloro- and 2'- and 4'-bromo-diphenyl-2-carboxylates; the mixed acids with conc. H_2SO_4 yield respectively mixtures of 4- and 2-chloro- and 4- and 2-bromo-fluorenones. Diazotised (I) gives no product with $PhNO_2$. The following are prepared from C_6H_6 and the appropriate NH_2·C_6H_3R·CO_2Me: 5-, m.p. 152° (*Me* ester, b.p. 180—190°/20 mm.), and 4-, m.p. 157°, *-chloro-*, 5-, m.p. 172° (*Me* ester, b.p. 185—195°/20 mm.), and 4-, m.p. 164°, *-bromo-*, and 4-*nitro-*, m.p. 173°, *-diphenyl-2-carboxylic acids*, yielding on ring-closure respectively 3-*chloro-*, m.p. 157°, 2-chloro- (II), m.p. 123°, 3-, m.p. 161°, and 2-, new m.p. 150°, -bromo-, and 2-nitro-, m.p. 219°, -fluorenones. (II) is also obtained by ring-closure of 4'-*chlorodiphenyl-2-carboxylic acid*, m.p. 161°, prepared by oxidation of 4'-*chloro-2-methyldiphenyl*, m.p. 288—290° (from diazotised *p*-C_6H_4Cl·NH_2 and PhMe). E. G. B.

Partial synthesis of the methyl*cyclo*pentenolone of wood tar. H. Gault and J. Burkhard (Compt. rend., 1937, **205**, 1416—1417; cf. Meyerfeld, A., 1912, i, 628).—2-Methyl*cyclo*pentanone is converted by gaseous Cl_2 or by Cl_2 in CCl_4 into 5 : 5-*dichloro-2-methyl*cyclo*pentanone* (or, possibly, the 4 : 5-Cl_2-isomeride), b.p. 90—95°/13 mm., hydrolysed by boiling H_2O to 3-methyl*cyclo*pentane-1 : 2-dione, m.p. 104° (phenylosazone, m.p. 136°), identical with the methyl*cyclo*pentenolone of Rojahn and Rühl. H. W.

Preparation of benzil from benzoin. E. V. Zmačinski and L. I. Malischevskaja (Compt. rend. Acad. Sci. U.R.S.S., 1937, **17**, 365—366).—Benzoin yields benzil (90%) and H_2S (96%) when heated with S at 230° for 1½ hr. A. Li.

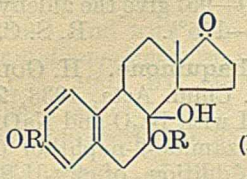
Reduction of benzil. I. A. Pearl and W. M. Dehn (J. Amer. Chem. Soc., 1938, **60**, 57—59).—Bz_2 [prep. in 90—95% yield from benzoin (I) by $CuSO_4$–NaOH] is reduced by KI–red P–HCl at 95° to deoxybenzoin (II) (70%) and β-deoxybenzoin pinacone (12%), by Zn–Hg–HCl at 15° to stilbene (85%) and CH_2Ph·CHPh·OH (10%), or (I) (90%), by Sn–Hg–HCl at 25° to (I) (96%) or at 75° to (II) (97%), by Al–Hg–HCl or Al–Hg–H_2O at 25° or by Mg–Hg–HCl at 5° to (I) (90%), by Al–HCl at 5° to (I) (90%) and *iso*didesyl (III) (5%), by Zn–NaOH at 100° to didesyl (30%), benzoin pinacone (IV) (10%), and (III) (6%), by Zn–aq. NH_3 at 95° to (II) (64%), by Zn–NH_4Cl at 25° to (I) (65—99%), and by Zn–H_3PO_4 at 100° to (IV) (10%). Zn–NaOH–EtOH gives 90% of OH·CPh_2·CO_2H, Zn–Hg–H_3PO_4 at <15° affords stilbene (55%) and *iso*stilbene (35%), whilst Al–Hg–aq. NH_3 yields hydrobenzoin (60%). Al–NaOH–EtOH, Zn–Hg–aq. NaOH, and Mg–Hg–H_2O are without effect. R. S. C.

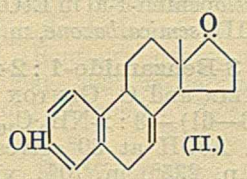
Reactions of maleic and dimethylmaleic anhydride with organo-metallic compounds. D. S. Tarbell (J. Amer. Chem. Soc., 1938, **60**, 215—216).—With 4 mols. of MgPhBr maleic anhydride gives COPh·CHPh·CH_2·COPh and a little COPh·CH_2·CHPh·CO_2H (I); with 1 mol. of MgPhBr some (I), but no COPh·CH:CH·CO_2H (II), is formed; thus 1 : 4-addition probably occurs. With the less reactive ZnPhCl, however, 26% of (II) is obtained. Dimethylmaleic anhydride, being also less reactive, with 1 mol. of MgPhBr gives β-benzoyl-α-methylcrotonic acid, dimorphic, m.p. 65—67° and 92—94°, and a little (?) β-*benzoyl-α-phenyl-α-methylbutyric acid* (III), m.p. 183—185°; with 2 mols. of MgPhBr it gives (III) and a *compound*, m.p. (? + solvent) 65—68°, 85—94°, or 90—93°, possibly stereoisomeric with (III). R. S. C.

Formation of acetoxy-β-diketones from bromo-α-diketones. A. H. Blatt (J. Washington Acad. Sci., 1938, **28**, 1—5).—Replacement of halogen in α-halogenoketones by addition to the CO group followed by C<O formation and ring opening (cf. A., 1929, 1072; 1933, 1297; 1937, II, 69) may involve shift of O from CO to an adjacent atom. A halogeno-α-diketone may then give a β-diketone. Thus COPh·CO·CHPhBr (I) with KOAc yields COPh·CH(OAc)·COPh (II) [presumably through COPh·C(OK)(OAc)·CHPhBr and COPh·C(OAc)<CHPh>O]. Similarly *p*-OMe·C_6H_4·CHBr·CO·COPh and *p*-OMe·C_6H_4·CO·CO·CHPhBr with KOAc both yield *α-benzoyl-α-*p*-anisoylmethyl acetate* (III), m.p. 70°. $CHBr(COPh)_2$, however, gives (II), not OAc·CHPh·CO·COPh, whilst *p*-OMe·C_6H_4·CO·CHBr·COPh gives (III), not *p*-OMe·C_6H_4·CH(OAc)·CO·COPh or *p*-OMe·C_6H_4·CO·CO·CHPh·OAc, suggesting that the oxide ring is not formed, but Br directly replaced. With *o*-$C_6H_4(NH_2)_2$, (I) gives 3-benzoyl-2-phenylquinoxaline, derived from $CO(COPh)_2$. With HI, there is no change of structure, (I) giving COPh·CO·CH_2Ph. With C_5H_5N, (I) gives a pyridinium salt, different from that formed by $CHBr(COPh)_2$, suggesting that the above rearrangements are not due to intermediate formation of COPh·CO·$CHPh^+$. E. W. W.

Equilin and its hydrogenation. A. Serini and W. Logemann [with, in part, Hohlweg] (Ber., 1938, **71**, [*B*], 186—191).—Addition of OsO_4 to equilin acetate in Et_2O and hydrolysis of the resultant ester gives the sec.-tert.-*glycol* [(I), R = H], m.p. 245°, which, with Ac_2O in cold C_5H_5N, gives the *diacetate* [(I), R = Ac], m.p. 215°, thus confirming the con-

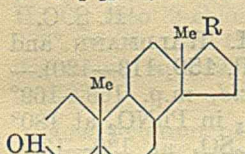
stitution (II) for equilin. Dihydroequilin is not hydrogenated (Raney Ni) in cold MeOH but becomes


(I.)


(II.)

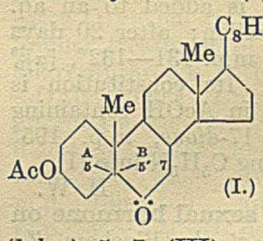
disproportionated to dihydroequilenin (III), m.p. 245°, and iso*œstradiol* (IV), $C_{18}H_{24}O_2$, m.p. 181°, $[\alpha]_D^{20}$ +18° in dioxan. If the temp. of the reaction is raised and the pressure of the H_2 diminished the formation of (III) is facilitated. In the reverse case the production of (III) can be suppressed but even then (IV) is not accompanied by œstradiol. (IV), BzCl, and cold 5% KOH give the corresponding *monobenzoate*, m.p. 190°, $[\alpha]_D^{20}$ +9·5° in dioxan, which is oxidised by CrO_3 in AcOH to iso*œstrone benzoate*, m.p. 196°, $[\alpha]_D^{20}$ +61° in dioxan, hydrolysed by N-MeOH–KOH to iso*œstrone*, $C_{18}H_{22}O_2$, m.p. 247°, $[\alpha]_D^{20}$ +94° in dioxan (*semicarbazone*, m.p. 270°). The œstrogenic activity of the *iso*-compounds is approx. one third of that of the corresponding œstrone compounds, and is roughly that of the equilin derivatives. Introduction of OH into ring II of equilin nullifies the œstrogenic activity. H. W.

Pregnan-3-ol-20-one. A. Butenandt and G. Müller (Ber., 1938, **71**, [*B*], 191—197).—If pregnanedione (I) is hydrogenated (PtO_2) in acid solution (Et_2O–AcOH) and the change is interrupted after the absorption of 2 H, the main product is n-*pregnan-3-ol-20-one* (II), m.p. 142—143°, $[\alpha]_D^{20}$ +101° in EtOH (*acetate*, m.p. 116·5°, $[\alpha]_D^{20}$ +86° in EtOH; *oxime*, m.p. 179°); the *digitonide*, m.p. 199—208°, requires 75% EtOH for its quant. separation. Hydrogenation (Pt-black) of (I) in neutral solution (Et_2O–EtOH) gives about 35% of (II) and epi*pregnan-3-ol-20-one* (III), m.p. 148—149°, $[\alpha]_D^{19}$ +114° in EtOH (*acetate*, m.p. 99°, $[\alpha]_D^{20}$ +123° in abs. EtOH; *oxime*, m.p. 224—226°), which does not give a ppt. with digitonin in 75% EtOH. (II) is converted by MgMeI in Et_2O into the corresponding *carbinol*, m.p. 168—171°, $[\alpha]_D^{20}$ +16° in EtOH, which loses H_2O when sublimed at 80°/high vac. and passes into the unsaturated *alcohol* (*A*) (R = :CMe_2), m.p. 141—142°, $[\alpha]_D^{20}$ +15° in EtOH; this is acetylated, ozonised in $CHCl_3$, and then converted into the acetate of ætiocholan-3-ol-17-one, isolated as the semicarbazone, m.p. 236—238° (the corresponding *oxime* has m.p. 188—189°). (II) is therefore (*A*) with R = Ac. Similarly, (III) and MgMeI give the corresponding *carbinol* (as *A*; R = ·CMe_2·OH), m.p. 190—201° (gradual decomp.), $[\alpha]_D^{20}$ +22° in EtOH, which is dehydrated by boiling AcOH–Ac_2O and then hydrolysed to the unsaturated *alcohol* (as *A*; R = :CMe_2), m.p. 164—165·5°, $[\alpha]_D^{20}$ +45° in EtOH, whence the known acetate of *epi*-ætiocholan-3-ol-17-one, thus establishing the structure of (III). Reduction of (II) with Na and $Pr^{\beta}OH$ gives a *n*-pregnanediol, m.p. 189—190·5°, $[\alpha]_D^{23}$ +44° in EtOH, which does not give a very sparingly sol. compound with digitonin and is possibly pregnane-3(β)-20(α)-diol (A., 1938, II, 12). The corresponding reduction of (III) leads essentially to the pregnanediol present in the urine of pregnancy. H. W.


(*A*.)

Preparation of *epiallo*pregnan-3-ol-20-one. G. Fleischer, B. Whitman, and E. Schwenk (J. Amer. Chem. Soc., 1938, **60**, 79).—*allo*Pregnanedione with H_2–PtO_2 in HBr–AcOH gives *allo-* (*acetate*, m.p. 144°, $[\alpha]_D^{22}$ +79·8° in EtOH) and *epiallo*-pregnan-3-ol-20-one, m.p. 176—178°, $[\alpha]_D$ +87·7° in EtOH (*acetate*, m.p. 141—142°, $[\alpha]_D^{22}$ +94·5° in EtOH). R. S. C.

Sterol group. XXXIV. Dibromination of 6-ketocholestanyl acetate. I. M. Heilbron, H. Jackson, E. R. H. Jones, and F. S. Spring (J.C.S., 1938, 102—107; cf. A., 1937, II, 344).—6-Ketocholestanyl acetate (I) has been dibrominated with the object of preparing steroid ketones containing unsaturated centres in rings A and B. (I) (prep. from cholesterol described) with Br (2 mols.) in Et_2O–AcOH at 0° gives the 5-Br-derivative (II) and in AcOH + a little HBr at room temp. (1 hr.), 5 : 7- (III), m.p. 152°, $[\alpha]_D^{20}$ −140° in $CHCl_3$, and (18 hr.) 5′ : 7- (IV), m.p. 129°, $[\alpha]_D^{20}$ −51·1° in $CHCl_3$, *-dibromo-6-ketocholestanyl acetates*. (II) with Br and HBr (≮1 mol. essential) in AcOH gives either (III) or (IV), whilst 7-bromo-6-ketocholestanyl acetate (V) gives only (III). With HBr in AcOH, (III) and (IV) revert to (V), so that (III) and (IV) are formed by simultaneous, not consecutive, reactions. Both with boiling C_5H_5N give 6-*keto*-3-*acetoxy*-$\Delta^{2:4}$-*cholestadiene*, m.p. 139—140°, $[\alpha]_D^{20}$ +27° in $CHCl_3$ [hydrolysed (MeOH–NaOMe) to 3 : 6-diketo-Δ^4-cholestene], and 7-*hydroxy*-6-*keto*-3-*acetoxy*-Δ^4-*cholestene*, m.p. 227—229° [*benzoate*, m.p. 136—137°; 3 : 7-(*OH*)$_2$-derivative, m.p. 220—222°]. (II), (III), and (V) do not react with C_5H_5N at room temp., whereas (IV) gives unidentified halogen-free mixtures. Similarly (II), (III), and (V) do not react with NaOAc in EtOH, whereas (IV) gives 6 : 7-diketocholestanyl acetate, 7-*bromo*-6-*keto*-3 : 5′-*diacetoxycholestane* (VI), m.p. 198° (decomp.), and 6-*keto*-3-*acetoxy*-7-*ethoxy*-Δ^4-*cholestene* (VII), m.p. 119—120°. (VI) is also obtained as sole product from (IV) and KOAc in EtOH, and with Al–Hg in moist Et_2O gives 6-keto-3 : 5′-diacetoxycholestane, m.p. 169—170°, hydrolysed to the corresponding 3 : 5′-(OH)$_2$-compound, m.p. 232°, different from the 3 : 5-dihydroxy-6-ketocholestane, m.p. 138°, obtained by hydrolysis of (II). (VII) with cold KOH–EtOH or hot MeOH–NaOMe gives 3-*hydroxy*-6-*keto*-7-*ethoxy*-Δ^4-*cholestene*, m.p. 113°. (IV) with KOAc in BuOH gives 6-*keto*-7-*methoxy*-$\Delta^{2:4:7}$-*cholestatriene*, m.p. 119—121°. E. G. B.


(I.)

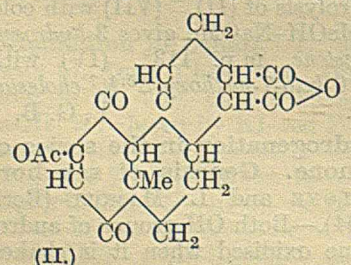
Biochemical dehydrogenation in the series of the testicular hormone. Genesis of sex hormones. A. Vercellone and L. Mamoli (Ber., 1938, **71**, [*B*], 152—154).—Both OH groups of androstene-3 : 17-diol become oxidised when it is shaken with O_2 in presence of impoverished yeast and PO_4 buffer at 32°; Δ^4-androstene-3 : 17-dione is formed. H. W.

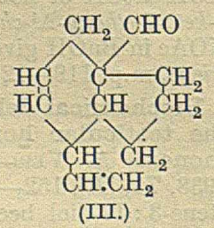
Biochemical transformation of dehydroandrosterone into androstenedione. Genesis of the testicular hormone. L. Mamoli and A. Vercellone (Ber., 1938, **71**, [*B*], 154—156).—Dehydroandrosterone (I) is smoothly dehydrogenated to Δ^4-androstenedione by impoverished yeast in an atm. of O_2, the yield being 70%. (I) is biochemically converted into Δ^4-testosterone in about 53—55% yield, which greatly exceeds that obtained with chemical reagents. Displacement of the double linking in androstenediol occurs during biochemical dehydrogenation. H. W.

Transformation of Δ^4-androstenedione into ætiocholane-3 : 17-dione by an enzymic extract of the testes of the stallion. A. Ercoli and L. Mamoli (Ber., 1938, **71**, [*B*], 156—158).—Finely divided Δ^4-androstenedione (I) is added to an aq. extract of the testes of the stallion; after 20 days at 37° *ætiocholane*-3 : 17-*dione*, m.p. 131—132°, $[\alpha]_D^{18}$ +113° in EtOH, is isolated. Its constitution is established by its bromination in AcOH containing HBr to 4-*bromoætiocholane*-3 : 17-*dione*, m.p. 195° (decomp.), which passes in boiling C_5H_5N into (I). H. W.

Increased activity of male sexual hormone on esterification. K. Miescher *et al.* (Biochem. Z., 1937, **294**, 39—60).—See A., 1938, III, 194. The following are described. *Androsterone* n-*butyrate*, m.p. 102—103°; *androstane*-3-cis-17-trans-*diol* 3-*propionate*, m.p. 120—121°, 3-n-*butyrate*, m.p. 124—125°, 3-*palmitate*, m.p. about 40°, 3 : 17-*dipropionate*, m.p. 121·5—122·5°; *dihydrotestosterone formate*, m.p. 141—142·5°, *propionate*, m.p. 121—121·7°, n-*butyrate*, *forms*, m.p. 90·5—91° and 100—101°, and n-*valerate*, m.p. 102·5—103°; *testosterone chloroformate*, m.p. 139—140·5°; *testosterone Me*, m.p. 140·5—141·5°, *Et*, m.p. 141—142°, *Pr*^{a}, m.p. 87—89°, *Bu*^{a}, an oil, *Ph*, m.p. 144·5—145·5°, *CH*$_2$*Ph*, m.p. 156·5—157°, and β-*diethylaminoethyl carbonate*, *hydrochloride* +0·5H_2O, m.p. 178—180°; *testosterone carbamate*, +0·5H_2O, m.p. 155—157°, N-n-*propylcarbamate*, m.p. 190—191°, *chloroacetate*, m.p. 123—124°, α-*bromopropionate*, m.p. 187—188°, α-*dimethylaminopropionate*, m.p. 83—85°, *phenylacetate*, m.p. 129—131° (corr.), and *crotonate*, m.p. about 158—159°.

Diene synthesis of polycyclic compounds, with or without angular substituents, from hexatriene. L. W. Butz (J. Amer. Chem. Soc., 1938, **60**, 216—217).—$\Delta^{\alpha\gamma\epsilon}$-Hexatriene (I) and 4-acetoxy-*p*-tolu-2 : 5-quinone in EtOH at 90—95° give 2-*acetoxy*-10-*methyl*-8-*vinyl*-5 : 8 : 9 : 10-*tetrahydronaphtha*-1 : 4-*quinone*, m.p. 192—195° after decomp. at 161—162°; the remainder of the reaction product with maleic anhydride in C_6H_6 at 150—160° gives 25% of the *substance* (II), decomp. 225°. (I) and *cyclo*penten-1-al in EtOH at 90—95° give the aldehyde (III) (*semicarbazone*, m.p. 173—175°). R. S. C.


(II.)


(III.)

3-Benzamido-1 : 2-naphthaquinone. H. Goldstein and G. Genton (Helv. Chim. Acta, 1938, **21**, 56—61).—3 : 2-NH_2·$C_{10}H_6$·OH with Bz_2O and NaOAc in AcOH at 80° gives 3-benzamido-2-naphthol (I), m.p. 235°, in 70% yield. Addition of 2N-H_2SO_4 to a solution of (I) in NaOH and $NaNO_2$ at 0° gives 1-*nitroso*-3-*benzamido*-2-*naphthol* (II), m.p. 202° (decomp.), which gives characteristically coloured lakes with $FeSO_4$, $FeCl_3$, $CoCl_2$, and $CuSO_4$. This is reduced by $SnCl_2$ and conc. HCl to 1-*amino*-3-*benzamido*-2-*naphthol* [*hydrochloride* (III); 1 : 3-*dibenzamido*-2-*naphthol*, m.p. 254°]. Oxidation of (III) with $FeCl_3$ in HCl affords 3-*benzamido*-1 : 2-*naphthaquinone* (IV), m.p. 199° (decomp.), the *oxime* of which is identical with (II). (IV) and *o*-$C_6H_4(NH_2)_2$,HCl yield 4-*benzamido*-1 : 2-*benzophenazine*, m.p. 220°. H at $C_{(4)}$ in (IV) is so mobile that (IV) is converted by HCl in AcOH into 4-*chloro*-3-*benzamido*-1 : 2-*dihydroxynaphthalene*, m.p. 160° (decomp.), oxidised by $FeCl_3$ to 4-*chloro*-3-*benzamido*-1 : 2-*naphthaquinone*, m.p. 175° (decomp.), whence 3-*chloro*-4-*benzamido*-1 : 2-*benzophenazine*, m.p. 276°. Passage of air through a solution of (IV) and NH_2Ph in EtOH at 70° gives 3-*benzamido*-4-*anilino*-1 : 2-*naphthaquinone*, m.p. 296—297°, converted by boiling glacial AcOH into 1 : 2-*diphenyl*-α-*naphthiminazole*-4 : 5-*quinone*, m.p. 312°, which with *o*-$C_6H_4(NH_2)_2$ affords the corresponding *phenazine*, m.p. 295°. M.p. are corr. H. W.

Method of ring-closure of 2-carboxydiaryl ketones. H. Waldmann (J. pr. Chem., 1938, [ii], **150**, 121—123).—Good yields of anthraquinones from *o*-CO_2H·C_6H_4·COAr by means of BzCl usually depend on the presence of acidic impurities, and addition of H_2SO_4 to the pure compounds often increases the yield. *o*-$C_6H_4(CO)_2O$ with (not without) a few drops of H_2SO_4 is an excellent reagent for ring-closure; examples are *o*-CO_2H·C_6H_4·COPh, 1-$C_{10}H_7$·CO·C_6H_4·CO_2H-*o*, 1 : 2-$C_{10}H_6Cl$·CO·C_6H_4·CO_2H-*o*, 2 : 3-$C_{10}H_6Bz$·CO_2H, 8-benzoyl-fluorene- and -fluorenone-1-carboxylic acid. R. S. C.

***lin*-Benzanthraquinones.** H. Waldmann and G. Polak (J. pr. Chem., 1938, [ii], **150**, 113—120).—o-1′-*Chloro*-2′-*naphthoylbenzoic acid*, m.p. 168—169° (*Me* ester, m.p. 101°), with P_2O_5 in $PhNO_2$ at 180° or (less satisfactorily) conc. H_2SO_4 at 130—135°, or its acid *chloride* (prep. from the 1′-OH-acid and PCl_5) alone or in $PhNO_2$ at about 210°, gives 1-chloro-2 : 3-benzanthraquinone, yellow, m.p. 261°, converted by NH_2Bz, $CuCl_2$, and NaOAc in $PhNO_2$ at 180° into the yellow vat dye, 1-*benzamido*-2 : 3-*benzanthraquinone*, m.p. 298°, by *p*-C_6H_4Me·SO_2·NH_2, K_2CO_3, and $Cu(OAc)_2$ in $PhNO_2$ at 210° into the 1-p-*toluenesulphonamido-quinone* (I), m.p. 231°, by NH_2Ph or *p*-C_6H_4Me·NH_2 and anhyd. NaOAc at 170—180° into the 1-*anilino*-, m.p. 244°, or 1-p-*toluidino-quinone*, m.p. 216°, respectively, and by Cu in $PhNO_2$ at 220—230° into 2 : 3 : 2′ : 3′-*dibenz*-1 : 1′-*dianthraquinonyl*, m.p. >350° (with Cu and cold H_2SO_4 gives 2 : 3 : 2′ : 3′-*dibenzhelianthrone*, m.p. >350°). With *p*-

$C_6H_4Me{\cdot}SO_3Me$ and K_2CO_3 in $C_6H_4Cl_2$ at 170—180° (I) gives 1-*methylamino*-2 : 3-*benzanthraquinone*, m.p. 209° (by way of the p-$C_6H_4Me{\cdot}SO_2{\cdot}$ derivative, m.p. 228·5°), and with conc. H_2SO_4 affords 1-*amino*-2 : 3-*benzanthraquinone*, m.p. 266° [Bentley's compound (J.C.S., 1907, **91**, 415), m.p. 290—292°, is impure], which affords (diazo-reaction) 1-*bromo*-2 : 3-*benzanthraquinone*, m.p. 235·5°. R. S. C.

Synthesis of hystazarin. H. Waldmann (J. pr. Chem., 1938, [ii], **150**, 99—106).—Gradual addition of *o*-$C_6H_4(CO)_2O$ and *o*-$C_6H_4(OH)_2$ to $AlCl_3$–NaCl at 110° and heating to 130—138° gives 3 : 4-*dihydroxybenzophenone*-2′-*carboxylic acid*, m.p. 207° (*Me* ester, m.p. 178°), converted by conc. H_2SO_4 at 100° into hystazarin (90%; diacetate, m.p. 210°; *dibenzoate*, m.p. 236°; *di*-p-*toluenesulphonate*, m.p. 204°) and alizarin (10%), separated by sublimation. 3 : 1 : 2-$C_6H_3Cl(CO)_2O$ gives similarly 3′- (or 6′-)*chloro*-3 : 4-*dihydroxybenzophenone*-2′-*carboxylic acid*, m.p. 187°, and thence 5-*chlorohystazarin* (90%), m.p. >300° (*diacetate*, m.p. 193°), and 5- (or 8-)chloroalizarin. 4 : 1 : 2-$C_6H_3Cl(CO)_2O$ gives 4′- (or 5′-)*chloro*-3 : 4-*dihydroxybenzophenone*-2′-*carboxylic acid*, m.p. 234°, and thence 6-*chlorohystazarin*, m.p. >310° (*diacetate*, m.p. 204·5°), and 6- (or 7-)chloroalizarin. 3 : 6 : 1 : 2-$C_6H_2Cl_2(CO)_2O$ gives 3′ : 6′-*dichloro*-3 : 4-*dihydroxybenzophenone*-2′-*carboxylic acid*, m.p. 205—206°, and thence about equal amounts of 5 : 8-*dichloro-hystazarin* (*diacetate*, m.p. 217°) and -*alizarin*, m.p. 257° (*diacetate*, m.p. 178°). R. S. C.

Nitration of hystazarin. H. Waldmann and E. Wider (J. pr. Chem., 1938, [ii], **150**, 107—112).—Hystazarin with 1 or 2 mols. of KNO_3 in H_2SO_4 gives the 1-NO_2-, m.p. 244°, or 1 : 4-$(NO_2)_2$-derivative, m.p. 224°, respectively. The Me_2 ether affords 1-*nitro*-2 : 3-*dimethoxyanthraquinone*, m.p. 233°. Reduction ($Na_2S_2O_4$) gives 1-*amino*- and 1 : 4-*diamino-hystazarin*, both m.p. >316°, and 1-*amino*-2 : 3-*dimethoxyanthraquinone*, m.p. 171·5°. The diamine with an excess of PhCHO and a little piperidine at 150° gives the *bisdiphenyloxazole*, m.p. >310°. *o*-$C_6H_4Cl{\cdot}OH$ and *o*-$C_6H_4(CO)_2O$ added to $AlCl_3$–NaCl at 130—150° give 3-chloro-4-hydroxybenzophenone-2′-carboxylic acid, m.p. 219°, converted by H_2SO_4 into 3-chloro-2-hydroxyanthraquinone, m.p. 266°, which gives the 1-NO_2-, m.p. 239°, and 1-NH_2-derivative, m.p. 231° (gives the *phenyloxazole*, m.p. >310°). R. S. C.

New product of the reaction between anthraquinone and alkali. N. N. Voroschcov, A. P. Alexandrov, and T. I. Berkova (Compt. rend. Acad. Sci. U.R.S.S., 1937, **17**, 361—363).—Aq. NaOH, Na_2SO_3, and anthraquinone in an autoclave at 210° (5—6 hr.) yield anthraquinol (44%), alizarin (2%), and 2 : 10-*dihydroxy*-9-*keto*-2 : 9-*dihydroanthracene* (I) (31%), m.p. 303—306° (decomp.). (I) heated alone yields 2-hydroxyanthraquinone but in benzenoid solvents gives dianthrone (identified by reduction and acetylation or methylation). (I) with Ac_2O + NaOH gives dianthrone and 2-acetoxyanthraquinone. A. Li.

Catalytic reduction and hydrogenation of hydroxyanthraquinones. K. Zahn and H. Koch (Ber., 1938, **71**, [*B*], 172—186).—Catalytic hydrogenation at >170°/20—80 atm. of 1-hydroxyanthraquinone (I) with a relatively small proportion of Ni–kieselguhr in PhCl gives exclusively 1-*hydroxy*-9-*anthrone* (II), m.p. 140—141° [whence 1 : 9-diacetoxyanthracene, m.p. 210—211° (lit. 148—149°)]. It appears that 1-hydroxyanthraquinol first results and this becomes transformed into 1-hydroxy-9 : 10-dihydroanthraquinol which spontaneously suffers transannelar loss of H_2O with formation of (II). Under similar conditions alizarin, chrysazin, and 1-hydroxy-4-methylanthraquinone afford respectively 1 : 2-dihydroxy-, m.p. 148—150°, 1 : 8-dihydroxy-, m.p. 177—179°, and 1-*hydroxy*-4-*methyl*-, m.p. 167—168°, -9-anthrone. 4-*Hydroxy*-1-*methyl*-9-*anthrone*, m.p. 223—225°, is obtained by reducing 1-acetoxy-4-methylanthraquinone with $Na_2S_2O_4$ at 65°. In all cases O vicinal to an α-OH is retained in the mol. Similar treatment of the corresponding ethers gives alkoxyanthrones with loss of O in *peri* position to α-OAlk. Thus 1-methoxyanthraquinone in PhCl affords 4-methoxy-9-anthrone, m.p. 142—143°, whence 9-*acetoxy*-4-*methoxyanthracene*, m.p. 130—132°. Alizarin Me_2 ether gives 3 : 4-dimethoxy-9-anthrone, m.p. 148—156°, and 4 : 5-dimethoxy-9-anthrone, m.p. 234—236° (*Ac* derivative, m.p. 216°), is obtained from chrysazin Me_2 ether. Quinizarin Me_2 ether (III) yields 1 : 4-*dimethoxy*-9-*anthrone*, m.p. 140—141° (whence 9-*acetoxy*-1 : 4-*dimethoxyanthracene*, m.p. 125—126°), also obtained by action of conc. H_2SO_4 at 15° on 2 : 5-dimethoxydiphenylmethane-2′-carboxylic acid, and transformed by $FeCl_3$ in hot AcOH into tetramethoxydianthrone, m.p. 248°. Catalytic hydrogenation of (I) in PhCl at 80—120°/70—50 atm. in presence of a larger proportion of Ni leads to 9 : 10-*dihydroxy*-1-*keto*-1 : 2 : 3 : 4-*tetrahydroanthracene* (IV), m.p. 170—171°, dehydrogenated to (I) when its alkaline solution is exposed to air. When cautiously treated with Ac_2O and KOAc at 60° it gives 9-*hydroxy*-1-*keto*-10-*acetoxy*- (V), m.p. 149—150°, and when more drastically treated it affords 1-*keto*-9 : 10-*diacetoxy*- (VI), m.p. 215—216°, -1 : 2 : 3 : 4-*tetrahydroanthracene*. Under extreme conditions 1 : 9 : 10-*triacetoxy*-3 : 4-*dihydroanthracene* (VII), m.p. 169—170°, results; its constitution follows from its alkaline hydrolysis and dehydrogenation to (I) and from the quantitative formation of a *dibromide*, decomp. 248—250°. Methylation of (IV) by cold NaOH and Me_2SO_4 affords 9-*hydroxy*-1-*keto*-10-*methoxy*-, m.p. 94° (*acetate*, m.p. 128—129°), whereas *p*-$C_6H_4Me{\cdot}SO_3Me$ and Na_2CO_3 in PhCl give 1-*keto*-9 : 10-*dimethoxy*-, m.p. 116—117°, -1 : 2 : 3 : 4-*tetrahydroanthracene*. Oxidation of (IV) with $Pb(OAc)_4$ in AcOH gives 1-*keto*-1 : 2 : 3 : 4-*tetrahydroanthraquinone*, m.p. 148—150°, isomerised when cautiously warmed in HCl containing C_5H_5N to 1-*hydroxy*-2 : 3-*dihydroanthraquinone*, which blackens when heated but melts if brought into a bath at 200°. 1 : 1-*Diacetoxy*-1 : 2 : 3 : 4-*tetrahydroanthraquinone* has m.p. 175—176°. (V) and $NHPh{\cdot}NH_2$ in boiling EtOH give the 1-*phenylhydrazone*, decomp. 234°, also obtained from (VI) or (VII), converted by alkaline hydrolysis in presence of air into 1-*benzeneazoanthraquinone*, m.p. 164°, reduced ($Na_2S_2O_4$) to 1-aminoanthraquinone. (IV) and NH_2Et in boiling aq. EtOH give 1-

ethylimino-9 : 10-*dihydroxy*-1 : 2 : 3 : 4-*tetrahydroanthracene*, m.p. 198—199° (10-*Ac* derivative, m.p. 159—160°) (converted by alkali and air into 1-*ethylaminoanthraquinone*, m.p. 124—125°), transformed by prolonged treatment with Ac_2O–C_5H_5N into 1-*acetethylamido*-9 : 10-*diacetoxy*-3 : 4-*dihydroanthracene*, m.p. 218—220°, which is similarly hydrolysed to 1-*acetethylamidoanthraquinone*, m.p. 153—154°. (IV), *p*-$C_6H_4Me{\cdot}NH_2$, and H_3BO_3 at 130—140° give a product, m.p. 290° (red at 200°), dehydrogenated in 50% MeOH containing a little alkali to 1-p-*toluidinoanthraquinone*, m.p. 156—157°. Exhaustive hydrogenation of (IV) at 120—130°/80—60 atm. in BuOH containing Ni leads to 9 : 10-*dihydroxy*-1-*keto*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydroanthracene* (VIII), m.p. 236—237° (*Ac*, m.p. 140°, and Ac_2, m.p. 215—216°, derivatives; *phenylhydrazone*, m.p. 181—183°), oxidised by $Pb(OAc)_4$ in AcOH to 1-*keto*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydroanthraquinone*, m.p. 150—152°. (II) is reduced [Ni in BuOH at 120—130° or red P and boiling HI (*d* 1·9)] to 9-*hydroxy*-1-*keto*-1 : 2 : 3 : 4-*tetrahydroanthracene*, m.p. 99° (Br_1-derivative, m.p. 138—139°), whence 1 : 9-diacetoxy-3 : 4-dihydroanthracene, m.p. 189—190°. Exhaustive hydrogenation of (II) in BuOH at 120—130°/70—50 atm. leads to a mixture of 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydroanthranol (Bz derivative, m.p. 127—128°) and its 1-keto-derivative (*phenylhydrazone*, m.p. 174—175°). Hydrogenation of quinizarin and its diacyl derivatives without loss of O has not been found possible. Treatment of (III) in PhCl with Ni and H_2 at 80—120°/60—40 atm. gives 1 : 4-*dimethoxy*-2 : 3 : 5 : 6 : 7 : 8-*hexahydroanthraquinone* (IX), m.p. 156°, whence 9 : 10-*diacetoxy*-1 : 4-*dimethoxy*-5 : 6 : 7 : 8-*tetrahydroanthracene*, m.p. 220—222°. 1 : 4-*Diethoxy*-2 : 3 : 5 : 6 : 7 : 8-*hexahydroanthraquinone*, m.p. 142—143°, similarly prepared, yields 9 : 10-*diacetoxy*-1 : 4-*diethoxy*-5 : 6 : 7 : 8-*tetrahydroanthracene*, m.p. 187—188°. Dehydrogenation of (IX) by $FeCl_3$ in hot AcOH gives 1 : 4-*dimethoxy*-5 : 6 : 7 : 8-*tetrahydroanthraquinone*, m.p. 153°; the corresponding *diethoxy*-compound has m.p. 129—131°. Hydrolysis of (IX) with H_2SO_4 affords 9 : 10-*dihydroxy*-1 : 4-*diketo*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydroanthracene* (X), m.p. 169—170° (1 : 4-*bisphenylhydrazone*, m.p. 235°), oxidised by $Pb(OAc)_4$ in AcOH to 1 : 4-*diketo*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydroanthraquinone*, m.p. (indef.) 155° [whence diacetyl-5 : 6 : 7 : 8-tetrahydroquinizarin (XI), m.p. 205—206°]. Enolising acetylation of (X) gives 1 : 4 : 9 : 10-*tetraacetoxy*-5 : 6 : 7 : 8-*tetrahydroanthracene*, m.p. 222—223°, also obtained from (XI) by reduction ($Na_2S_2O_4$, dil. AcOH) and subsequent acetylation. H. W.

Substituted anthraquinones.—See B., 1938, 140.

β-Phellandrene. A. K. Macbeth, G. E. Smith, and T. F. West (J.C.S., 1938, 119—123).—The α-nitrosite (I) of *l*-β-phellandrene from Canada balsam has m.p. 101—102°, $[\alpha]_D$ +165·3° in $CHCl_3$, and the α-nitrosite (II) of *d*-β-phellandrene from water-fennel oil has m.p. 102—103°, $[\alpha]_D$ −165·7° in $CHCl_3$; these vals. are very close to those of α-phellandrene derivatives. The mutarotation of β-phellandrene α-nitrosite proceeds slowly and [α] does not fall to half the initial val. With NaOH, the nitrosite gives nitrophellandrene, reduced to cuminal; (I) yields a nitrophellandrene, $[\alpha]_D$ −78·8°, and (II) affords the compound, $[\alpha]_D$ +107·5° in EtOH. Oxidation of (I) and (II) leads, according to conditions, to phellandrol or 4-*iso*propyl-Δ^2-*cyclo*hexene-1-one. The absorption spectrum of β-phellandrene in C_6H_{12} shows a max. at 2312 A. with log ε 3·96. F. R. S.

Catalytic oxidation of camphene. B. N. Rutovski and A. D. Belogolovov (Prom. Org. Chim., 1937, **4**, 673—676).—Camphene (I)–air–steam mixtures are passed over a Cr_2O_3–SnO_2 catalyst at 150° and 350°. The (I) is recovered unchanged, except for about 5% oxidised to CO_2. Identical results were obtained in presence of AcOH, or with bornyl acetate in place of (I). Borneol or *iso*borneol gives camphor, in 71 and 48% yield, respectively. R. T.

Dialkyl-α-camphoramic acids. P. Goissedet and R. Despois (Compt. rend., 1937, **205**, 1239—1241).—Me *cis*-*d*-camphorate with $NHEt_2$ at 190—200° under pressure affords a neutral product, camphoric acid, and diethyl-α- and -β-camphoramic acid. *d*-*cis*-Camphoryl chloride (1 mol.) with $NHMe_2$ (4 mols.) in C_6H_6 at 5° affords *dimethyl*-α-d-cis-*camphoramdimethylamide*, m.p. 91°. The following are prepared similarly: *methylethyl*-α-d-cis-*camphoramethylmethyl*-, m.p. 61°, *diethyl*-α-d-cis-*camphoramdiethyl*-, m.p. 130° (also from *l*-*cis*-camphoryl chloride), *dibutyl*-α-d-cis-*camphoramdibutyl*-, b.p. 222°/1 mm., and *di*iso*amyl*-α-d-cis-*camphoramdi*iso*amyl*-, b.p. 232°/1·5 mm., and *diethyl*-l-trans-*camphoramdiethyl-amide*, m.p. 80°. Dialkyl-α-camphoramic acids (cf. A., 1908, i, 860) with $SOCl_2$ afford acid chlorides which react with primary and secondary amines to give the tetra-alkyldiamides. The following are prepared: *methylethyl*-α-d-cis-*camphoram-dimethyl*-, m.p. 74°, and *-diethyl*-, b.p. 182°/2 mm., *dimethyl*-α-d-cis-*camphoram-methylethyl*-, m.p. 54—55°, and *-diethyl*-, m.p. 41—42°, *diethyl*-α-d-cis-*camphoram-dimethyl*-, m.p. 56°, *-methylethyl*-, m.p. 86°, *-methyl*-, m.p. 117°, and *-ethylamide*, b.p. 185°/2·5 mm. J. L. D.

Bornyl esters of oxalic and tartaric acid. E. B. Abbot, A. McKenzie, and J. O. McB. Ross (Ber., 1938, **71**, [*B*], 16—27).—Treatment of anhyd. $H_2C_2O_4$ with (−)-borneol (I) and HCl at 100° gives *di*-(−)-*bornyl oxalate* (II), m.p. 106·5°, $[\alpha]_D^{20}$ −59·1° in $CHCl_3$, also obtained from (I) and $(COCl)_2$ in C_5H_5N at room temp. *Di*(+)-*bornyl oxalate* (III), obtained similarly by the esterification method, has m.p. 106·5°, $[\alpha]_D^{20}$ +58·8° in $CHCl_3$. When mixed with an equal wt. of (II) it gives *di*-dl-*bornyl oxalate* (IV), m.p. 107·5°, also obtained from $H_2C_2O_4$ and *dl*-borneol in presence of HCl. This is shown by Roozeboom's method not to be a *dl*-conglomerate. All mixtures of (II) and (III) melt sharply at the same temp. so that an unbroken series of mixed crystals exists. As by-product of the prep. of (II) a liquid, sol. in alkali, is obtained which sooner or later solidifies and then consists of a mixture of (II) and $H_2C_2O_4$. Partial hydrolysis of (II) also gives a liquid which, when distilled under diminished pressure, affords CO_2 and (−)-bornyl formate, b.p. 65—67° 1 mm., $[\alpha]_{5461}^{20}$ −54·1° in EtOH. The isolation of (+)-bornyl (−)-bornyl oxalate could not be achieved. Treatment of the freshly prepared liquid derived from the

semi-hydrolysis of (III) with (I) yielded (IV) as sole isolable product.

(+)-Tartaric acid is converted by (+)-borneol and HCl into *di*-(+)-*bornyl* (+)-*tartrate* (V), m.p. 117·5—118·5°, $[\alpha]_D^{15·5}$ +71·4°, $[\alpha]_{5461}^{20}$ +81·8° in $CHCl_3$. *Di*-(−)-*bornyl* (+)-*tartrate* (VI) has m.p. 132·5—133·5°, $[\alpha]_D^{17}$ −6·2° in $COMe_2$, $[\alpha]_{5461}^{20}$ −8·1° in $CHCl_3$. Admixture of (V) and (VI) in equal amounts in $COMe_2$ and removal of the solvent gives a residue with m.p. 95—105°, $[\alpha]_{5461}^{20}$ +36·5° in $CHCl_3$; it gives homogeneous (VI) when repeatedly cryst. from aq. EtOH and is regarded provisionally as *di*-dl-*bornyl* (+)-*tartrate*. The m.p. curve of mixtures of (V) and (VI) is generally of the conglomerate type but mixtures with 30—45% of (VI) melt sharply at 100° and show that the components form mixed crystals within these limits. Partial hydrolysis of the requisite esters affords (+)-*bornyl H* (+)-*tartrate* (VII), m.p. 130·5—131·5°, $[\alpha]_D^{9}$ +51·8°, $[\alpha]_{5461}^{9}$ +58·9° in EtOH, and (−)-bornyl H (+)-tartrate (VIII), m.p. 157·5—158·5°, $[\alpha]_D^{16}$ −6·5°, $[\alpha]_{5461}^{20}$ −8·3° in EtOH. Equal quantities of (VII) and (VIII) yield dl-*bornyl H* (+)-*tartrate*, m.p. 140—145°, $[\alpha]_{5461}^{20}$ +25·3° in EtOH, which is partly resolved by a single crystallisation from $CHCl_3$. The diastereoisomeric esters form a continuous series of mixed crystals. The action of (+)-borneol on (VIII) leads to a mixture of esters, m.p. 90—100°, $[\alpha]_{5461}^{20}$ +46·2° in $CHCl_3$, which crystallises unchanged from aq. EtOH. Small amounts of (VI) are isolated from the products of the interaction of (I) with (VII). (+)-Diacetyltartaric anhydride and (I) at 100° afford the glassy (−)-*bornyl H* (+)-*diacetyltartrate*, $[\alpha]_D^{13}$ −12·3°, $[\alpha]_{5461}^{20}$ −15·1° in EtOH. H. W.

Menthyl and bornyl malonate. E. B. Abbot, E. W. Christie, and A. McKenzie (Ber., 1938, **71**, [*B*], 9—15; cf. A., 1934, 777).—Esterification of $CH_2(CO_2H)_2$ by (+)-menthol at 100° gives *di*-(+)-*menthyl malonate* (I), m.p. 59—60°, $[\alpha]_D^{20}$ +80·2° in $CHCl_3$, transformed by partial hydrolysis into (+)-*menthyl H malonate*, m.p. 57—58°, $[\alpha]_D^{18·5}$ +70·6° in $CHCl_3$. Equal wts. of (I) and di-(−)-menthyl malonate in $COMe_2$ afford, after removal of the solvent, r-*dimenthyl malonate*, m.p. 54·5—55·5°, also obtained by esterifying $CH_2(CO_2H)_2$ with *dl*-menthol, but (+)-menthyl (−)-menthyl malonate could not be obtained. Esterification of $CH_2(CO_2H)_2$ by (−)-borneol and HCl at 100° yields *dl*-(−)-*bornyl malonate* (II), b.p. 219—220°/6 mm., m.p. 31°, $[\alpha]_D^{20}$ −41·9°, $[\alpha]_{5461}^{20}$ −49·6° in $COMe_2$, and (−)-*bornyl H malonate* (III), m.p. 65—66°, $[\alpha]_D^{20}$ −36·8°, $[\alpha]_{5461}^{20}$ −43·3° in $CHCl_3$, also obtained by partial hydrolysis of (II). *Di*-(+)-*bornyl malonate* (IV), b.p. 217—218°/6 mm., $[\alpha]_D^{20}$ +41·3°, $[\alpha]_{5461}^{20}$ +49·3° in $COMe_2$, and (+)-*bornyl H malonate* (V), m.p. 65—66°, $[\alpha]_D^{20}$ +36·2°, $[\alpha]_{5461}^{20}$ +43·2° in $CHCl_3$, are described. Equal amounts of (II) and (IV) lead to r-*dibornyl malonate*, b.p. 217—218°/6 mm., which after being seeded with (II) solidifies to a form, m.p. 36°, which passes into a second *variety*, m.p. 46°, when cryst. from aq. MeOH. Equal amounts of (III) and (IV) give dl-*bornyl H malonate*, m.p. 70—71°. The m.p. curve shows the existence of a continuous series of mixed crystals which exhibits a temp. max. at equimol. concns. of the components. The formation of a true racemic compound is not, however, completely excluded by such a graph since a racemate can give mixed crystals with each antimeride. Treatment of (III) with *d*-borneol or of (V) with *l*-borneol in absence of a catalyst gives a normal ester of m.p. about 51—53°, so that (+)-*bornyl* (−)-*bornyl malonate* appears to have been produced, but the products are invariably optically active so that in consequence of the formation of mixed crystals it appears impossible to obtain the product completely free from isomerides. The product of the action of *dl*-borneol on $CH_2(CO_2H)_2$ in presence of HCl or on $CH_2(COCl)_2$ is a mixture, b.p. 219—221°/6 mm., m.p. 40—44°, which could not be separated into its components. The asymmetric synthesis of $OH·CHPh·CH_2·CO_2H$ is effected by condensing (−)-menthyl H malonate with PhCHO in C_5H_5N followed by hydrolysis; the crude material has $[\alpha]_D^{19}$ −4° in EtOH and contains $CHPh{:}CH·CO_2H$, whilst $[\alpha]_D$ −18·9° is recorded for the homogeneous acid. H. W.

Constitution of caryophyllene. H. N. Rydon (Chem. and Ind., 1938, 123—125).—Two alternative formulæ are suggested and used for discussing the behaviour of caryophyllene: $CR_2{-}CH·CH_2{-}\!-\!-\!-CMe{:}CH$ / $CR'_2·CH·CH(CMe{:}CH_2)·CH_2$ with R = Me, R′ = H, or R = H, R′ = Me. F. R. S.

Architecture of the polyterpenes. L. Ruzicka (Angew. Chem., 1938, **51**, 5—11).—A review of the development of the knowledge of sesquiterpenes, diterpenes, pentacyclic triterpenes, and of biologically important natural products of unknown constitution due to the adoption of the isoprene hypothesis and application of new methods of dehydrogenation. H. W.

Synthesis of polyterpenoid compounds. IV. J. W. Cook and C. A. Lawrence (J.C.S., 1938, 58—63).—4-Methoxy*cyclo*hexanone, $Et_2C_2O_4$, and Na give *Et* 4-*methoxy*cyclo*hexanone*-2-*glyoxylate*, b.p. 116°/0·4 mm. [*Cu*^{II} compound, m.p. 161—163° (decomp.); *bis*-2 : 4-*dinitrophenylhydrazone*, m.p. 224—227° (decomp.)], which when heated affords *Et* 4-*methoxy*cyclo*hexanone*-2-*carboxylate*, b.p. 131—133°/10 mm. [2 : 4-*dinitrophenylhydrazone*, m.p. 129—131° (decomp.)], in 25% yield. This keto-compound (Na derivative) and γ-iodobutyronitrile afford *Et* 4-*methoxy*-2-γ-*cyanopropyl*cyclo*hexanone*-2-*carboxylate*, b.p. 155°/0·2 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 123—126°), hydrolysed to γ-(2-*keto*-5-*methoxy*cyclo*hexyl*)*butyric acid* (I), b.p. about 185°/1 mm. (*semicarbazone*, m.p. 178—178·5°), in 25% yield, and the *anhydride* of a γ-2-keto*cyclo*hexenylbutyric acid, b.p. 251—260°/0·4 mm. This anhydride is hydrolysed to an acid (*semicarbazone*, m.p. 219—220·5°) and isomerised by $Ba(OH)_2$ to an acid [*semicarbazone*, m.p. 213·5—215° (decomp.)]. The ester of (I) and MgMeI give γ-(5-methoxy-2-methyl-Δ^1-*cyclo*hexenyl)butyric acid, cyclised with loss of MeOH to 1-keto-9-methylhexahydronaphthalene (?), b.p. 150°/30 mm. [2 : 4-*dinitrophenylhydrazone*, m.p. 224° (decomp.); *semicarbazone*, m.p. 214—216° (decomp.)], and not the required 6-OMe-compound.

1-Ethinyl*cyclo*hexanol (p-*nitrobenzoate*, m.p. 64—64·5°; 3 : 5-*dinitrobenzoate*, m.p. 104·5—106°) is reduced (Pd–H_2) to 1-*vinyl*cyclo*hexanol*, b.p. 67—68°/

10 mm. (p-*nitrobenzoate*, m.p. 101—102°; 3 : 5-*dinitrobenzoate*, m.p. 122—123°), which with $KHSO_4$ gives 1-*vinyl*-Δ^1-cyclo*hexene*, b.p. 145°. 1-Ethylcyclohexanol yields a p-*nitrobenzoate*, m.p. 73—74°, and a 3 : 5-*dinitrobenzoate*, m.p. 127—127·5°. The hexene and maleic anhydride afford $\Delta^{4:10}$-*octahydronaphthalene*-1 : 2-*dicarboxylic anhydride*, m.p. 52—53°, of which the *acid*, m.p. 131—132·5° (*diphenacyl* ester, m.p. 139·5—140·5°), is isomerised (NaOH) to a *lactonic acid*, m.p. 176—176·5° (*phenacyl* ester, m.p. 131—131·5°). The hexene and *p*-benzoquinone in MeOH yield 1 : 4-*diketodecahydrophenanthrene*, m.p. 84—85·5°, and in tetralin form 9 : 10-*diketo-octadecahydro*-1 : 2 : 5 : 6-*dibenzanthracene*, m.p. 200—203° (decomp.). A similar series of reactions gives 2-*methyl*-1-*ethinyl*cyclo*hexanol*, b.p. 83—84°/21 mm. (p-*nitrobenzoate*, m.p. 135—136°; 3 : 5-*dinitrobenzoate*, m.p. 76·5—79°); 2-*methyl*-1-*vinyl*cyclo*hexanol*, b.p. 86·5—90°/30 mm. (p-*nitrobenzoate*, m.p. 71—72°; 3 : 5-*dinitrobenzoate*, m.p. 120—120·5°); 2-*methyl*-1-*ethyl*cyclo*hexanol*, b.p. 81—84°/23 mm. (3 : 5-*dinitrobenzoate*, m.p. 105·5—107·5°); 1-*methyl*-2-*vinyl*-Δ^1-cyclo*hexene*, b.p. 156—157°; and 9-methyl-$\Delta^{4:10}$-octahydronaphthalene-1 : 2-dicarboxylic anhydride, m.p. 114—114·5°, and its acid, m.p. 179—181° (cf. Meggy *et al.*, A., 1937, II, 456). F. R. S.

Constitution of insulin. III. Acetylation of insulin by keten. K. G. Stern and A. White (J. Biol. Chem., 1938, **122**, 371—379).—The activity of insulin is dependent on its phenolic OH- but not on its NH_2-groups. With $CH_2{:}CO$ in a p_H 5·7 M-acetate buffer, best in a dialysis thimble, it gives first (in 5 min. at room temp.) a *polyacetylinsulin* in which all the NH_2 but none of the OH are acetylated; this has approx. the same physiological activity as insulin. Further treatment (complete after 30 hr.) acetylates the tyrosine OH-groups, giving a series of *polyacetylinsulins* of which the activity, greatly diminished, can be partly regenerated by dil. alkali. E. W. W.

Lignin.—See A., III, 251.

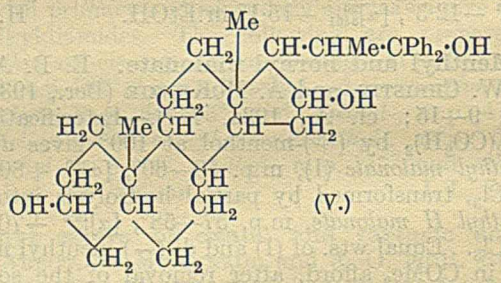
Derivatives of ψ-bufotalin.—See B., 1938, 226.

Constituents of *Ceanothus Americanus*. I. Ceanothic acid. P. J. Julian, J. Pikl, and R. Dawson (J. Amer. Chem. Soc., 1938, **60**, 77—79).—The root bark yields bitter, non-phenolic *ceanothic acid*, $OH{\cdot}C_{27}H_{41}(CO_2H)_2$, dimorphic, m.p. 354° and 359° (*Ba* salt), which with CH_2N_2, but not with HCl–MeOH, affords a Me_2 ester, m.p. 223° (*Ac* derivative, m.p. 157°, hydrolysed by acid to the ester), and, when heated above the m.p., loses H_2O and CO_2 to give a *lactone*, $C_{28}H_{42}O_2$, m.p. 234°. The acid thus contains a γ-OH. It has no hæmostatic action. R. S. C.

Rottlerin. H. Brockmann and K. Maier (Naturwiss., 1938, **26**, 14—15).—The yellow transformation product, m.p. 139—140° (higher-melting form 181—183°), obtained by boiling rottlerin with EtOH, PhMe, or AcOH gives BzOH on oxidation. On thermal decomp. it, like rottlerin itself, yields methylphloracetophenone. Catalytic reduction (2 H) gives a *product*, m.p. 210—211°. Rottlerin with CH_2N_2 gives a Me_2 derivative, m.p. 245—247°, catalytically reduced to *tetrahydrorottlerin* Me_2 *ether*, m.p. 192—193°, also obtained by methylating tetrahydrorottlerin (cf. A., 1938, II, 66). W. O. K.

Action of nitrous acid on the methyl ether of rottlerin. K. S. Narang, J. N. Ray, and B. S. Roy (Chem. and Ind., 1938, 134).—The Me ether of rottlerin with $NaNO_2$–AcOH gives a substance, m.p. 207° (decomp.). As this substance is best represented as $C_{36}H_{40}O_{11}N_2$, rottlerin is probably $C_{31}H_{30}O_8$ (cf. A., 1937, II, 66) and the ether is $(OMe)_5$; the $(OAc)_5$-derivative has m.p. 214°. F. R. S.

Sarsasapogenin. I. Investigation of the side-chain. L. F. Fieser and R. P. Jacobsen (J. Amer. Chem. Soc., 1938, **60**, 28—33).—The prep. of sarsasapogenin and sarsasapogenone (I) is modified. Sarsasapogenin acetate (II) and acid give up to 17% of the ketone, $C_8H_{14}O_3$, but other products are indefinite; HCl–AcOH and (I) give 26% of the ketone, and HBr–$CHCl_3$ at 100° gives iso*sarsasapogenone*, m.p. 182—185° [*oxime*, m.p. 176—179° (decomp.)], also degraded to the ketone by acid. This degradation is probably a mixture of cleavage and isomerisation. With relatively little CrO_3 (II) gives the lactone acetate (III), m.p. 184·5—185·5°, of Farmer and Kon (A., 1937, II, 203; the hydrolysis and conversion into the deoxylactone is confirmed) and *sarsasapogenoic acid* (IV), $C_{27}H_{42}O_5$, m.p. 190—191° [*acetate*, m.p. 155·5—156·5°; *Me* ester, m.p. 130—131° (*benzoate*, dimorphic, m.p. 128·8—129·3° and 125·5—126·5°)]. With MgPhBr in PhMe (III) gives the *diphenylcarbinol* (V), m.p. 162—164° (*acetate*, m.p. 192·5—193·5°). With hot NaOH–aq. MeOH (IV) gives

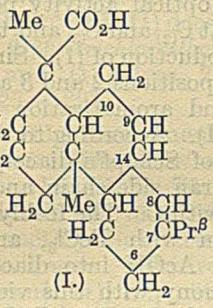


(V.)

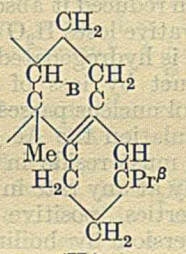
anhydrosarsasapogenoic acid, $C_{27}H_{40}O_4$, m.p. 244—246° (decomp.; sinters from 239°) (*Me* ester *acetate*, m.p. 147—148°), which gives cryst. oxidation and reduction products and reduces $KMnO_4$. Tschesche and Hagedorn's acid, m.p. 221—222° (A., 1935, 1126), isomeric with (IV) and now called tigogenoic acid, differs from (IV) only in the configuration at $C_{(5)}$. Hydrogenation of (IV) gives an *acid*, $C_{27}H_{42}O_4$, m.p. 174—180°, and NH_2OH–EtOH at 135° gives a *compound*, $C_{27}H_{44}O_5N_2$, m.p. 247° (decomp.). R. S. C.

Dehydroabietic acid and the structure of pine resin acids. L. F. Fieser and W. P. Campbell (J. Amer. Chem. Soc., 1938, **60**, 159—170).—The coupling of p-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ with 27 unsaturated compounds is reported. Doubly unsaturated, conjugated compounds couple, whether or not the ethylenic linkings are in one ring; lack of conjugation prevents coupling. The presence of CO introduces anomalies. Abietic acid (I) couples to give the *azo*-compound, m.p. 154—158° (decomp.); this and the absorption spectrum prove conjugation. By analogy

with sterol derivatives the absorption max. at 2725 A. and the abnormal reaction with maleic anhydride indicate that the ethylenic linkings are in different rings. Positions 9 : 10 and 8 : 14 are excluded by the failure of (I) to lactonise. Position 7 : 8 is indicated by isolation of $Pr^{\beta}CO_2H$ from the $KMnO_4$-oxidation products of pure (I), m.p. 168—172°, $[\alpha]_D$ −92°. Therefore, the following formula is adopted for (I).

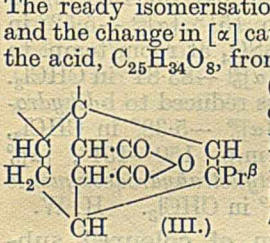


(I.)



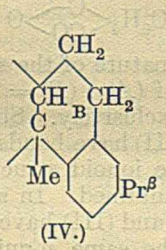
(II.)

The ready isomerisation of *l*-pimaric acid (II) to (I) and the change in $[\alpha]$ caused thereby, the production of the acid, $C_{25}H_{34}O_8$, from the maleic anhydride adduct (III) of (II), and the absence of $Pr^{\beta}CO_2H$ from the oxidation products of (II) indicate the formulæ shown for (II) and (III). With SeO_2 (I) gives 6-*hydroxyabietic acid*, m.p. 153—155° (with loss of H_2O), and

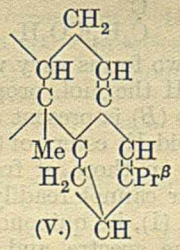


(III.)

+0·5H_2O, "double" m.p. 120—130° (decomp.) and 150—155° (decomp.), $[\alpha]_D^{25}$ −125° in EtOH (*Me* ester, m.p. 75—77·5°, $[\alpha]_D$ −96° in EtOH), which gives an acidic *Na* salt, $(C_{20}H_{30}O_4)_4,C_{20}H_{29}O_3Na,2H_2O$, m.p. 167—170° (decomp.), $[\alpha]_D^{25}$ −114° in EtOH, with H_2–PtO_2 gives a mixture of (? stereoisomeric) *dihydroabietic acids*, m.p. 157° (clears at 165°), and in boiling AcOH readily loses H_2O to give *dehydroabietic acid* (IV), m.p. 171—172°, $[\alpha]_D^{25}$ −61° in EtOH, saturated to Br and $KMnO_4$, and having an absorption spectrum typical of similar compounds containing an aromatic ring. The Na salt of the OH-acid at



(IV.)



(V.)

175—200° under N_2 loses H_2O and gives the unsaturated *anhydrohydroxyabietic acid* (? V), m.p. 167·5—169·5°, $[\alpha]_D^{25}$ +21° in EtOH (*Me* ester, b.p. 174—178°/3 mm.), reduced (H_2–PtO_2) to a *tetrahydroabietic acid*, m.p. 164—164·5°, $[\alpha]_D^{25}$ +26° in EtOH, and giving $Pr^{\beta}CO_2H$ when oxidised. Nitration of (IV) gives the (? 6 : 8-)$(NO_2)_2$-derivative, m.p. 178—185° (decomp.), $[\alpha]_D^{25}$ +49° in $COMe_2$ (*Me* ester, m.p. 189—189·5°, $[\alpha]_D^{25}$ +53° in $COMe_2$), previously reported as "dinitroabietic acid" and also obtained from a "pinabietic acid." It is now obtained from abietic acid which has been heated at 260—270° and in 50—60% yield from α-pyroabietic acid, m.p. 171—172°, $[\alpha]_D$ +41° in EtOH. It is considered that heating (I) produces a mixture of (IV) and reduced acids by disproportionation and that the α-pyro-acid is really impure (IV), a view supported by its absorption spectrum, which is weaker than, but otherwise identical with, that of (III). M.p. are corr.

R. S. C.

Arylamides of furoylacetic acid.—See B., 1938, 140.

Preparation of furanic ketones containing several ethylenic linkings. N. MAXIM and (MLLE.) M. POPESCU (Bull. Soc. chim., 1938, [v], **5**, 49—53).—The marked halochromic effect of the furan nucleus and of ethylenic linkings when associated with CO in aromatic ketones is illustrated as follows (cf. Maxim and Popescu, A., 1935, 626). ε-*Keto*-ε-*p-tolyl*-α-*furyl*-$\Delta^{\alpha\gamma}$-*pentadiene*, m.p. 77°, yellow, from *p*-C_6H_4Me·COMe and furylacraldehyde (I) [from MeCHO and C_4H_3O·CHO (II)]; ε-*keto*-ι-*phenyl*-α-*furyl*-$\Delta^{\alpha\gamma\zeta\theta}$-*nonatetraene*, m.p. 103°, orange-yellow, from CHPh:CH·CHO and ε-keto-α-furyl-$\Delta^{\alpha\gamma}$-hexadiene (III) [from $COMe_2$ and (I)]; ε-*keto*-αι-*difuryl*-$\Delta^{\alpha\gamma\zeta\theta}$-*nonatetraene*, m.p. 121°, orange-yellow, from (I) and (III); ε-*keto*-α-*furyl*-η-*dimethylaminophenyl*-$\Delta^{\alpha\gamma\zeta}$-*heptatriene*, m.p. 121°, red prisms, from *p*-NMe_2·C_6H_4·CHO and (III); ε-*keto*-η-*piperonyl*-α-*furyl*-$\Delta^{\alpha\gamma\zeta}$-*heptatriene*, m.p. 119°, orange-yellow, from piperonal and (III); ε-*keto*-η-*anisyl*-α-*furyl*-$\Delta^{\alpha\gamma\zeta}$-*heptatriene*, m.p. 99°, yellow, from *p*-OMe·C_6H_4·CHO and (III); ε-*keto*-αλ-*difuryl*-$\Delta^{\alpha\gamma\zeta\theta\kappa}$-*undecapentaene*, m.p. 129°, orange-red, from (III) and α-2-furyl-$\Delta^{\alpha\gamma}$-pentadienal [from (II) and excess of MeCHO]. E. G. B.

Halochromy of furanic and pyrrolic ketones with conjugated double linkings. N. MAXIM and I. COPUZEANU (Bull. Soc. chim., 1938, [v], **5**, 57—63).—The colours of various furanic ketones with two double linkings, C_4H_3O·CH:CH·CO·CH:CH·C_6H_4·R (I) when solid and in H_2SO_4 or HCl solution indicate that the nature and position of R have little halochromic effect. Only OMe and CH_2O_2 have much effect, the colour then inclining towards red or violet. Comparison with earlier results (Maxim and Popescu, A., 1935, 626) for furanic ketones with one double linking shows that the second double linking has a marked halochromic effect, the colours changing from yellow to red or violet. Comparison with the colours of various pyrrolic ketones with a single double linking, C_4H_3NH·CO·CH:CH·C_6H_4·R (II), shows that the pyrrole nucleus has hardly any while the furan nucleus has a very marked halochromic effect. OMe and CH_2O_2 have a halochromic effect with (II) similar to that with (I). Absorption spectra of (I) and (II) in $CHCl_3$, H_2SO_4, and HCl show that replacement of $CHCl_3$ by H_2SO_4 or HCl sometimes causes a shift of the first band >1500 A., while the no. of bands is increased 2—3 times. With the exception of OMe, CH_2O_2, and NMe_2, the nature and position of R have little effect on the no. and position of bands. The ethylenic linking and the furan nucleus cause a marked displacement of bands, whilst the pyrrole nucleus has no effect. If dry HCl is passed through solutions of (I) in C_6H_6, reddish-violet compounds are formed,

rapidly losing HCl in air. Various theories of halochromy are outlined. E. G. B.

Pechmann dyes. Supposed isomerism with Kugel dyes. P. CHOVIN (Compt. rend., 1937, **205**, 677—680).—The red dye (I) prepared by Bogert and Ritter (A., 1925, i, 255) by a reaction of Kugel's and stated to be isomeric with the red Pechmann dye (II) is shown to be identical with (II). The white dihydrated acid given by alkaline hydrolysis of (I) yields (II) on dehydration. Differences in colour and reflexion of crystals of (I) and (II) are due to conditions of prep. Thus (II) cryst. from Ac_2O gives either (I) or (II) according to the rate of cooling. Similarly (I) prepared by Kugel's method (A., 1898, i, 198) yields either (I) or (II). All preps. of (I) and (II) and their mixtures melt at 317° and their absorption spectra are identical. E. G. B.

Anthoxanthins. XVI. Synthesis of herbacetin. L. J. GOLDSWORTHY and R. ROBINSON (J.C.S., 1938, 56—58).—2 : 4-Dihydroxy-ω : 3 : 6-trimethoxyacetophenone, anisic anhydride, and Na anisate give 7-*hydroxy*-3 : 5 : 8 : 4′-*tetramethoxyflavone*, m.p. 269—270°, demethylated to 3 : 5 : 7 : 8 : 4′-*pentahydroxyflavone*, m.p. 278—280°, identical with herbacetin. The $(OH)_5$-compound yields a $(OAc)_5$-compound, m.p. 189—191°, and a $(OMe)_5$-compound, m.p. 156—158°. F. R. S.

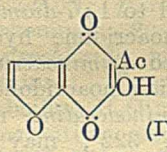
Lichen substances. LXXXVII. Usnic acid. IV. Y. ASAHINA, M. YANAGITA, and S. MAYEDA [with, in part, S. KAWAMURA] (Ber., 1937, **70**, [*B*], 2462—2469; cf. A., 1936, 1262; Curd and Robertson A., 1937, II, 347).—Usnic acid (I) with abs. EtOH at 150° gives Et acetylusnetate (II), m.p. 150° [*monosemicarbazone*, m.p. 196° (decomp.)], which is probably (II) since it is hydrolysed by alkali partly to *usnetic acid*, $C_{14}H_{14}O_6$, m.p. 202° (decomp.) (*Et* ester, m.p. 147°), and partly to CO_2 and acetylusnetol [deacetyldecarbousnic acid], m.p. 197—198°. Triacetyldecarbousnic acid is optically inactive in $CHCl_3$. Usnonic acid, which contains 1 O more in its mol. than does (I), into which it is readily transformed by Zn and AcOH, is transformed by EtOH at 100—105° into *Et* r-iso*hydroxyacetusnetate*, $C_{18}H_{20}O_8$ (III), m.p. 145° (decomp.), hydrolysed by conc. KOH to r-iso*hydroxyusnetic acid*, m.p. 186° after giving a brown-red distillate at about 175°. (III) is deoxidised by Zn and AcOH to Et acetusnetate, m.p. 149°. Similarly, d-*usnonic acid*, m.p. 143—144° (decomp.) after becoming red at about 135°, $[\alpha]_D^{21}$ +388·6° in $CHCl_3$, is converted by EtOH at 100—105° into *Et* d-iso*hydroxyacetusnetate*, m.p. 124° (decomp.), $[\alpha]_D^{22}$ +127·4° in $CHCl_3$. From this it follows that O very probably enters not in the 1 : 3-diketo-side-chain but in the previously-assumed coumarone nucleus in which an asymmetric C is initially present. To explain the structure of this unknown nucleus it must be recognised that (I) when transformed into decarbousnic acid forms a true phloroglucinol nucleus and loses its optical activity whereas when oxidised by $KMnO_4$ it adds 1O and the usnonic acid thus formed yields an alcoholysis product with asymmetric C. Hence (I) is probably *A*. On oxidation with $KMnO_4$ it first adds 2 OH at $C_{(2)}$ and $C_{(3)}$ and then loses H_2O with production of usnonic acid (as *A*, but with OH at 4). During lactone fission migration of the quinol OH is no longer possible so that the optical activity persists. When reduced it absorbs H at $C_{(2)}$ and $C_{(3)}$ and the H_2-derivative loses H_2O with production of (I). Similarly (III) is hydrogenated in the positions 2 and 3 and the product by loss of H_2O and aromatisation of the quinol nucleus passes into (II). According to the new formulation the Ac groups of Schöpf's diacetylusnic acid must reside in the furan side-chain and exist partly at any rate in union with C. The feebly acidic properties, positive reaction with $FeCl_3$, and the conversion by boiling 60% AcOH into diacetyldecarbousnic acid are in harmony with this view. *d*-Diacetylusnic acid is reduced (Pd–C in EtOAc) to d-*dihydrodiacetylusnic acid*, m.p. 151°, $[\alpha]_D^{20}$ +5·52° in $CHCl_3$, hydrolysed by conc. H_2SO_4 at room temp. to l-*dihydrousnic acid*, m.p. 150°, $[\alpha]_D^{20}$ −83·84° in $CHCl_3$. Similarly, *l*-diacetylusnic acid is reduced to l-*dihydrodiacetylusnic acid*, m.p. 151°, $[\alpha]_D^{20}$ −5·38° in $CHCl_3$, whence d-*dihydrousnic acid*, m.p. 150—151°, $[\alpha]_D^{20}$ +81·73° in $CHCl_3$. d-*Diacetyltetrahydrodeoxyusnic acid* has m.p. 194°, $[\alpha]_D^{20}$ +27·7° in $CHCl_3$. H. W.

Structure and absorption of coloured substances. Isomeric forms of fluorescein. P. RAMART-LUCAS (Compt. rend., 1937, **205**, 1409—1411).—Measurements of the absorption spectra of fluorescein (I) and its Me_2 ether (II) and of resorcinolbenzein (III) show that (I) can yield an equilibrium mixture of the coloured, fluorescent quinonoid form (*A*) and the colourless, non-fluorescent, lactoid variety (*B*). The relative proportions of the two forms vary with the nature of the solvent. In EtOH the mol. proportion of (*A*) : (*B*) = 1 : 140. In Et_2O (*B*) is present almost exclusively. Since the quinonoid Et esters of (I) and (III) have bands superposable on those of free (I) the ionoid structure of Wizinger cannot readily be maintained. In alkaline solution (I), its quinonoid ester, and (III) have nearly the same spectra and hence the same *p*-quinonoid structure; the presence of CO_2H does not considerably modify the absorption of the two former substances. In MeOH–HCl, (I) and (II) afford hydrochlorides of closely similar spectra, and they therefore have the same structure. This cannot be lactoid since they have visible colour and the lactoid di-ether cannot assume the *p*-quinonoid form. It is probable that they should be assigned the *o*-quinonoid formula with oxonium O, as generally used for the hydrochloride of (I). H. W.

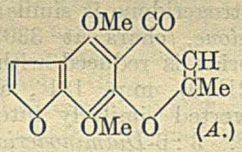
Dioxan and its derivatives. VI. Action of di- and tri-chloro- and di- and tri-methyl deriv-

atives of ethyl alcohol on 2 : 3-dichloro-1 : 4-dioxan. J. Böeseken, F. Tellegen, and M. Plusjé (Rec. trav. chim., 1938, **57**, 73—78).—2 : 3-Dichloro-1 : 4-dioxan (I) with $CCl_3·CH_2·OH$ in C_6H_6 yields 3-*chloro*- (II), b.p. 160—190°/20 mm., m.p. 77—78°, converted by boiling EtOH into 3-*ethoxy*-, b.p. 88—95°/20 mm., and by $Cl·[CH_2]_2·OH$ in C_6H_6 into 3-β-*chloroethoxy*-2-βββ-*trichloroethoxy*-1 : 4-*dioxan*, b.p. 180—183°. With $CHCl_2·CH_2·OH$ and $CH_2Bu^{\gamma}·OH$ (II) does not react. With $Pr^{\beta}OH$, (II) yields 2-βββ-*trichloroethoxy*-3-iso*propoxy*-, b.p. 155—165°, and (I) gives 2 : 3-*di*iso*propoxy*-1 : 4-*dioxan*, b.p. 123—129°. E. I.

Natural chromones. I. Constitution of kellin (from *Ammi visnaga*). E. Späth and W. Gruber (Ber., 1938, **71**, [*B*], 106—113; cf. A., 1931, 73).—Kellin (I), m.p. 154—155° (vac.), is $C_{14}H_{12}O_5$. It is smoothly converted by 1% aq. KOH into AcOH and kellinone [5-hydroxy-3 : 6-dimethoxy-4-acetylbenzfuran] (II), m.p. 99—101° [*acetate*, m.p. 73·5—74°; *Et ether* (III), b.p. 120—130° (bath)/1 mm., and its *semicarbazone*, m.p. 166—167° (vac.; slight decomp.)], which gives a green colour with $FeCl_3$. Oxidation of (II) in abs. EtOH with fuming HNO_3 gives the *ketone* (IV), m.p. 170—172° (vac.; decomp.),



(IV.)



(*A*.)

thus establishing the position of the OMe in (I) and (II). Oxidation of (I) with alkaline H_2O_2 gives furan-2 : 3-dicarboxylic acid. Ozonisation of (III) leads to 2-*hydroxy*-3 : 6-*dimethoxy*-4-*ethoxy*-5-*acetylbenzaldehyde*; this is completely ethylated with KOH and Et_2SO_4 and then oxidised by $KMnO_4$ in aq. $COMe_2$ to 3 : 6-*dimethoxy*-2 : 4-*diethoxyacetophenone*-5-*carboxylic acid* (V), the *Me* ester of which affords a *semicarbazone*, m.p. 202—204° (vac.; decomp.). Decarboxylation of (V) by Cu powder in boiling quinoline leads to 3 : 6-*dimethoxy*-2 : 4-*diethoxyacetophenone*, b.p. 120—130° (bath)/0·05 mm., characterised as the *semicarbazone*, m.p. 184—187° (vac.; decomp.). This is obtained synthetically from 2 : 4-dihydroxy-3 : 6-dimethoxyacetophenone. Therefore (I) is *A*. Ac_2O and NaOAc at 160° convert (II) into 3-*acetylkellin*, m.p. 195—196°, which with aq. Na_2CO_3 gives AcOH and (I). H. W.

Pyrrole-2-carboxylic acid and amides derived therefrom. N. Maxim, I. Zugravescu, and I. Fulga (Bull. Soc. chim., 1938, [v], **5**, 44—48).—An improved prep. of pyrrole-2-carboxylic acid is from its Et ester, prepared from Mg pyrryl bromide and $ClCO_2Et$ (cf. Oddo, A., 1909, i, 672). With PCl_5 it gives the chloride, from which are obtained the *diethylamide*, m.p. 99·5°, *methyl*-, m.p. 147°, and *ethyl*-, m.p. 123°, *-anilides*, and *diphenylamide*, m.p. 173°. E. G. B.

Dimethyloxindoles. A. Wahl and V. Livovschi (Compt. rend., 1937, **205**, 738—740).—Cyclisation of 2 : 4-dimethylchloroacetanilide with $AlCl_3$ affords a *compound*, $C_{10}H_{11}ON$, m.p. 153°, different from 5 : 7-dimethyloxindole (carbomesyl) prepared by Wispek (A., 1883, 1095) as it does not react with aldehydes and is probably a methyldihydrocarbostyril. 2 : 6-Dimethylchloroacetanilide similarly affords a *dimethyloxindole*, m.p. 170° (*benzylidene* derivative, m.p. 212°), so that the structures of 4 : 7- and 5 : 7-dimethyloxindole (cf. A., 1937, II, 115) remain in doubt. J. L. D.

Isatin derivatives and indigoid vat dyes.—See B., 1938, 143.

Complex salts of amino-acids and peptides.—See A., I, 155.

Preparation of 8-nitro-6-methoxyquinoline. I. P. Strukov (Prom. Org. Chim., 1937, **4**, 523—524).—Glycerol 350, 85% H_3AsO_4 160, *m*-nitro-*p*-anisidine 160, and H_2SO_4 160 g. are heated under reduced pressure at 100—110° until distillation of H_2O ceases; heating is then continued under reflux at 115—120°, with gradual addition of 120 g. of H_2SO_4 during 2·5 hr. The product is poured into ice-H_2O after 7 hr., and the ppt. of 8-nitro-6-methoxyquinoline (78% yield) is dried at 50°. R. T.

Condensation of acetylene with aromatic amines in presence of Cu_2Br_2. XV. N. Kozlov and L. Olifson (J. Gen. Chem. Russ., 1937, **7**, 2301—2305).—NH_2Ph or *o*-, *m*-, or *p*-toluidine, $COMe_2$, and C_2H_2 in presence of CuBr yield respectively 2 : 4-dimethyl- or 2 : 4 : 8-, 2 : 4 : 7-, or 2 : 4 : 6-trimethyl-quinoline. R. T.

Modifications of cobalt quinaldinate. N. K. Dutt (J. Indian Chem. Soc., 1937, **14**, 572—573).—By mixing cold neutral solutions of a Co salt with Na quinaldinate a cream-coloured *Co quinoline*-2-*carboxylate*, $+2H_2O$, is formed. Hot and slightly acid solutions give a red variety (anhyd.), obtainable from the first by heating above 160°. F. L. U.

Synthesis of *iso*quinoline derivatives. II. W. Krabbe, H. H. Böhlk, and K. H. Schmidt (Ber., 1938, **71**, [*B*], 64—76; cf. A., 1936, 1124).—Substituted vinylamines are formed frequently if not invariably as intermediate products of the conversion of acylamidocarbinols into *iso*quinoline derivatives according to Pictet and Gams. $NH_2·CH_2·CPh_2·OH$ (I) is transformed by cold Ac_2O into *diphenylacetamidomethylcarbinol*, m.p. 141°, which is converted by P_2O_5 in boiling C_6H_6 into *acet*-ββ-*diphenylvinylamide*, m.p. 166°, or under more drastic conditions into 4-*phenyl*-1-*methyl*isoquinoline, m.p. 80° (*hydrochloride*; *picrate*, m.p. 206°). This has the same action as papaverine on the smooth muscle but is badly resorbed when administered parenterally. $NH_2·CHPh·CPh_2·OH$ is converted by short treatment with boiling Ac_2O into its N-*Ac* derivative, m.p. 260°, transformed by P_2O_5 in boiling PhMe into *acet*-αββ-*triphenylvinylamide*, m.p. 90°, and 3 : 4-*diphenyl*-1-*methyl*isoquinoline, m.p. 156° [*hydrochloride*; *picrate*, m.p. 196° (decomp.)]. β-*Benzamido*-ααβ-*triphenylethyl alcohol*, m.p. 273°, passes under somewhat drastic conditions into 1 : 3 : 4-*triphenyl*isoquinoline, m.p. 191° (*hydrochloride*; *picrate*, m.p. 156°). Gradual addition of anhyd. HCO_2H to (I) in PhMe affords the corresponding *formate*, m.p. 153—157° (slight decomp.), which passes at 160° into *diphenylformamidomethylcarbinol*, m.p. 167° after softening at 140°; this when rapidly distilled under

atm. pressure gives *form*-ββ-*diphenylvinylamide*, m.p. 174°, or when treated with P_2O_5 in boiling xylene 4-*phenyl*isoquinoline, m.p. 82° (*hydrochloride*, m.p. 185—195° after softening; *picrate*, m.p. 209—210°), also obtained similarly from the amide. It is oxidised by $KMnO_4$ to *o*-$C_6H_4Bz{\cdot}CO_2H$ and 3-*phenylpyridine*-4 : 5-*dicarboxylic acid*, m.p. 225—230°, decarboxylated by distillation with CaO to 3-phenylpyridine. Ozonisation of benz-ββ-diphenylvinylamide in $CHCl_3$ gives a solid *ozonide* (converted by boiling H_2O into $COPh_2$ and NH_2Bz) or in HCO_2H gives $COPh_2$ and formylbenzamide, m.p. 112°. The amide with boiling KOH–EtOH–H_2O gives only a pale, resinous product from which an individual could not be isolated; with HCl–EtOH–H_2O the main products are $CHPh_2{\cdot}CHO$ and BzOH or EtOBz. Restricted treatment of (I) with P_2O_5 in boiling C_6H_6 gives *di*-αα-*diphenylvinylamine*, m.p. 144—146°. 1 : 4-Diphenyl*iso*quinoline (*hydrochloride*) has m.p. 131°. H. W.

Complexes of polynitro-compounds. II. Compounds of polynitro-substances with derivatives of 1-keto-1 : 2 : 3 : 4-tetrahydrocarbazole. A. Kent and D. McNeil (J.C.S., 1938, 8—11).—The following have been prepared: cyclo*hexane*-1 : 2-*dione*-1-m-*tolylhydrazone*, m.p. 156—158°, -1-(6′-*cyano*-m-*tolylhydrazone*), m.p. 123°, -2-(4′-*nitrophenylhydrazone*)-1-(6′-*cyano*-m-*tolylhydrazone*), m.p. 214—215°, and -1-*o*-*carboxyphenylhydrazone*, m.p. 185—186°; 4-*methyl*cyclo*hexane*-1 : 2-*dione*-2-*phenylhydrazone*, m.p. 139—141°; 1-*keto*-2-*methyltetrahydrocarbazole*-p-*nitrophenylhydrazone*, m.p. 226—228°; 1-*keto*-3-, m.p. 194—195° (p-*nitrophenylhydrazone*, m.p. 265—267°), and 1-*keto*-4-*methyltetrahydrocarbazole*, m.p. 131° (p-*nitrophenylhydrazone*, m.p. 227—229°); 1-*keto*-*tetrahydrocarbazole*-8-*carboxylic acid*, m.p. 279—281° (p-*nitrobenzyl* ester, m.p. 189°); 1-*keto*-6-*methyltetrahydrocarbazole*-p-*nitrophenylhydrazone*, m.p. 260° (decomp.); and 1-*keto*-5(or 7)-, m.p. 160—161°, and -7(or 5)-*methyltetrahydrocarbazole*, m.p. 196°. These substances yield the following *mol. compounds*, where X is *s*-$C_6H_3(NO_2)_3$, Y is picric acid, Z is *m*-$C_6H_4(NO_2)_2$, and K is 1-ketotetrahydrocarbazole: XA, m.p. 180°, XA_2, m.p. 186—187°, and YA_2, m.p. 154—155° (A = 2-methyl-K); XB_2, m.p. 187—188°, and YB_2, m.p. 169° (B = 3-methyl-K); XC_2, m.p. 177°, and YC_2, m.p. 157—159° (C = 4-methyl-K); XD_2, m.p. 190—192°, and YD_2, m.p. 158—159° [D = 5 (or 7)-methyl-K]; XE, m.p. 174—176°, YE, m.p. 156—158°, and ZE (E = 6-methyl-K); XF_2, m.p. 201—203°, and YF_2, m.p. 183° [F = 7 (or 5)-methyl-K]; XG, m.p. 179—180°, YG, m.p. 161—162°, and ZG_2, (G = 8-methyl-K); XP, m.p. 229—231°, and YP, m.p. 212—214° (decomp.) (P = 5 : 6-benzo-K); and XQ, m.p. 240—241°, and YQ, m.p. 220—222° (decomp.) (Q = 7 : 8-benzo-K). The properties of the compounds are discussed. F. R. S.

***meso*-Derivatives of acridine. VIII. New method of preparation of *N*-alkylacridones.** N. S. Drozdov (J. Gen. Chem. Russ., 1937, **7**, 2292—2297).—5-Phenoxyacridine derivatives react with *p*-$C_6H_4Me{\cdot}SO_3H$ esters to yield 10-alkylacridones, of which the following appear to be new: 3 : 10-*dimethylacridone*, m.p. 150—151°, 3-*methoxy*-, m.p. 147—148°, 2-*chloro*-7-*methoxy*-10-*methyl*-, m.p. 245—246°, and -10-*ethyl*-*acridone*, m.p. 223—225°. 2-Chloro-5-phenoxy-7-methoxyacridine when heated in acid solution yields 2-*chloro*-7-*methoxyacridone*, m.p. >300°, from which 2-*chloro*-7-*methoxy*-5-p-*dimethylaminophenylacridine*, m.p. 197·5—198°, is obtained by heating at 100° with $NPhMe_2$ and $POCl_3$. R. T.

Chemotherapeutic studies in the acridine series. III. 4-Amino-, 1 : 3-, 1 : 7-, and 3 : 6-diamino-acridines. A. Albert and W. H. Linnell (J.C.S., 1938, 22—26).—*o*-$C_6H_4Cl{\cdot}CO_2Na$, 3 : 5-$(NO_2)_2C_6H_3{\cdot}NH_2$, and Cu give 3′ : 5′-*dinitrodiphenylamine*-2-*carboxylic acid* (I), m.p. 263°; the 4 : 3′-*acid*, m.p. 229°, is similarly obtained. Reduction of the $(NO_2)_2$-acid with $SnCl_2$–AcOH yields 2′ : 4′-*diaminodiphenylamine*-2-*carboxylic acid hydrochloride*, m.p. 252°, the stannichloride of which with Sn–HCl affords a compound, described as 1 : 3-diaminoacridone (Jourdan, A., 1885, ii, 987), and apparently a lactam, which is acetylated to 2′ : 4′-*bisacetamidodiphenylamine*-2-*carboxylic acid* 1 : 2-*lactam*, m.p. 307°. $POCl_3$ and (I) give 2 : 4-*dinitroacridone*, and 5 : 4′-dinitrodiphenylamine-2-carboxylic acid with $POCl_3$ yields 5-*chloro*-2 : 7-*dinitroacridine*, m.p. 233°. 1 : 3-Dinitroacridine is reduced ($SnCl_2$–AcOH) to 1 : 3-*diaminoacridine*, m.p. 225° (decomp.), and 1 : 7-dinitroacridone is similarly reduced to 1 : 7-*diaminoacridone*, chars at 330°. 4-Aminoacridone hydrochloride is reduced with Na–Hg to 4-*aminoacridine* (+$2H_2O$), m.p. 181°, and 1 : 7-diaminoacridone is converted similarly into 1 : 7-*diaminoacridine*, m.p. 126°. 3 : 6-*Diaminoacridine*, m.p. 322°, may be similarly obtained. The presence of 1- and 4-NH_2 substituents leads always to compounds which are non-fluorescent in alcoholic solution, even when the corresponding substances without these groups fluoresce actively. The preliminary bacteriological tests indicate that all the compounds containing a 1-NH_2 are without antiseptic effect, whereas the 4-(as well as the 5-, 3-, and 2-)NH_2 greatly increases the antiseptic activity. F. R. S.

5-*iso*Butyl- and -propyl-5-crotylbarbituric acid.—See B., 1938, 226.

Glyoxalines. II. R. Weidenhagen and H. Wegner (Z. Wirts. Zuckerind., 1937, **87**, 755—777; cf. A., 1935, 1380, 1507).—*p*-Toluoylcarbinyl acetate, $Cu(OAc)_2$, CH_2O, and NH_3 in MeOH at 100° afford 4(5)-p-*tolylglyoxaline*, m.p. 116—117° (*Cu* derivative; *picrate*, m.p. 210°). 4(5)-p-*Ethylphenyl*-, m.p. 127—128° (*Cu* derivative; *picrate*, m.p. 197°), and 4(5)-p-iso*propylphenyl*-, m.p. 114—115° (*Cu* derivative; *picrate*, m.p. 186—187°), -*glyoxaline* are obtained similarly. These compounds generally depress the blood pressure but have little action on the uterus. The halogen in 4(5)-p-*chlorophenyl*-, m.p. 147° (*Cu* compound; *picrate*, m.p. 219—220°), and 4(5)-p-*bromophenyl*-, m.p. 142° (*Cu* salt; *picrate*, m.p. 142°), -*glyoxaline* is so firmly combined that it cannot be replaced by other substituents. 2′-*Furyl*-4(5)-*phenylglyoxaline*, m.p. 180° (decomp.) [*Cu* compound; *hydrochloride*, m.p. 275—276°; *picrate*, m.p. 204° (decomp.)], is obtained from benzoylcarbinol, $Cu(OAc)_2$, and furfuraldehyde. 4(5)-β-*Naphthylglyoxaline* (I), m.p. 170—171° [*Cu* derivative; *picrate*, m.p. 215°; *hydrochloride*, m.p. 219—220° after slight softening;

nitrate, m.p. 185° (decomp.)], is described. Addition of the requisite amounts of I to an alkaline solution of (4)5-*p*-carboxyphenylglyoxaline gives *monoiodo-*, m.p. 240° (decomp.), or *di-iodo-*, m.p. 234—235° (decomp.), -p-*carboxyphenylglyoxaline*. 2 : 5-*Di-iodo*-4(5)-p-*sulphophenylglyoxaline dihydrate* is obtained similarly. These compounds are highly toxic. Attempted iodination of glyoxaline-4(5)-carboxylic acid causes decarboxylation with production of 2 : 4 : 5-tri-iodoglyoxaline. 4(5)-Phenylglyoxaline with anhyd. K_2CO_3 and pyridinium-1-sulphonic acid at 10—15° gives 4(5)-*phenylglyoxaline*-1-*sulphonic acid*, which becomes translucent at 210° (*K* salt). 4(5)-β-*Naphthylglyoxaline*-1-*sulphonic acid*, becoming translucent at 200—210°, m.p. indef. (*K* salt), and *glyoxaline*-1-*sulphonic acid*, m.p. 221—222° (*K* salt), are obtained similarly. With fuming H_2SO_4 at 100° (I) yields 4(5)-*sulpho*-β-*naphthylglyoxaline*, m.p. indef. The prep. of the following *-glyoxalines* demonstrates the possibility of extension of the synthesis to acyloins: 4 : 5-dimethyl-; 2 : 4 : 5-trimethyl-; 4 : 5-diphenyl-, m.p. 218° (*picrate*, m.p. 231—232°); 2 : 4 : 5-triphenyl-, m.p. 265—266° (*picrate*, m.p. 235°, after slight softening); 4 : 5-*difuryl-*, m.p. 162—163° (decomp.) [*Cu* compound; *hydrochloride*, m.p. 196° (decomp.); *picrate*, m.p. 222—223° (decomp.) after darkening]; 2 : 4 : 5-*trifuryl-*, m.p. 202° (decomp.) (*hydrochloride*, m.p. 141°; a picrate could not be obtained). Fructose, $Cu(OAc)_2$, CH_2O, and NH_3 in boiling H_2O afford 4(5)-hydroxymethylglyoxaline, apparently with intermediate formation of $CO(CH_2{\cdot}OH)_2$. The following monoalkylamides are obtained by heating the requisite Me or Et ester and primary amine at about 160°: *glyoxaline*-4(5)-*carbmethylamide*, m.p. 145° after slight softening (*picrate*, m.p. 196°); *-ethylamide*, m.p. 161—162° (*picrate*, m.p. 193—194°); *-propylamide*, m.p. 121—122° (*picrate*, m.p. 150°); *-allylamide*, m.p. 130° (*picrate*, m.p. 171—172°). These compounds have only slight toxicity but the pharmacological action is unimportant. The method cannot be applied to the prep. of the dialkylamides. However, the acid is transformed by slightly moist PCl_5 at 110—120° into *glyoxaline*-4(5)-*carboxyl chloride* which with an aq. solution of the requisite *sec.* amine gives the following *glyoxaline*-4(5)-*carb-dimethylamide*, b.p. 165—170°/0·4 mm., m.p. 90—91° [*oxalate*, m.p. 204° (decomp.); *picrate*, m.p. 200—202°]; *-diethylamide*, b.p. 168—175°/0·4 mm. [*oxalate*, m.p. 166° (slight decomp.); *picrate* (+1H_2O), m.p. (anhyd.) 158—159°]; *-dipropylamide*, b.p. 180—190°/0·4—0·5 mm., m.p. 69—70° [*oxalate*, m.p. 160—161°; *picrate* (+1H_2O), m.p. (anhyd.) 147—148°]. *o*-Diamines of the C_6H_6 series react with aldehydes in H_2O or EtOH in presence of $Cu(OAc)_2$ and the benziminazoles separate as complex Cu salts when the mixtures are gently warmed or heated not above 100°. The complexes in hot H_2O or H_2O–EtOH are decomposed by H_2S and the bases usually separate pure and in good yield from the filtrates from the CuS, after concn. if necessary. The following *-benziminazoles* are thus obtained: 2-methyl-, m.p. 175—176°; 2-ethyl-, m.p. 174—175°; 2-*n*-propyl-, m.p. 157—159°; 2-*iso*propyl-, m.p. 228°; 2-n-*butyl-*, m.p. 149—151°; 2-iso*butyl-*, m.p. 186—187°; 2-*n*-amyl-, m.p. 159—161°; 2-n-*hexyl-*, m.p. 136—138°; 2-*dimethylheptadienyl-* (probably a mixture of stereoisomerides), m.p. (indef.) 102° after softening; 2-phenyl-, m.p. 290°; 2-o-*nitrophenyl-*, m.p. 190—193° [*hydrochloride*, m.p. 291° (decomp.)]; 2-*m*-nitrophenyl- (+1H_2O), m.p. 204°; 2-*p*-nitrophenyl- [hydrochloride, m.p. 310° (decomp.)]; 2-4′-*hydroxy*-3′-*methoxyphenyl-*, m.p. 221—222°; 2-p-*anisyl-*, m.p. 228—230°; 2-3′ : 4′-*methylenedioxyphenyl-*, m.p. 249°; 2-*styryl-*, m.p. 201—202°; 2-furyl-, m.p. 285—286°. *Et* 2-*ethyl-*, m.p. 151°, and 2-*hexyl-*, m.p. 238—240°, *-benziminazole*-5-*carboxylate* are described. 1 : 2-$C_{10}H_6(NH_2)_2$ and the requisite aldehyde afford 2-iso*propyl-*, m.p. 239—240° (*Cu* salt), and 2-*hexyl-*, m.p. 199—202°, -1′ : 2′-*naphthiminazole*. H. W.

Action of ammonia on benzil. D. Davidson, M. Weiss, and M. Jelling (J. Org. Chem., 1937, **2**, 319—327).—The course of the reaction of NH_3 with benzil (I) and the structures of the products, viz., benzilimide (II), benzilam (III), imabenzil (IV), and lophine (V), are discussed. (II) is shown to be *N*-desylbenzamide (McKenzie and Barrow, J.C.S., 1913, **103**, 1331) [*oxime*, m.p. 197—203° (corr.)], synthesised by benzoylation of COPh·CHPh·NH_2, and not 2-hydroxy-2 : 4 : 5-triphenyloxazoline (Japp, *ibid.*, 1886, **49**, 473). PhCHO, (I), and NH_3 give (V) only and a course for the reaction between (I) and NH_3 is therefore suggested which avoids PhCHO as an intermediate (Japp, *loc. cit.*). With NH_3 (I) gives COPh·CPh(OH)·NH_2 (VI), which with (I) gives COPh·CPh(OH)·N:CPh·COPh, the labile :C(Ph)·C(O)· linking of which is readily hydrolysed to COPh·CPh(OH)·N:CHPh (VII) and BzOH. Cyclodehydration of (VII) gives (III) (2 : 4 : 5-triphenyloxazole) by way of (II). This mechanism is analogous to that of the formation of α-acylaminoacids from NH_3 and α-keto-acids. The formation of (V) from NH_3, PhCHO, and (I) in EtOH is explained by formation of $CHPh(NH_2)_2$ and condensation of this with (I) to yield $\begin{matrix}CPh{:}N\\CPh{:}N\end{matrix}>CHPh$, which changes into (V) (2 : 4 : 5-triphenylglyoxaline). The mechanism is analogous to the formation reaction of hydrobenzamide. When (I) reacts with NH_3, (V) is formed from (II) by action of NH_3, which explains the absence of (II) in the later stages of the reaction, while (III) does not react with NH_3 and is thus among the final products. (IV), which is a primary product but disappears later, is converted by acids into (II), (I), and NH_3, and is assumed to be formed by condensation of (VI) with (II), *i.e.*, is 5 : 6-dihydroxy-1-benzoyl-2 : 3 : 5 : 6-tetraphenyl-1 : 2 : 5 : 6-tetrahydropyrazine.

Benzil and NH_4OAc in boiling glacial AcOH give (V) (90%) with some (III), owing to the suitability of AcOH as a medium for converting acyldesylamines into glyoxalines by NH_3. Thus (II) and *N-desylacetamide* (VIII), m.p. 137° (corr.), give respectively (V) and 4 : 5-diphenyl-2-methylglyoxaline (IX), m.p. 243° (corr.), under these conditions. With NH_2Ph, (II) and (VIII) give respectively tetraphenylglyoxaline, m.p. (new) 221° (corr.), and 1 : 4 : 5-*triphenyl*-2-*methylglyoxaline*, m.p. 197° (corr.). With fused NH_4OAc or HCO_2NH_4, (I) gives at high temp. mainly

(III). The prep. of glyoxalines from (I), RCHO, and NH_3 is improved by using AcOH as solvent; RCHO may be replaced by their NH_3 derivatives or reversible polymerides. Thus (I), NH_4OAc, and $(CH_2)_6N_4$, paraldehyde, and PhCHO (or hydrobenzamide) in AcOH give nearly quant. yields of 4 : 5-diphenylglyoxaline, (IX), and (V), respectively. E. G. B.

Action of ammonia on benzoin. D. Davidson, M. Weiss, and M. Jelling (J. Org. Chem., 1937, **2**, 328—334).—Benzoin (I) with NH_3 in AcOH gives mainly amarone (II) (tetraphenylpyrazine; cf. Japp and Wilson, J.C.S., 1886, **49**, 825), 4 : 5-diphenyl-2-methylglyoxaline (III), and some dihydroamarone (IV). The probable course of the reaction is conversion of (I) into OH·CHPh·CPh:NH (V), tautomerising to COPh·CHPh·NH_2 (VI), which condenses either with itself to give (IV), oxidising to (II), or with AcOH to give its Ac derivative, which with NH_3 gives (III). Formation of (IV) is shown by the orange colour of the reacting mixture. Destruction of this by HNO_3 yields a further ppt. of (II). The yield of (II) is a max. in presence of air. The above mechanism is confirmed by replacement of (I) by the hydrochloride of (VI), when the yields of (II) and (III) are not affected. In $EtCO_2H$ instead of AcOH, the Et analogue is formed in place of (III). In anhyd. AcOH–HCO_2H, *N-desylformamide*, m.p. 122°, is formed, giving, with NH_3, 4 : 5-diphenylglyoxaline. The initial formation of (V) in the reaction in AcOH is confirmed by replacing (I) by its esters, when oxazoles are formed in addition to glyoxalines. Thus esters COPh·CHPh·O·CO·R (R = Me or Ph) with NH_3 give the corresponding 2-substituted-4 : 5-diphenyloxazoles (VII). The intermediates NH_2·CPh:CPh·O·CO·R are probably formed, giving either (VII) by cyclodehydration or OH·CPh:CPh·NH·CO·R and COPh·CHPh·NH·CO·R by successive acyl migration and tautomerisation. The last two with NH_3 give 2-substituted 4 : 5-diphenylglyoxalines. E. G. B.

Heteropolar compounds. IV. New derivatives of 2-thio-4-hydroxy-1 : 2 : 3 : 4-tetrahydroquinazoline. C. V. Gheorghiu and B. Arventi (Bull. Soc. chim., 1938, [v], **5**, 38—43; cf. A., 1937, II, 351).—The effect of 4-substitution on the ionic dissociation of 2-thion-4-hydroxy-1 : 2 : 3 : 4-tetrahydroquinazoline has been studied by the prep. of the following derivatives by condensation of *o*-NH_2·C_6H_4·COPh with the appropriate thiocarbimide alone or in EtOH: 4-*hydroxy*-2-*thion*-3 : 4-*diphenyl*-, m.p. 183°, -4-*phenyl*-3-α-*naphthyl*-, m.p. 171—174°, 4-*phenyl*-3-β-*naphthyl*-, m.p. 219°, and 4-*phenyl*-3-*allyl*-, m.p. 175—180°, -1 : 2 : 3 : 4-*tetrahydroquinazolines*. The ionic dissociations of these compounds, as shown by the duration of the coloration produced in solutions in inert solvents by heat, are > those of the corresponding 2-thion-4-ethoxy-3-allyl-, -3-phenyl-, and -3-*o*-tolyl-tetrahydroquinazolines. This is to be expected on the assumption that dissociation occurs by fission of the ring between atoms 3 and 4. Ph and α- and β-$C_{10}H_7$ in the 3-position have much the same effect on dissociation, while allyl has a much greater effect. E. G. B.

Action of (A) chloropyridine, (B) 2-chloroquinoline, on anthranilic acid. O. Seide and G. V. Tschelincev (J. Gen. Chem. Russ., 1937, **7**, 2314—2317, 2318—2323).—(A) The substance "α-quinoquinoline," obtained by Reissert (A., 1895, i, 244) from 2-chloropyridine-5-carboxylic acid and anthranilic acid (I), and by Räth (A., 1931, 852) from 2-chloropyridine and (I), and termed by him "pyracridone," is 2 : 3-dihydrobenzquinazolone-4, prepared by Seide (A., 1925, i, 159) from 2-aminoquinoline and *o*-C_6H_4Cl·CO_2H. Räth's work is repeated, and his various products are shown to have been wrongly identified. In particular, "2-oxalylaminopyridine-3-carboxylic acid" is shown to be impure 4-hydroxyquinazoline (II), "2-aminopyridine-3-carboxylic acid hydrochloride" is the hydrochloride of (II), and "2-aminopyridine-3-carboxylic acid" is (II); "pyracridone hydrazone" is the hydrazide of 2-pyridylanthranilic acid.

(B) Bose and Sen's synthesis (A., 1932, 66) of benzquinazocolone (III) [*hydrochloride*, $+H_2O$; *picrate*, m.p. 203°; *platinichloride*, decomp. at 327°; *chromate*, decomp. at 170°; *methiodide*, m.p. 122° (decomp.)], and its hydrolytic conversion into *N*-2-quinolylanthranilic acid (IV) are confirmed. The Na salt of (IV) and PhI in presence of Cu-bronze (3 hr. at the b.p.) yield *N-phenyl*-N-2-*quinolylanthranilic* acid, m.p. 221—222° (decomp.), which with H_2SO_4 at 100° gives N-2-*quinolylacridone*, m.p. 270°. In aq. KOH (12 hr. at room temp.) (III) and $KMnO_4$ yield 9 : 10-diketo-1′ : 2′ : 3 : 2-(3′-indolenino)-3 : 4-dihydroquinazoline and 4-keto-2-2′-carboxyphenyl-3 : 4-dihydroquinazoline. R. T.

New derivatives of pyrimidine. W. Huber and H. A. Hölscher (Ber., 1938, **71**, [*B*], 87—100).—The following compounds have been prepared for comparison with the products of the degradation of vitamin-B_1. The *picrate*, m.p. 273—275° (decomp.), and *hydrochloride*, m.p. 240° (decomp.), of 2 : 6-diamino-, the *picrate*, m.p. >300°, and *hydrochloride*, m.p. 284° (decomp.), of 4 : 6-diamino-5-ethylpyrimidine, and the *picrate*, m.p. >300°, and *hydrochloride*, m.p. >300°, of 2 : 6-diamino-4 : 5-dimethylpyrimidine. 4 : 6-*Dihydroxy*-2-*ethylpyrimidine*, m.p. 299° (decomp.) (*Na* and *Cu* salts), is obtained from propionamidine hydrochloride, $CH_2(CO_2Et)_2$, and NaOEt. 4 : 6-Dihydroxy-2 : 5-dimethylpyrimidine is converted by boiling $POCl_3$ into 4 : 6-*dichloro*-2 : 5-*dimethylpyrimidine*, m.p. 39°, which with NH_3–EtOH at 180° affords 4(6)-*chloro*-6(4)-*amino*-2 : 5-*dimethylpyrimidine*, m.p. 196—197°, whence by NH_3–EtOH at 250° 4 : 6-*diamino*-2 : 5-*dimethylpyrimidine*, m.p. 225—226° [*picrate*, m.p. 285° (decomp.); *hydrochloride*, m.p. 330° with elimination of HCl]. 2-Amino-4 : 6-dimethylpyrimidine in H_2O at 0° with Br in excess affords an intensely red-brown *perbromide*, which when treated successively with SO_2 and NH_3 gives 5-*bromo*-2-*amino*-4 : 6-*dimethylpyrimidine*, m.p. 183—184° (*picrate*, m.p. 201—203°), from which Br is removed by Cu-bronze or $CuSO_4$ and NH_3–EtOH at 240°. Cautious addition of 4 : 6-dihydroxy-2-methylpyrimidine to HNO_3 (*d* 1·52) at ≯20° gives 5-*nitro*-4 : 6-*dihydroxy*-2-*methylpyrimidine*, decomp. 270—280°, which with freshly distilled $POCl_3$ under

strictly defined conditions affords 4 : 6-*dichloro*-5-*nitro*-2-*methylpyrimidine*, m.p. 37°, converted by NH_3–EtOH at 0° into 5-*nitro*-4 : 6-*diamino*-2-*methylpyrimidine*, m.p. 234—235° (decomp.) [*picrate*, m.p. 233—235° (decomp.); *hydrochloride*, slow decomp. 200—220° with loss of NH_4Cl]. Acetamidine hydrochloride and the Na derivative of urethanoformylacetic ester in H_2O containing a slight excess of NaOH gradually yield 5-*urethano*-4-*hyldroxy*-2-*methylpyrimidine*, m.p. 260—261° (decomp.) (*picrate*, m.p. 180—182°; *hydrochloride*, m.p. >300°). 5-Urethano-4-hydroxy-2-methylpyrimidine with conc. HCl at 120—130° furnishes 4 : 5-*dihydroxy*-2-*methylpyrimidine*, m.p. 231° (decomp.) (K_2 salt). Et_2 acetosuccinate, ψ-ethylthiocarbamide hydrobromide, and KOH yield *Et* 6-*hydroxy*-2-*ethylthiol*-4-*methylpyrimidine*-5-*acetate*, m.p. 163°. The following condensations of derivatives of $CH_2(CN)_2$ with amidines and carbamide derivatives are effected by dissolving equiv. amounts of the reactants in EtOH, the amidine or carbamide component being liberated by the requisite amount of NaOEt. Thus are prepared: 6-*amino*-2-*ethylpyrimidine*-5-*nitrile*, m.p. 198° (*picrate*, m.p. 198·5°), hydrogenated (Pd–C in AcOH containing HCl at room temp.) to 6-*amino*-5-*aminomethyl*-2-*ethylpyrimidine*, m.p. 229°; 6-*amino*-2-*phenylpyrimidine*-5-*nitrile*, m.p. 226° (decomp.) (*picrate*, m.p. 196°), whence 6-*amino*-2-*phenyl*-5-*aminomethylpyrimidine dihydrochloride*, m.p. 291—292° (corresponding *dipicrate*, m.p. 226—227°); 6-*amino*-2-*ethylthiolpyrimidine*-5-*nitrile*, m.p. 141°; 2 : 6-*diaminopyrimidine*-5-*nitrile*, gradual decomp. >300°; *ethoxyethylidenemalonodinitrile*, m.p. 87°; 6-*amino*-2 : 4-*dimethylpyrimidine*-5-*nitrile*, m.p. 220·5°; 6-*amino*-2 : 4-*dimethyl*-5-*aminomethylpyrimidine*, m.p. 192—193° (decomp.). H. W.

Pyrimidine derivatives.—See B., 1908, 140.

Synthesis of *r*-6-methoxytryptophan and of harmine; action of acetaldehyde on tryptophan. D. G. HARVEY and W. ROBSON (J.C.S., 1938, 97—101).—$Et_2C_2O_4$, KOEt, and *o*-nitro-*p*-tolyl Me ether give the K derivative of Et *o*-nitro-*p*-methoxyphenylpyruvate, which with aq. NH_3–$FeSO_4$ yields NH_4 6-methoxyindole-2-carboxylate, decarboxylated to 6-methoxyindole; this with $CHCl_3$ and KOH affords 6-methoxyindole-3-aldehyde and 3-chloro-7-methoxyquinoline. The aldehyde with hydantoin in $C_5H_{11}N$ gives 5-(6′-*methoxyindolal*)*hydantoin*, m.p. 311—315°, which is reduced (H_2S) to 5-(6′-*methoxyindolylmethyl*)*hydantoin*, m.p. 220°, converted by aq. NH_3 into 6-*methoxytryptophan* (I), m.p. 263—268°; this compound could not be demethylated. *l*-Tryptophan and MeCHO give 3-*methyl*-3 : 4 : 5 : 6-*tetrahydro*-4-*carboline*-5-*carboxylic acid*, m.p. 295—299°, oxidised ($K_2Cr_2O_7$) to harman in 75% yield. MeCHO and (I) afford 11-*methoxy*-3-*methyl*-3 : 4 : 5 : 6-*tetrahydro*-4-*carboline*-5-*carboxylic acid* (+H_2O), m.p. 244—246°, oxidised to harmine in 40% yield. F. R. S.

3-Carbazyl-2-indole. S. M. SCHERLIN and A. J. BERLIN (J. Gen. Chem. Russ., 1937, **7**, 2275—2277).—*N*-Acetylcarbazole and CH_2Cl·COCl in CS_2 and $AlCl_3$ (30 min. at 100°, followed by 2 hr. at room temp.) yield *N-acetyl*-3-*chloroacetylcarbazole*, m.p. 175—177°, hydrolysed to 3-*chloroacetylcarbazole*, m.p. 207—209° (decomp.). This when heated at 120—130° for 3 hr. yields 3-*carbazyl*-2-*indole*, m.p. >300°. R. T.

Phenazine. (I.) Action of methyl sulphate on phenazine, 1-methoxyphenazine, and 1-hydroxyphenazine. H. HILLEMANN (Ber., 1938, **71**, [*B*], 34—41).—Treatment of phenazine in $PhNO_2$ with Me_2SO_4 for 7 min. at 100° gives phenazine methosulphate (I), m.p. 155—157°, whereas more protracted action leads to 2-*methylphenazine methosulphate* (II), m.p. 185—186° (decomp.), also obtained from (I) and Me_2SO_4. Still more protracted action affords charred matter and a green powder of variable composition, decomp. >250°. Quant. hydrogenation of the blood-red solution of (I) in EtOH gives a max. green intensity after absorption of 1 H. Complete hydrogenation is achieved by addition of 2 H and the solution then becomes colourless. If to this solution an equiv. amount of (I) is added, dark green crystals of the semiquinonoid *compound*, m.p. 158°, not identical with (II), are obtained. NH_3 in excess and (I) in MeOH give a blue solution from which $CHCl_3$ removes a black powder of indefinite m.p. With alkali (I) gives a blue solution from which only phenazine could be isolated, whilst SO_2 transforms (I) into dark green *crystals* which darken at 200° and have m.p. >360°. Similarly short interaction of 1-methoxyphenazine and Me_2SO_4 at 100° gives 1-*methoxyphenazine methosulphate* (III), m.p. 171—172°, reduced in EtOH by 1 H to a green and by 2 H to a colourless compound. Addition of an equiv. amount of (III) to this colourless solution followed by picric acid gives the semiquinonoid *picrate*, m.p. 195—196°. More protracted action causes the introduction of Me into the nucleus with production of 1-*methoxy*-3 : 7-*dimethylphenazine methosulphate*, m.p. 168—170° (decomp.). 1-Hydroxyphenazine and Me_2SO_4 rapidly yield the corresponding methosulphate (IV) whereas more prolonged action leads to 1-*hydroxy*-3-*methylphenazine methosulphate*, m.p. 163—165°. After very protracted change an unidentified almost black compound, m.p. >250°, is obtained. Mild hydrolysis of (IV) in MeOH by CH_2N_2 in Et_2O or by H_2O followed by NaOAc affords pyocyanine [aurichloride, m.p. 177° (decomp.)].

Pyrogallyl carbonate and CH_2N_2 in abs. Et_2O yield the *carbonate*, m.p. 111—113°, of the 1-Me ether, hydrolysed by boiling H_2O to *pyrogallol* 1-*Me ether*, b.p. 148—149°/24 mm. Condensation of the corresponding *o*-quinone with *o*-$C_6H_4(NH_2)_2$ is accompanied by oxidation leading to the production of 2 : 3-diamino- and 3-amino-2-hydroxy-phenazine; addition of H_3BO_3 brings no improvement. Replacement of PbO_2 by $Pb(OAc)_4$, CrO_3, *o*-benzoquinone, tetrabromo-*o*-benzoquinone, or Bz_2O_2 was a failure or gave no advantage. Condensation of $PhNO_2$ with *o*-anisidine and KOH at 140° to 160° gives small amounts of 2-methoxyazobenzene, m.p. 40—41°, but not 1-methoxyphenazine. H. W.

Phenazine. II. 5 : 10-Dimethyldihydrophenazine. H. HILLEMANN (Ber., 1938, **71**, [*B*], 42—46).—Gradual addition of phenazine methiodide or *methochloride* (obtained by treating phenazine

methosulphate successively with picric acid and HCl in MeOH) to MgMeI in Et_2O gives 5 : 10-dimethyldihydrophenazine (I), m.p. 151—152°, and phenazine (II) derived from initial material which has not entered into the reaction. The constitution of (I) follows from its formation by the successive action of LiEt and MeI on 5-methyldihydrophenazine. The latter substance is readily autoxidised and passage of air through its solution in C_6H_6 causes rapid development of a bluish-red colour; in one instance it was possible to isolate from such a solution almost black, very unstable *crystals*, m.p. 116—118° after softening at 100°, which are more conveniently prepared from I and Li 5-methyldihydrophenazine. Addition of picric acid to a solution of equal parts of (I) and (II) in EtOH leads to a *picrate*, decomp. 190°, of undecided structure. Attempts to prepare (I) from *o*-$C_6H_4(NHMe)_2$ and *o*-$C_6H_4(NH_2)_2$,2HCl in a sealed tube at 220° and from *o*-$C_6H_4(NHMe)_2$ and *o*-$C_6H_4(OH)_2$ at 200—210° were not successful. *o*-$C_6H_4I_2$, *o*-$C_6H_4(NHMe)_2$, K_2CO_3, and Cu powder in boiling amyl alcohol give a *substance*, $C_{11}H_{10}N$ or $C_{22}H_{20}N_2$, m.p. 191°, which has not been identified. *o*-$C_6H_4Br{\cdot}NH_2$, $PhNO_2$, K_2CO_3, and Cu powder afford essentially (II). H. W.

Phenazine. III. Position of the methyl group in pyocyanine and attempted synthesis of *iso*pyocyanine. H. Hillemann (Ber., 1938, **71**, [*B*], 46—52).—1-Hydroxyphenazine methosulphate is reduced by Zn dust and dil. HCl to leucopyocyanine (I); this with $(COCl)_2$ in $CHCl_3$–C_5H_5N yields the *oxalyl* compound (II), m.p. 218—222° (decomp.) after softening at 209° in a sealed capillary. Since this compound is hydrolysed by prolonged shaking with H_2O the ·CO·CO· group must be attached to N and O; this is possible only if in (I) Me is attached to N remote from O. The analogous *compound* formed from $COCl_2$ has m.p. 221—222° (decomp.), and is too unstable to recrystallise. In unsuccessful attempts to synthesise *iso*pyocyanine (III) the following experiments have been performed. 1 : 2 : 6-$C_6H_3Cl(NO_2)_2$ and *o*-$NO_2{\cdot}C_6H_4{\cdot}NHMe$ are converted by K_2CO_3 and CuI in boiling amyl alcohol into 2 : 2′ : 6-*trinitrodiphenylmethylamine*, m.p. 221—223°. *o*-$NH_2{\cdot}C_6H_4{\cdot}NHMe$ and 2 : 6-dinitrophenyl *p*-toluenesulphonate in boiling C_6H_6 yield 2 : 6-*dinitro*-2′-*aminodiphenylmethylamine* or 2 : 6-*dinitro*-2′-*methylaminodiphenylamine*, m.p. 177°. Ring-closure to the phenazonium system could not be achieved. 3-Nitro-2-aminophenol (IV) is reduced by $Na_2S_2O_4$ to 2 : 3-*diaminophenol*, m.p. 166°. CH_2N_2 and (IV) give only small amounts of 3-nitro-2-aminoanisole, the bulk of the CH_2N_2 appearing to be decomposed catalytically. 3-Nitro-2-aminophenetole, *o*-$C_6H_4I{\cdot}NO_2$, K_2CO_3, and Cu powder yield 2 : 2′-*dinitro*-6-*ethoxydiphenylamine*, m.p. 123—125°, converted by KOH and Me_2SO_4 in boiling $COMe_2$ into 2 : 2′-*dinitro*-6-*ethoxydiphenylmethylamine*, m.p. 125—127°, which could not be hydrolysed satisfactorily. It is reduced by $SnCl_2$ in AcOH to the *compound*, $C_{15}H_{19}ON_3$, m.p. 103—105°. H. W.

Alloxazine, *iso*alloxazine (flavin), and lumazine groups. I. Synthesis of 6- or 7-phenyl- and 6 : 7-diphenyl-lumazines. K. Ganapati (J. Indian Chem. Soc., 1937, **14**, 627—632).—Phenylglyoxal hydrate with 4 : 5-diaminouracil sulphate (I) gives 6- or 7-*phenyl-lumazine*, m.p. >330° (*Me*$_2$ derivative, m.p. 278°). Benzil and (I) afford 6 : 7-*diphenyl-lumazine*, m.p. 310—315°. Piperil (improved prep.) with (I) yields 6 : 7-*di*-(3 : 4-*methylenedioxyphenyl*)*lumazine*, m.p. >330°, in small amount, whilst with camphorquinone and (I), 2′ : 3′-*camphorolumazine*, m.p. >320°, is obtained. F. R. S.

Phthalocyanine-like pigments related to the porphyrins. C. E. Dent (J.C.S., 1938, 1—6).—Phthalimideneacetic acid dihydrate (I) in H_2O at 80° gives *methylenephthalimidine* (II), m.p. 120—125°, which polymerises on heating. Phthalonitrile, (II), and $CuCl_2$ yield *Cu tetrabenzotriazaporphin*. 4-Chlorophthalonitrile, (I), and CuCl afford *Cu trichlorotetrabenzotriazaporphin*. *Cu* and *Me phthalimideneacetates*, m.p. 125—127°, do not give pigments in appreciable yield. The new pigments are green to blue and resemble in properties the phthalocyanines. Benzylidene- and ethylidene-phthalimidine have been prepared by new and improved methods. F. R. S.

Light absorption and constitution of some chlorophyll derivatives.—See A., I, 10.

Light absorption of porphin dyes; relation to structure.—See A., I, 59.

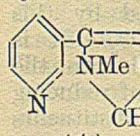
Action of light on porphyrins. I. Conversion of ætioporphyrin-I into bilirubinoid dyes. H. Fischer and K. Herrle (Z. physiol. Chem., 1938, **251**, 85—96).—Ætioporphyrin-I in C_5H_5N and in presence of O_2 and NaOEt undergoes photochemical decomp. into a mixture which is separated by treatment with HCl and chromatographic adsorption on Al_2O_3 into a *porphyrin*, $C_{32}H_{38}O_{5\text{ or }6}N_4$, decomp. 320°, *ætioglaucobilin*, $C_{31}H_{38}O_2N_4$, m.p. 238°, a red *ketone*, $C_{31}H_{36}O_3N_4$, m.p. 244° (*Cu* salt), reduced by Na–Hg to (?) ætio*meso*bilirubinogen and by $Na_2S_2O_4$, and two isomeric dicyclic *aldehydes*, $C_{16}H_{20}O_2N_2$. The mechanism of the production of these compounds is discussed. W. McC.

Reaction of salts or esters and anhydrides of monobasic acids with some cyclic ammonium salts containing reactive methyl groups. T. Ogata (Proc. Imp. Acad. Tokyo, 1937, **13**, 360—363).—A summary of published work (A., 1934, 422; 1936, 869). The product of interaction of 2-methylbenzthiazole ethiodide and A'_2O–MOA (A = acyl; M = metal or alkyl) depends on the relative strengths of AOH and A′OH, the radical from the stronger acid forming the 8-substituent of the resulting trimethinethiocyanine. F. R. G.

Aneurin. IX. New synthesis of thiochrome. Synthesis of aneurin. F. Bergel and A. R. Todd (J.C.S., 1938, 26—28).—2-*Thio*-7-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-1 : 3 : 6 : 8-*benztetrazine*, m.p. 275—277° (decomp.), obtained from 4-amino-2-methyl-5-aminomethylpyrimidine hydrochloride and $CS(NH_2)_2$ or KCNS, with Me α-chloro-γ-acetoxypropyl ketone (I) gives thiochrome. 4-Amino-2-methyl-5-thioformamidomethylpyrimidine, (I), and AcOH afford O-

acetylaneurin chloride hydrochloride, m.p. 205—207°, which is an intermediate product, not hitherto isolated, in the synthesis of aneurin (cf. A., 1937, II, 216). The existence of a low-melting modification of aneurin chloride hydrochloride is confirmed. F. R. S.

***N*-Methylmyosmine.** E. Späth, J. P. Wibaut, and F. Kesztler (Ber., 1938, **71**, [*B*], 100—106).—Attempts to resolve an old specimen of dihydronicotyrine (I) into its optical antipodes (cf. Oosterhuis and Wibaut, A., 1936, 1276) by 4 : 6 : 4′ : 6′-tetranitro-2 : 2′-diphenic acid give a product with small $[\alpha]_D$ but the experiments are devoid of constitutional significance since specimens of (I), when preserved, pass into a mixture of nicotine and nicotyrine. Oxidation of (I) by $KMnO_4$ in dil. H_2SO_4 gives $NHMe{\cdot}[CH_2]_2{\cdot}CO_2H$, identified as β-p-*toluenemethylsulphonamidopropionic acid*, m.p. 110—111° (prep. from $CH_2I{\cdot}CH_2{\cdot}CO_2H$ described). Therefore (I) is *A* and may also be regarded as *N*-methylmyosmine.



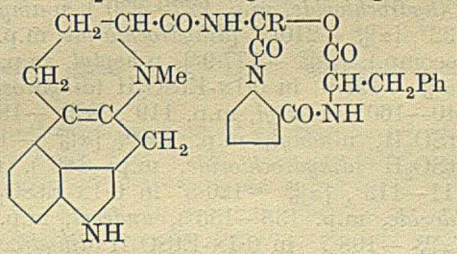
(*A*.)

The nicotine synthesis of Späth and Bretschneider can therefore be simplified since 3-pyridyl 3′-1′-methyl-2′-pyrrolidonyl ketone is converted by 12N-HCl at 130° into (I), catalytically reduced (Pd-sponge in AcOH) to *dl*-nicotine. The structure *A* has been assigned by Noga (A., 1915, i, 711) to *iso*nicoteine; this is not identical with (I) but may possibly be 2 : 3′-dipyridyl or nicotyrine. The nicoteine of Pictet and Rotschy does not appear to be homogeneous. The dihydronicotyrine obtained from iodonicotyrine by Pictet and Crépieux is identical with (I). H. W.

Alkaloids of *Ammodendron Conollyi*. Constitution of ammodendrine. A. Orékhov and N. Proskurnina (Bull. Soc. chim., 1938, [v], **5**, 29—38).—The *sec*.-base ammodendrine (I), $C_{12}H_{20}ON_2$, $[\alpha]$ 0°, probably contains :N·CO·. With alkalis it gives a *base*, $C_{10}H_{18}N_2$, and AcOH, and so is $C_{10}H_{18}(NH)(NAc)$. Hydrogenation (Pt–H_2) of (I) gives *dihydroammodendrine* (II) [*N-Me* derivative (*methiodide*, m.p. 177—180°)], which with alkalis gives AcOH and 2 : 3′-dipiperidyl. Methylation of (I) followed by hydrogenation and hydrolysis gives *N*-methyl-2 : 3′-dipiperidyl, identical with that obtained by methylation and hydrogenation of *r*-anabasine. Therefore (II) is 1-acetyl-3-α-piperidylpiperidine. The position of the double linking in (I) is uncertain. It is the only base of this type known in the Leguminosæ and occurs in *A. Conollyi* with *d*-sparteine (III), the ratio of (I) to (III) varying with age, indicating possible interconversion. This hypothesis is supported by the simultaneous presence of sparteine alkaloids and anabasine in *Anabasis aphylla*. E. G. B.

Synthesis of salsolidine. E. Späth and F. Dengel (Ber., 1938, **71**, [*B*], 113—119; cf. A., 1933, 907).—6 : 7-Dimethoxy-1-methyl-3 : 4-dihydro*iso*quinoline, obtained by the action of P_2O_5 on *N*-acetylhomoveratrylamine, is reduced by Zn and 2N-HCl or catalytically (Pd-sponge in MeOH containing AcOH at 40—45°) to dl-6 : 7-*dimethoxy*-1-*methyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline (= *dl*-salsolidine) (I), b.p. 180° (bath)/1 mm., m.p. 53—53·5° [hydrochloride, m.p. 196—197°; picrate, m.p. 201—201·5° (decomp.); picrolonate, m.p. 241° (decomp.); *Bz* derivative, m.p. 127—128° (vac.); the consts. differ considerably from those recorded by Proskurnina and Orékhov, A., 1937, II, 394]. Pd-sponge dehydrogenates (I) at 180° to 6 : 7-dimethoxy-1-methyl*iso*quinoline, m.p. 107—108°. Successive treatments of (I) with *d*- and *l*-tartaric acid in H_2O give l-*salsolidine* (II), m.p. 47·5—48·5°, $[\alpha]_D^{16}$ −59·7° in abs. EtOH, and d-*salsolidine* (III), m.p. 47·5—48·5° (vac.), $[\alpha]_D^{16}$ +59·9° in EtOH. Equal amounts of (II) and (III) give (I), m.p. 53°. The *hydrochlorides* of (II) and (III) have m.p. 235—236°, $[\alpha]_D^{18}$ −24·8° in H_2O, and m.p. 235—236°, $[\alpha]_D^{17}$ +25·3° in H_2O, respectively. The *picrates*, m.p. 193—194° (decomp.), and *picrolonates*, m.p. 235·5—236° (decomp.), of (II) and (III) are described. The optically active products are not racemised extensively when heated with 5% HCl at about 90° or similarly with 5% KOH or alone at 150°/0·01 mm. Oxidation of (I) with $KMnO_4$ gives *m*-hemipinic acid, identified as the ethylimide. CH_2O and anhyd. HCO_2H convert (III) into non-cryst. d-*carnegine*, b.p. 100° (bath)/0·01 mm., $[\alpha]_D^{19}$ +24·6° in EtOH. l-*Carnegine* has $[\alpha]_D^{18}$ −24·4° in EtOH. The *picrates* and *picrolonates* of the active bases have m.p. 222° (decomp. in open tube) and m.p. 205—206°, respectively. H. W.

Ergot alkaloids. XIII. Precursors of pyruvic and *iso*butyrylformic acids. W. A. Jacobs and L. C. Craig (J. Biol. Chem., 1938, **122**, 419—423).—Ergotinine is hydrogenated (Adams–Shriner PtO_2 in AcOH at 3 atm.) to a product which with KOH–MeOH yields *iso*butyrylformic acid (I), further hydrogenated in EtOH to α-hydroxyvaleric acid, which is not, however, detected in the former hydrogenation. Ergotamine similarly hydrogenated gives no nitroprusside reaction of $AcCO_2H$ until the product is hydrolysed. It is suggested that the precursors of (I) and $AcCO_2H$ from regotinine–ergotoxine (II)



and from ergotamine–ergotaminine (III) are $OH{\cdot}CPr^{\beta}(NH_2){\cdot}CO_2H$ and $OH{\cdot}CMe(NH_2){\cdot}CO_2H$, respectively, and that the formula represents (II) (R = Pr^{β}) and (III) (R = Me). E. W. W.

Microscopical examination of ergot alkaloids. III. Ergosine and ergosinine (ergoclavine). A. Kofler (Arch. Pharm., 1938, **276**, 40—45; cf. A., 1937, II, 393).—The crystallo-optical properties of ergosine, m.p. 208—212° (micro), and ergosinine, anhyd., m.p. 210—215°, and +MeOH, m.p. 190—192° or 210—215° (micro), are described. R. S. C.

Modified cinchona alkaloids. V. β-*iso*Quinotoxine and the stereochemistry of the parent bases. W. Solomon (J.C.S., 1938, 6—8).—β-*iso*Quinotoxine has $[\alpha]_D^{15}$ −33·8° in 0·1N-H_2SO_4 [*H tartrate*, m.p. 192—194° (decomp.), $[\alpha]_D^{15}$ −12·0° in

H_2O; *neutral tartrate* (+$2H_2O$), m.p. 162—166° (decomp.), $[\alpha]_D^{15}$ −12·0° in H_2O; *sulphate* (+$3{\cdot}5H_2O$), m.p. 198—199° (decomp.), $[\alpha]_D^{15}$ −25·2° in H_2O]. The evidence is thus in favour of the lævorotatory configuration of the fourth C of the cinchona alkaloid mol. F. R. S.

Cinchona and other alkaloids in bird malaria. III. G. A. H. Buttle, T. A. Henry, W. Solomon, J. W. Trevan, and E. M. Gibbs (Biochem. J., 1938, **32**, 47—58).—See A., 1938, III, 224. The following are described: *ethers* of *apo*quinine: *Pr*$^{\alpha}$, $[\alpha]_D^{15}$ −286·8° [*hydrochloride*, m.p. 249—251° (decomp.), $[\alpha]_D^{15}$ −172°], *Pr*$^{\beta}$, $[\alpha]_D^{15}$ −288° [*hydrochloride*, m.p. 254—257° (decomp.)], *Bu*$^{\alpha}$, m.p. 162—164°, $[\alpha]_D^{15}$ −280·7° [*hydrochloride*, m.p. 219° (decomp.)], n-*amyl*, m.p. 143—145·5°, $[\alpha]_D^{15}$ −268·1° [*hydrochloride*, m.p. 234·5—236·5° (decomp.)], iso*amyl*, m.p. 185°, $[\alpha]_D^{15}$ −269·7° (*hydrochloride*, m.p. 201—205°), n-*hexyl*, m.p. 135—137°, $[\alpha]_D^{15}$ −273·5° in 0·1N-$EtSO_3H$ (*hydrochloride*, m.p. 223—225°), n-*heptyl*, m.p. 137—140°, $[\alpha]_D$ −263·5° in 0·1N-$EtSO_3H$ (*hydrochloride*, m.p. 172—176°), n-*octyl*, m.p. 141—143°, $[\alpha]_D^{15}$ −232·5° in 0·1N-$EtSO_3H$ (*hydrochloride*, m.p. 90—145°), sec-*octyl*, $[\alpha]_D^{15}$ −225·6° in 0·1N-$EtSO_3H$ (*H oxalate*, decomp. 120°), n-*nonyl*, m.p. 138—141°, $[\alpha]_D$ −211·6° in 0·1N-$EtSO_3H$ (*hydrochloride*, m.p. 100—120°), n-*decyl*, m.p. 124—127°, $[\alpha]_D^{15}$ −177·6° in 0·1N-$EtSO_3H$ (*hydrochloride*, m.p. 90—115°), n-*undecyl*, m.p. 124—129°, $[\alpha]_D^{15}$ −164·6° in 0·1N-$EtSO_3H$ (*hydrochloride*, m.p. 100—120°), *cetyl*, m.p. 103—106°, $[\alpha]_D^{15}$ −132·7° in 0·1N-$EtSO_3H$ (*hydrochloride*, m.p. 90—110°). *Ethers* of *isoapo*quinidine: *Et* [*sulphate*, m.p. 140—145 (anhyd.), $[\alpha]_D^{15}$ −43·4°], n-*amyl* (*H sulphate*, m.p. 173°, $[\alpha]_D^{20}$ +26·2°), iso*amyl* [*sulphate*, m.p. 130° (decomp.), $[\alpha]_D^{20}$ +31·7° in 0·1N-H_2SO_4], n-*hexyl* (*H sulphate*, m.p. 175°, $[\alpha]_D^{20}$ +24·9° in 0·1N-HCl), n-*heptyl* (*H sulphate*, m.p. 170°, $[\alpha]_D^{20}$ +25·3° in 0·1N-HCl), n-*octyl* (*H sulphate*, m.p. 161°, $[\alpha]_D^{20}$ −5·1° in 0·1N-HCl). *Ethers* of dihydrocupreine: *Pr*$^{\beta}$, $[\alpha]_D$ −226° (*hydrochloride*, m.p. 227—230°), n-*amyl*, m.p. 130—132°, $[\alpha]_D^{15}$ −210·2° [*dihydrochloride*, m.p. 240—243 (decomp.), $[\alpha]_D^{15}$ −177·9°], n-*heptyl*, m.p. 130—132°, $[\alpha]_D^{15}$ −198·9° in 0·1N-$EtSO_3H$ (*dihydrochloride*, m.p. 140—160°), n-*octyl*, m.p. 119°, $[\alpha]_D^{15}$ −186·3° in 0·1N-$EtSO_3H$, n-*nonyl*, m.p. 130°, $[\alpha]_D^{15}$ −146° in 0·1N-$EtSO_3H$ (*dihydrochloride*, m.p. 180°), n-*decyl*, m.p. 111—113°, $[\alpha]_D^{15}$ −120·8° in 0·1N-$EtSO_3H$ (*dihydrochloride*, m.p. 135—155°), *undecyl*, m.p. 107—109°, $[\alpha]_D^{15}$ −108·7° in 0·1N-$EtSO_3H$ (*dihydrochloride*, m.p. 130—150°). J. N. A.

Alkaloids from the bark of *Strychnos henningsii*. III. Isolation of a second crystalline alkaloid. M. M. Rindl and M. L. Sapiro (Trans. Roy. Soc. S. Africa, 1936, **23**, 361—365).—The bark of *S. henningsii* contains 5—6% of a mixture of alkaloids. The cryst. alkaloid previously isolated is probably $C_{22}H_{25}O_4N_2{\cdot}OMe$. A second alkaloid $C_{22}H_{24}O_3N_2(OMe)_2$, m.p. 214·5—215·0°, subliming at 190—200°/0·03 mm., gives colour reactions with Froehde's reagent similar to those of colubrine (cf. A., 1931, 1312). H. J. E.

Atisan from *Aconitum heterophyllum*, Wall, and anthorin from *Aconitum anthora*. A. Goris (Compt. rend., 1937, **205**, 1007—1009).—*A. heterophyllum* contains atisan (I), an *isomeride* (iso*atisan*) (II) (*hydrochloride*, m.p. 331·5°, $[\alpha]_D$ +10·62°; *hydriodide*, m.p. 272°), and an *alkaloid* insol. in Et_2O. *A. anthora* yields anthorin (identical with atisan) and *ψ-anthorin*. Jowett's artisan (J.C.S., 1896, **69**, 1518) is a mixture of (I) and (II). J. D. R.

Influence of substitution in the nucleus on the reduction potential, the dissociation constants, and the surface activity of phenylarsinic acid. B. Breyer (Ber., 1938, **71**, [*B*], 163—171).—Determination of the reduction potentials of $PhAsO_3H_2$ and its 4-Me, 4-NHAc-, 4-OMe-, 2 : 4-Cl_2-, 4-OH- and 4-NH_2-derivatives by the polarographic method of Heyrovsky and Shikata shows that the influence of the substituents corresponds with the sequence: Me < NHAc < OMe < 2Cl < OH < NH_2. $NO_2{\cdot}C_6H_4{\cdot}AsO_3H_2$ cannot be investigated by this method since reduction first affects $\cdot NO_2$. It is remarkable that the introduction of Cl into the aromatic nucleus increases the difficulty of reducing $PhAsO_3H_2$. Generally the halogens as substituents appear to exert a somewhat uncertain influence. Anti-auxochrome action appears to predominate with Cl and to a smaller extent with Br, whereas I can reveal auxochrome activity. Determination of the dissociation consts. with the quinhydrone electrode places the negativising groups in the sequence NO_2 > Cl and the positivising groups in the order NHAc < Me < OMe < OH < NH_2. The surface activities of the acids and their derivatives are determined polarographically, the diminution of the O_2-max. being measured. If the val. of $PhAsO_3H_2$ is unity those of the Me, OH, NH_2, OMe, 2 : 4-Cl_2, and NHAc derivatives are 1·0, 1·5, 1·5, 3·0, 3·5, 8·5, and 22·2 respectively. It appears that the closing of the polar NH_2 or OH increase the surface activity in a degree ≫ calc. by the method of Bennett and Mitchell. H. W.

o-Arsenated phenoxyalkanols. S. B. Binkley and C. S. Hamilton (J. Amer. Chem. Soc., 1938, **60**, 134—135).—*o*-$NO_2{\cdot}C_6H_4{\cdot}OK$ and $CH_2Cl{\cdot}CHMe{\cdot}OH$ give β-o-*nitrophenoxy*iso*propyl alcohol*, b.p. 223—225°/25 mm., reduced (H_2–Raney Ni at 2 atm.) in MeOH to the *NH*$_2$*-alcohol*, m.p. 75°, which affords (Bart) β-o-*arsinophenoxy*iso*propyl alcohol*, m.p. 167° (*Na* salt). HNO_3 (*d* 1·5) converts this into β-4-*nitro*-2-*arsinophenoxy*iso*propyl nitrate*, m.p. 186°, hydrolysed by hot 3N-HCl to the *NO*$_2$*-alcohol*, m.p. 165—167°, which is hydrogenated to β-4-*amino*-2-*arsinophenoxy*iso*propyl alcohol*, +$2H_2O$ and anhyd., m.p. 184° (*Na* salt). SO_2–HI reduces this base to 5-*amino*-2-β-*hydroxy*-n-*propoxyphenylarsinoxide*, amorphous, m.p. 125—128°, and 2-β-*hydroxy*-n-*propoxyphenylarsinoxide*, amorphous, m.p. 115—120°, and the 5-*NO*$_2$-derivative, amorphous, m.p. 152—154°, thereof are similarly obtained. Reduction by H_3PO_2 gives 2 : 2′-*di*-β-*hydroxy*-n-*propoxyarsenobenzene*, m.p. 121—124°. Attempts to oxidise the CH·OH to CO and to condense *o*-OH·$C_6H_4{\cdot}AsO_3H_2$ with $CH_2Cl{\cdot}CHMe{\cdot}OH$ failed. R. S. C.

Organic arsenic compounds.—See B., 1938, 227.

Isomorphous relationships of some analogous organic derivatives of oxygen, sulphur, and selenium. N. M. Cullinane and C. A. J. Plummer (J.C.S., 1938, 63—67).—The results of observ-

ations of temp.–concn. diagrams of binary mixtures of (*a*) diphenylene oxide (I), sulphide (II), and selenide (III), and (*b*) diphenylene dioxide (IV), disulphide (V), and diselenide (VI), are in harmony with the periodic relationships of the elements O, S, and Se. In series (*a*), (II) and (III) and (I) and (II) yield continuous series of solid solutions, whilst (I) and (III) exhibit only partial solid solubility. The system (V)–(VI) shows that an unbroken series of solid solutions is present, whereas the systems (IV)–(V) and (IV)–(VI) exhibit eutectics with negligible solid solution formation. The spatial configurations of the mols. are discussed in the light of the results. F. R. S.

Configuration of heterocyclic compounds. VI. Examination of derivatives of seleno-xanthone and phenoxselenine. (Miss) M. C. Thompson and E. E. Turner. VII. **Some derivatives of phenoxtellurine.** (Miss) I. G. M. Campbell and E. E. Turner (J.C.S., 1938, 29—36, 37—42).—VI. 2-Selenocyano-4′-methyldiphenyl ether, prepared by diazotising the corresponding 2-NH_2-compound and adding KCNSe, could not be oxidised satisfactorily. 2-*Acetamido*-4′-*methyldiphenyl ether*, m.p. 92°, is oxidised ($KMnO_4$) to the -4′-*carboxy*-compound, m.p. 211°, hydrolysed to 2-*amino*-4′-*carboxydiphenyl ether*, m.p. 137°. The diazotised acid and KCNSe give 2-*selenocyano*-4′-*carboxydiphenyl ether*, m.p. 178°, oxidised (HNO_3) to 4′-*carboxydiphenyl ether* 2-*seleninic acid*, m.p. 212° (decomp.), which (85% H_2SO_4; aq. $K_2S_2O_5$) gives *phenoxselenine*-2-*carboxylic acid*, m.p. 251° [*dibromide*, m.p. 214° (decomp.)]. This acid could not be resolved through the following salts: *cinchonidine*, m.p. 211°; *d*- and *l*-α-phenylethylamine, *l*-base *salt*, m.p. 207°, $[\alpha]_{5791}^{20}$ −3·5° in MeOH; *brucine salt trihydrate*, $[\alpha]_{5791}^{20}$ −10·3° to 6·2° in $COMe_2$, giving inactive acids. Selenoxanthone-1-carboxylic acid could not be resolved through the *l*-CHPhMe·NH_2 or *strychnine* salt, m.p. 240—243°, $[\alpha]_{5461}^{20}$ +3·5° in $CHCl_3$. 2′ : 4′-*Dichloro*-2-*nitro*-4-*carboxydiphenyl ether*, m.p. 207—209°, obtained from 2 : 4-$C_6H_3Cl_2$·OH and 3 : 4-NO_2·C_6H_3Cl·CO_2H, is reduced (aq. NH_3–$FeSO_4$) to the -2-NH_2-compound, m.p. 199° (*Ac* derivative, m.p. 232°), the diazo-derivative of which with KCNSe gives the -2-*selenocyano*-derivative, m.p. 247—248° (decomp.). This compound is oxidised (HNO_3) to 2′ : 4′-*dichloro*-4-*carboxydiphenyl ether* 2-*seleninic acid*, decomp. >176°, which gives (H_2SO_4; $K_2S_2O_5$) 6 : 8-*dichlorophenoxselenine*-2-*carboxylic acid*, m.p. 309°, which could not be resolved through the d-α-*phenylethylamine salt*, m.p. 250—256°, $[\alpha]_{5791}^{20}$ +4·2° in EtOH. The acid with NaOH affords 5 : 5′-*dicarboxy*-2 : 2′-*di*-(2′ : 4′-*dichlorophenoxy*)*diphenyl diselenide* (+2AcOH), m.p. 278° (decomp.). 2-*Nitro*-4-*carboxy*-3′ : 5′-*dimethyldiphenyl ether*, m.p. 179—181°, prepared from *m*-xylenol and 3 : 4-NO_2·C_6H_3Cl·CO_2H, is reduced to the 2-NH_2-*acid*, m.p. 173° (*Ac* derivative, m.p. 219°), the diazo-derivative of which with KCNSe yields the 2-*selenocyano*-compound, m.p. 233° (decomp.). This substance with NaOH forms 5 : 5′-*dicarboxy*-2 : 2′-*di*-(4′-m-*xylenoxy*)*diphenyl diselenide* (+AcOH), m.p. 239—243°. 2-*Carboxyphenoxselenine* 10-*oxide*, m.p. 217—218°, obtained by oxidation (H_2O_2) of the -carboxylic acid, could not be resolved through the *nor*-d-ψ-*ephedrine* salt, m.p. 180°, $[\alpha]_{5791}^{20}$ +16·7° to +17·4° in aq. MeOH. The non-resolvability of the compounds is discussed. Selenanthren has a folded structure.

VII. 2-Aminophenoxtellurine could not be resolved through the *H* d-*tartrate*, m.p. 158—159° (decomp.), $[\alpha]_{5791}^{20}$ +2·45° in EtOH, or d-*camphorsulphonate*, m.p. 182—185° (decomp.), $[\alpha]_{5791}^{20}$ +14·0° to 15·6° in EtOH. 4-Chloro-4′-methyldiphenyl ether and $TeCl_4$ when heated together give a poor yield of a dichloride, reduced to 2-*chloro*-8-*methylphenoxtellurine*, m.p. 67—68°. 2-Amino-4′-methyldiphenyl ether, diazotised and treated with $HgCl_2$ and then Cu at low temp., gives 2-*chloromercuri*-4′-*methyldiphenyl ether*, m.p. 140°, which with $TeCl_4$ forms 4′-*methyldiphenyl ether* 2-*telluritrichloride*, m.p. 180—185° (decomp.), converted by heating into 2-*methylphenoxtellurine* 10 : 10-*dichloride*, m.p. 274—275°. The dichloride is reduced to 2-*methylphenoxtellurine*, m.p. 50—52°, which could not be oxidised. A similar series of reactions with 2-amino-4′-carboxydiphenyl ether gives 2-*chloromercuri*-4′-*carboxydiphenyl ether*, m.p. 220° (decomp.), 4′-*carboxydiphenyl ether* 2-*telluritrichloride*, m.p. 205—206° (decomp.), 2-*carboxyphenoxtellurine* 10 : 10-*dichloride*, m.p. 319°, and *phenoxtellurine*-2-*carboxylic acid*, m.p. 231—233°. This acid could not be resolved through the *nor*-d-ψ-*ephedrine* salt, m.p. 144—145°, also (+3H_2O), $[\alpha]_{5791}^{20}$ +16·8° in EtOH; *strychnine* salt, m.p. 198—200° (decomp.), $[\alpha]_{5791}^{20}$ −14·5° in $CHCl_3$; *quinine* salt, m.p. 211°, $[\alpha]_{5791}^{20}$ −125·1° in $CHCl_3$; *cinchonidine* salt, m.p. 206°, $[\alpha]_{5791}^{20}$ −59·4°; d-α-*phenylethylamine* salt, m.p. 205°, $[\alpha]_{5791}^{20}$ +3·80° to 4·19° in MeOH; and l-*menthyl* ester, m.p. 123—125°, $[\alpha]_{5791}^{20}$ −51·9° to −52·2° in $COMe_2$. It is probable that the phenoxtellurine mol., although folded, is flexible. F. R. S.

Recent progress in the chemistry of the proteins. P. Rondoni (Chim. e l'Ind., 1938, **16**, 65—73).—A review.

Proteins and proteolytic enzymes.—See A., III, 148.

Micro-determination of carbon and hydrogen. A. Elek (Ind. Eng. Chem. [Anal.], 1938, **10**, 51—52).—Suggested improvements in the Pregl technique include the use of Ag gauze in place of Ag thread in the combustion train, an improved electric heater and absorption tubes, the use of pure O_2 from liquid air, and employment of two specially designed boats and capillary tubes in the analysis of easily subliming and volatile substances. F. N. W.

Micro-determination of carbon and hydrogen. E. J. Schtuber and M. E. Maurit (J. Gen. Chem. Russ., 1937, **7**, 2523—2531).—Directions for conducting micro-determination of C and H by a modified Pregl procedure are given. R. T.

Weighing tube for volatile liquids in carbon–hydrogen and Dumas nitrogen semimicro-determinations. V. A. Aluise (Ind. Eng. Chem. [Anal.], 1938, **10**, 56).—Use of a U-shaped capillary tube, centrifuged after filling and prior to sealing, overcomes the necessity of using $KClO_3$ in the Pregl straight weighing tube. F. N. W.

Distillation of ammonia in Kjeldahl determinations with the Parnas–Wagner apparatus. J. K. Parnas (Acta Biol. Exp., 1937, **11**, 107—110).—Bartosiewicz's modification (A., 1937, II, 129) is criticised. R. T.

Micro-determination of phosphorus in organic compounds. E. I. Aizenschtadt (Zavod. Lab., 1937, **6**, 1014—1016).—Minor modifications of Pregl's method are described. R. T.

Titration with mixed indicators. A. Zipero-vitsch (Ukrain. Biochem. J., 1937, **10**, 441—444).—CO_2H groups are determined using a 0·5% solution of mixed thymol- and phenol-phthaleins as indicator, whereby the colour change point is broader than with a single indicator. P. G. M.

Application of the Raman effect to the analysis of organic mixtures. J. Goubeau (Angew. Chem., 1938, **51**, 11—15).—The application of the Raman effect to qual. and quant. org. analysis is described. The sensitivity of the process is discussed. The method may be used (*a*) for testing the purity of a substance, (*b*) for identifying a substance (for which purpose it has several advantages over m.p. and b.p. determinations), (*c*) for analysing mixtures of many, or difficultly separable, constituents, *e.g.*, motor fuels, (*d*) the detection of classes of compounds. Quant. analysis depends on the determination of the intensity of the Raman lines. A. J. M.

Cause of error in the determination of the diene value. S. Sabetay and Y. R. Naves (Bull. Soc. chim., 1937, [v], **4**, 2105—2107).—$CH_2Ph{\cdot}CH_2{\cdot}OH$, $CH_2Ph{\cdot}OH$, n-$C_8H_{17}{\cdot}OH$, geraniol, menthol, borneol, cholesterol, and ricin all react when heated with maleic anhydride. Thus the "diene val." of an oil or fat, determined by the method of Kaufmann (A., 1936, 966) or of Sandermann (B., 1937, 1370), may be quite misleading if alcohols are present. E. W. W.

Determination of pentoses and other reducing sugars.—See A., III, 162.

[Microchemical detection of acetic acid.]—See A., I, 157.

Colour test for pentoses. H. Tauber (Proc. Soc. Exp. Biol. Med., 1937, **37**, 600—601).—1 g. of benzidine is dissolved in 25 c.c. of glacial AcOH. If 0·5 c.c. of this solution is added to one drop of a solution of arabinose, xylose, or ribose containing 0·05 mg. of the sugar, which is then boiled and cooled, a stable cherry-red colour develops. V. J. W.

Biochemistry of carbohydrates. XXIX. Determination of non-amino-sugars by the Dische and Tillmans–Philippi methods. H. Hisamura (J. Biochem. Japan, 1937, **26**, 359—372).—Tabulated data and curves indicate the accuracy obtainable in the colorimetric determination of non-amino-sugars (glycuronic acid, glucose, mannose, galactose, arabinose, xylose) at various concns. by the orcinol method of Tillmans and Philippi (Ozaki, A., 1937, III, 87) and the indole and phloroglucinol methods of Dische (A., 1926, 1282). The reduction in colour due to mixing a sugar with either another sugar or an amino-sugar is indicated. F. O. H.

Potentiometric determination of polypeptides and amino-acids. III. Titration of amino-acids and peptides in presence of sugars. E. W. Balson and A. Lawson (Biochem. J., 1938, **32**, 230—234; cf. A., 1936, 1006).—The changes in p_H observed when a sugar is added to a NH_2-acid buffer are due only to the acidic function of the sugar. The product of the reaction has an acid K not very different from that of the NH_2-acid itself. Hence the electrometric method cannot be used for studying the equilibrium. The p_H optimum curves obtained for CH_2O titration by Frankel and Katchalsky (A., 1937, II, 402) are inconsistent with the accepted theory. J. N. A.

Determination of adrenaline.—See A., III, 162.

Determination of the phellandrenes by means of maleic anhydride. N. F. Goodway and T. F. West (J.S.C.I., 1938, **57**, 37—38).—The maleic anhydride iodometric method (A., 1937, II, 272, 296) for determining conjugated compounds is not applicable to β-phellandrene (I). Diene val. rose slowly to 31·8 in 10 hr., equiv. to 17% of (I), although the H_2 absorption corresponded with 77%. The diene val. of the α-phellandrene indicated 45% purity, H_2 absorption corresponding with 70%. T. F. W.

Colour reaction of tannic acid. E. Durio and M. Garino (Annali Chim. Appl., 1937, **27**, 523—525).—The application of the red colour given with aq. I and $NaHCO_3$ to the detection and determination of tannin (*e.g.*, in plant extracts) is described. F. O. H.

Determination of histidine. R. J. Block (Proc. Soc. Exp. Biol. Med., 1937, **37**, 580—582).—Histidine is pptd. from the protein dialysate by $AgNO_3$ and the Ag is removed by H_2S. The histidine in solution can be determined colorimetrically as a Br-compound or gravimetrically as an insol. compound with nitranilic acid. V. J. W.

Turbidimetric titration of small amounts of nicotine. L. D. Goodhue (Ind. Eng. Chem. [Anal.], 1938, **10**, 52—54).—A photo-electric apparatus including a special titration cell is used. 0·05—0·75 mg. of nicotine and 2 c.c. of silicotungstic acid solution (5 g. per l.) are pipetted into the cell and 4 drops of 1·5N aq. HCO_2H (to retard crystallisation), 4 drops of 2% aq. irish moss extract (to prevent flocculation), and 10 c.c. of H_2O are added, and the mixture is titrated with standard aq. nicotine formate (0·5 g. per l.), the end-point being the point of max. turbidity, which is indicated photo-electrically. F. N. W.

Titration constants of anserine, carnosine, and related compounds.—See A., I, 144.