BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

JULY, 1941.

I.—ALIPHATIC.

Photolysis of ethyl iodide in various solvents [and determination of ethyl iodide].—See A., 1941, I, 275.

Cadmium-photosensitised reactions of propane.—See A., 1941, I, 275.

Kinetics of oxidation of hydrocarbons.—See A., 1941, I, 270.

Chromium oxide gel catalysts for dehydro-cyclisation of *n*-heptane.—See A., 1941, I, 274.

High-pressure chlorination of paraffins.—See B., 1941, II, 133.

Catalytic polymerisation of ethylene at atmospheric pressure. XI. Influence of hydrogen and nitrogen. XII. Action of acetylene. Y. Konaka (*J. Soc. Chem. Ind. Japan*, 1940, **43**, 363B; cf. B., 1938, 762).—XI. The presence of H_2 diminishes the yield of polymeride oil over Ni, Co, or Fe catalysts. N_2 acts merely as a diluent.

XII. C_2H_2 alone yields little oil but $C_2H_2 + H_2$ (1 : 1) give a good yield of mainly aromatic oil, of lower distillation range than the oil from C_2H_4, which is paraffinic. Although present in the polymerisation products of C_2H_4, C_2H_2 is not to be regarded as the main intermediate product. A. R. PE.

Catalytic polymerisation of ethylene at atmospheric pressure. IX, X.—See B., 1941, II, 134.

Polymerisation of olefines. III. Polymeric olefines from methyl*iso*propylcarbinol. F. C. Whitmore and W. A. Mosher (*J. Amer. Chem. Soc.*, 1941, **63**, 1120—1123; cf. A., 1941, 756).—$CHMePr^{\beta}$·OH and 75% H_2SO_4 at 76—80° give (cf. Drake *et al.*, A., 1934, 1329). $CHMeBu^{\gamma}$·CMe:CHMe (45), CMe_2Et·CH_2·CMe:CHMe (I) (35), C_2HMe_3 (1), CMeEt:CHMe (3), $COMePr^{\beta}$ (1), $CHMeBu^{\gamma}$·CMe:CH_2 (2), other nonenes (1), and higher polymerides (5%). Reaction mechanisms are postulated. COMe·CH_2·CMe_2Et and MgMeI give CMe_2Et·CH_2·CMeEt·OH, b.p. 86°/30 mm., dehydrated by 75% H_2SO_4 at 80° to a 20 : 1 and by $CuSO_4$ to a 6 : 1 mixture of (I) and CMe_2Et·CH:CMeEt. COMe·CHMeBu^{γ} and COEt·CHMeBu^{γ} do not react with MgRI. R. S. C.

Property of conjugated systems. J. Kenner (*Nature*, 1941, **147**, 482).—In a compound X·$[CH{:}CH]_n$·Y the conjugated system is an electronic conductor between the covalent groups X and Y, and there must be a correspondence between such chemical properties of the compound as leave the conjugated system intact and those of the covalent compound XY. The val. of this generalisation as a means of insight into the reactivity, and its mechanism, of the compound XY has been overlooked. Its bearing on the nitration of paraffins, the mechanism of nitrosation of $NHMe_2$, and the mechanism of certain inorg. reactions is discussed. L. S. T.

Absorption spectrum of squalene.—See A., 1941, I, 192.

Removal of substituents from vinyl polymerides. II. F. T. Wall (*J. Amer. Chem. Soc.*, 1941, **63**, 821—824; cf. A., 1940, II, 202).—The removal of Cl from polyvinyl chloride or a co-polymeride of vinyl chloride and acetate by Zn is treated statistically when the polymeride is made up of "head to head–tail to tail" units. The results are compared with previously derived equations for structures involving 1–2 or 1–3 removal of Cl_2. It is proved rigorously that different removal rates of 1–2 and 1–3 Cl_2 pairs have no effect on the final % of Cl in a randomly oriented polymeride. W. R. A.

Catalytic dehydration and dehydrogenation of butyl and amyl alcohol. V. I. Komarewsky and J. T. Stringer (*J. Amer. Chem. Soc.*, 1941, **63**, 921—922).—Passage of $Bu^{\alpha}OH$, *n*- or *iso*-C_5H_{11}·OH over Al_2O_3–Cr_2O_3 (cf. A., 1939, II, 491) at 575—625°/128—155 mm. (apparatus described) gives 20·4—49·3% of olefine (dehydration by Al_2O_3), 1·8—15·9% of diene [$(CH_2{:}CH)_2$, CHMe:CH·CH:CH_2, or isoprene, respectively; mixed dehydration–dehydrogenation], considerable amounts of aldehyde (dehydrogenation by Cr_2O_3; decomposed during the reaction to CO, CO_2, and paraffins), and free C. Over Al_2O_3 alone more olefine is formed but no diene. R. S. C.

Use of methylallyl chloride in the synthesis of compounds with conjugate unsaturation. C. D. Hurd and J. L. Abernethy (*J. Amer. Chem. Soc.*, 1941, **63**, 976—977).—$CH_2{:}CMe·CH_2Cl$ (I) and HOCl give *ββ′-dichloro*-tert.-*butyl alcohol*, b.p. 72—73°/23 mm., converted by KCN in hot aq. MeOH into $(CN·CH_2)_2CMe·OH$, an oil, which with HCl–abs. EtOH gives an OH-ester and thence by distillation with I yields $CO_2Et·CH_2·CMe{:}CH·CO_2Et$ (*α-CHPh:* derivative, softens at ~170°, decomp. 175—200°). With aq. Br–KBr or I–HgO, (I) gives *β-chloro-β′-bromo-*, b.p. 84—85°/20 mm., and *-β′-iodo*-tert.-*butyl alcohol*, b.p. 101—103° (decomp.)/18 mm., respectively. R. S. C.

Effect of zinc chloride on octyl alcohol. M. M. Gerasimov and V. E. Glushnev (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, **29**, 462—465).—Interaction of octyl alcohol (I) vapour at 225—325° with $ZnCl_2$ distributed on pumice gives hexenes, heptenes, octenes, $CMe_2{:}CH_2$, CHMe:CH_2, C_2H_4, and H_2 and saturated hydrocarbons due to "cracking" of (I). The yield of H_2 and unsaturated hydrocarbons is the greater the higher is the temp. Aldehydes are present in the fractions of high b.p. J. L. D.

Preparation of αγ-butylene glycol from aldol by high-pressure hydrogenation. I. Reaction with nickel catalyst prepared electrolytically. II. Reaction with mixed catalyst of nickel and alumina. H. Nagai (*J. Soc. Chem. Ind. Japan*, 1941, **44**, 41—43B, 43B).—Aldol has been hydrogenated to OH·CHMe·$[CH_2]_2$·OH, varying the temp., time, amount and pressure of H_2, and amount of catalyst. Optimum results are obtained with 10% of catalyst and a H_2–aldol ratio >77 : 23 by vol., at 80° and >30 atm. pressure.

II. Addition of Al_2O_3 to the catalyst reduces the reaction rate and the yield. A. LI.

Catalytic preparation and interconversion of simple and mixed esters. V. N. Ipatieff and R. L. Burwell, jun. (*J. Amer. Chem. Soc.*, 1941, **63**, 969—971).—Passage of MeOH over "solid H_3PO_4" at 350°/55 atm. gives 86—87% of Me_2O. At 336°/60 atm. MeOH + EtOH gives similarly Me_2O, MeEtO, and Et_2O (largely decomposed to C_2H_4). MeOH + CH_2Ph·OH at 350°/50 atm. gives similarly CH_2Ph·OMe. Me_2O + Et_2O are decomposed by the catalyst at 450°. In an autoclave Me_2O and Et_2O are equilibrated by the catalyst at 150°. R. S. C.

Structure of the Cori ester. M. L. Wolfrom and D. E. Pletcher (*J. Amer. Chem. Soc.*, 1941, **63**, 1050—1053).—The structure of the Cori ester (I) as *d*-glucopyranose 1-phosphate is confirmed. Synthetic (I) (Cori *et al.*, A., 1938, II, 39) has $[\alpha]^{20}_{5892\cdot5}$ +78°, $[\alpha]^{20}_{5461}$ +90° in H_2O, is hydrolysed by 5% HCl at 60° to glucose (isolated as Et_2 mercaptal penta-acetate), and is characterised as K_2 salt, +$2H_2O$ [mol. wt. (cryoscopy; H_2O) normal; does not reduce Fehling's solution], which consumes 2 HIO_4 giving 1 HCO_2H and no CH_2O. R. S. C.

Cetyl 3 : 5-dinitrobenzoate, m.p. 72·3°.—See A., 1941, III, 367.

Absorption of oxygen by mercaptans in alkaline solution. J. Xan, E. A. Wilson, L. D. Roberts, and N. H. Horton (*J. Amer. Chem. Soc.*, 1941, **63**, 1139—1141).—RSH in aq. NaOH absorb more O_2 than is required for formation of R_2S_2 (reason unknown). The rate of absorption of O_2 increases with the concn. of alkali, when allowance is made for decrease in the solubility of O_2 in the solution. The rate of absorption is R = Pr$^{\alpha}$ > Bu > *n*-amyl > CH_2Ph > Ph. R. S. C.

Sulphonation of *iso*butylene. I. β-Methylpropene-αγ-disulphonic acid and related compounds. C. M. Suter and J. D. Malkemus (*J. Amer. Chem. Soc.*, 1941, **63**, 978—981).—Addition of SO_3 (4·38) and then of *iso*-C_4H_8 (2·2) to dioxan (3 mols.) in $(CH_2Cl)_2$ at 0°, warming to 50°, and keeping at 0° gives 30% of *dioxan β-methylpropene-αγ-disulphonate* (**I**), whence the *Ba* (**II**), +5H_2O (1 H_2O retained at 115°/10 mm.; unsaturated to $KMnO_4$), *Na*$_2$, $(NH_4)_2$, and $(NH_3Ph)_2$ (**III**) salts are prepared. $SOCl_2$ converts (**I**) into the acid *anhydride* (**IV**), m.p. 167—170°, which is only slowly hydrolysed by H_2O or aq. alkali, reacts only slowly with Br–CCl_4 or –H_2O, and with NH_2Ph in EtOAc gives (**III**). PCl_5 at 100° converts (**IV**), (**I**), or (**II**) into the *disulphonyl chloride* (**V**), m.p. 79·2—79·8°, which gives the *diamide*, m.p. 152·5—154°, and *dianilide*, m.p. 171·5—172·5°, at 180—210° gives SO_2 and (?) $CH_2Cl{\cdot}CMe{:}CHCl$, and with 3 : 5-$(NO_2)_2C_6H_3{\cdot}CO_2Ag$ gives products, m.p. 56—57° and 139—142° (not derived from *cis*- or *trans*-$OH{\cdot}CH_2{\cdot}CMe{:}CHCl$). $CH_2Cl{\cdot}CMe{:}CH_2$ and 2·25% HOCl at ~15° give $OH{\cdot}CMe(CH_2Cl)_2$ and thence by aq. Na_2SO_3 at 70—90°, followed by PCl_5 at 100°, (**V**). Hydrogenation of (**III**) to $CHMe(CH_2{\cdot}SO_3NH_3Ph)_2$ [prepared from $CHMe(CH_2Cl)_2$] failed. SO_3–dioxan and Bu$^{\gamma}$OH at 0—5° give dioxan H sulphate and only a trace of org. acid. R. S. C.

Radioactive carbon as tracer in synthesis of propionic acid from carbon dioxide by propionic acid bacteria.—See A., 1941, III, 536.

Thermal transformations of thallous formate.—See A., 1941, I, 278.

Substituted acetylenes and their derivatives. XLII. Preparation, properties, and derivatives of α-acetylenic acids. A. O. Zoss and G. F. Hennion (*J. Amer. Chem. Soc.*, 1941, **63**, 1151—1153; cf. Campbell amd Eby, A., 1941, II, 81).—C_2HNa in liquid NH_3 at −35° is treated with RBr and then with $NaNH_2$ at −45°. The resulting crude $CR{:}CNa$ is treated in Et_2O, C_6H_6, or PhMe with CO_2 at −50° and then with saturated aq. $NaHSO_4$, giving thus good yields of $CR{:}C{\cdot}CO_2H$ with 5% of C_2R_2. $CR{:}C{\cdot}CO_2Me$ (prep. by H_2SO_4–MeOH) with HgO–Et_2O,BF_3–$CCl_3{\cdot}CO_2H$–MeOH gives $OMe{\cdot}CR{:}CH{\cdot}CO_2Me$ (purified by distillation with a trace of *p*-$C_6H_4Me{\cdot}SO_3H$), with liquid NH_3–MeOH gives $CR{:}C{\cdot}CO{\cdot}NH_2$, and with $NHPh{\cdot}NH_2$ at 130° gives the pyrazolone. Addition of Br to the acid in CCl_4 gives $CRBr{:}CBr{\cdot}CO_2H$. Thus are obtained Δ$^{\alpha}$-*n*-pentinenoic, m.p. 50·0° [*dibromide*, m.p. 35—38·5°, b.p. 126°/6 mm. (another fraction containing 66·42% of Br had m.p. 40·2—43·7°, b.p. 118—125·5°/6 mm.); Me ester, b.p. 47°/10 mm.; *amide*, m.p. 146—146·5°], -hexinenoic, m.p. 24·5—25°, b.p. 111°/10 mm. (Me ester, b.p. 65°/10 mm.; *dibromide*, b.p. 125°/2 mm.; *amide*, m.p. 81·5—82°), -heptinenoic, b.p. 122°/10 mm. (Me ester, b.p. 72°/10 mm.; *dibromide*, b.p. 142°/7 mm.; *amide*, m.p. 68—69°), and -octinenoic acid, b.p. 133°/10 mm. (Me ester, b.p. 94°/10 mm.; *dibromide*, b.p. 146°/2 mm.; *amide*, m.p. 89—90°), *Me β-methoxy-*Δ$^{\alpha}$-n-*pentenoate*, b.p. 59·5°/10 mm., *-hexenoate*, b.p. 76°/10 mm., *-heptenoate*, b.p. 88°/10 mm., and *-octenoate*, b.p. 100°/10 mm., 1-phenyl-3-ethyl-, m.p. 100—110·5°, *-n*-propyl-, m.p. 110·5—111°, -n-*butyl-*, m.p. 83—83·5°, and *-n*-amyl-, m.p. 95·5—96°, -pyrazolone. R. S. C.

Synthesis of Δ$^{\alpha}$-pentadecenoic and -heptadecenoic acids. W. M. Lauer, W. J. Gensler, and E. Miller (*J. Amer. Chem. Soc.*, 1941, **63**, 1153—1155).—The following general synthesis is devised, increasing the C chain by one unit. $CH_2R{\cdot}CO_2H \rightarrow CHRBr{\cdot}CO_2H \rightarrow$ (+KOH) $OH{\cdot}CHR{\cdot}CO_2H \rightarrow$ [+$Pb(OAc)_4$–AcOH; 60°] RCHO (obtained also, less well, by pyrolysis) → [+$CH_2(CO_2H)_2$–C_5H_5N at room temp. and later 100°] $CHR{:}CH{\cdot}CO_2H$. Thus are obtained *n*-$C_{12}H_{25}{\cdot}CHO$, b.p. 150—155°/28 mm. (semicarbazone, m.p. 105·5—106·5°; 2 : 4-*dinitrophenylhydrazone*, m.p. 107—108°), *n*-$C_{14}H_{29}{\cdot}CHO$, b.p. 155—160°°/12—14 mm. (semicarbazone, m.p. 108—109°; 2 : 4-*dinitrophenylhydrazone*, m.p. 107·5—108°), Δ$^{\alpha}$-*heptadecenoic*, m.p. 57·5° (*amide*, m.p. 110—110·5°; p-*bromoanilide*, m.p. 115—116°), and *-pentadecenoic acid*, m.p. 47·5—48° (*amide*, m.p. 111·5—112·5°; p-*bromoanilide*, m.p. 114—114·5°). The structure of the acids is proved by ozonolysis in $CHCl_3$ to give RCHO. R. S. C.

Chemistry of fatty acids. VII. Multiple nature of linoleic and linolenic acids prepared by the bromination–debromination procedure. Purification of these acids by repeated low-temperature crystallisation. N. L. Matthews, W. R. Brode, and J. B. Brown (*J. Amer. Chem. Soc.*, 1941, **63**, 1064—1067; cf. A., 1940, II, 266).—Debromination of linoleic (**I**) and linolenic (**II**) acid bromides and crystallisation of the products from light petroleum at ~ −60° shows the presence of ~12 and ~15%, respectively, of isomerides in the products, whence existence of isomerides in the "natural" acids is inferred. (**I**), m.p. −5·2° to −5·0°, and (**II**), m.p. −11·3° to −11·0° (hexabromide no. 96·0), are reported. R. S. C.

Geometric isomerism of linolenic acids. Elaidolinolenic acid. J. P. Kass, J. Nichols, and G. O. Burr (*J. Amer. Chem. Soc.*, 1941, **63**, 1060—1063).—Heating the Et esters of the acids from linseed oil with Se–N_2 at 205—215°, followed by hydrolysis and treatment with Br, gives *elaidolinolenic acid hexabromide* (**I**), m.p. 169—170° (Et ester, m.p. 114—115°), and Et_2O-sol. bromides. Zn and HCl–EtOH convert (**I**) into Et elaidolinolenate, b.p. 138°/1 mm., hydrolysed to the *acid* (**II**), m.p. 29—30°, f.p. 29·5—30°, I val. (Wijs) 271·8, and CNS val. 149·7 (absorbs 3 H_2). Pure (**II**) gives only 31% of (**I**), whence it follows that formation of more than one bromide from linolenic acid is not evidence for existence of a β-isomeride. R. S. C.

Malonatomanganiates.—See A., 1941, I, 278.

Hydrogen bridges and isomerism. H. C. Brown (*J. Amer. Chem. Soc.*, 1941, **63**, 882—883).—Polemical against Reimer *et al.* (A., 1940, II, 374; 1941, II, 102). W. R. A.

Wound hormones of plants. V. Synthesis of analogues of traumatic acid. J. English, jun. (*J. Amer. Chem. Soc.*, 1941, **63**, 941—943; cf. A., 1940, III, 271).—Et H sebacate and boiling $SOCl_2$ give the ester *chloride*, b.p. 129—130°/1 mm., and thence by H_2–Pd in xylene (no "poison") Et θ-aldehydo-*n*-nonoate, b.p. 130°/2 mm. Condensation of $CO_2H{\cdot}[CH_2]_n{\cdot}CHO$ and $CH_2(CO_2H)_2$ by C_5H_5N at room temp. and subsequent hydrolysis by 2N-NaOH–EtOH gives $CO_2H{\cdot}[CH_2]_n{\cdot}CH{:}CH{\cdot}CO_2H$ and some $CO_2H{\cdot}[CH_2]_{n-1}{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CO_2H$ (*A*), but by $NPhMe_2$–MeOH or $N([CH_2]_2{\cdot}OH)_3$ gives mainly (*A*); the isomerides are best separated by adsorption on C from Et_2O. Thus are obtained Δ$^{\alpha}$-*nonene-αι-*, m.p. 103°, *-n*-decene-*ακ-*, m.p. 165°, and *-n-tridecene-αν-*, m.p. 108·5°, Δ$^{\beta}$-*n*-nonene-*αι-*, m.p. 90°, *-n-decene-ακ-*, m.p. 109°, and *-tridecene-αν-dicarboxylic acid*, m.p. 104°. $([CH_2]_3{\cdot}CHBr{\cdot}CO_2Et)_2$ (prep. from the acid chloride by Br, followed by EtOH) with $NPhMe_2$ at 180° gives Δ$^{\alpha\eta}$-*octadiene-αθ-dicarboxylic acid*, m.p. 236—239° (decomp.), hydrogenated (1 mol. of H_2; Pt; EtOH) to Δ$^{\alpha}$-n-*octene-αθ-dicarboxylic acid*, m.p. 173°. $CO(CH_2{\cdot}CO_2Et)_2$, $I{\cdot}[CH_2]_4{\cdot}CO_2Et$, and NaOEt–EtOH give an undistillable ester, which in boiling conc. HCl gives n-*undecan-ζ-one-αλ-dicarboxylic acid*, m.p. 114° (*Et* ester, b.p. 180°/0·5 mm.), hydrogenated (PtO_2; 30—40 lb.; Et_2O–EtOH) to n-*undecan-ζ-ol-αλ-dicarboxylic acid*, m.p. 102—103°, which with PI_3 at 100° gives an oily I-acid, converted by 25% KOH–EtOH into Δ$^{\epsilon}$-n-*undecene-αλ-dicarboxylic acid*, m.p. 72°. n-*Nonan-ε-one-*, m.p. 111°, and n-*nonan-ε-ol-αι-dicarboxylic acid*, m.p. 95°, but not the unsaturated acid, are similarly prepared. Other methods of prep. failed. The unsaturated acids are all plant wound hormones, more active than the saturated acids. M.p. are corr. R. S. C.

Crystalline sodium salt of pantothenic acid. N. Gätzi-Fichter, H. Reich, and T. Reichstein (*Helv. Chim. Acta*, 1941, **24**, 185—187).—*Na pantothenate*, m.p. 121—122°, $[\alpha]_D^{13}$ +29°±1·5° in H_2O, is obtained from the Ba salt and Na_2SO_4 with subsequent crystallisation from EtOH with addition of $COMe_2$ or Et_2O or by addition of α-hydroxy-ββ-dimethylbutyrolactone to NaOMe–MeOH containing β-alanine. It is very hygroscopic. *Na* l-*pantothenate* has m.p. 120—122°, $[\alpha]_D^{15}$ −27·4°±2·5° in H_2O. H. W.

Use of Bunte salts in synthesis. II. Preparation of derivatives of thiol-aliphatic acids. G. G. Stoner and G. Dougherty (*J. Amer. Chem. Soc.*, 1941, **63**, 987—988; cf. A., 1940, II,

159).—$CH_2Cl{\cdot}CO_2Na$ and aq. $Na_2S_2O_3$ give $SO_3Na{\cdot}S{\cdot}CH_2{\cdot}CO_2Na$, oxidised by I in hot H_2O to $(S{\cdot}CH_2{\cdot}CO_2H)_2$. *dl*-$(CHMeBr{\cdot}CO_2Na)_2$ gives similarly $(S{\cdot}CHMe{\cdot}CO_2H)_2$, and $Cl{\cdot}[CH_2]_2{\cdot}CO_2H$ gives $(S{\cdot}[CH_2]_2{\cdot}CO_2H)_2$. $Cl{\cdot}[CH_2]_3{\cdot}CN$ with $Na_2S_2O_3$ in boiling EtOH and later I gives *di-γ-thiolbutyronitrile* (70%), an oil, hydrolysed by hot conc. HCl to $(S{\cdot}[CH_2]_3{\cdot}CO_2H)_2$. $CO_2H{\cdot}[CH_2]_n{\cdot}S{\cdot}SO_3Na$ (prep. as above) with HCl and RCHO or COR_2 gives *S*-methylene-, m.p. 126—127° (cf. lit.), *S*-benzylidene-, m.p. 124° (cf. lit.), *S-o*-nitrobenzylidene-, m.p. 124° (lit. 122—123°), and *S-iso*propylidene-di(thiolacetic acid), m.p. 129° (cf. lit.), *S*-methylene-, m.p. 149—152° (lit. 155—156°), *S*-benzylidene-, m.p. 149—150° (lit. 138—140°), S-iso*propylidene*-, m.p. 174°, and S-*α'-methylpropylidene-di-(α-thiolpropionic acid)*, m.p. 126—127°, S-*methylene*-, m.p. 142°, S-*benzylidene*-, m.p. 90°, and S-iso*propylidene-di-(β-thiolpropionic acid)*, m.p. 70°.

R. S. C.

δ-Valerosultone. T. Nilsson (*Svensk Kem. Tidskr.*, 1940, **52**, 324—325).—$Br{\cdot}[CH_2]_4{\cdot}SO_3Na$ in aq. $AgNO_3$ at 55° for 4 hr. gives *δ-valerosultone* (**I**), liquid, polymerising on keeping. Hydrolysis of (**I**) in dil. aq. solution at 60° is unimol. and is thus not catalysed by H'.

M. H. M. A.

[Photolytic] reactions of the acetyl radical.—See A., 1941, I, 276.

Photolysis of glyoxal and acetaldehyde.—See A., 1941, I, 276.

High-temperature photolysis of acetone and the action of free methyl radicals on propane.—See A., 1941, I, 276.

Synthesis of methyl vinyl ketone by hydration of vinylacetylene under pressure.—See B., 1941, II, 135.

Acetylene derivatives. XIV. Synthesis of ββ-dialkyldivinyl ketones by isomerisation of *tert.*-vinylethylcarbinol. XV. Vinyl ketones and their polymerisation. I. N. Nazarov. XVI. Action of ethylene oxide on vinylethinylcarbinols. Esterification of β-hydroxyethyl ethers of vinylethinylcarbinols with organic acids. I. N. Nazarov and V. M. Romanov (*Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1940, 545—551, 552—558, 559—570).—XIV. The general reaction $OH{\cdot}CRR'{\cdot}C{\equiv}C{\cdot}CH{:}CH_2 + R''OH \rightarrow OR''{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH{:}CRR'$ takes place in presence of $HgSO_4$ (12 hr. at 35—40°) (R'' = Me, R = R' = Me, Et, Pr^a; R = *Me*, R' = *Et*, b.p. 91—93°; R = Me, R' = Pr^a; RR' = $[CH_2]_5$). When heated with *p*-$C_6H_4Me{\cdot}SO_3H$ the keto-ethers eliminate R''OH, yielding the ketones $CH_2{:}CH{\cdot}CO{\cdot}CH{:}CRR'$ (R = R' = Me, *Et*, b.p. 59—60°/5 mm., *Pr*^{a}, b.p. 80—81°/5 mm.; R = *Me*, R' = *Et*, b.p. 50—51°/6 mm., R' = *Pr*^{a}, b.p. 73—74°/10 mm.; RR' = $[CH_2]_5$, b.p. 98·5—101°/12 mm.). The ketones are hydrogenated to the saturated ketones, $COEt{\cdot}CH_2{\cdot}CHRR'$ [R = R' = Me, *Et*, b.p. 179—181° (*carbazone*, m.p. 127—128°), *Pr*^{a}, b.p. 209—211° (*semicarbazone*, m.p. 89—90°); R = *Me*, R' = *Et*, b.p. 161—162° (*carbazone*, m.p. 92—93°), R' = *Pr*^{a}, b.p. 178—180° (*semicarbazone*, m.p. 64—65·5°)].

XV. The keto-ethers described above are hydrogenated (Pt catalyst) to keto-ethers, $OMe{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CHRR'$, which when distilled from *p*-$C_6H_4Me{\cdot}SO_3H$ give ketones, $CH_2{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CHRR'$ (R = R' = *Me*, b.p. 41—42°/22 mm., *Et*, b.p. 65—66°/11 mm., *Pr*^{a}, b.p. 90—91°/12 mm.; R = *Me*, R' = *Et*, b.p. 40—41°/7 mm.; R = *Me*, R' = *Pr*^{a}, b.p. 72—73°/16 mm.; RR' = $[CH_2]_5$, b.p. 96°/12 mm.). The ketones readily polymerise to elastic, transparent products.

XVI. Carbinols of the type $OH{\cdot}CRR'{\cdot}C{\equiv}C{\cdot}CH{:}CH_2$ are obtained by condensation of ketones CORR' with $CH{\equiv}C{\cdot}CH{:}CH_2$ (R = R' = Me, *Pr*^{a}, b.p. 83°/4 mm.; R = Me, R' = Et; R = Me, R' = Pr^a; RR' = $[CH_2]_5$). The carbinols condense with 1 or 2 mols. of $(CH_2)_2O$ to yield the mono- and di-glycyl ethers, $OH{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CRR'{\cdot}C{\equiv}C{\cdot}CH{:}CH_2$ [R = R' = *Me*, b.p. 80—81°/4 mm. (*acetate*, b.p. 92—93°/5 mm.; *propionate*, b.p. 102—104°/4 mm.; *butyrate*, b.p. 110—113°/4 mm.; iso*butyrate*, b.p. 98—100°/2·5 mm.; *valerate*, b.p. 120—121°/4 mm.); R = R' = *Pr*^{a}, b.p. 108—109°/3 mm.; R = *Me*, R' = *Et*, b.p. 89—90°/5 mm. (*butyrate*, b.p. 129—131°/4 mm.); R = *Me*, R' = *Pr*^{a}, b.p. 96—97°/4 mm.; RR' = $[CH_2]_5$, b.p. 118—119°/3 mm.], and $OH{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CRR'{\cdot}C{\equiv}C{\cdot}CH{:}CH_2$ (R = R' = *Me*, b.p. 103—104°/2 mm.; R = R' = *Pr*^{a}, b.p. 140—142°/4 mm.; R = *Me*, R' = *Et*, b.p. 125—127°/4 mm.; R = *Me*, R' = *Pr*^{a}, b.p. 135—137°/4 mm.; RR' = $[CH_2]_5$, b.p. 149—150°/3 mm.). All the above products polymerise on keeping to transparent gels, the tenacity of which falls with increasing mol. wt. of R and R'.

R. T.

Photolysis of diacetyl in the near ultra-violet.—See A., 1941, I, 276.

Preparation of *d*-mannose. H. S. Isbell (*J. Res. Nat. Bur. Stand.*, 1941, **26**, 47—48).—The prep. from ivory nut shavings is described in detail.

J. W. S.

***iso*Propylidene derivative of the mercaptals of monosaccharides. VI. Crystalline 2-methyl-*d*-mannose and its α-methylglucofuranoside, dimethyl acetal, and dibenzyl mercaptal.** E. Pacsu and S. M. Trister (*J. Amer. Chem. Soc.*, 1941, **63**, 925—928; cf. A., 1940, II, 365).—The "4-"methylmannose (**I**) of Pacsu *et al.* (A., 1930, 70) is shown to be the 2-derivative (cf. Munro *et al.*, A., 1936, 826) and the structure of intermediates is modified accordingly. Mannose $(CH_2Ph)_2$ mercaptal (modified prep. from α-methyl-*d*-mannofuranoside) gives the (mainly 3 : 4-5 : 6-)$(CMe_2)_2$ derivative, a syrup, $[\alpha]_D^{21}$ +59·5° in $(CHCl_2)_2$, converted by NaOMe–MeI (twice) into the syrupy 2-Me derivative, whence conc. HCl in boiling 80% EtOH yields 83% of 2-methylmannose $(CH_2Ph)_2$ mercaptal (**II**), m.p. 117°, $[\alpha]_D^{21}$ −43·1° in C_5H_5N, +39·5° in $CHCl_3$. With HgO–$HgCl_2$ in MeOH at 60°, (**II**) gives *2-methyl-α-methylmannofuranoside* (**III**), m.p. 82°, $[\alpha]_D^{25}$ +129·5° in H_2O, with a little *2-methylmannose Me$_2$ acetal* (**IV**), m.p. 111—112°, $[\alpha]_D^{21}$ −11·3° in H_2O. N-HCl at 100° hydrolyses (**III**) to (**I**), m.p. 136—137° (lit. a syrup), $[\alpha]_D^{20}$ +7·0° → +4·5° in 24 hr. in H_2O, which, according to the conditions, yields phenylglucosazone or *2-methylmannose-phenylhydrazone*, m.p. 163°, [α] −49·1° → −60·7° in 24 hr. in C_5H_5N. Hydrolysis of (**IV**) by 0·05N-HCl at 21° gives 2-methyl-α- and -β-methylmannofuranoside (increased lævorotation) and then more slowly (**I**). The data of Pacsu *et al.* (*loc. cit.*) for (**II**) probably refer in error to the glucose analogue.

R. S. C.

Hydrolysis of turanose in alkaline solution. H. S. Isbell (*J. Res. Nat. Bur. Stand.*, 1941, **26**, 35—46).—Treatment of turanose (**I**) with aq. $Ca(OH)_2$ at 20° leads to a decrease in rotation, the final val. being in accord with the view that hydrolysis occurs to glucose and *d*-fructose instead of the normal Lobry de Bruyn interconversion. A solution of (**I**) in N-KOH turns brown and becomes lævorotatory, the loss in [KOH] according with the view that the hydrolysis products enolise and decompose to yield saccharic acids. Alkaline oxidation of 0·17 mol. of fructose yields 2·9 g. and of (**I**) 1·8 g. of cryst. K *d*-arabate (**II**). Lactulose yields no (**II**) but forms the K salt of a dibasic acid, presumably 3-*β-d*-galactopyranosido-*d*-arabonic acid. These differences in behaviour and the differences in Cu-reducing vals. are discussed with reference to the effect of the glycosidic linking on the behaviour of the sugars in alkaline solution.

J. W. S.

[Degradation of long-chain molecules.] H. Mark and R Simha (*Trans. Faraday Soc.*, 1941, **37**, 244).—A note on a recent paper by the authors (cf. A., 1940, II, 268).

F. L. U.

Separation of starch into its two constituents. E. Pacsu and J. W. Mullen (*J. Amer. Chem. Soc.*, 1941, **63**, 1168—1169).—When an adsorbent (best, cotton; also activated C, fuller's earth, or Al_2O_3) is added to cold 1% maize-starch paste, the amylose is adsorbed. Cold H_2O then removes the α-amylose (**I**), which can be recovered by pptn. by EtOH. Final elution with hot H_2O extracts the β-amylose (**II**) giving a clear aq. solution, which rapidly ppts. a degraded, insol. form; pptn. by EtOH gives a similar material. Addition of C_5H_5N during distillation of the aq. solution of (**II**) gives a solution of (**II**) in C_5H_5N, whence (**II**) is pptd. by EtOH. (**I**) and (**II**) have $[\alpha]_D^{20}$ +145° in 20% NaOH and differ only in that (*a*) (**I**) contains 0·020% of P and (**II**) contains no P, and (*b*) (**I**) gives a purple and (**II**) a deep blue colour with I.

R. S. C.

Fractionation of wheat starch.—See B., 1941, III, 68, 98, 150.

Starch. IX. Degradation by β-amylase and the law of mass action. K. H. Meyer and J. Press (*Helv. Chim. Acta*, 1941, **24**, 50—58).—The degradation of sol. starch (**I**) (Zulkowski) by β-amylase is a reaction of zero order; until degradation has reached 35—40% the quantity of maltose (**II**) formed in unit time is const. In conc. solution [0·6—1·4% of (**I**)] this is not remarkable but the concn. of terminal groups may be considered const. in more dil. solution in which concn. has a marked influence on the rate of reaction. The evidence points to the existence of an additive compound

of enzyme and substrate in equilibrium with its products of dissociation. The reaction is inhibited by (II). In alkaline solution (p_H 4·8) amylose from maize or potato starch is degraded ~65% as rapidly as (I). H. W.

Starch. XI. Residual dextrin from maize starch (erythro-granulose). K. H. Meyer, M. Wertheim, and P. Bernfeld (*Helv. Chim. Acta*, 1941, **24**, 212—216).—Amylopectin (I), obtained by the cautious removal of amylose from maize starch, is solubilised by CCl_3·$CH(OH)_2$ and subjected to the action of β-amylase (II) in H_2O; all the terminal groups of (I) are found in the residual dextrin (III). Possibly the very slow attack of (II) on (III) is due to the liberation of maltose or glucose. H. W.

Starch. X. Degradation of glycogen by β-amylase. K. H. Meyer and J. Press (*Helv. Chim. Acta*, 1941, **24**, 58—62).—Glycogen (I) obtained by Brücke's method is much more slowly attacked than sol. starch by β-amylase (II) but with a high concn. of enzyme it is possible to achieve 45% degradation with formation of 55% of residual dextrin. Lyoglycogen, isolated without use of alkali and containing about ⅓ its wt. of protein (III), is not attacked by (II) in a solution which has been made alkaline and then neutralised. If (III) is removed by tungstic acid the residual (I) is more rapidly attacked than Brücke's (I). H. W.

Factors in the methylation of cellulose acetate and of cellulose dissolved in benzyltrimethylammonium hydroxide. G. G. Johnston (*J. Amer. Chem. Soc.*, 1941, **63**, 1043—1050).—The amount of methylation of cellulose acetate (I) achieved in one operation increases as the degree of polymerisation decreases. Repeated methylation gives products containing 1% less OMe than theoretical for trimethylation. Higher OMe is achieved only after reacetylation, which involves further depolymerisation. Only in $COMe_2$ is methylation of (I) easier than that of cellulose. Fine division increases the ease of methylation. Methylation and deacetylation in $COMe_2$ are initially slow, owing to the immiscibility of $COMe_2$ with conc. NaOH, but accelerate as the product ppts. and thus comes in contact with NaOH. In CH_2Ph·NMe_3·OH the reaction rate is normal as the solution is homogeneous, but methylation ceases at ~43% of OMe owing to insolubility of the product. Cohesive forces (H or OH linkings) are responsible for the incomplete methylation. R. S. C.

Amination in liquid ammonia.—See B., 1941, II, 134.

Treatment of simple aliphatic amines with nitrous acid. F. C. Whitmore and R. S. Thorpe (*J. Amer. Chem. Soc.*, 1941, **63**, 1118—1120; cf. A., 1932, 1022).—Yields of ROH from NH_2R and HNO_2 are R = Me 0, Et 60, Pr^{α} 7, and Pr^{β} 32% (also 28% of C_3H_6) with traces of Et and Pr ethers. Failure of the reaction with NH_2Me is due to hydrolysis of the nitrite occurring more readily than its decomp. R. S. C.

Reductive alkylation of ammonia and amines with aldehydes and ketones. Preparation of ethylamines from acetaldehyde.—See B., 1941, II, 135.

Manufacture of amino-fatty acid derivatives.—See B., 1941, II, 137.

Molecular refraction of ions of *l*-aspartic acid.—See A., 1941, I, 194.

Azlactones. III. Acylation of amino-acids in pyridine. H. E. Carter, P. Handler, and C. M. Stevens (*J. Biol. Chem.*, 1941, **138**, 619—626).—70% yields of acetyl-, *butyryl*-, m.p. 86—87°, iso*butyryl*-, m.p. 105—106°, *valeryl*-, m.p. 84—85°, *γ-methylvaleryl*-, m.p. 129—130°, and *trimethylacetyl-phenylalanine*, m.p. 124—125°, and the corresponding *acyl*-dl-*valines*, m.p. —, 148—149°, 165—167°, 105—106°, 144—146°, and 98—99°, are obtained from the NH_2-acid and acid chloride in C_5H_5N below 40°. *dl*-Valine with BzCl in C_5H_5N gives a mixture of benzoyl-*dl*-valine and -*dl*-valylvaline, m.p. 170—205°. Leucine behaves similarly. Benzoyl-*dl*-phenylalanine with BzCl or (poor yield) AcCl or Ac_2O yields the azlactone, which with NH_2Ph affords the anilide. Benzoyl-*dl*-alanyl-, *acetyl*-dl-*phenylalanyl*-, m.p. 211—212°, and n-*valeryl*-dl-*valyl*-*anilide*, m.p. 164—165°, are similarly prepared. Benzoyl-*dl*-phenylalanylglycine, m.p. 225—237°, and n-*valeryl*-dl-*valyl*-dl-*valine*, m.p. 180—183°, are obtained in poor yield from the azlactone and NH_2-acid in C_5H_5N at room temp. A. Li.

Synthesis of β-hydroxynorvaline. M. Botvinnik, E. Morozova, and G. Samsonova (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **30**, 133—136).—Equimol. amounts of Δ^{α}-pentenoic acid (I) with $Hg(OAc)_2$ in cold MeOH give a mixture of Hg derivatives of β-methoxyvaleric acid which when treated with aq. KBr–Br gives α-bromo-β-methoxyvaleric acid (II), converted by 25% aq. NH_3 under pressure at 100° for 2 hr. into α-amino-β-methoxyvaleric acid, which with boiling 48% HBr gives β-hydroxynorvaline (cf. Abderhalden *et al.*, A., 1934, 638). (I) with $AgNO_3$ and Br in MeOH at 5—15° gives (II) (cf. West *et al.*, A., 1938, II, 129). J. L. D.

Benzoylation of amino-acids. H. E. Carter and C. M. Stevens (*J. Biol. Chem.*, 1941, **138**, 627—629).—*l-p*-Methoxyphenylalanine with excess of BzCl in aq. $NaHCO_3$ gives the partly racemised Bz derivative (I) (75—85%), and an oil hydrolysed to BzOH and (I). Similar products are obtained from *dl*-alanine and *dl-O*-methyl*allo*threonine. Bz derivatives of > 16 NH_2-acids, and some β-phenylpropionyl derivatives, have been prepared without racemisation in 0·5N-NaOH. An explanation of this difference is suggested. A. Li.

Sulphur in proteins. VI. Alkaline decomposition of cysteine. H. V. Lindstrom and W. M. Sandstrom (*J. Biol. Chem.*, 1941, **138**, 445—450).—Uvitic, uvitonic, and thiolacetic acids are produced by the action of boiling 2N-$Ba(OH)_2$ on cysteine (I), or on a mixture of its primary decomp. products, $AcCO_2H$, H_2S, and NH_3. The residue after extraction of the products from (I) with Et_2O and then boiling alkaline $Pb(OAc)_2$ contains alanine (II), which stabilises (I) in NaOH or KOH, but not in $Ba(OH)_2$. It is concluded that (II), when formed, condenses with $AcCO_2H$ in presence of NaOH or KOH, inhibiting further decomp. of (I). A. Li.

Dehydration of hydroxy-amino-acids. M. M. Botvinnik, M. A. Prokofiev, and N. D. Zelinski (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **30**, 129—132).—β-Hydroxyvaline (I) (1 mol.) with Bz_2O (3 mols.) at 150°/1 hr. gives the azlactone (II) of α-benzamido-β-methylcrotonic acid (III), hydrolysed (N-NaOH at 100°) to (III). When (II) is boiled with N-HCl for 5·5 hr., $COPr^{\beta}$·CO_2H is formed. (III) gives (II) on brief boiling with Ac_2O, or when heated with Bz_2O at 120—125° for 20 min. The sulphate of (I) is not dehydrated when fused with Bz_2O. Similarly, α-amino-β-hydroxybutyric acid, or its Bz derivative, with Bz_2O yields the azlactone, m.p. 95° (cf. Carter *et al.*, A., 1939, II, 423), hydrolysed (N-NaOH at 80°) to α-benzamidocrotonic acid, m.p. 193—195°. J. L. D.

New sulphur-containing amino-acid (lanthionine) from sodium carbonate-treated wool. M. J. Horn, D. B. Jones, and S. J. Ringel (*J. Biol. Chem.*, 1941, **138**, 141—149).—Hydrolysis (conc. HCl) of wool previously boiled with 2% aq. Na_2CO_3, concn. of the hydrolysate, and pptn. of the EtOH solution of the residue with C_5H_5N yields *ββ′-diamino-ββ′-dicarboxydiethyl sulphide* (*lanthionine*), decomp. 304° (softening at 270°) (*NN′-Bz*$_2$ derivative, m.p. 205—206°), with two other compounds with similar properties and the same N content. A. Li.

Synthesis of new sulphur-containing amino-acid [lanthionine] isolated from sodium carbonate-treated wool. V. du Vigneaud and G. B. Brown (*J. Biol. Chem.*, 1941, **138**, 151—154).—Cysteine (from cystine and Na in liquid NH_3) with CH_2Cl·$CH(NH_2)$·CO_2Me,HCl and KOH yields lanthionine (preceding abstract) [*NN′-dicarbobenzyloxy*-derivative, m.p. 138—140° (corr.)]. A. Li.

High-pressure reduction of fatty acid amides. II. S. Ueno and S. Takase (*J. Soc. Chem. Ind. Japan*, 1941, **44**, 29—30B).—The amides of palmitic (I), hexoic, octoic, stearic, lauric, and myristic acid have been hydrogenated in dioxan to the corresponding *sec.* amines [*e.g.*, C_7H_{15}·$CO·NH_2 \rightarrow (C_8H_{17})_2NH$], varying temp., pressure, time, and quantity of catalyst (Cu–Cr_2O_3 with a trace of Ba) and of solvent. Optimum results are obtained at 270—290°/180—200 atm. for 1 hr., with 3 times as much dioxan as amide. From (I) n-*cetylamine* (*hydrochloride*, m.p. 130—133°) is also obtained. With little or no solvent the amides decompose. A. Li.

Action of halogens on αβ-unsaturated ureides. C. J. Cavallito and C. S. Smith (*J. Amer. Chem. Soc.*, 1941, **63**, 995—998).—*trans*-CHMe:CH·COCl and $CO(NH_2)_2$ in CCl_4 give trans-*crotonylcarbamide*, which with Br–CCl_4 at 0—5° gives a *dibromide*, m.p. 150°. trans-*Cinnamylcarbamide* and aq. Br give the *dibromide*, m.p. 180°. Maleamic and maleic acids

also give dibromides (*αβ*-dibromosuccinamic acid has m.p. 170°), but *succinuric acid* does not react. Maleuric acid (I) with Br in H_2O or CCl_4 at 0—10° gives *β-bromomaleuric acid* (II), m.p. 147°, hydrolysed by H_2O at room temp. to *β-hydroxymaleuric acid* (III), m.p. 230—270°. With Br–H_2O at 30—35°, (I), (II), or (III) gives *tribromopyruvylcarbamide* (IV), m.p. 260° [N-*Cl*-derivative (V), m.p. 210°; N-*Ag* salt, with alkali gives $CHBr_3$]. I does not react with (I). IBr and (I) in H_2O at 0—10° give *β-iodomaleuric acid*, m.p. 150—155°, converted by IBr at 30° into *tri-iodopyruvylcarbamide*, m.p. 220° [also obtained from (II) by IBr], and by Br into (IV). (IV) is a mild sedative and (V) is antiseptic. M.p. are corr. (decomp.). R. S. C.

Sebacic acid mononitrile. B. S. Biggs and W. S. Bishop (*J. Amer. Chem. Soc.*, 1941, **63**, 944).—Distillation of $([CH_2]_4\cdot CO\cdot NH_2)_2$ (crude or pure) or $([CH_2]_4\cdot CO_2NH_4)_2$ gives 50—55% of $([CH_2]_4\cdot CN)_2$, b.p. 204°/16 mm., and 35% of *ω-cyano-n-nonoic acid* (I), m.p. 51·5—52° (purified by way of the Ba salt). With NaOMe–Me_2SO_4–MeOH (I) gives *Me ω-cyano-n-nonoate* (II), b.p. 178°/16 mm. $CO_2H\cdot[CH_2]_8\cdot CO_2Me$ with $SOCl_2$ and then aq. NH_3 gives *Me n-decoamate*, m.p. 77·4°, which with P_2O_5 in boiling $(CHCl_2)_2$ gives (II). R. S. C.

Purification of lecithin.—See A., 1941, III, 368.

Dimethyl silicon dichloride and methyl silicon trichloride. W. F. Gilliam, H. A. Liebhafsky, and A. F. Winslow (*J. Amer. Chem. Soc.*, 1941, **63**, 801—803).—*Si Me_2 dichloride*, b.p. 69·0—70·2°/744·5 mm., and *Si Me trichloride*, b.p. 66·2—67°/765·8 mm., have been prepared by a Grignard reaction between MgMeCl and $SiCl_4$ in Et_2O and Bu^{α}_2O respectively. W. R. A.

Polymeric methyl silicon oxides. E. G. Rochow and W. F. Gilliam (*J. Amer. Chem. Soc.*, 1941, **63**, 798—800).—Polymeric Si Me oxides (I) have been prepared by direct hydrolysis of the product obtained by action of MgMeBr on $SiCl_4$, and by hydrolysis of mixtures of $SiMeCl_3$ and $SiMe_2Cl_2$. (I) are intermol. condensation products of Me silicols. The properties and thermal stability of the products obtained by using various Me/Si ratios are recorded. Resins prepared by both methods are identical, and appear to consist essentially of a siloxane network in which Me are attached directly to Si. W. R. A.

Redistribution reaction. X. Relative affinity of mercury and lead for methyl and ethyl radicals. G. Calingaert, H. Soroos, and H. Shapiro (*J. Amer. Chem. Soc.*, 1941, **63**, 947—948; cf. A., 1940, II, 295).—Equilibration of $HgMe_2$ (2) with $PbEt_4$ (3 mols.) by $AlCl_3$ gives a random equilibrium mixture, for which the relative affinity const. is 3·4 in good agreement with that (4·5±0·4) determined previously (A., 1940, II, 300) for a mixture in different proportions. R. S. C.

II.—HOMOCYCLIC.

Catalytic dehydrogenation of *cyclo*pentane in presence of chromic oxide.—See A., 1941, I, 273.

Mechanism of catalytic hydrogenation of phenol under high pressure. VII. Comparison of hydrogenated products of *cyclo*hexanol and *cyclo*hexane. S. Andō (*J. Soc. Chem. Ind. Japan*, 1940, **43**, 355—356B; cf. B., 1938, 903).—Both *cyclo*hexane (I) and *cyclo*hexanol (II) when hydrogenated at 380°/200 atm. over MoS_3 produced methyl*cyclo*pentane (III), the yield from (II) being > that from (I), and it is concluded that *cyclo*hexene rather than (I) is the intermediate in the conversion of (II) into (III), whilst (II) is an intermediate in the hydrogenation of PhOH. A. R. Pe.

***cis–trans*-Isomeric stilbenes. V. Stereoisomeric forms of 2 : 4′-dinitrostilbene; phenanthrene syntheses. III.** P. Ruggli and A. Dinger (*Helv. Chim. Acta*, 1941, **24**, 173—185).—Protracted heating of *p*-$NO_2\cdot C_6H_4\cdot CH_2\cdot CO_2Na$ and *o*-$NO_2\cdot C_6H_4\cdot CHO$ with Ac_2O and $ZnCl_2$ at 70° gives 2′ : 4-*dinitrostilbene-7-carboxylic acid* (I), m.p. 185°; piperidine as condensing agent causes evolution of CO_2. Reduction (Raney Ni–EtOH–EtOAc) of (I) gives 2′ : 4-*diaminostilbene-7-carboxylic acid*, m.p. 186° (*Ac_2* derivative, m.p. 240°), converted by diazotisation and subsequent boiling with EtOH into phenanthrene-9-carboxylic acid, m.p. 252° (yield 18%). Decarboxylation of (I) in quinoline containing Cu chromite at 220° gives a mixture from which cis-2′ : 4-*dinitrostilbene* (II), m.p. 140°, is isolated. (II) (or the mixture) is not appreciably affected by boiling HCl–EtOH, quinoline, or $PhNO_2$ but with $PhNO_2$ containing a trace of I at 205—210° yields pure trans-2′ : 4-*dinitrostilbene* (III), m.p. 140°. (II) is reduced (Raney Ni in EtOAc) to cis-2′ : 4′-*diaminostilbene* (IV), m.p. 105° (*Ac_2* derivative, m.p. 180°), transformed into phenanthrene. 2′ : 4 : 4′-Trinitrostilbene is reduced by $(NH_4)_2S$ in EtOH to 2′ : 4-*dinitro-4′-aminostilbene*, m.p. 202° (*hydrochloride*; *Ac* derivative, m.p. 237°), converted by diazotisation and boiling with EtOH into (III), catalytically reduced (Raney Ni in EtOAc) to trans-2′ : 4-*diaminostilbene*, m.p. 125—126° (*Ac_2* derivative, m.p. 241°). This, when diazotised and then boiled with EtOH containing a little Cu powder, yields stilbene. It is also obtained by isomerisation of (IV) by slow distillation under 13 mm. Bromination of (III) in $CHCl_3$ affords a 73% yield of a *dibromide* (V), m.p. 212°, and an uncrystallisable resin. Under similar conditions (II) gives (V) in 16% yield with a resin from which a *bromide*, m.p. 165°, could be isolated in small amount. Warm C_5H_5N transforms (V) into (III) in 72% yield. Passage of Cl_2 through (III) in boiling $CHCl_3$ gives a *dichloride* (VI), m.p. 125—126°, whereas a *dichloride*, m.p. 204°, is derived from a mixture of (II) and (III). (VI) is converted by NaOH into a *substance*, $C_{14}H_8O_{2\cdot5}N_2$, m.p. 244°, probably owing to ring formation. H. W.

Synthesis of tricyclic hydrocarbons related to stilbœstrol. A. A. Plentl and M. T. Bogert (*J. Amer. Chem. Soc.*, 1941, **63**, 989—995).—Slow addition of indan-1-one (I) in Et_2O to $CH_2Ph\cdot MgCl$–Et_2O gives 65% of 1-*benzylideneindane* (purified by adsorption of impurities on Al_2O_3), b.p. 157—157·5°/2 mm., which probably contains 1-benzylindene since only poor yields of BzOH and (I) are obtained by $KMnO_4$ in aq. K_2CO_3 and $COMe_2$, respectively. CHPhMeBr and CN·CPhNa·CO_2Et (II) in hot EtOH give *Et α-cyano-αβ-diphenyl-n-butyrate*, b.p. 157°/0·2 mm., and some CHPhMe·CHPh·CN, m.p. 133° (lit. 129—130°), both converted by 1 : 2 HCl–AcOH at 200° into CHPhMe·CHPh·CO_2H, forms, m.p. 186° (lit. 181°) (*amide*, m.p. 193°) and 135° (lit. 133—134°) (*amide*, m.p. 173—174°), which with boiling $SOCl_2$, followed by $AlCl_3$ in CS_2, gives *2-phenyl-3-methylindan-1-one*, m.p. 86° (2 : 4-*dinitrophenylhydrazone*, m.p. 204°; no semicarbazone), converted by MgEtI–Et_2O, followed by Ac_2O, into *2-phenyl-3-methyl-1-ethylindene*, an oil. Ph·$[CH_2]_2$·Br and (II) in dioxan give *Et α-cyano-αγ-diphenyl-n-butyrate*, b.p. 174—175°/0·5 mm., and thence, as above, *αγ-diphenyl-n-butyric acid*, m.p. 76°, and 1-*keto*-2-*phenyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 79° (2 : 4-*dinitrophenylhydrazone*, m.p. 204°; no semicarbazone), 1-*hydroxy*-2-*phenyl*-1-*ethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 129°, and 2-*phenyl*-1-*ethyl*-3 : 4-*dihydronaphthalene*, b.p. 80—90° (bath)/0·1 mm. Attempts to condense CHPhMe·MgBr and (I) failed, since only $(CHPhEt)_2$ was obtained. R. S. C.

Formation of ions from compounds with conjugated double bonds: hydrocarbon salts. J. Weiss (*Nature*, 1941, **147**, 512; cf. A., 1940, II, 247).—Salts of coronene, 1 : 2-benzperylene, 3 : 4-benzpyrene, and anthracene with ClO_4', SO_4'', and P_2O_7'''' as anions have been prepared from the hydrocarbon and an oxidising agent [CrO_3, $K_3Fe(CN)_6$, or H_2O_2] in presence of the moderately conc. acids at room temp. Deeply coloured, H_2O-sol. salts are formed even from the sulphonated hydrocarbons. *Anthracene perchlorate* (I), $[C_{14}H_{10}]^{\cdot}[ClO_4]'$, m.p. >110° (decomp.), gives dark brown crystals (absorption spectrum in $COMe_2$ given). H_2O decomposes (I), but not the salts of the higher-mol. hydrocarbons. The deep colour of the solutions is due to the positive hydrocarbon ion, and univalent ions, [hydrocarbon]$^{\cdot}$[anion]′, have been observed. The well-known hydrocarbon polynitro-compounds are present to an appreciable extent as ionic compounds of the type [hydrocarbon]$^{\cdot}$[NO_2-compound]′ and [NH_2-compound]$^{\cdot}$-[NO_2-compound]. L. S. T.

1-Methylphenanthrene. I. Conversion of retene into 1-methylphenanthrene. T. Hasselstrom (*J. Amer. Chem. Soc.*, 1941, **63**, 1164—1165).—1-Methylphenanthrene [derived phenazine, new m.p. 183·5° (corr.)] (with propylene and an oily by-product) is obtained (97 g.) by boiling retene (250 g.) with dehydrated fuller's earth and thus becomes readily available. R. S. C.

Syntheses in the phenanthrene and triphenylene series. L. F. Fieser and W. H. Daudt (*J. Amer. Chem. Soc.*, 1941, **63**, 782—788).—*dl*-$(CHMe\cdot CO)_2O$ (I), m.p. 88—89°, b.p. 234—237° (prep.: Bone *et al.*, J.C.S., 1899, **75**, 839), and

1-$C_{10}H_7$·MgBr in boiling Et_2O–C_6H_6–N_2 give mixed *β*-1-*naphthoyl-α-methyl*-n-*butyric acids* (**II**) (66·5%; the Friedel–Crafts reaction is less satisfactory), whence a small amount of a pure *acid*, m.p. 151·2—151·4°, is isolated. (**II**) enolises readily and in HCl–AcOH or $-Ac_2O$ at room temp. or with boiling HCl–MeOH gives *γ*-1-*naphthyl-αβ-dimethyl-Δβ-crotonolactone*, m.p. 96—97°, which reduces Tollens' reagent but gives no Legal reaction. Hydrogenation (Cu chromite; 140°/1500—2500 lb.) of the Na salt of (**II**) in H_2O gives 81·5% of *γ*-1-*naphthyl-αβ-dimethyl*-n-*butyric acid*, *forms*, m.p. 107·5—108·5° and 114—115°, cyclised by HF to 1-*keto*-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (**III**) (88·5%), an oil, whence a small amount of crystals, m.p. 91—98°, is obtained. Clemmensen–Martin reduction and dehydrogenation (Pd–C; 300—330°) converts (**III**) into 2 : 3-dimethylphenanthrene (**IV**). MgMeBr and (**III**) in C_6H_6 give a carbinol, which with Pd–C at 300°, later 300—350°, gives 1 : 2 : 3-*trimethylphenanthrene* (42·5%), m.p. 63·8—64·8° [picrate, m.p. 187—188°; $C_6H_3(NO_2)_3$ compound, m.p. 200·7—201·5°]. 2-$C_{10}H_7$·MgBr and (**I**) give similarly *β*-2-*naphthoyl-α-methyl*-, m.p. 149—153° (*enol lactone*, m.p. 126—127·5°), and *γ*-2-*naphthyl-αβ-dimethyl*-n-*butyric acid*, m.p. 83—84°, and thence by HF or, probably better, $ZnCl_2$–Ac_2O, 4-*keto*-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (**V**), m.p. 93·4—94·5° after softening. Interaction of crude (**V**) with MgMeBr, dehydration at 200°, and removal of adsorbable (Al_2O_3) material gives an oil, which with Pd–C gives 17% of 2 : 3 : 4-*trimethylphenanthrene*, m.p. 62·8—63·8° [picrate, m.p. 113—114°; $C_6H_3(NO_2)_3$ compound, m.p. 139—140°]. $Al(OPr^{\beta})_3$ reduces (**V**) in PhMe to 4-*hydroxy*-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 111—114·5° [dehydrogenated to (**IV**)], converted by HCl–C_6H_6 into the chloride, which with $CH_2(CO_2Et)_2$ and NaOEt–EtOH–C_6H_6 and later boiling 40% KOH gives 2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydro*-4-*phenanthrylmalonic acid*, m.p. 188—190° (gas). Heating at 200° then gives 2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydro*-4-*phenanthrylacetic acid*, m.p. 110—123°, cyclised by HF to 1-*keto*-3 : 4-*dimethyl*-1 : 2 : 2a : 3 : 4 : 5-*hexahydropyrene*, *forms*, m.p. 204·5—206·5° and 197—202°. Mg 9-phenanthryl bromide and (**I**) give, as above, *β*-9-*phenanthroyl-α-methylbutyric acid*, m.p. 170—171·5° (slight previous softening) [picrate, m.p. 176—177°; $C_6H_3(NO_2)_3$ compound, m.p. 188·5—189·2°; *enol lactone*, m.p. 216—218°], *γ*-9-*phenanthryl-αβ-dimethyl*-n-*butyric acid*, m.p. 158—163° [$C_6H_3(NO_2)_3$ compound, m.p. 174—175·5°], 1-*keto*-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydrotriphenylene* (**VI**), m.p. 132—138°, 1 : 2 : 3-*trimethyltriphenylene*, m.p. 109·8—110·6° [picrate, m.p. 186—186·5°; $C_6H_3(NO_2)_3$ compound, m.p. 203·7—204·1°], (by Zn–Hg–PhMe–HCl) 2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydrotriphenylene* (**VII**), m.p. 158—167° [picrate, m.p. 154—158°; $C_6H_3(NO_2)_3$ compound, m.p. 158—160°], [from (**VII**) by Pd–C] 2 : 3-*dimethyltriphenylene* (**VIII**), m.p. 156·7—157·2° [$C_6H_3(NO_2)_3$ compound, m.p. 237—237·7°], and [from (**VI**) by Pd–C, which gives also some (**VIII**)] 1-*hydroxy*-2 : 3-*dimethyltriphenylene*, m.p. 167·5—168·5° [$C_6H_3(NO_2)_3$ compound, 239—240°; picrate, m.p. 210·5—211·5°]. 1-$C_{10}H_7$·CH:CHMe and $(CH_2CO)_2O$ at 100° give (?) 3-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-1 : 2-*dicarboxylic anhydride* (77·5%), m.p. 271·8—272°, unaffected by HCl–AcOH–Ac_2O and dehydrogenated by S to 3-*methylphenanthrene*-1 : 2-*dicarboxylic anhydride*, m.p. 332—333°. M.p. are corr. R. S. C.

Action of acids on β-hydroxy-sulphonamides. T. L. Cairns and J. H. Fletcher (*J. Amer. Chem. Soc.*, 1941, **63**, 1034—1035).—*iso*Butylene oxide (**I**) and boiling aq. NH_3 give $OH·CMe_2·CH_2·NH_2$ (**II**). Steam-distillation of the *N*-*p*-$C_6H_4Br·SO_2$ derivative of (**II**) with 75% H_2SO_4 or 48% HBr gives *p*-$C_6H_4Br·SO_2·NH_2$ and $Pr^{\beta}CHO$ (isolated as *methone* derivative, m.p. 148—150°) (cf. A., 1939, II, 496). *β*-*p*-*Bromobenzenesulphonyl*-tert.-*butyl alcohol*, m.p. 89—90·5°, gives similarly EtCHO, but *p*-$C_6H_4Br·SO_2·NH·[CH_2]_2·OH$ is unaffected. The fission is catalysed by acid, since it is not effected by P_2O_5 or AcCl. R. S. C.

Catalytic reduction of nitrobenzene in the liquid phase.—See B., 1941, II, 173.

Reductive alkylation of hindered aromatic primary amines. W. S. Emerson, F. W. Neumann, and T. P. Moundres (*J. Amer. Chem. Soc.*, 1941, **63**, 972—974).—Reductive alkylation of NH_2Ar by RCHO (cf. A., 1940, II, 11) in acid media can be accomplished if polymeride formation is prevented by substitution of Ar at positions 2, 4, and 6. Zn–Hg–AcOH–conc. HCl is an effective reducing agent. Thus, mesidine with CH_2O gives 2 : 4 : 6 : 1-$C_6H_2Me_3·NMe_2$ (**I**) (70%) [*hydrochloride*, m.p. 155—156° (decomp.); also obtained similarly from 2 : 4 : 6 : 1-$C_6H_2Me_3·NO_2$ (**II**)], with RCHO gives *N*-*iso*butyl- (91%), b.p. 267—277° [*hydrochloride*, m.p. 148—150° (decomp.); *Ac* derivative, m.p. 71·5—72·5°], and *N*-*iso*amyl-mesidine (94%), b.p. 155—165°/20 mm. [*Bz* derivative, m.p. 92—93°; hydrochloride, an oil; also obtained from (**II**) (61%)], and with $COMe_2$ gives 18% of *N*-*iso*propylmesidine, b.p. 118—123°/3 mm. NH_2Ph gives similarly 31% of $NHPhPr^{\beta}$. (**I**) is also obtained by using HCO_2H as reducing agent, which, however, fails in other cases. R. S. C.

Synthesis and toxicity of N^1-*p*-fluorophenylsulphanilamide. G. P. Hager, E. B. Starkey, and C. W. Chapman (*J. Amer. Pharm. Assoc.*, 1941, **30**, 65—68).—*p*-$NO_2·C_6H_4·N_2·BF_4$ (from *p*-$NO_2·C_6H_4·N_2Cl$ and $NaBF_4$; cf. Dunker *et al.*, A., 1937, II, 39) is converted into *p*-$C_6H_4F·NO_2$ and thence *p*-$C_6H_4F·NH_2$, which with *p*-$NHAc·C_6H_4·SO_2Cl$ in $COMe_2$–C_5H_5N affords the N^4-Ac derivative, m.p. 190°, of N^1-*p*-fluorophenylsulphanilamide (**I**), m.p. 166·5° (corr.) (sinters 162—165°, softens 165°) (cf. Suter *et al.*, A., 1940, II, 164). For toxicity of (**I**), cf. A., 1941, III, 526. F. O. H.

Phosphoric acid derivatives of sulphanilamides.—See B., 1941, III, 161.

4-Aminodiphenyl-4′-sulphonamide. C. K. Donnell, J. H. Dietz, and W. T. Caldwell (*J. Amer. Chem. Soc.*, 1941, **63**, 1161—1162).—*p*-$C_6H_4Ph·NO_2$ and $ClSO_3H$ at, successively, <15°, room temp., and 60° give *p*-$NO_2·C_6H_4·C_6H_4·SO_3Cl$-*p* (94%), m.p. 178°, and thence the amide, which is reduced by Sn–HCl–EtOH to *p*-$NH_2·C_6H_4·C_6H_4·SO_2·NH_2$-*p*, m.p. 263° (corr.). R. S. C.

Reaction of aldehydes with amines. III. *N′*-Acetyl-*NN*-dibenzyl-*m*-phenylenediamine. F. G. Singleton and C. B. Pollard (*J. Amer. Chem. Soc.*, 1941, **63**, 998—999).—*m*-$NH_2·C_6H_4·N(CH_2Ph)_2$ (A., 1941, II, 102) with RCHO gives Schiff's bases, but with Ac_2O at room temp. affords *N′-acetyl*-NN-*dibenzyl*-m-*phenylenediamine*, m.p. 144—145°, which with RCHO and H_2SO_4 in boiling EtOH (tube at 100°, if necessary) gives 44—80% of 4 : 4′-*bisdibenzylamino*-2 : 2′-*diacetamidotriphenylmethane*, m.p. 228°, 4 : 4′-*bisdibenzylamino*-2 : 2′-*diacetamido*-3″ : 4″-*dimethoxy*-, m.p. 231°, -2″-, m.p. 244°, and -4″-*methoxy*-, m.p. 224°, -3″-, m.p. 216°, and -4″-*methyl*-, m.p. 218°, -3″ : 4″-*methylenedioxy*-, m.p. 225°, and -4″-*hydroxy*-3″-*methoxy*-, m.p. 196°, -*triphenylmethane*, 2″-, m.p. 239°, 3″-, m.p. 211°, and 4″-*nitro*-, m.p. 251°, 2″-, m.p. 242°, and 4″-*chloro*-, m.p. 248°, and 2″-*chloro*-5″-*nitro*-, m.p. 240°, -4 : 4′-*bisdibenzylamino*-2 : 2′-*diacetamidotriphenylmethane*, 4 : 4′-*bisdibenzylamino*-2 : 2′-*diacetamidodiphenylmethane*, m.p. 241°, αα-4 : 4′-*bisdibenzylamino*-2 : 2′-*diacetamidodiphenylethane*, m.p. 172°, -*propane*, m.p. 230°, -n-*butane*, m.p. 245°, and -n-*hexane*, m.p. 201°, and α-*phenyl*-ββ-4 : 4′-*bisdibenzylamino*-2 : 2′-*diacetamidodiphenylethane*, m.p. 184°. Small amounts of Schiff's bases, acridines, and CRR′$_2$·OH are also formed. M.p. are corr. R. S. C.

Isomerism of diazoaminoazo-compounds. F. P. Dwyer (*J. Proc. Roy. Soc. N.S. Wales*, 1940, **74**, 169—174; cf. A., 1939, II, 543).—Diazoaminoazobenzene, purplish-red quinonoid form (**I**), $PhN_2·N:C_6H_4:N·NHPh$, m.p. 121—122°, is obtained by neutralising *p*-$NPh:N·C_6H_4·N_2Cl$ with Na_2CO_3, and coupling with NH_2Ph. (**I**) dissolves in C_5H_5N to a deep red solution, and addition of light petroleum then gives (after 2—3 days) brownish-yellow needles, m.p. 138—139°, of the triazen *form* (**II**), $PhN_2·NH·C_6H_4·N_2Ph$, m.p. 138—139°, which is best obtained by allowing a saturated solution of (**I**) in amyl acetate to evaporate slowly. A mixture of (**I**) and (**II**) melts at 142—143° (softens at 138°), indicating probable salt formation between the acidic (**I**) and feebly basic (**II**). When a solution of the crude salt from (**I**) or (**II**) and MeOH–NaOAc–$AgNO_3$–C_5H_5N in C_5H_5N at 85° is cooled to 25°, the orange-yellow *Ag* salt (**III**), decomp. 200—205°, of (**II**), separates. When a solution of (**III**) in C_5H_5N at 85° is cooled rapidly to 20°, filtered, and the filtrate mixed with MeOH at −10°, the *Ag* salt (**IV**), probably dimeric, m.p. 195—200° (explodes at 205°), of (**I**) separates. (**III**) or (**IV**) and MeI–$COMe_2$ afford the same *N*-Me derivative, m.p. 84—85°. A. T. P.

Reactivity of phenols towards paraformaldehyde.—See A., 1941, I, 214.

2-Nitro-4-*tert.*-alkylphenols.—See B., 1941, II, 178.

2 : 5-Dialkylphenols.—See B., 1941, II, 177.

Polymorphic forms of substituted phenols. R. T. Arnold, H. Klug, J. Sprung, and H. Zaugg (*J. Amer. Chem. Soc.*, 1941, **63**, 1161).—Forms, m.p. 53—54° and 62° (stable), of 5 : 6 : 7 : 8-tetrahydro-β-naphthol and, m.p. 39·5—40° and 49—50° (stable), of 4-hydrindenol are prepared by alkali fusion of the Na sulphonates and from the diazonium salts, respectively. R. S. C.

Exploration of methods for preparation of stilbene derivatives. II. Unsymmetrical stilbenes. W. H. Linnell and H. S. Shaikmahamud (*Quart. J. Pharm.*, 1941, **14**, 64—72; cf. A., 1940, II, 167).—*p*-OMe·C_6H_4·[CHBr]$_2$·CO_2H [from *p*-OMe·C_6H_4·CH:CH·CO_2H, prep. of which by Knoevenagel's reaction gives a little of (?) *p*-OMe·C_6H_4·CH:$C(CO_2H)_2$, m.p. 204°] with dry PhOH at >50°/30 mm., followed by treatment of the product with aq. Na_2CO_3, affords 4′-*hydroxy*-4-*methoxystilbene* (**I**), m.p. 209—210° [*acetate*, m.p. 167—168° (opaque), 182—183° (clear)], and 41·3% of (probably) p-*hydroxy*-β-p′-*anisylcinnamic acid*, m.p. 185—186° (*Me ether Me ester*, m.p. 86—87°, hydrolysed to the *Me ether*, m.p. 137—138°), presumably formed by addition of PhOH to *p*-OMe·C_6H_4·C:C·CO_2H. *Et* β-*hydroxy*-β-p-*acetoxyphenyl*-α-*ethylvalerate*, m.p. 85° (from *p*-OAc·C_6H_4·COEt, CHBrEt·CO_2Et, and Zn in C_6H_6), with $SOCl_2$–C_5H_5N in dry Et_2O yields Et *p*-acetoxy-αβ-diethylcinnamate, b.p. 162—164°/5 mm. (from which no stilbene derivative could be obtained by heating its dibromide with PhOH), hydrolysed by 25% MeOH–KOH to p-*hydroxy*-αβ-*diethylcinnamic acid*, m.p. 133° (**II**) and 119—121° (probably *cis*- and *trans*-forms); (**II**) is methylated to p-*methoxy*-αβ-*diethylcinnamic acid* (**III**), m.p. 63—64°. *Et* β-*hydroxy*-β-p-*anisyl*-α-*ethylvalerate*, m.p. 71—72° (from *p*-OMe·C_6H_4·COEt as above), similarly yields (**III**) (mixture of isomerides). (**III**) and the corresponding *p*-OAc-compound give dibromides which decompose on removal of solvent; bromination of (**III**) and direct addition of PhOH, however, gives an *acid*, m.p. 125—126° [probably either *p*-OMe·C_6H_4·C(:CHMe)·CEtBr·CO_2H or *p*-OMe·C_6H_4·CEtBr·C(:CHMe)·CO_2H]. (*p*-OMe·C_6H_4·CH:$)_2$ (**IV**) is obtained by methylation of (**I**) and from *p*-OMe·C_6H_4·N_2Cl, *p*-OMe·C_6H_4·CH:CH·CO_2H, and 33% aq. CH_2Cl·CO_2Na in boiling $COMe_2$; the corresponding stilbene derivative could not be similarly obtained from (**III**) (both forms) or *p*-OH·C_6H_4·CH:CH·CO_2H. (**I**), (**IV**), (*p*-OH·C_6H_4·CH:$)_2$, new m.p. 288—289° [from (**IV**) and Na in $C_2H_4(OH)_2$], and its diacetate were examined for œstrogenic activity (cf. A., 1941, III, 509). F. O. H.

Structures of arylhydrazones of unsymmetrically substituted quinones. L. I. Smith and W. B. Irwin (*J. Amer. Chem. Soc.*, 1941, **63**, 1036—1043).—*m*-Cresol and *p*-NO_2·C_6H_4·N_2Cl (**I**) in aq. NaOH give 4′-*nitro*-4-*hydroxy*-2-*methylazobenzene*, m.p. 163—164° (*acetate*, m.p. 132—133°), reduced by $Na_2S_2O_4$ in aq. EtOH to 2 : 1 : 5-NH_2·C_6H_3Me·OH, which is oxidised, best by steam-distillation with $Fe_2(SO_4)_3$, to *p*-toluquinone (**II**). *o*-Cresol and (**I**) give 4′-*nitro*-4-*hydroxy*-3-*methylazobenzene* (**III**), m.p. 205—206° (decomp.) (*acetate*, m.p. 144·5—146°), also obtained (in only 28% yield, cf. below) from (**II**) by *p*-NO_2·C_6H_4·NH·NH_2 (**IV**), and reduced by $Na_2S_2O_4$ to 5 : 1 : 2-NH_2·C_6H_3Me·OH. *s*-*m*-Xylenol and (**I**) give 4′-nitro-4-hydroxy-2 : 6-dimethylazobenzene, m.p. 167—168° (decomp.) (*acetate*, m.p. 133—133·5°), and thence 2 : 1 : 3 : 5-NH_2·$C_6H_2Me_2$·OH, m.p. 179—180° (decomp.) [lit. 180·5—181·5° (decomp.)], oxidised by $Fe_2(SO_4)_3$ to *m*-xyloquinone (**V**) and by $FeCl_3$ to 3-*chloro*-2 : 6-*dimethyl*-p-*benzoquinone*, m.p. 55·5—57°. (**IV**) and (**V**) give 4′-*nitro*-4-*hydroxy*-3 : 5-*dimethylazobenzene* (77%), m.p. 182—183° (decomp.) (*acetate*, m.p. 192—193°), reduced by $Na_2S_2O_4$ to 5 : 1 : 3 : 2-NH_2·$C_6H_2Me_2$·OH. 1 : 3 : 4 : 5-$C_6H_2Me_2$·OH (**VI**) and *p*-NO_2·C_6H_4·N_2HSO_4 (**Ia**) (prep. by *iso*-C_5H_{11}·O·NO) in AcOH give 4′-*nitro*-4-*hydroxy*-2 : 3 : 6-*trimethylazobenzene* (68% at 10°; 90%, less pure, in H_2O), m.p. 165·5—166·5° (decomp.) (*acetate*, m.p. 133—134°), reduced to 3 : 1 : 2 : 4 : 6-NH_2·C_6HMe_3·OH. ψ-Cumoquinone (**VII**), (**IV**), and H_2SO_4 in EtOH give 4′-*nitro*-4-*hydroxy*-2 : 3 : 5-*trimethylazobenzene* (73%), m.p. 227—228° (decomp.) (*acetate*, m.p. 165°), reduced to 6-*amino*-ψ-*cumenol* [4-*amino*-2 : 3 : 6-*trimethylphenol*], m.p. 136—137° (decomp.) (*hydrochloride*, chars slightly ~225°), which with $FeCl_3$ gives (**VII**), isolated as quinol diacetate. Durenol and (**Ia**) in AcOH at 14—15° give 94% and duroquinone (**VIII**) and (**IV**) give 53% of 4′-*nitro*-4-*hydroxy*-2 : 3 : 5 : 6-*tetramethylazobenzene*, m.p. 174—174·5° (decomp.) (*acetate*, m.p. 143—144°), reduced to *aminodurenol*, m.p. 177—178·5° [179—183° (decomp.)], which gives (**VIII**) by oxidation. 2 : 4 : 1-$(NO_2)_2C_6H_2$·N_2Cl (**IX**) and (**VI**) in AcOH at 15—16° give 2′ : 4′-*dinitro*-4-*hydroxy*-2 : 3 : 6-*trimethylazobenzene*, m.p. 188·5—189° (decomp.) (*acetate*, m.p. 155—156°), whence reduction and then oxidation gives only a trace of (**VII**). (**VII**) with 2 : 4 : 1-$(NO_2)_2C_6H_2$·NH·NH_2 (**X**) in H_2SO_4–EtOH gives 2′ : 4′-*dinitro*-4-*hydroxy*-2 : 3 : 5-*trimethylazobenzene* (90%), m.p. 220—221° (decomp.), and with *p*-SO_3H·C_6H_4·NH·NH_2 in aq. EtOH gives a compound, m.p. 224—228° after decomp. Durenol and (**IX**) give 2′ : 4′-*dinitro*-4-*hydroxy*-2 : 3 : 5 : 6-*tetramethylazobenzene* (95%), orange, m.p. 199—200° (decomp.) (*acetate*, m.p. 181·5—182°), also obtained in a [? polymorphous (*X*-ray)] *form*, deep red, m.p. 197—197·5° (190—191°) (decomp.), from (**VIII**) and (**X**). Reduction of the $(NO_2)_2$-compounds gives inseparable mixtures. The azo-compounds and their acetates are purified by adsorption of impurities on Al_2O_3. R. S. C.

Alkylpyrocatechol esters of phosphorous acid. A. E. Arbuzov and F. G. Valitova (*Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1940, 529—544).—Esters, RP·OR′, where R = *o*-$C_6H_4<^{O}_{O}>$ and R′ = Me (+*CuBr*, m.p. 130—135°), Et (+*CuBr*, m.p. 142—145°), Pr^{α} (+*CuI*, m.p. 138°), Pr^{β} (+*CuCl*, m.p. 143°; +*CuI*, m.p. 178—179°), Bu^{α} (+*CuCl*, m.p. 202°), and Bu^{β} (+*CuCl*, m.p. 208—210°) are obtained from RPCl and NaOR′ in Et_2O. The esters readily isomerise to RPR′:O, which with H_2O gives RPR′(OH)$_2$ and *o*-OH·C_6H_4·O·P(OH)·R′:O. With CH_2PhBr, RP·OR′ react as follows: RP·OR′ + CH_2PhBr → RPO·CH_2Ph + R′Br. R. T.

Reaction between 2-methylnaphthaquinone and magnesium phenyl bromide. (Miss) H. M. Crawford (*J. Amer. Chem. Soc.*, 1941, **63**, 1070—1073; cf. A., 1940, II, 82; Smith *et al.*, A., 1939, II, 543).—2-Methyl-1 : 4-naphthaquinone and MgPhBr give in poor yield 1 : 4-*dihydroxy*-1 : 2-*diphenyl*-2-, m.p. 189—190° [with $K_2Cr_2O_7$ gives COPhMe and *o*-C_6H_4Bz·CO_2H (**I**)], and -3-*methyl*-1 : 2-*dihydronaphthalene* (**II**), m.p. 196·5—197° (or, in one experiment, a *substance*, m.p. 218—220°). (**II**) is oxidised to (**I**), BzOH, and *substances*, m.p. 243—244° (**III**) and 215—217°, and is dehydrated, best by $ZnCl_2$–HCl–C_6H_6, to 3 : 4-*diphenyl*-2-*methyl*-1-*naphthol* (**IV**), m.p. 181—182° [*acetate* (**V**), m.p. 176—177°, obtained also from (**II**) by Ac_2O]. $K_2Cr_2O_7$–AcOH–H_2O oxidises (**IV**) to 3 : 4-diphenyl-1 : 2-naphthaquinone, but (**V**) gives (**III**). (**II**), (**IV**), and (**V**) have no vitamin-*K* activity in 5-mg. doses, but 2-methyl-1 : 4-naphthaquinone has a potency of 2000 units per mg. R. S. C.

Interactions between polycyclic hydrocarbons and sterols in mixed surface films at the air–water interface.—See A., 1941, I, 257.

Isolation of a new phytosterol, campesterol. E. Fernholz and H. B. MacPhillamy (*J. Amer. Chem. Soc.*, 1941, **63**, 1155—1156).—Rapeseed oil yields brassicasterol (acetate bromide insol. in Et_2O–AcOH) and *campesterol* (**I**), $C_{28}H_{48}O$, m.p. 157—158°, $[\alpha]_D^{23}$ −33° in $CHCl_3$ (*acetate*, m.p. 137—138°, $[\alpha]_D^{23}$ −35° in $CHCl_3$; *benzoate*, m.p. 158—160°, $[\alpha]_D^{23}$ −8·6° in $CHCl_3$; 3 : 5-*dinitrobenzoate*, m.p. 202—203°, $[\alpha]_D^{23}$ −6·0° in $CHCl_3$; absorbs 1 O from BzO_2H; sol. acetate bromide). (**I**) is also obtained from soya-bean oil (by way of the bromide; with stigmasterol) and wheat-germ oil (directly), but not cotton-seed or tall oil. R. S. C.

Constitution of campesterol. E. Fernholz and W. L. Ruigh (*J. Amer. Chem. Soc.*, 1941, **63**, 1157—1159).—Campesterol (**I**) is shown to differ from 22 : 23-dihydrobrassicasterol only in configuration at $C_{(24)}$. Its acetate is hydrogenated (H_2–PtO_2–AcOH; later reacetylation) to *campestanyl acetate* (**II**), m.p. 143—144°, $[\alpha]_D^{23}$ +18·3° in $CHCl_3$, and oxidised (CrO_3–90% AcOH; 95°; later hydrolysis by 2N-NaOH) to β-3-hydroxy-nor*allo*cholanic acid, (?) *d*-Me γδ-dimethylamyl ketone (*semicarbazone*, m.p. 152—153°, $[\alpha]_D^{24}$ +11·9° in $CHCl_3$, does not depress the m.p. of the *l*-isomeride), and $COMe_2$. 5% KOH–EtOH hydrolyses (**II**) to *campestanol*, m.p. 146—147°, $[\alpha]_D^{24}$ +31° in $CHCl_3$ (3 : 5-*dinitrobenzoate*, m.p. 198°, $[\alpha]_D^{24}$ +22° in $CHCl_3$). (**I**) gives *i*-campesteryl *p*-toluenesulphonate, m.p. 150—152°, and thence *i*-*campesteryl Me ether*, m.p. 61—63°, $[\alpha]_D^{24}$ +62° in $CHCl_3$. R. S. C.

Sterols. CXX. Anterior pituitary gland extracts. R. E. Marker and E. L. Wittbecker (*J. Amer. Chem. Soc.*, 1941, **63**, 1031—1032).—$COMe_2$ extracts from anterior pituitary glands

(ox) cholesterol (only sterol), Na stearate, *substances* (*a*), $C_8H_{10}O_4N_4$ or $C_{10}H_{13}O_5N_5$, m.p. 281—284°, and (*b*) $C_{20}H_{40}O_2$, m.p. 96—98°, a *carbinol*, m.p. 79—81°, and the known hydrocarbon, $C_{28}H_{58}$. R. S. C.

Effect of *ortho*-substitution on bacteriostatic properties of phenylacetic acid. C. F. Feasley and B. H. Gwynn [with E. F. Degering and P. A. Tetrault] (*J. Amer. Pharm. Assoc.*, 1941, **30**, 41—45).—Slow addition of HNO_3 (*d* 1·41) to *p*-$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO_2H$ in boiling AcOH–I yields 2-*iodo*-4-*nitrophenylacetic acid*, m.p. 236°, reduced (H_2, colloidal Pt, EtOH) to 2-*iodo*-4-*aminophenylacetic acid*, m.p. 184°. For bacteriostatic properties of these and related compounds, cf. A., 1941, III, August. F. O. H.

Normal and alkaline esters of *m*-aminomandelic acid and related compounds. L. S. Fosdick and J. C. Calandra (*J. Amer. Chem. Soc.*, 1941, **63**, 1101—1103; cf. A., 1938, II, 322).—Crude *m*-$NO_2{\cdot}C_6H_4{\cdot}CH(OH){\cdot}CN$ (prep. described) with HCl–ROH gives *Me*, m.p. 66°, Et, m.p. 63°, *Pr*$^{\alpha}$, m.p. 73°, *Pr*$^{\beta}$, m.p. 57°, and *Bu*$^{\alpha}$ m-*nitromandelate*, m.p. 65°, hydrogenated (PtO_2; 45 lb.) to the *NH*$_2$-*esters*, m.p. 139°, 55°, 101°, 146°, and 110°, respectively. *Cl*·$[CH_2]_2$ m-*nitromandelate*, m.p. 76°, gives *Cl*·$[CH_2]_2$ m-*aminomandelate*, m.p. 91°, which with $NHEt_2$ at 100° gives $NEt_2{\cdot}[CH_2]_2$ *m*-aminomandelate, unstable (*hydrochloride*, m.p. 133°). The NH_2-esters have little or no anæsthetic activity. M.p. are corr. R. S. C.

Reaction of anhydrous rare earth bromides with ethyl benzoate.—See A., 1941, I, 278.

Alkamine esters of *p*-fluorobenzoic acid and their salts. L. S. Fosdick and E. E. Campaigne (*J. Amer. Chem. Soc.*, 1941, **63**, 974—975).—*p*-$C_6H_4F{\cdot}CO_2H$ is obtained in 16% yield from *p*-C_6H_4MeF or from *p*-$C_6H_4Br{\cdot}NH_2$ (by way of *p*-C_6H_4BrF and *p*-$C_6H_4F{\cdot}MgBr$) and in 20% yield from NH_2Ph (by way of PhF and *p*-$C_6H_4F{\cdot}COMe$). *Di-ethyl-*, b.p. 136—137°/7 mm. (*hydrochloride*, m.p. 124—126°; *borate*, *B*,5HBO_2), *-propyl-*, b.p. 149—150°/7 mm. (*hydrochloride*, m.p. 115—117°; *borate*, *B*,5HBO_2), *-butyl-aminoethyl*, b.p. 168—169°/7 mm. (*hydrochloride*, m.p. 115—116°; *borate*, *B*,5HBO_2), *di-ethyl-*, b.p. 148—149°/7 mm. (*hydrochloride*, m.p. 122—124°; *borate*, *B*,7HBO_2), *-propyl-*, b.p. 161—161·5°/7 mm. (*hydrochloride*, m.p. 124—126°; *borate*, *B*,6HBO_2), and *-butyl-aminopropyl*, b.p. 175·5—177°/6 mm. (*hydrochloride*, m.p. 100°; *borate*, *B*,6HBO_2), p-*fluorobenzoate* are described; they are efficient, non-toxic, but irritant anæsthetics. R. S. C.

4 : 5-Dinitro-2-methoxybenzoic acid. H. Goldstein and A. Jaquet (*Helv. Chim. Acta*, 1941, **24**, 30—37).—4 : 2 : 1-$NO_2{\cdot}C_6H_3(OMe){\cdot}CO_2H$ (obtained by oxidation of 4 : 1 : 2-$NO_2{\cdot}C_6H_3Me{\cdot}OMe$ with $KMnO_4$) with HNO_3 (*d* 1·52) and conc. H_2SO_4 at 0° gives 4 : 5-*dinitro*-2-*methoxybenzoic acid* (**I**), m.p. 144°, transformed by conc. NH_3 at room temp. into 5-*nitro*-4-*amino*-2-*methoxybenzoic acid* (**II**), m.p. 248° (*Ac* derivative, m.p. 193°), which is converted (diazo-reactions) into 5 : 2 : 1-$NO_2{\cdot}C_6H_3(OMe){\cdot}CO_2H$ and 4-*iodo*-5-*nitro*-2-*methoxybenzoic acid*, m.p. 227°. (**I**) and KOH–MeOH at 50° give 5-*nitro*-2 : 4-*dimethoxybenzoic acid*, m.p. 220° (Me ester, m.p. 150°), reduced ($SnCl_2$–conc. HCl) to 5-*amino*-2 : 4-*dimethoxybenzoic acid*, m.p. 199° (*Ac* derivative, m.p. 217°). (**I**) is transformed by boiling 7% NaOH into 5-*nitro*-4-*hydroxy*-2-*methoxybenzoic acid*, m.p. 192°. When heated with the requisite base, (**I**) is converted into 5-*nitro*-4-*dimethylamino*-, m.p. 208°, 5-*nitro*-4-*anilino*-, m.p. 204°, 5-*nitro*-4-*phenylhydrazino*- (**III**), m.p. 193°, and 5-*nitro*-4-*hydrazino*-, m.p. 237° (*Ac*, m.p. 256°, and *CMe*$_2$:, m.p. 242°, derivatives), -2-*methoxybenzoic acid*. (**III**) is transformed by boiling glacial AcOH into 3-*oxido*-6-*methoxy*-2-*phenylbenztriazole*-5-*carboxylic acid*, m.p. 208°. (**I**) is slowly transformed by Na_2S_2 in boiling EtOH into *di*-6-*nitro*-3-*methoxy*-4-*carboxyphenyl disulphide*, m.p. 264° (decomp.). M.p. are corr. H. W.

Chlorination of derivatives of *o*-orsellinic acid. T. J. Nolan and D. Murphy (*Sci. Proc. Roy. Dublin Soc.*, 1941, **22**, 315—319).—Et *o*-orsellinate and Cl_2 in CCl_4 at room temp. give the 4 : 6-Cl_2-derivative (**I**), m.p. 158—161°, hydrolysed (boiling 5% aq. KOH) to 2 : 4-*dichloro-orcinol*, m.p. 121°, converted by CH_2N_2–$COMe_2$ into the Me_2 ether, an oil. Equimol. amounts of Me *o*-orsellinate (**II**) and Cl_2 in $CHCl_3$–CCl_4 at room temp. give *Me* 4 : 6-*dichloro*-*o*-*orsellinate* (+0·5H_2O) (**III**), m.p. 117°. (**II**) with excess of Cl_2 in $CHCl_3$–CCl_4 at room temp. affords *Me* 3 : 3 : 5 : 5-*tetrachloro*-2 : 4-*diketo*-6-*methyl*-2 : 3 : 4 : 5-*tetrahydrobenzoate*, m.p. 132—134°, converted by $SnCl_2$ in AcOH–HCl at room temp. into (**III**). (**I**) with excess of CH_2N_2 in Et_2O–$COMe_2$, followed by hydrolysis (boiling 5% aq. KOH), gives 4 : 6-*dichloro*-3 : 5-*dimethoxy*-*o*-*toluic acid*, m.p. 135—136°. Equimol. amounts of *o*-orsellinic acid and CH_2N_2 in Et_2O–$COMe_2$ give Me 3-hydroxy-5-methoxy-*o*-toluate (**IV**), m.p. 63—65°, which with a small excess of Cl_2 in $CHCl_3$–CCl_4 gives *Me* 4 : 6-*dichloro*-3-*hydroxy*-5-*methoxy*-*o*-*toluate* (**V**), m.p. 79—81°. With excess of Cl_2, (**IV**) gives *Me* 3 : 3 : 5 : 5-*tetrachloro*-2-*keto*-4-*methoxy*-6-*methyl*-2 : 3 : 4 : 5-*tetrahydrobenzoate*, m.p. 144—146°, reduced ($SnCl_2$–AcOH–HCl) to (**V**). J. L. D.

Manufacture of unsaturated aldehydes.—See B., 1941, III, 161.

Reactions of 2 : 8-dihydroxy-1-naphthaldehyde. R. Adams and D. E. Burney (*J. Amer. Chem. Soc.*, 1941, **63**, 1103—1107).—2 : 8 : 1-$(OH)_2C_{10}H_5{\cdot}CHO$ (**I**) [prep. from 2 : 8-$C_{10}H_6(OH)_2$ by $Zn(CN)_2$–HCl in 34—38% yield] and its derivatives do not react in the tautomeric forms characteristic of the gossypol series. (**I**) gives a normal phenylhydrazone and *oxime* (**II**), m.p. 161—162°, dehydrated by Ac_2O at room temp. to 2-*hydroxy*-peri-*naphthoxazine* (**III**), m.p. 190—191°, the *Me ether* (prep. by CH_2N_2–Et_2O or K_2CO_3–Me_2SO_4–$COMe_2$), m.p. 111—112°, of which with boiling Ac_2O–NaOAc gives 8-*acetoxy*-, m.p. 94·5—96°, and thence by HCl 8-*hydroxy*-2-*methoxy*-1-*naphthonitrile* (**IV**), m.p. 194—195°. 10% KOH–MeOH converts (**III**) into (**IV**). The *Ac* derivative, m.p. 159—160°, of (**III**) is obtained by Ac_2O from (**II**) or (**III**) and is converted by boiling Ac_2O–NaOAc into 2-*acetoxy*-peri-*naphthoacetimidolactone*, m.p. 100—101° [also obtained similarly from (**II**) or (**III**)]. Conc. HCl at room temp. then gives 2-*hydroxy*-peri-*naphtholactone* (90%), m.p. 193—194° (*acetate*, m.p. 134—135°), the *Me ether* (prep. by CH_2N_2–Et_2O or K_2CO_3–Me_2SO_4–$COMe_2$), m.p. 128—129°, of which with hot Me_2SO_4–aq. NaOH gives *Me* 2 : 8-*dimethoxy*-1-*naphthoate*, m.p. 131—132°. 2 : 8-*Dimethoxy*-1-*naphthaldehyde* [prep. from (**I**) by Me_2SO_4–K_2CO_3–$COMe_2$], m.p. 90—91° (*phenylhydrazone*, m.p. 126—127°), gives the *oxime*, m.p. 137—139°, dehydrated by boiling Ac_2O to 2 : 8-*dimethoxy*-1-1-*naphthonitrile*, m.p. 148—149°, which is also obtained from (**IV**) by Me_2SO_4–NaOH. M.p. are corr. R. S. C.

Metallic derivatives of acetomesitylene. H. Gilman and R. G. Jones (*J. Amer. Chem. Soc.*, 1941, **63**, 1162—1163).—The MgBr derivative of acetomesitylene (**I**), prepared by MgPhBr, gives the Michler's ketone test. The Li and Na derivatives (prep. by LiPh and NaPh, respectively) regenerate 97 and 86%, respectively, of (**I**) and give the Michler's ketone test. R. S. C.

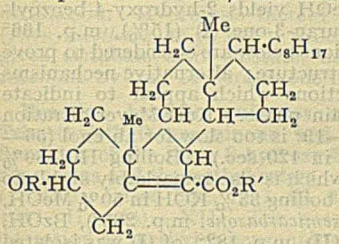
Hydroxyalkyl ethers of substituted acylphenols.—See B., 1941, II, 177.

Naphthalene series. VI. Synthesis of 2-propyl-1-naphthol and properties of 2-propionyl-1-naphthol. R. D. Desai, A. Hamid, and H. P. Shroff. **VII. Attempted synthesis of 4-stearyl-, 4-palmityl-, and 4-lauryl-1-naphthol.** R. D. Desai and W. S. Waravdekar (*Proc. Indian Acad. Sci.*, 1941, **13**, A, 33—38, 39—42).—VI. α-$C_{10}H_7{\cdot}OH$ with hot $EtCO_2H$ and $ZnCl_2$ yields 2-propionyl-1-naphthol (**I**) (*picrate*, m.p. 88°; *semicarbazone*, m.p. 304°; *phenylhydrazone*, m.p. 78°; p-*nitrophenylhydrazone*, m.p. 232°; *Me ether*, m.p. 45°). (**I**) with $AlCl_3$ in $PhNO_2$ at room temp. gives a *compound*, $C_{28}H_{22}O_4$, m.p. >300°, and with Br in AcOH–I (trace) yields 4-bromo-2-propionyl- (**II**) and 4-*bromo*-2-α-*bromopropionyl*-1-*naphthol* (**III**), m.p. 145°. (**II**) with NaOAc and Ac_2O at 180—185° yields 6-bromo-2 : 3-dimethyl-1 : 4-α-naphthapyrone, new m.p. 225°, hydrolysed (10% NaOH) to 1 : 4 : 2-OH·$C_{10}H_5Br{\cdot}CO_2H$. (**III**) with 10% NaOH yields 4-*bromo*-2-*lactyl*-1-*naphthol*, m.p. 214°, and with NaOMe in MeOH affords 4-*bromo*-2-*acrylyl*-1-*naphthol*, m.p. 204°, and 5-*bromo*-2-*methylnaphthacoumaranone*, m.p. 252°. HNO_3 (*d* 1·5; 1 mol.) and (**I**) in AcOH give 4-*nitro*-2-*propionyl*-1-*naphthol*, m.p. 162°, which with NaOAc and Ac_2O at 100—140° yields 6-*nitro*-2 : 3-*dimethyl*-1 : 4-α-*naphthapyrone*, m.p. 226°, hydrolysed (10% NaOH) to 4 : 1 : 2-$NO_2{\cdot}C_{10}H_5(OH){\cdot}CO_2H$; with 2 or >2 mols. of HNO_3, 2 : 4 : 1-$(NO_2)_2C_{10}H_5{\cdot}OH$ is formed. Reduction (Clemmensen) of (**I**) yields 2-*propyl*-1-*naphthol* (**IV**), b.p. 165°/6 mm. (*picrate*, m.p. 113°; *Me ether*, b.p. 145°/6 mm.), and (?) 2-*propyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthol*, b.p. 120—121°/7 mm. (**IV**) with PhN_2Cl yields 4-*benzeneazo*-2-*propyl*-1-*naphthol*, m.p. 180°, and the *phenylhydrazone*, m.p. 112°, of 2-*propyl*-1 : 4-*naphthaquinone*, m.p. 243°.

VII. α-$C_{10}H_7{\cdot}OH$, stearyl chloride, and $ZnCl_2$ in $PhNO_2$ at

room temp. yield 2- (80%) and 4-*stearyl*-1-*naphthol* (6%), m.p. 159—160°. α-$C_{10}H_7$·OMe similarly yields 70% of 1-*methoxy*-4-*stearylnaphthalene*, m.p. 125—126° (with some 4 : 4′-dimethoxy-1 : 1′-dinaphthyl), which with $AlCl_3$ in C_6H_6 gives only $C_{17}H_{35}$·CO_2H and α-$C_{10}H_7$·OH, but is reduced (Clemmensen) to 1-*methoxy*-4-*octadecylnaphthalene*, m.p. 202—203°. Similar methods yield 1-*methoxy*-4-*palmityl*- (which with $AlCl_3$ in C_6H_6 gives only $C_{15}H_{31}$·CO_2H and α-$C_{10}H_7$·OH), -*hexadecyl*-, m.p. 224—225°, -*lauryl*-, m.p. 111—112°, and -*dodecyl*-*naphthalene*, m.p. 165—166°. A. Li.

[Relation between] structure and absorption spectra of αβ-unsaturated ketones. R. B. Woodward (*J. Amer. Chem. Soc.*, 1941, **63**, 1123—1126).—The following corrections convert absorption max. of αβ-unsaturated ketones in the solvent named into max. in abs. EtOH : MeOH −1, $CHCl_3$ 0, Et_2O +6, hexane +7 mμ. Structure and the position of absorption max. are strictly correlated as follows: CO·CH:CHR or $CO·CR:CH_2$ 225±5, CO·CH:CRR′ or CO·CR:CHR′ 239±5, CO·CR:CR′R″ 254±5 mμ. It is suggested that the substances (absorption max. <230 mμ.) obtained (Heilbron *et al.*, A., 1938, II, 103) from halogeno-6-ketocholestanyl acetates by basic reagents have the annexed structure.



R. S. C.

Colour reaction for phenolic steroids (naturally occurring œstrogens). I. S. Kleiner (*J. Biol. Chem.*, 1941, **138**, 783—784).—Œstrone (**I**), œstriol, and œstradiol with *o*-$C_6H_4(CO)_2O$ and $SnCl_4$ at 116—120° yield characteristic phthalein colours not given by non-phenolic steroids. Quant. results may be obtained with as little as 0·25 μg. of (**I**). A. Li.

Absorption spectra in relation to quinones : 1 : 4-naphthaquinone, anthraquinone, and their derivatives.—See A., 1941, I, 238.

1-Alkylamino-4-hydroxyanthraquinones.—See B., 1941, II, 179.

III.—TERPENES.

Detection and estimation of α-terpinene by means of the diene synthesis. R. M. Gascoigne (*J. Proc. Roy. Soc. N.S. Wales*, 1940, **74**, 353—358).—Combination (modified method of Birch, B., 1938, 981) of α-terpinene (**I**) (purified by method of Richter *et al.*, A., 1930, 1172) and maleic anhydride (**II**) to the adduct, m.p. 60—61°, is quant. at room temp.; 94% purity of (**I**) was shown by this method. (**I**) regenerated from its dihydrochloride is absorbed to the extent of 44% by (**II**). The product from α-terpineol and dil. H_2SO_4 on reacting with (**II**) (modified method of Diels *et al.*, A., 1938, II, 330) gives a 52% content of (**I**). (**I**) and *p*-O:C_6H_4:O in EtOH afford *α-terpinene–benzoquinone adduct*, m.p. 87—88°, in 29% yield. A. T. P.

Configuration of the nickel salt of formylcamphor.—See A., 1941, I, 238.

Fission of the *cyclo*propane ring of α-thujene. R. M. Gascoigne (*J. Proc. Roy. Soc. N.S. Wales*, 1940, **74**, 359—364).—α-Thujene (**I**) (from *Eucalyptus dives* oil), b.p. 152—153°/760 mm., $[\alpha]_D^{21}$ +19·61°, and warm 5% HCl–EtOH afford α- (**II**) and γ-terpinene (**III**) (does not react with maleic anhydride). Probably (**I**) changes into (**III**), which partly isomerises to (**II**). (**I**) heated with maleic anhydride yields the α-terpinene adduct, the *dl*-α-phellandrene adduct, and *p*-cymene; any (**III**) formed would be immediately isomerised. (**I**) and *p*-O:C_6H_4:O in HCl–EtOH afford the α-terpinene–*p*-benzoquinone adduct. A. T. P.

Volatile vegetable substances. XIII. α- and β-Vetivone. Y. R. Naves and E. Perrottet (*Helv. Chim. Acta*, 1941, **24**, 3—29).—α- (**I**) and β-Vetivone (**II**) are steric isomerides and their mol. structure should be interpreted on an approx. tetrahedral basis modified by constraint due to cyclisation and to space relationships. (**I**) (2 : 4-*dinitrophenylhydrazone*, m.p. 149°) purified through its semicarbazone, m.p. 222—223°, $[\alpha]_D$ +334·20°±0·40° in AcOH, has b.p. 126—127°/0·85 mm., 144—144·5°/2·0 mm., m.p. 51—51·5°, $[\alpha]_D$ +238·25° in EtOH; it rapidly alters on exposure to air. (**II**) (2 : 4-*dinitrophenylhydrazone*, m.p. 190·5—191°), similarly purified through the semicarbazone, m.p. 228—229°, $[\alpha]_D$ −71·10° in AcOH, has b.p. 130—132°/1·15 mm., 141—142°/2 mm., m.p. 44—44·5°, $[\alpha]_D$ −38·92° in EtOH. Various colour reactions of (**I**) and (**II**) are recorded. Dehydrogenation of (**I**) by Se at 260—280° and then at 280—300° affords vetivazulene (2·3%; picrate, m.p. 122—122·5°), eudalinol, m.p. 85—85·5° (phenylurethane, m.p. 135°), and a non-azulenic neutral fraction which does not give a well-defined picrate or styphnate. Ozonolysis of (**I**) gives 1 mol. of $COMe_2$ and smaller proportions of CH_2O and HCO_2H; with (**II**) the results are similar but the amounts of CH_2O and HCO_2H are less. The *sesquiterpenes* [(**III**) and (**IV**)] derived from the semicarbazones of (**I**) and (**II**) (Wolff–Kishner) have b.p. 124°/4·2 mm., α_D +98·64°, and b.p. 103—103·5°/2·8 mm., α_D −33·76°; (**III**) gives an intense blue colour becoming olive-green with Br–$CHCl_3$ whereas (**IV**) decolorises the reagent. Hydrogenation (PtO_2 in AcOH at 70°) of (**III**) affords *α-vetivane*, b.p. 102—103°/2·2 mm., α_D −3·21°, whilst (**IV**) yields *β-vetivane* (**V**), b.p. 101—102°/2·3 mm., α_D −2·96°; neither gives a colour with Br–$CHCl_3$, or $C(NO_2)_4$. Similar hydrogenation of (**I**) and (**II**) gives closely related products, b.p. 106°/2·4 mm., α_D −3·92° and b.p. 94—94·5°/1·65 mm., α_D −1·85°, very like the decahydro-S- and -Se-guaiazulene of Ruzicka and Haagen-Smit. The attempted isomerisation of (**V**) by $AlCl_3$ gives a hydrocarbon, $C_{15}H_{28}$, b.p. 98—99°/3·2 mm., α_D ±0° which is scarcely affected by Se at 280—300°. The alcoholic fraction obtained by the hydrogenation of (**II**) contains *tetrahydro-β-vetivol* [*β-vetivanol*] (**VI**), m.p. 108—108·5°, $[\alpha]_D$ 0° in EtOH (3 : 5-*dinitrobenzoate*, m.p. 161—161·5°; *allophanate*, m.p. 196—196·5°; the *allophanate* of the isomeric β-vetivanol, m.p. 76—76·5°, has m.p. 218—218·5°). (**VI**) is oxidised (CrO_3 in AcOH) to *tetrahydro-β-vetivone* [*β-vetivanone*], b.p. 134—136°/2 mm., m.p. 38° (*semicarbazone*, m.p. 198·5—199°). Partial hydrogenation (Raney Ni; EtOH) of (**II**) gives 6 : 7-dihydro-β-vetivol, m.p. 108·5—109°, α_D ±0° (3 : 5-dinitrobenzoate, m.p. 129·5—130°; *allophanate*, m.p. 221—221·5°). *Tetrahydro-α-vetivol* [*α-vetivanol*], b.p. 132·5—134°/2·5 mm., α_D ±0° (*allophanate*, m.p. 225·5—226°; non-cryst. 3 : 5-dinitrobenzoate), obtained by hydrogenation of (**I**), is oxidised to *tetrahydro-α-vetivone* [*α-vetivanone*] (*semicarbazone*, m.p. 224·5—225°; isomeric 2 : 4-*dinitrophenylhydrazones*, m.p. 95—95·5° and 131·5—132°, respectively). H. W.

IV.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Sterols. CXV. Sapogenins. XLIV. Relation between diosgenin and cholesterol. R. E. Marker and D. L. Turner (*J. Amer. Chem. Soc.*, 1941, **63**, 767—771).—Diosgenin (**I**) and Zn–Hg in conc. HCl–EtOH give *tetrahydrodiosgenin* (**II**), m.p. 178—179° [*triacetate* (**III**), m.p. 119·5°; *tribenzoate*, m.p. 166—167°], whence H_2–PtO_2 at 3 atm. in AcOH yields *tetrahydrotigogenin*, m.p. 195—197° [*triacetate*, m.p. 67—68°, also obtained by similar hydrogenation of (**III**); *tribenzoate*, m.p. 162°]. SeO_2 in boiling 97% AcOH, followed by KOAc, and finally EtOH–KOH, oxidises (**III**) to a *tetrahydroxycholestene*, m.p. 196°, converted by boiling HCl–EtOH into 16 : 27-*dihydroxy*-3-*keto*-Δ^4-*cholestene*, m.p. 163—164°. Treatment of (**II**) with PBr_3 in boiling C_6H_6, then with KOAc–AcOH, and finally with Na–PrOH gives Δ^5-cholestene (reduced catalytically to cholestane) and cholesterol. Diosgenin acetate and CrO_3 in AcOH at 50—53° give an *acid*, $C_{27}H_{40}O_5$, decomp. 226° (rapid heating to 200°), 7-*ketodiosgenin acetate* (**IV**), m.p. 197°, and unchanged material. NaOEt–EtOH at 180° converts the *semicarbazone*, decomp. 282°, of (**IV**) into (**V**) (below) (small yield). With boiling 15% KOH–EtOH, (**IV**) gives (?) 7-*keto*-3 : 5-*dihydrotigogenin*, $C_{27}H_{38}O_3$, m.p. 197—198°. 4-Dehydrotigogenone with Zn–Hg–HCl–EtOH or Zn–HCl–EtOH gives 4-*dehydrodeoxytigogenin*, m.p. 145·5—146°, and with $Al(OPr^\beta)_3$–$Pr^\beta OH$ gives 3 : 5-*dehydrodeoxytigogenin* (**V**), m.p. 168—169°, reduced (H_2–Pd–$BaSO_4$–Et_2O) to deoxytigogenin. Treating (**I**) with *p*-O:C_6H_4:O in PhMe and then with $Al(OPr^\beta)_3$ gives, after removal of acids and carbinols, 4 : 6-*dehydrotigogenone*, m.p. 205—207°. Chlorination of (**I**) gives *chlorodeoxydiosgenin*, m.p. 211—213°, hydrogenated (PtO_2; AcOH) to 3-*chlorodeoxytigogenin* (**VI**), m.p. 204—207°. An *isomeride*, m.p. 210—212°, of (**VI**) is obtained from tigogenin by PCl_5 and $CaCO_3$ in $CHCl_3$ at 20° and in boiling quinoline

gives 2-*dehydrodeoxytigogenin*, m.p. 163—166°. 4-Dehydrotigogenone and $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ give 4-*dehydro*epi*tigogenin*, m.p. 208—210° [in boiling Ac_2O gives (?) (**V**)], and a *product*, m.p. 167—169° (digitonide; dehydrated at 100°/vac.).

R. S. C.

Sterols. CXXI. Sapogenins. XLVIII. Bromosarsasapogenin and bromodiosgenin. R. E. Marker, D. L. Turner, A. C. Shabica, and P. R. Ulshafer (*J. Amer. Chem. Soc.*, 1941, **63**, 1032—1034).—The Br of bromosarsapogenin (**I**) is shown to be at $C_{(23)}$. The acetate of (**I**) and CrO_3 at 60° give 3-hydroxy-16-ketobisnorcholanic acid. Diosgenin acetate (**II**), Br, and a drop of HBr in AcOH at 20° give the 5 : 6 : 23-Br_3-derivative (**III**), m.p. 172° (decomp.), converted by KI in boiling EtOH into 23-*bromodiosgenin acetate*, m.p. 177—179° (decomp.) or 197—198° (decomp.), which is reduced by Zn–AcOH to (**II**), is hydrolysed by boiling 1% KOH–EtOH to *bromodiosgenin*, m.p. 195° (decomp.), is oxidised by SeO_2 (with subsequent hydrolysis) to 23-*bromo*-4-*hydroxydiosgenin*, m.p. 203° (decomp.), and with CrO_3–AcOH–H_2O at 50° gives (?) 7 : 16-*diketo*-3-*acetoxy*-Δ^5-*bisnorcholenic acid*, m.p. 226—227° (*semicarbazone*, decomp. 195°), and a small amount of 23-*bromo*-7-*ketodiosgenin acetate*, decomp. 214°. With 1% EtOH–KOH followed by CrO_3–AcOH at 20° and then KI–EtOH, (**III**) gives 23-*bromo*-4-*dehydrotigogenone*, decomp. 214°.

R. S. C.

Sterols. CXVI. Sapogenins. XLV. *iso*Sarsasapogenin configuration. R. E. Marker, D. L. Turner, R. B. Wagner, and P. R. Ulshafer (*J. Amer. Chem. Soc.*, 1941, **63**, 772—774).—Reactions are described supporting the view that sapogenins having the *iso*sarsasapogenin differ from those having the sarsasapogenin configuration only in configuration at $C_{(22)}$. Tigogenin and $H_2S_2O_8$–AcOH at 25° give allo*pregnane*-3(β) : 16 : 20-*triol*, m.p. 235—237° (*triacetate*, m.p. 166°; *tribenzoate*, m.p. 204°), also obtained from tigogenin acetate by 30% H_2O_2 in AcOH at 70° and later KOH–EtOH. *epi*-Tigogenin gives ($H_2S_2O_8$) allo*pregnane*-3(α) : 16 : 20-*triol*, m.p. 210—212° (*triacetate*, m.p. 148—150°), whilst smilagenin affords the same pregnane-3(β) : 16 : 20-triol, m.p. 223—226°, as is obtained (A., 1940, II, 376) from sarsasapogenin. Diosgenin and MgEtBr in Et_2O, later boiling C_6H_6, give 22-*ethyldihydrodiosgenin*, m.p. 211—214° (*di*-p-*nitrobenzoate*, m.p. 183—184°), hydrogenated (PtO_2–AcOH; 35 lb.) to 22-*ethyldihydrotigogenin*, m.p. 192—194° (*di*-p-*nitrobenzoate*, m.p. 183—184°), which is obtained also from tigogenin by MgEtBr and with CrO_3 in 90% AcOH at 15° gives the *keto-acid*, $C_{29}H_{46}O_4$, m.p. 221—223°. Smilagenin and MgEtBr give a 22-*ethyldihydro*-derivative, m.p. 161—162° (*diacetate*, m.p. 89—91°), isomeric with that obtained from sarsasapogenin.

R. S. C.

V.—HETEROCYCLIC.

Co-ordination compounds with furfuraldoxime as a chelate group. I. Additive compounds with metallic salts. A. Bryson and F. P. Dwyer (*J. Proc. Roy. Soc. N.S. Wales*, 1940, **74**, 107—109).—β-Furfuraldoxime and $CuCl_2,2H_2O$–EtOH, Cu_2Cl_2–EtOH, $AgNO_3$–aq. EtOH, aq. $AgClO_4$, Ag_2SO_4–aq. EtOH, $NiCl_2,6H_2O$–EtOH, or $CoCl_2,6H_2O$–EtOH, respectively, afford *compounds*, $Cu(C_5H_5O_2N)_2Cl_2$, $Cu(C_5H_5O_2N)_2Cl$, $Ag(C_5H_5O_2N)_2NO_3$, $Ag(C_5H_5O_2N)_2ClO_4$, $Ag_2(C_5H_5O_2N)_4SO_4$, $Ni(C_5H_5O_2N)_4Cl_2$, and $Co(C_5H_5O_2N)_4Cl_2$, respectively. α-Furfuraldoxime does not give additive compounds with metallic salts, but rearranges to give an additive compound of the β-oxime.

A. T. P.

Furfuraldoxime as a chelate group. II. Palladium compounds with α-(*syn*)furfuraldoxime. A. Bryson and F. P. Dwyer (*J. Proc. Roy. Soc. N.S. Wales*, 1940, **74**, 240—246).—Pd alone of the common metals forms complexes with α-furfuraldoxime (**I**) (cf. A., 1935, 752, and *J. Proc. Roy. Soc. N.S. Wales*, 1935, **68**, 107). (**I**) and Na chloropalladite in aq. EtOH–NaOAc afford *Pd bis-α-furfuraldoxime* (**II**), $Pd(C_5H_4O_2N)_2$ (*monomeric* form), decomp. without melting; keeping the solid or a conc. solution in $COMe_2$, at room temp. converts it into the trimeric *form* (**III**), $[Pd(C_5H_4O_2N)_2]_3$, decomp. without melting. (**I**) can be recovered from either form. Structural formulæ are given. (**II**) in cold C_5H_5N yields *bispyridine palladous oximate* (**IV**), $Pd(C_5H_4O_2N)_2,2C_5H_5N$ (C_5H_5N is lost at 100—110°), converted by cold dil. HCl into $Pd(C_5H_5N)_2Cl_2$. (**IV**) is sol. in H_2O or $CHCl_3$, indicating an equilibrium between the true ionic oximate form and a covalent form. In boiling $CHCl_3$ with C_5H_5N or *p*-$C_6H_4Me{\cdot}NH_2$, (**III**) shows no evidence of further co-ordination. (**III**) and C_5H_5N at 80—90° give *bispyridine Pd bisfurfuraldoxime*, $[Pd(C_5H_4O_2N)_2]_3,2C_5H_5N$, gradually decomp. in C_5H_5N at 90° to give (**IV**). (**II**) or (**III**) and $(CH_2{\cdot}NH_2)_2$–C_6H_6–$CHCl_3$ afford the same *ethylenediamine compound* (**V**), $Pd(C_5H_4O_2N)_2,C_2H_8N_2$, sol. in H_2O or $CHCl_3$, and considered to be ethylenediamine palladous oximate in equilibrium with ethylenediamine Pd bisfurfuraldoxime. (**V**) and $(CH_2{\cdot}NH_2)_2$–$CHCl_3$ give the ionic H_2O-sol. bisethylenediamine *compound*.

A. T. P.

2-Hydroxy-4-benzoyl-2 : 5-diphenylfuran-3-one. R. E. Lutz, J. M. Smith, jun., and A. H. Stuart (*J. Amer. Chem. Soc.*, 1941, **63**, 1143—1148).—COPh·CO·CH:CPh·ONa and BzCl in boiling Pr^{β}_2O give benzoates [including COPh·CH:C(OBz)·COPh and (?) COPh·CO·CH:CPh·OBz], whence 10% NaOH–aq. MeOH yields 2-hydroxy-4-benzoyl-2 : 5-diphenyl-2 : 3-dihydrofuran-3-one (**I**) (15%), m.p. 166° (cf. A., 1936, 1524). Reactions below are considered to prove that (**I**) has only the furan structure; alternative nechanisms are set out for those reactions which appear to indicate existence of (**I**) in open-chain phase. Kurt-Meyer titration with Br–EtOH at −16° to −19° is too slow for an enol (56—60% in 1, 74% in 5, 99% in 120 sec.). Boiling HCl–80% EtOH has no effect on (**I**), which is also remarkably stable to alkali. Hydrolysis requires boiling 33% KOH in 50% MeOH, yielding then a substance (*semicarbazone*, m.p. 285°), BzOH, and $(CHO)_2$. The *benzoate* (**II**), m.p. 182°, of (**I**) was isolated in poor yield as intermediate in the prep. of (**I**) and was also obtained (~80%) from (**I**) by Bz_2O–H_2SO_4 at room temp. (not by BzCl) or (20%) from the Ag salt of (**I**) by BzCl in boiling Pr^{β}_2O. Ac_2O and a drop of H_2SO_4 convert (**I**) at 25° into its *acetate*, m.p. 120·5°, which in 10% KOH–MeOH–H_2O at 60° regenerates (**I**). With HCl–MeOH at room temp., (**I**) or (**II**) gives 4-*benzoyl*-2-*methoxy*-2 : 5-*diphenyl*-2 : 3-*dihydrofuran*-3-*one* (**III**), m.p. 131°, also obtained (15%) from the Ag salt of (**I**) and MeI in boiling Pr^{β}_2O and converted by *o*-$C_6H_4(NH_2)_2$ into 2-*phenyl*-3-*dibenzoylmethylquinoxaline* (**V**), m.p. 157° (cf. below), and by O_3 in $CHCl_3$ into BzOH (37%; no $BzCO_2H$ is isolated). 4-*Benzoyl*-2-*ethoxy*-2 : 5-*diphenyl*-2 : 3-*dihydrofuran*-3-*one*, m.p. 83°, is similarly obtained from (**II**) by HCl–EtOH. Boiling (**I**) in $SOCl_2$ gives, probably, the 2-Cl-compound, since the oily product is converted by NaOMe–MeOH at 0° into (**III**). Br and (**I**) in EtOH at 0° give *β-bromo-β-benzoyl-αδ-diphenylbutan-αγδ-trione* (**V**), m.p. 114·5°, which with KI regenerates (**I**) and with HCl–MeOH gives (**III**) and a small amount of a product, m.p. 110°. (**IV**) is obtained slowly at the b.p. from (**I**) in EtOH but immediately from (**V**) or (**VI**) (see below); it gives a slowly deepening $FeCl_3$ colour and with NaOMe gives an unstable enolic form, m.p. 60—65°, which gives an immediate deep $FeCl_3$ colour; with boiling NH_2OH–or $NHPh{\cdot}NH_2$–NaOAc or a little HCl in boiling 75% EtOH, (**IV**) gives 2-phenyl-3-phenacylquinoxaline, m.p. 166° (cf. *loc. cit.*); with CrO_3–AcOH it gives 2-hydroxy- and 2-carboxy-3-phenylquinoxaline and BzOH. CH_2N_2–Et_2O and (**I**) give OMe·CPh:C(COPh)·CO·COPh (**VI**), an oil, the structure of which is proved by the following reactions. At 25° (**VI**) readily gives (**IV**); with O_3 in $CHCl_3$ at 0° it gives BzOH, $BzCO_2H$, and MeOBz; with boiling HCl–AcOH or 2% KOH in boiling 70% MeOH it gives (**I**) (50%); with MeOH–HCl it gives (**III**); with NaOMe at 25° it gives a substance, m.p. 119—121°. M.p. are corr.

R. S. C.

Synthesis of 2-hydroxy-4-benzoyl-2 : 5-diphenylfuran-3-one by way of benzoyldiphenylfuran and bromotribenzoylethylene. R. E. Lutz and J. M. Smith, jun. (*J. Amer. Chem. Soc.*, 1941, **63**, 1148—1150).—The structure of 2-hydroxy-4-benzoyl-2 : 5-diphenyl-2 : 3-dihydrofuran-3-one (**I**) is confirmed by a synthesis proving attachment of the Bz to C. $CH_2Bz{\cdot}CHBrBz$ [best prepared from $(CHBz:)_2$ by HBr–AcOH] and H_2SO_4–Ac_2O give 3-bromo-2 : 5-diphenylfuran, the Grignard reagent from which with CO_2 gives 2 : 5-diphenyl-3-furoic acid and with (best) Bz_2O–Et_2O at 0° (later room temp.) gives 3-benzoyl-2 : 5-diphenylfuran (**II**), m.p. 77° (oxime, m.p. 173—176°; *semicarbazone*, m.p. 225°) (and in both cases also some bis-2 : 5-diphenyl-3-furyl). With Br–CCl_4 or PBr_5 at 25° [not by the method of Kohler *et al.* (A., 1919, i, 533)], (**II**) gives the 4-Br-derivative, m.p. 119·5—120°, which with HNO_3–AcOH at 50° gives *β-bromo-γ-benzoyl-αδ-diphenyl-*Δ^{β}*-butene-αδ-dione* [*bromotribenzoylethylene*] (54%), m.p. 101°. This is converted by H_2–Pd–$BaSO_4$ into (**II**), by Zn dust in AcOH at 25° or 50° into a substance (poor yield), m.p. 167—169°, by HCl–MeOH at room temp. into 2-methoxy-4-benzoyl-2 : 5-diphenyl-2 : 3-dihydrofuran-3-one [hydrolysed to (**I**)], by H_2SO_4–Ac_2O into

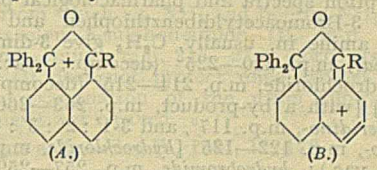
2-acetoxy-4-benzoyl-2 : 5-diphenyl-2 : 3-dihydrofuran-3-one [and thence (**I**)], by 2% KOH in boiling MeOH into CHBz:CBz·OH, by NaOMe–MeOH at 25° into CHBz:CBz·OMe, and by NH_3–MeOH at room temp. into CHBz:CBz·NH_2. M.p. are corr. R. S. C.

Derivatives of coumaran. VII. Synthesis of *iso*tubanol and *iso*tubaic acid. R. L. Shriner and M. Witte (*J. Amer. Chem. Soc.*, 1941, **63**, 1108—1110; cf. A., 1940, II, 20).—3-Hydroxy-2-keto-1 : 2-dihydrobenzfuran, $COMe_2$, and KOH in abs. EtOH at room temp. give the 1-CMe_2: derivative, m.p. 121° (*phenylurethane*, m.p. 143°), converted by BzCl–Na_2CO_3–aq. $COMe_2$ into 2-*keto*-1-*benzoyloxy*-1-*iso*propylidene-1 : 2-*dihydrobenzfuran*, m.p. 160°. H_2–PtO_2 in abs. EtOH containing a little HCl at 48 lb. then gives 2-hydroxy-3-benzoyloxy-1-*iso*propyl-1 : 2-dihydrobenzfuran, an oil, dehydrated to *iso*tubanol benzoate by distillation. Hydrolysis thereof by NaOH gives *iso*tubanol (*phenylurethane*, m.p. 142°), which with NaOMe–MeOH–CO_2 gives *iso*tubaic acid (acetate, new m.p. 153°; prep. from rotenone by way of *iso*rotenone modified). R. S. C.

Reaction between quinones and metal enolates. XIII. Trimethylethylbenzoquinone and sodiomalonic ester. XIV. Synthesis of the three 6-hydroxy-3-carboxy-*Bz*-dimethylethyl-coumarins and their ethyl esters. L. I. Smith and J. W. Opie (*J. Amer. Chem. Soc.*, 1941, **63**, 932—936, 937—940; cf. A., 1941, II, 144).—XIII. The success and direction of condensation of methyl-*p*-benzoquinones with $CHNa(CO_2Et)_2$ (**I**) depend on the nature of other substituents. Whereas the Br of 1 : 2 : 3 : 5 : 6 : 4-O:C_6Me_3Br:O causes unidirectional reaction (*loc. cit.*), replacement of the Br by Et gives a much less marked effect. 1 : 2 : 3 : 5 : 6 : 4-O:C_6Et_4:O [prepared from 1 : 2 : 4 : 5-$C_6H_2Et_4$ by way of the $(NO_2)_2$-, m.p. 149—151° (lit. 143—145°), and $(NH_2)_2$-compound], m.p. 60—62° (lit. 56—58°), does not condense with (**I**). 1 : 2 : 3 : 5 : 6 : 4-O:C_6Me_3Et:O (similar prep. improved), m.p. 43—45°, with (**I**) in boiling C_6H_6 gives 40% of the derived *quinol*, m.p. 169—170° (*diacetate*, m.p. 136—136·5°), and a red Na salt, hydrolysed to a mixture, whence adsorption on Al_2O_3, fractional elution, and crystallisation gives material, m.p. 185°, shown by thermal analysis to be a binary mixture of *Et* 6-*hydroxy*-7 : 8-*dimethyl*-5-*ethyl*- (**II**) and 6-*hydroxy*-5 : 8-*dimethyl*-7-*ethyl*-*coumarin*-3-*carboxylate* (**III**), and material, m.p. 150—152°, shown similarly to be a ternary mixture of (**II**), (**III**), and *Et* 6-*hydroxy*-5 : 7-*dimethyl*-8-*ethylcoumarin*-3-*carboxylate* (**IV**).

XIV. Ethyl-*o*-, -*m*-, and -*p*-xyloquinone, respectively, with Zn–AcOH–H_2O give 2 : 3-*dimethyl*-5-, m.p. 160—160·5°, 2 : 6-*dimethyl*-3-, m.p. 158—158·5°, and 2 : 5-*dimethyl*-3-*ethylquinol*, m.p. 158—159°, the *diacetates*, m.p. 90—91°, (**V**) 65—66°, and 74·5—75·5°, of which with Me_2SO_4–KOH–MeOH give the oily Me_2 ethers. With CH_2O–HCl–H_2 these give 2 : 5-*dimethoxy*-3 : 4-*dimethyl*-6-, m.p. 61—62°, -4 : 6-*dimethyl*-3-, m.p. 60—62°, and -3 : 6-*dimethyl*-4-, m.p. 81—82°, *-ethylbenzyl chloride*, which with boiling KOAc–AcOH give the corresponding *acetates*, m.p. 30—40°, an oil, and m.p. 54·5—56·5°, respectively, and thence by KOH–aq. EtOH the *alcohols*, m.p. 116·5—118°, 107—108°, and 127·5—128·5°, respectively. CrO_3–AcOH at <50° then gives 2 : 5-*dimethoxy*-3 : 4-*dimethyl*-6-, m.p. 53—54°, -4 : 6-dimethyl-3-, an oil, and -3 : 6-dimethyl-4-, an oil, -ethylbenzaldehyde, which with (**I**) in EtOH at room temp. and later boiling 48% HBr give 6-*hydroxy*-7 : 8-*dimethyl*-5-, m.p. 223—224° [Et ester (**II**), m.p. 180°], -5 : 7-*dimethyl*-8-, m.p. 232—234° [Et ester (**IV**), m.p. 173—174·5°], and -5 : 8-*dimethyl*-7-, m.p. 250° [Et ester, (**III**), m.p. 199—201°], *-ethylcoumarin*-3-*carboxylic acid*. CH_2O–HCl converts (**V**) into 2-*hydroxy*-5-*acetoxy*-4 : 6-*dimethyl*-3-*ethylbenzyl chloride*, m.p. 144·5—146°, which with Na and $CH_2(CO_2Et)_2$ in boiling Et_2O gives *Et* 6-*acetoxy*-5 : 7-*dimethyl*-8-*ethyl*-3 : 4-*dihydrocoumarin*-3-*carboxylate*, m.p. 128·5—129·5°. The corresponding Me_3 compound could not be dehydrogenated. R. S. C.

Reaction between lactones and Grignard reagents. I. Diphenyl-1 : 8-naphthalide. T. A. Geissman and L. Morris (*J. Amer. Chem. Soc.*, 1941, **63**, 1111—1114).—Only 1 mol. of MgRHal reacts with diphenyl-1 : 8-naphthalide (**I**) to give 1 : 8-$C_{10}H_6<^{CPh_2}_{CR(OH)}>O$. Thus are obtained 1-iso*butyryl*- (**II**), m.p. 176°, *-propionyl*- (**III**), m.p. 142—143°, -n-*valeryl*- (**IV**), m.p. 114—115°, -iso*valeryl*-, m.p. 135—136° (decomp.), and -benzoyl- (**V**), m.p. (+C_6H_6) ~115° (decomp.), (anhyd.) 200—201° (lit. 202°), -8-α-hydroxybenzhydrylnaphthalene semiketal. In H_2SO_4 the primary alkyl ketones give deep yellow colours and with HCl–AcOH–$FeCl_3$ (**III**), (**IV**), and (**V**) give *ferrichlorides*, m.p. 150—153° (decomp.), 134—135° (decomp.), and 148—150° (decomp.), respectively; the structures (*A*) and (*B*) are assigned to the cations. The semiketals decompose at or slightly > the m.p., yielding (**I**) and [from (**II**)] the paraffin (C_3H_8) or [from (**III**)] the olefine (C_2H_4) and H_2. With NaOAc in boiling AcOH, (**III**) and (**II**) give 1 : 1-*diphenyl*-3-*ethylidene*-, m.p. 134°, and *-propylidene*-peri-*naphthopyran*, 1 : 8-$C_{10}H_6<^{CPh_2}_{C(:CRR')}>O$, m.p. 190—194°, respectively.



R. S. C.

Effect of unsaturated chromophores on pyronine dyes. II. Dyes obtained from maleic and succinic acids. I. N. D. Dass and J. D. Tewari (*Proc. Indian Acad. Sci.*, 1941, **13**, **A**, 68—76; cf. A., 1931, 1426).—Condensation of maleic and succinic acids with 1 : 2 : 3-$C_6H_3(OH)_3$, *o*- and *m*-cresol, and *m*-NH_2·C_6H_4·OH in presence of H_2SO_4 yields *maleins*, m.p. ≮300°, 228°, 155°, and 225° (changing colour at 212°), and *succineins*, m.p. 290°, 230° (blackening at 195°), 112°, and 198° (changing colour at 120°), respectively. *Pyrocatechol-malein*, m.p. 148°, and *-succinein*, m.p. 290°, are prepared without condensing agent and purified by $SnCl_4$. *Phenolmalein* (H_2SO_4) has m.p. 195° (blackening at 170°), *β-naphtholmalein* ($ZnCl_2$), 140° (softening at 133°), *α-naphtholsuccinein* (H_2SO_4), 185°, and m-*phenylenediamine-malein* and *-succinein*, 285° and 210° (changing colour at 192°) respectively. Except those from *m*-NH_2·C_6H_4·OH, the maleins are more coloured than the succineins. *m*-$C_6H_4(OH)_2$ with CO_2H·CH_2·CHBr·CO_2H gives a product (**I**) similar to resorcinolmalein (**II**), and with $(CO_2H·CHBr)_2$ yields an acetylenic compound (**III**) (darkens at 250°, then decomp.). Bromination of (**II**) or (**I**) and of (**III**) yields Br_4-compounds, m.p. 185° and 220° (contracting at 183°) respectively. Dyes of this series crystallise with $1H_2O$. Absorption max. of these compounds are given. A. Li.

Benzopyrone series. III. Synthesis of coumarino- and flavono-α-methyl-7 : 8-dihydrofurans. B. Krishnaswamy and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1941, **13**, **A**, 43—48).—Umbelliferone with CH_2:CH·CH_2Br and K_2CO_3 in $COMe_2$ yields 7-*allyloxy*-, m.p. 79—80°, transformed by heating at 195—200°/20 mm. into 7-*hydroxy*-8-*allyl*-*coumarin*, m.p. 162—163°. This with $HgCl_2$ in EtOH yields 2′-*chloromercurimethyl*-, m.p. 233—235°, which with I in KI gives 2′-*iodomethyl*-, m.p. 168—169°, reduced (Na + EtOH) to 2′-*methyl*-2′ : 3′-*dihydrocoumarino*-(7 : 8-5′ : 4′)-*furan*, m.p. 148—149°. By similar reactions 7-allyloxy-4-methylcoumarin yields 4-methyl-8-allylumbelliferone, 4-*methyl*-2′-*chloromercurimethyl*-, m.p. 225—227°, and -2′-*iodomethyl*-, m.p. 158—159°, and 2 : 4-*dimethyl*-2′ : 3′-*dihydrocoumarino*-(7 : 8-5′ : 4′)-*furan*, m.p. 182—183°, and 3-*methoxy*-7-*allyloxy*-, m.p. 107—108°, yields 7-*hydroxy*-3-*methoxy*-8-*allyl*-*flavone*, m.p. 243—244°, 3-*methoxy*-2′-*chloromercurimethyl*-, decomp. ~200°, -2′-*iodomethyl*-, m.p. 205—206°, and -2′-*methyl*-2′ : 3′-*dihydroflavono*-(7 : 8-5′ : 4′)-*furan*, m.p. 133—134°. A. Li.

Hæmorrhagic sweet clover disease. V. Identification and synthesis of the hæmorrhagic agent. M. A. Stahmann, C. F. Huebner, and K. P. Link. **VI. Synthesis of the δ-diketone derived from the hæmorrhagic agent through alkaline degradation.** C. F. Huebner and K. P. Link (*J. Biol. Chem.*, 1941, **138**, 513—527, 529—534).—V. A method of mass isolation of the compound $C_{19}H_{12}O_6$ (**I**), m.p. 288—289° (Campbell *et al.*, A., 1941, III, 23) [*diacetate*, m.p. 250—252° (decomp.)], is described. (**I**) yields, with KOH at 300°, *o*-OH·C_6H_4·CO_2H, with 30% EtOH–KOH or 10% aq. NaOH, *αγ-disalicoylpropane* (**II**), m.p. 101—102° (*Me ether*, m.p. 86—88°) (which, fused with KOH, gives *o*-OH·C_6H_4·CO_2H), with NH_2Ph at 180°, 4-anilo-3 : 4-dihydrocoumarin, m.p. 262—263°, and with NHPh·NH_2, a *diphenylhydrazone*, $C_{21}H_{10}O_2N_4$, m.p. 189—189·5°. (**I**) is 3 : 3′-methylenebis-(4-hydroxycoumarinyl) (Anschütz, A., 1909, i, 663) (from 4-hydroxycoumarin and CH_2O), which shows hæmorrhagic activity in rabbits.

VI. (II) with N_2H_4,HCl and NaOAc yields a *compound*, $C_{17}H_{16}O_2N_2$, m.p. 252°, which gives a yellow colour with aq. NH_3. *o*-OMe·C_6H_4·CO·CH_2·CO_2Et (from *o*-OMe·C_6H_4·CO_2Me and EtOAc), new m.p. 130—131°, with Na and CH_2I_2 in C_6H_6 yields a product hydrolysed (cold 10% NaOH) to the *Me*$_2$ *ether*, m.p. 86—88, of (II). Ph glutarate with $AlCl_3$ in CS_2 yields (II). A. Li.

Isosteric compounds. III. *tert.*-**Dibenzthienyl amino-alcohols.** A. Burger and H. W. Bryant (*J. Amer. Chem. Soc.*, 1941, **63**, 1054—1057; cf. A., 1939, II, 386).—Dibenzthiophen and phenanthrene are not isosteric. They are not isomorphic; their absorption spectra and pharmacological properties are dissimilar. 3-Bromoacetyldibenzthiophen and the appropriate *sec.* amine in, usually, C_6H_6 give 3-dimethylamino- [*hydrochloride*, m.p. 220—225° (decomp.; vac.)], -diethylamino- [hydrochloride, m.p. 214—215° (decomp.; vac.) (lit. 200—202°)] [with a by-product, m.p. 263—266° (decomp.; vac.)], *-piperidino-*, m.p. 117°, and 3-1′ : 2′ : 3′ : 4′-*tetrahydro*-iso*quinolino-*, m.p. 122—125° [*hydrochloride*, m.p. 244—246° (decomp.; vac.); *hydrobromide*, m.p. 257—259° (decomp.; vac.)], *-acetyldibenzthiophen*, hydrogenated (PtO_2; MeOH) as hydrohalide to 3-β-dimethylamino- [*hydrochloride*, m.p. 228—228·5° (decomp.; vac.); *acetate hydrochloride*, m.p. 206—208° (decomp.; vac.)], *-diethylamino-* (I), m.p. 59—60° [*hydrochloride*, m.p. 163—164°; *acetate hydrochloride*, m.p. 188—192° (decomp.; vac.)], *-piperidino-* (II), m.p. 88—89° [*hydrochloride*, m.p. 225—229° (decomp.; vac.); *acetate hydrochloride*, m.p. 220—225°], and -1′ : 2′ : 3′ : 4′-*tetrahydro*-iso*quinolino-*, m.p. 106—107° [*hydrochloride*, m.p. 243—244° (decomp.; vac.); *hydrobromide*, m.p. 250—252° (decomp.; vac.)], *-α-hydroxyethyldibenzthiophen*. 3-Acetyldibenzthiophen (III), paraformaldehyde, and the appropriate *sec.* amine hydrochloride in boiling *iso*-C_5H_{11}·OH (IV) or *cyclo*hexanol (V) give 3-β-dimethylamino- [*hydrochloride*, m.p. 192—195° (decomp.; vac.)], -diethylamino- [*hydrochloride*, m.p. 150—151°; prep. in (V); in (IV) a non-basic substance, m.p. 82—82·5°, is formed], -piperidino- [*hydrochloride*, m.p. 201—203° (decomp.; vac.)], and -1′ : 2′ : 3′ : 4′-*tetrahydro*iso*quinolino-*, m.p. 106—107° [*hydrochloride*, m.p. 197—198° (decomp.; vac.)], *-propionyldibenzthiophen*, hydrogenated as above to 3-*γ-dimethylamino-* (VI), m.p. 118° (*hydrochloride*, m.p. 137—139°; *acetate hydrochloride*, m.p. 149—150°), *-piperidino-* (VII), m.p. 102° [*hydrochloride*, m.p. 201—201·5° (decomp.; vac.); *acetate hydrochloride*, m.p. 185—186°], and -1′ : 2′ : 3′ : 4′-*tetrahydro*iso*quinolino-*, m.p. 136° [*hydrochloride*, m.p. 183—185°; *acetate hydrochloride*, m.p. 193—196° (decomp.; vac.)], *-β-hydroxy-*n*-propyldibenzthiophen*. 1-*β-Piperidinopropionyl-*, m.p. 112° [*hydrochloride*, m.p. 229—232° (decomp.; vac.)], and 1-*γ-piperidino-β-hydroxy-*n*-propyl-*, m.p. 105°, *-dibenzthiophen* are similarly prepared. Boiling $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ reduces (III) to 3-*α-hydroxyethyldibenzthiophen*, m.p. 76—77° (oily *acetate*). Analgæsic and other physiological properties of (I), (II), (VI), and (VII) are reported. R. S. C.

Preparation and attempted resolution of 2 : 2-dimethylethyleneimine. T. L. Cairns (*J. Amer. Chem. Soc.*, 1941, **63**, 871—872).—NH_2·CMe_2·CH_2·OH (I) distilled with aq. H_2SO_4 (first up to 115°/atm. pressure and later 150—170°/25—30 mm.) gives 2 : 2-*dimethylethyleneimine* (II), b.p. 69—70°, stable to $KMnO_4$ and converted by dil. H_2SO_4 into NH_2·CH_2·CMe_2·OH. *d*-CHMePh·NH_2,HCl and $COCl_2$ in boiling PhMe give *l-α*-phenylethylcarbimide, b.p. 82—83°/12—14 mm., $[\alpha]_D^{24}$ −2° in C_6H_6, which with NH_3–C_6H_6 gives *d-α*-phenylethylcarbamide, m.p. 121—122°, $[\alpha]_D^{25}$ +48·8° in abs. EtOH, and with (II) in C_6H_6 gives d-1-*α-phenylethylcarbamyl*-2 : 2-*dimethylethyleneimine* (III), m.p. 104—105°, $[\alpha]_D^{25}$ +48° in C_6H_6. Mutarotation of (III) occurs in boiling C_6H_6, but is due solely to decomp. R. S. C.

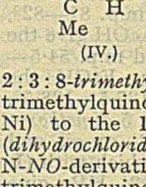
Aminoethanol derivatives possessing local anæsthetic activity. F. C. MacIntosh and T. S. Work (*Quart. J. Pharm.*, 1941, **14**, 16—25).—7 : 1-OMe·$C_{10}H_6$·CO·CH_2·NMe_2 (from the bromide and $NHMe_2$ in MeOH–Et_2O) is reduced (H_2, PtO_2, MeOH–HCl) to 7-methoxy-1-naphthyldimethylaminomethylcarbinol (an oil) [*hydrochloride*, m.p. 209°; *picrate*, m.p. 158° (sinters at 95°)]. Similarly, condensation of COPh·CH_2Br with piperidine (I) and reduction of the resultant base affords *phenylpiperidinomethylcarbinol hydrochloride*, m.p. 195°. C_6H_{13}Ph (prep. from hexoylbenzene by Clemmensen or Wolff–Kishner reduction) with CH_2Cl·COCl and $AlCl_3$ in CS_2 yields p-*hexylphenacyl chloride*, m.p. 32°, b.p. 154—156°/0·9 mm., which with (I) in Et_2O and subsequent reduction affords *p*-hexylphenylpiperidinomethylcarbinol (*picrate*, m.p. 133—135°); similarly PhBu gives p-*butylphenacyl chloride* (II), b.p. 142—144°/2 mm., the corresponding piperidino-ketone (an oil) (III), and *p*-butylphenylpiperidinomethylcarbinol (an oil) (*picrate*, m.p. 137—138°). *p*-Butylphenylethylpiperidinomethylcarbinol (*hydrochloride*, m.p. 178°) was prepared from (III) and MgEtI in Et_2O; the corresponding methylcarbinol (*hydrochloride*, m.p. 186°) was obtained from (II) and MgMeI (which yielded an oil and a cryst. *substance*, $C_{12}H_{16}O$, m.p. 121°) and subsequent treatment of the resulting oil with (I). *α-Chlorotridecan-β-one*, m.p. 46° (from lauryl chloride and CH_2N_2 in Et_2O, the resultant diazoketone, m.p. 44°, being decomposed in Et_2O by dry HCl), with (I) in Et_2O gives a piperidino-ketone, reduced to piperidinomethylundecylcarbinol (*picrate*, m.p. 69—70°). The above compounds of the type OH·CRR′·CH_2·N:R″, together with others previously described (A., 1940, II, 356), were examined for local anæsthetic activity (cf. A., 1941, III, 528). F. O. H.

p-**Piperidinobenzonitrile, m.p. 55°.**—See A., 1941, I, 271.

Synthesis of dihydroindole, dihydrothionaphthen, and dihydrobenzofuran. G. M. Bennett and M. M. Hafez (*J.C.S.*, 1941, 287—288).—*o*-Amino-β-phenylethyl alcohol (O-*Bz* derivative, m.p. 168°) when heated with HCl and made alkaline or with $PhSO_2Cl$ and cold aq. alkali gives indoline (*p*-C_6H_4Me·SO_2, m.p. 99°, and *Ac* derivatives, m.p. 105°). Diazotisation of the alcohol in H_2SO_4 and treatment with $NaHCO_3$ affords 2 : 3-dihydrobenzofuran and introduction of S by the Leuckhardt process followed by warming with acid yields dihydrothionaphthen. F. R. S.

Vitamin-B_6.—See B., 1941, III, 161.

Petroleum bases. II. Amino- and hydroxy-derivatives. Chemistry of diazo-oxides. L. R. Modlin, jun., and A. Burger (*J. Amer. Chem. Soc.*, 1941, **63**, 1115—1118).—5-Hydroxy-2 : 3 : 8-trimethylquinoline (I) (A., 1940, II, 288) and HNO_3 (*d* 1·5) at 0° give the 6-*NO*$_2$-derivative, m.p. (+EtOH or anhyd.) 152—152·5°, converted by CH_2N_2–EtOH–MeOH into the *Me ether* (II), m.p. 128—129°, also obtained by nitrating 2 : 3 : 8 : 5-$C_{10}H_4Me_3$·OMe at −10°. $SnCl_2$–HCl reduces (II) to 6-*amino-5-methoxy-*, m.p. 137—138° [*hydrochloride*, m.p. 255—259° (decomp.)], converted by HBr into 6-amino-5-hydroxy-2 : 3 : 8-trimethylquinoline (III), unstable [*hydrobromide*, m.p. 330—335° (decomp.; vac.)]. Treating the dihydrobromide of (III) with $NaNO_2$ in 17% HCl at −5° and then with $CO(NH_2)_2$ and pouring the mixture into boiling H_2O gives 2 : 3 : 8-*trimethylquinoline*-6-*diazo*-5-*oxide* (IV), darkens at 167°, decomp. 228° (vac.). With $Na_2S_2O_4$ in boiling aq. EtOH, (IV) gives (I), and with NH_2OH,HCl and C_5H_5N in boiling EtOH gives 2 : 3 : 8-*trimethylquinoline*-5 : 6-*quinonedioxime*, m.p. 189—190° (decomp.; vac.), which in boiling 10% NaOH gives 2 : 3 : 8-*trimethylquinolinofurazan*, m.p. 130°. 5-Amino-2 : 3 : 8-trimethylquinoline is hydrogenated (PtO_2–EtOH or Raney Ni) to the 1 : 2 : 3 : 4-*H*$_4$-derivative, b.p. 110°/0·1 mm. (*dihydrochloride*, decomp. >300°; *Ac*$_2$, m.p. 152°, and N-*NO*-derivative, cryst.), also obtained from 5-nitro-2 : 3 : 8-trimethylquinoline by H_2–PtO_2–EtOH. Hydrogenation of (I) gives similarly 5-hydroxy-2 : 3 : 8-trimethyl-1 : 2 : 3 : 4-tetrahydroquinoline (65%) [*hydrochloride*, m.p. 258—263° (decomp.)], and an alkali-insol. oil. R. S. C.



(IV.)

Synthesis and pharmacology of dialkylmalonylguanidines. O. H. Miller and L. Fischer (*J. Amer. Pharm. Assoc.*, 1941, **30**, 45—47).—The following were prepared by treatment of the appropriate dialkylmalonic Et_2 ester with guanidine hydrochloride in presence of NaOEt at 80—90° for 60 hr.: *diethyl-*, *ethyl*iso*propyl-*, *ethyl-*n*-butyl-*, *ethyl*iso*amyl-*, and *ethylphenylmalonylguanidine* (all m.p. >300°). For pharmacology of above compounds, cf. A., 1941, III, August. F. O. H.

Pyrimidines. CLXIX. Action of 5 : 5-bromo-oxyhydrouracil on ethylenethiocarbamide. T. B. Johnson and C. O. Edens (*J. Amer. Chem. Soc.*, 1941, **63**, 1058—1060).—5 : 5-Dibromo- or -dichloro-hydroxydihydrouracil in boiling EtOH oxidises ethylenethiocarbamide (I) to $(CH_2$·NH_2,HHal$)_2$, S, and the substance (II), $C_6H_{10}N_4S$, m.p. 218—220°, of Jaffe *et al.* (A., 1894, i, 437). (II) is *di*-4 : 5-*dihydro*-2-*glyoxalinyl sulphide*. It is obtained from (I) (*loc. cit.*) or $(CH_2$·$NH_2)_2$ by

$CSCl_2$, reaction proceeding by way of $CH_2{\cdot}NH{>}CH_2{-}N{>}C{\cdot}S{\cdot}CSCl$ and, from (I), $[CH_2{\cdot}NH{>}CH_2{-}N{>}C{\cdot}S]_2CS$. R. S. C.

5-Amino-1-aryl-3-methylpyrazoles. F. Bell (*J.C.S.*, 1941, 285—287).—The methods of preparing 5-amino-1-phenyl-3-methylpyrazole (I) are reviewed; the most satisfactory is from $NHPh{\cdot}NH_2$ and diacetonitrile, which give cyanoacetonephenylhydrazone, converted by 6N-HCl into (I). Similarly *o*-$C_6H_4Cl{\cdot}NH{\cdot}NH_2$ affords *cyanoacetone-o-chlorophenylhydrazone*, m.p. 74—77°, and *5-amino-1-(2′-chlorophenyl)-3-methylpyrazole hydrochloride* (+$2H_2O$), m.p. 123—126°, and 2 : 5-$C_6H_3Cl_2{\cdot}NH{\cdot}NH_2$ (II) yields *cyanoacetone-2 : 5-dichlorophenylhydrazone*, m.p. 112—114°, and *5-amino-1-(2′ : 5′-dichlorophenyl)-3-methylpyrazole hydrochloride*, m.p. 214—220°. $CH_2Ac{\cdot}CO_2Et$ and (II) give *Et acetoacetate 2 : 5-dichlorophenylhydrazone*, m.p. 66—68°, which with $POCl_3$ affords *5-chloro-1-(2′ : 5′-dichlorophenyl)-3-methylpyrazole*, b.p. 195°/25 mm. F. R. S.

Chloral amides. VII. H. W. Hirwe and P. Y. Kulkarni (*Proc. Indian Acad. Sci.*, 1941, **13**, **A**, 49—52; cf. A., 1940, II, 220).—Chloral and *o*-$NH_2{\cdot}CO{\cdot}C_6H_4{\cdot}NH_2$,HCl at 60—70° yield *4-keto-2-trichloromethyl-1 : 2 : 3 : 4-tetrahydroquinazoline*, m.p. 202° (*Ac* derivative, m.p. 194—195°), stable towards HCl. Chloral, warmed with the appropriate amide, yields *chloral-2-* (I), m.p. 172—173°, *-3-*, m.p. 164—165°, and *-4-acetamido-*, m.p. 259—260°, *-2-*, m.p. 168—169°, *-3-*, m.p. 232—233°, and *-4-benzamido-* (requires long heating), m.p. 212—213°, and *-5-bromo-2-acetamido-* (II), m.p. 171—172°, and *-benzamido-benzamide*, m.p. 171°. (I) with Br in glacial AcOH yields (II), hydrolysed (10% NaOH) to *6-bromo-4-keto-2-methyl-3 : 4-dihydroquinazoline*. A. Li.

Triazine and glyoxaline series. A. H. Cook and D. G. Jones (*J.C.S.*, 1941, 278—282).—Polymerisation of the appropriate nitrile with $ClSO_3H$ affords the kyaphenine; *tri-o-methylkyaphenine*, m.p. 110°, is prepared from *o*-$C_6H_4Me{\cdot}CN$. *m-Nitrokyaphenine*, m.p. 206°, is obtained by heating a mixture of PhCN, *m*-$NO_2{\cdot}C_6H_4{\cdot}COCl$, NH_4Cl, and $AlCl_3$; the *p-compound*, m.p. 218°, is similarly prepared. *m*-$NO_2{\cdot}C_6H_4{\cdot}CN$ with BzCl gives *di-m-nitrokyaphenine*, m.p. 253°, and the *p-compound*, m.p. 297°, is obtained similarly, whilst *p*-$NO_2{\cdot}C_6H_4{\cdot}CN$ and *p*-$NO_2{\cdot}C_6H_4{\cdot}COCl$ yield *dinitrocyanobenzophenone*, m.p. 218°. Nitration (KNO_3–H_2SO_4) of tri-*p*-methylkyaphenine gives the NO_2-derivative, m.p. 239°, whilst with fuming HNO_3 the m-$(NO_2)_3$-compound, m.p. 305—307°, also obtained by polymerisation of 2 : 1 : 4-$NO_2{\cdot}C_6H_3Me{\cdot}CN$, is prepared. *Dinitrotri-p-chlorokyaphenine*, m.p. 348°, is formed by nitration. Reduction of the corresponding NO_2-derivative with $NHPh{\cdot}NH_2$ affords m-, m.p. 214°, and p-*amino-*, m.p. 273° (decomp.) (*Ac* derivative, m.p. 315°), and m-*aminotri-*p-*methyl-*, m.p. 231°, and *di-*m-*nitrotri-*m-*amino-*p-*methyl-kyaphenine*, m.p. 261°. Reduction (Zn–AcOH) of tri-*p*-chlorokyaphenine yields *tri-*p-*chlorolophine*, m.p. 268°. Condensation of benzil with the appropriate aldehyde and NH_4OAc gives 4 : 5-*diphenyl-2-ethyl-*, m.p. 229°, 4 : 5-*diphenyl-2-*iso*propyl-*, m.p. 248°, 2-o-*hydroxyphenyl-4* : 5-*diphenyl-*, m.p. 209°, 2-p-*methoxyphenyl-4* : 5-*diphenyl-*, m.p. 229°, 2-o-, m.p. 230°, 2-m-, m.p. 309°, and 2-p-*nitrophenyl-4* : 5-*diphenyl-*, m.p. 240°, 4-p-*nitrophenyl-2* : 5-*diphenyl-*, m.p. 229°, 2-o-*hydroxyphenyl-4-p-nitrophenyl-5-phenyl-*, m.p. 217°, and 2-m-*nitrophenyl-4-p-nitrophenyl-5-phenyl-glyoxaline*, m.p. 226° and 256°, and *2-phenyl-*, m.p. 314°, and 2-o-*nitrophenyl-4* : 5 : 9′ : 10′-*phenanthriminazole*, m.p. 267°. Reduction ($NHPh{\cdot}NH_2$) affords 2-o-, m.p. 196°, and 2-m-*aminophenyl-4* : 5-*diphenyl-*, m.p. 283° (decomp.), and 4-p-*aminophenyl-2* : 5-*diphenyl-glyoxaline*, m.p. 245° (decomp.). Most of the new glyoxalines exhibit chemiluminescent properties recalling those of lophine. F. R. S.

Bile pigments from choleglobin and verdohæmochromogen. —See A., 1941, III, 447.

Addition compounds of morpholine. H. M. Haendler and G. McP. Smith (*J. Amer. Chem. Soc.*, 1941, **63**, 1164).—Morpholine gives 2 : 1 additive *compounds* with $ZnCl_2$, softens at 200—210°, later melts, $ZnBr_2$, decomp. 230—240°, $CdBr_2$, decomp. 250—252°, CdI_2, decomp. 205—210°, $HgBr_2$, decomp. 131—135°, $CdCl_2$, and $HgCl_2$. Co and Cu^{II} halides react, but the Cu^{II} compounds are very sensitive to H_2O. R. S. C.

Reactions of monoalkylanilines with ββ-dichlorodiethyl ether. 4-Phenylmorpholine. H. C. Brill, C. N. Webb, and H. S. Hakbedel (*J. Amer. Chem. Soc.*, 1941, **63**, 971—972).—$(Cl{\cdot}[CH_2]_2)_2O$ and NHPhAlk give *N*-phenylmorpholine (I), the yield being higher if Alk is Me or Et than if it is Bu^{α} or *iso*amyl. The alkiodide of (I) may be an intermediate. R. S. C.

Stable derivative of 4-amino-3-hydroxybenzenesulphonamides. J. V. Scudi and R. P. Buhs (*J. Amer. Chem. Soc.*, 1941, **63**, 879—880).—Benzoxazolone (prep. in 50% yield from *o*-$OH{\cdot}C_6H_4{\cdot}NH_2$ by $COCl_2$–C_5H_5N) and $ClSO_3H$ at 10—15° and later 60° give the 5-sulphonyl chloride, m.p. 182—183° (corr.), from which aq. NH_3 and boiling NH_2Ph–dioxan give benzoxazolone-5-sulphon-amide (I), m.p. 269—270° (decomp.), and *-anilide*, m.p. 215—216° (corr.), respectively. Ingestion of (I) does not protect mice against hæmolytic streptococci; examination of the urine shows that the oxazolone ring is not cleaved. R. S. C.

Dimorpholine salts.—See B., 1941, II, 178.

Thiazoline-*m*-cresol. Functional derivatives and substitution products. W. F. Hart and J. B. Niederl (*J. Amer. Chem. Soc.*, 1941, **63**, 945—947).—2-5′-Hydroxy-*o*-tolyl-5-methylthiazoline (A., 1939, II, 347) gives by standard methods the *methiodide*, m.p. 166°, *Me*, m.p. 107—108° (*picrate*, m.p. 117°; *methiodide*, m.p. 160°), Et (*hydrochloride*, m.p. 156°; *picrate*, m.p. 118°; *methiodide*, m.p. 148°), Pr^{α} (*hydrochloride*, m.p. 183°; *picrate*, m.p. 121°; *methiodide*, m.p. 101°), Pr^{β} (*hydrochloride*, m.p. 190°; *picrate*, m.p. 107°; *methiodide*, m.p. 93°), Bu^{α} (*hydrochloride*, m.p. 180°; *picrate*, m.p. 111°; *methiodide*, m.p. 108°), allyl (*hydrochloride*, m.p. 163°; *picrate*, m.p. 112°; *methiodide*, m.p. 117°), n-$C_{12}H_{25}$ (*hydrochloride*, m.p. 148°; *methiodide*, m.p. 82°), cetyl (*hydrochloride*, m.p. 143°; *methiodide*, m.p. 66°), and $NEt_2{\cdot}[CH_2]_2$ (*dihydrochloride*, m.p. 189°) ether, oxyacetic acid derivative [carboxymethyl ether?] (*hydrochloride*, m.p. 230°; *Na* salt; *Et* ester *hydrochloride*, m.p. 184°), *phenylurethane*, m.p. 105° (*hydrochloride*, m.p. 167°), *NO_2-*, m.p. 144° (*hydrochloride*, m.p. 180°), and *NH_2-*derivative, m.p. 224° (*dihydrochloride*, m.p. 250°). 15% oleum at 100° gives the *sulphonic acid*, m.p. 300° (*Na* salt). NaOMe–MeOH at 80° and then, after removal of the MeOH, CO_2 at 170—175° gives the *4′-carboxylic acid*, m.p. 219—220° [*hydrochloride*, m.p. 225—230°; *Na* salt; *Me*, m.p. 76—77° (*hydrochloride*, m.p. 181—183°; *methiodide*, m.p. 172—175°), and *Et* ester, m.p. 77—78° (*hydrochloride*, m.p. 173—175°; *methiodide*, m.p. 161—163°; *picrate*, m.p. 142—143°)]. R. S. C.

Amino-analogue of vitamin-B_1. D. Price and F. D. Pickel (*J. Amer. Chem. Soc.*, 1941, **63**, 1067—1069).—4-Methyl-5-thiazolylacetamide (prep. from the Et ester by aq. NH_3 at room temp.) and $POCl_3$ at 115—120° give *4-methyl-5-thiazolylacetonitrile* (I), b.p. 92—93°/2 mm. (*picrate*, m.p. 171°), hydrogenated (Raney Ni–EtOH or Pd– or ZrO_2–AcOH–HCl) to 4-methyl-5-β-aminoethylthiazole, b.p. 82—85°/2 mm. (*picrate*, m.p. 227°), which with 6-amino-2-methyl-5-bromomethylpyrimidine dihydrobromide in $Bu^{\alpha}OH$ at 120—125° gives *3-6′-amino-2′-methyl-5′-pyrimidylmethyl-4-methyl-5-β-aminoethylthiazolium bromide dihydrobromide* (II), m.p. 250—251° (derived picrate, m.p. 204—206°). (I) and the appropriate thiazole derivative give similarly *3-6′-amino-2′-methylpyrimidylmethyl-4-methyl-5-cyanomethylthiazolium bromide hydrobromide* (III), +H_2O, m.p. 231—232° (derived picrate, m.p. 199—200°). (II) and, by hydrolysis, (III) give the Pauly reaction. (II), but not (III), gives the thiochrome reaction. (II) has no vitamin-B_1 activity. R. S. C.

***Erythrophleum* alkaloids. IV. Coumingine, a crystalline alkaloid from the bark of *E. couminga* (H. Baillon) and its relationship to cassaine.** L. Ruzicka, G. Dalma, and W. E. Scott (*Helv. Chim. Acta*, 1941, **24**, 63—76).—The powdered bark is extracted with Et_2O and the alkaloid mixture is crystallised from $COMe_2$–H_2O; the crude alkaloid is purified by adsorption on Al_2O_3 followed by elution with C_6H_6–Et_2O and crystallisation from Et_2O, thereby giving homogeneous *coumingine* (I), $C_{28}H_{45}O_6N$, m.p. 142°, $[\alpha]_D^{20}$ −70°±1° in 95% EtOH [*hydrochloride*, m.p. 195° (vac.); *oxime*, m.p. 165°]. Pure (I) does not react with cold or hot Ac_2O–C_5H_5N whereas crude (I) gives an *acetate*, $C_{30}H_{47}O_7N$, m.p. 154—155°. Hydrogenation (PtO_2 in AcOH at room temp.) of (I) affords *dihydrocoumingine*, m.p. 95—96°, $[\alpha]_D^{20}$ +8°±1° in EtOH (very hygroscopic *hydrochloride*, m.p. 160—162°). Acid hydrolysis of (I) gives *coumingic acid* (II), $C_{24}H_{36}O_6$, m.p. 200° (vac.),

$[\alpha]_D^{20}$ $-81°\pm3°$ in 95% EtOH [*Me* ester, m.p. 217—218° (high vac.), $[\alpha]_D^{20}$ $-83°\pm1°$ in 95% EtOH, and its *oxime*, m.p. 124—125°], and $NMe_2\cdot[CH_2]_2\cdot OH$. Alkaline hydrolysis of (I) affords cassaic acid (III), m.p. 223—224° (high vac.), $[\alpha]_D^{20}$ $-123°\pm1°$ in 95% EtOH, also identified as the Me ester, m.p. 188—189°, $[\alpha]_D^{20}$ $-124°\pm2°$ in 95% EtOH, and its Ac derivative, new m.p. 150°; (III) is also obtained by the alkaline hydrolysis of (II). (III) is oxidised by CrO_3 in AcOH to diketocassenic acid, m.p. 249° (high vac.), $[\alpha]_D^{20}$ $-152°\pm2°$ in 95% EtOH (Me ester, m.p. 132—133°, $[\alpha]_D^{20}$ $-156°\pm2°$ in 95% EtOH). (I) is an ester of cassaine with an acid $C_4H_8O_3$ which contains the O atom of unknown function in (I). H. W.

VI.—ORGANO-METALLIC COMPOUNDS.

Preparation of organo-bismuth compounds from diazonium compounds. H. Gilman and H. L. Yablunky (*J. Amer. Chem. Soc.*, 1941, **63**, 949—954).—Determination of Bi in org. compounds is modified. *Compounds*, (*a*) *o*-$C_6H_4Me\cdot N_2Cl,BiCl_3$, decomp. 82°, (*b*) $(ArN_2Cl)_2,BiCl_3$ in which Ar = Ph, decomp. 94°, α-, decomp. 120°, and β-$C_{10}H_7$, decomp. 118°, *o*-, decomp. 160°, and *p*-C_6H_4Cl, decomp. 154°, *o*-, decomp. 155°, and *p*-C_6H_4Br, decomp. 147° (fuses at 120°), *p*-C_6H_4I, decomp. 129°, *o*-, decomp. 153°, and *p*-$C_6H_4\cdot OMe$, decomp. 145°, *o*-$C_6H_4\cdot CO_2Me$ (I), decomp. 122°, *o*- (II), decomp. 115°, and *p*-$C_6H_4\cdot CO_2Et$, unstable, decomp. 91°, and *p*-$C_6H_4\cdot SO_2\cdot NH_2$, decomp. 123°, and (*c*) $(ArN_2Cl)_3,BiCl_3$ in which Ar = *p*-tolyl, decomp. 127° (fuses at 110°), and *p*-C_6H_4Ph, decomp. 121°, are prepared. With (best) Cu-bronze in abs. EtOH and later N_2H_4, these compounds usually give $BiAr_3$ in poor yield, examples being Ar = p-C_6H_4Br (III), m.p. 144·5—145°, Ph, *o*- and *p*-tolyl (IV), α-$C_{10}H_7$, *p*-C_6H_4Cl, *o*- and *p*-$C_6H_4\cdot OMe$; some ArCl and $(ArN:)_2$ are also formed. With Cu-bronze in abs. EtOH, (I) gives *Bi di-o-carbomethoxyphenyl chloride* (10·3%), m.p. 180—181°, and *o-carbomethoxyphenyl dichloride* (1·95%), m.p. 220—221°, but (II) gives *Bi di-o-carbethoxyphenyl chloride* (6·5%), m.p. 147—148°; these chlorides are unusually stable. Presence of NaI during the decomp. leads to $BiPh_3$, but not (III) or (IV). Similar decomp. of *p*-$C_6H_4Br\cdot N_2Cl,ZnCl_2$ gives *p*-C_6H_4BrCl (46·7%) and of PhN_2Cl,BF_3 gives (NPh_2). R. S. C.

Organic mercury derivatives of basic triphenylmethane dyes: dimercuri-derivatives of malachite-green. L. Chalkley (*J. Amer. Chem. Soc.*, 1941, **63**, 981—987).—Colourless, but not coloured, compounds of the $CHPh_3$ dye series are readily mercurated. The coloured compounds resemble quaternary salts in their resistance to $Hg(OAc)_2$. $(p\text{-}NMe_2\cdot C_6H_4)_2CPh\cdot CN$ (I) and $Hg(OAc)_2$–AcOH in boiling EtOAc, followed by KOH–MeOH, give 4 : 4′-*bisdimethylamino*-3-*hydroxymercuri*-3′-*methoxymercuritriphenylacetonitrile*, decomp. >200° (variable), converted by irradiation (ultra-violet) in 1% AcOH–MeOH into the impure dye, 4 : 4′-bisdimethylamino-3-hydroxymercuri-3′-cyanomercuritriphenylcarbinol (cf. A., 1940, II, 239). A more convenient synthesis utilises acid-labile colourless compounds CAr_2X (X = OH, OMe, NH_2), which in "non-ionising" org. solvents exist mainly in the colourless form, are thus readily mercurated, and are then transformed into the coloured mercurials by acid in, *e.g.*, H_2O or EtOH. Isolation of the coloured mercurial is often difficult, *e.g.*, [4 : 3-$NMe_2\cdot C_6H_3(Hg\cdot OAc)]_2CPh\cdot CN$ is more sol. in EtOH or EtOAc than is (I). Details are given for conversion of $(p\text{-}NMe_2\cdot C_6H_4)_2CPh\cdot OH$ by $Hg(OAc)_2$ in EtOAc at 70° and later 56° into 4 : 4′-*bisdimethylamino*-3 : 3′-*di*(*acetoxymercuri*)*triphenylcarbinol*, +*x*AcOH and solvent-free, decomp. >∼115°, hydrolysed by 2N-KOH–MeOH to the $(HgOH)_2$-compound (II), decomp. >200°, whence NaCl–MeOH–H_2O–AcOH (little) ppts. the impure $(HgCl)_2$-compound. Hg_1 derivatives cannot be obtained free from Hg_2 compounds. In solutions of the Hg compounds the coloured and colourless forms are in equilibrium, the relative amounts depending on the concn. of acid present and on the temp. (more dye at higher temp.); this complicates isolation. Aq. solutions of (I) become coloured at p_H 13—11·4, but those of (II) only at p_H 7. In acid baths, (II) dyes silk at 1 in 5×10^6, but the colour is somewhat lighter than is given by (I). In weakly alkaline or neutral baths, (II) exhausts onto silk, giving only slightly coloured fibres. The Hg derivatives are surface-active. R. S. C.

VII.—PROTEINS.

Origin of the humin formed by the acid hydrolysis of proteins. IX. Hydrolysis in presence of djenkolic and thiazolidine-4-carboxylic acids. H. A. Lillevik and W. M. Sandstrom (*J. Amer. Chem. Soc.*, 1941, **63**, 1028—1030; cf. A., 1924, i, 762).—Hydrolysis of djenkolic (I) or thiazolidine-4-carboxylic acid by 20% HCl gives CH_2O and cysteine + cystine (isolated), the reaction being confirmed by polarographic and colorimetric analysis and by condensation of CH_2O with tryptophan (II). (I) may be the aldehyde responsible for humin formation from gelatin and (II). $(CH_2O)_3$ is less effective than these acids. R. S. C.

Separation of amino-acids by means of copper salts. III. Hydrolysis of gliadin. Dicarboxylate fraction; isolation of *r*-glutamic acid as hydrolysis product. B. W. Town (*Biochem. J.*, 1941, **35**, 417—432).—40·4% of glutamic acid has been isolated from gliadin; 5% of this is obtained as *r*- and 95% as *l*(+)-glutamic acid. *r*-Glutamic acid gives a 3 : 5-*dinitrobenzoyl* derivative, m.p. 204° as compared with 104° for the same derivative of the *dl*-mixture, which, on hydrolysis and rebenzoylation, gives only 4·5% of the compound of m.p. 204°. Similar treatment of the high-melting derivative yields 42·6% of the same compound, thus indicating the presence of the *r*-compound as a definite hydrolysis product. 0·43% of aspartic acid and 0·18% of serine have also been isolated from the dicarboxylic acid fraction, the presence of the latter tending to interfere with crystallisation of the other acids. P. G. M.

Hydrogen linking in protein structure.—See A., 1941, I, 245.

VIII.—ANALYSIS.

Electric heating mortar for use in carbon and hydrogen micro-combustions.—See A., 1941, I, 283.

Application of the grating microspectrograph to the problem of identifying organic compounds.—See A., 1941, I, 282.

Colour reactions of aliphatic acids. G. Roeder (*J. Amer. Pharm. Assoc.*, 1941, **30**, 74—76).—Colour reactions of the following substances with hot Ac_2O in presence of an org. base or an alkali salt of a carboxylic acid are described: malonic, aconitic, citric, cetylcitric, tartaric, acetonedicarboxylic, ascorbic, and *d-iso*ascorbic acid, glucono-*d*- and glucoheptono-lactone. Hydroxydimethylbutyrolactone does not give a colour. F. O. H.

Determination of threonine by periodate. L. A. Shinn and B. H. Nicolet (*J. Biol. Chem.*, 1941, **138**, 91—96).—Threonine (I) is determined in protein hydrolysates by oxidation (HIO_4), removal of MeCHO in a current of CO_2, absorption in $NaHSO_3$, and titration. Casein contains 3·5% and gelatin 1·4% of (I). A. Li.

Decolorisation of acid digestion mixtures for determination of nicotinic acid. T. E. Friedemann and C. J. Barborka (*J. Biol. Chem.*, 1941, **138**, 785—786).—A decolorisation technique is described involving digestion with dil. HCl and treatment with $ZnSO_4$ and NaOH. A. Li.

Determination of carotene.—See A., 1941, III, 455.

Simplification of the Petering–Wolman–Hibbard method for determination of chlorophyll and carotene. H. G. Petering, E. J. Benne, and P. W. Morgal (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 236; cf. A., 1940, III, 549).—Instead of adding $Ba(OH)_2,8H_2O$ to the aq.-$COMe_2$ extract, saturated aq. $Ba(OH)_2$ is added to the $COMe_2$ extract in amount sufficient to remove all the chlorophyll, and the mixture treated as in the original procedure (*loc. cit.*). J. D. R.

Detection of quinicine and cinchonicine. J. W. Millar and S. J. Dean (*J. Amer. Pharm. Assoc.*, 1941, **30**, 52—53).—$PhN_2\cdot SO_3H$ reagent gives reliable tests for quinicine (I) and cinchonicine (II) in aq. or EtOH solution and in presence of the parent alkaloid or alkaloidal salts; dinitrothiophen reagent is also satisfactory, excepting in presence of the alkaloidal salts. A modified Lipkin test (Br–aq. NH_3, followed by extraction with $CHCl_3$) differentiates between quinine and (I) and cinchonine and (II), whilst $K_4Fe(CN)_6$ reagent differentiates between (I) and (II). F. O. H.

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