BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

APRIL, 1942.

I.—ALIPHATIC.

Mechanism and kinetics of substitution at a saturated carbon atom.—See A., 1942, I, 148.

Production of saturated hydrocarbons.—See B., 1942, II, 2.

Dehydrogenation of paraffins and paraffin–olefine mixtures.—See B., 1942, II, 2.

Chemical reaction by the use of the thermal diffusion apparatus of Clusius and Dickel. I. Thermal polymerisation of methane. K. Hirota (*Bull. Chem. Soc. Japan*, 1941, **16**, 274—278).—The thermal polymerisation of CH_4 to higher hydrocarbons and H_2 is much more effective when carried out in a thermal diffusion column, 42% conversion and 87% of H_2 being obtained. F. J. G.

Effects of a high-voltage discharge on the thermal decomposition of ethane.—See A., 1942, I, 151.

Thermal behaviour of *n*-hexane.—See B., 1942, II, 1.

Action of sulphur on hydrocarbons under high pressure. W. Friedmann (*Refiner*, 1941, **20**, 395—406).—Experimental data obtained by autoclaving S with *n*-heptane, *iso*octane (**I**), or *iso*decane (**II**) at 280° are presented. The following general conclusions are reached. (1) The normal hydrocarbons change into branched systems, especially those which, under the directional influence of S, tend to form a five-membered ring with S in the bridge. (2) The branched hydrocarbons give simultaneously thiophanes and sulphides, *e.g.*, Me_2S. (3) Thiophanes react further with S forming (*a*) thiophens from normal paraffins, with partly dehydrogenated products as intermediates, (*b*) thiophthen (and probably thiophthanes) from normal paraffins, (*c*) polythiophanes or thiophane polysulphides from (**I**), and (*d*) dithienyls (probably hydrogenated dithienyls as an intermediate product) from (**II**). R. B. C.

Synthesis and properties of hydrocarbons of high mol. wt. J. N. Cosby and L. H. Sutherland (*Refiner*, 1941, **20**, 471—480).—Pure hydrocarbons of high mol. wt. are prepared, as a basis for establishing the chemical composition of lubricating oils. Pure intermediates are used, and the general procedure is the Grignard prep. of alcohols, followed by dehydration and hydrogenation, with careful purification at each stage by selective adsorption on SiO_2 gel or distillation. Purity is determined by time–temp. m.p. curve. In all cases, 85—95% of the final distillate has a const. val. for n, and vals. for η, d, heat of vaporisation, and dispersion are also given and their relation to constitution is discussed. The following are prepared: λ-, m.p. 0°, b.p. 180°/0·5 mm. (all b.p. recorded are at 0·5 mm.), ι-, m.p. 1·3°, b.p. 179°, η-, m.p. 3·2°, b.p. 180°, and ε-n-*butyldocosane*, m.p. 20·8°, b.p. 183°; η-n-*hexyl*-, m.p. 19·3°, b.p. 196°, and ι-n-*octyldocosane*, m.p. 8·6°, b.p. 209°; λ-n-*decyl*-, m.p. 8·7°, b.p. 215°, λ-α-*decahydronaphthyl*-, glass at −40°, b.p. 222°, λ-n-*amyl*-, m.p. −9·1°, b.p. 178°, λ-(γ-*amyl*)-, glass at −40°, b.p. 175°, λ-cyclo*hexyl*-, m.p. −7·2°, b.p. 197°, and λ-*phenyl-heneicosane*, m.p. 20·8°, b.p. 191°; λ-*phenyl*-Δ^{κ}-*heneicosene*, glass at −40°, b.p. 190°; ι-p-*tolyloctadecane*, glass at −40°, b.p. 173°; η-n-*hexyleicosane*, m.p. 10·2°, b.p. 181°; αα-*di*cyclo*hexyl*-, m.p. 37·6°, b.p. 193°, and αα-*diphenyl-tetradecane*, m.p. 17·9°, b.p. 194°; αα-*diphenyl*-Δ^{α}-*tetradecene*, m.p. 16·3°, b.p. 192°; ι-n-*octylheptadecane*, m.p. −13·8°, b.p. 172°; ι-n-*octyl*-Δ^{0}-*heptadecene*, glass at −40°, b.p. 181°; α-cyclo*hexyl*-γ-(β-cyclo*hexylethyl*)*hendecane*, glass at −40°, b.p. 195°; λ-*n*-decyldocosane, m.p. 1°, b.p. 222°/0·5 mm. A. T. P.

Activation energy of ionic substitution.—See A., 1942, I, 148.

Mechanism and kinetics of elimination reactions.—See A., 1942, I, 148.

Mechanism and kinetics of additions to olefinic compounds. G. Williams (*Trans. Faraday Soc.*, 1941, **37**, 749—763).—Addition of halogen to a double linking takes place most readily in strongly dissociating solvents, by an ionic mechanism; less readily in dissociating solvents such as AcOH by a mol. two-stage mechanism; and still less readily in non-dissociating solvents by catalytic mechanisms. Preliminary experiments are described in which the bromination of CH_2:CHBr at 300° is shown not to result in homogeneous addition; the effect of high temp. is to suppress surface addition and to promote substitution. F. L. U.

Reaction product of olefines with sulphuric acid.—See B., 1942, II, 1.

Polymerisation of olefines induced by free radicals.—See A., 1942, I, 151.

Preparation of palladium and platinum synthetic high polymeride catalysts and relationship between particle size and rate of hydrogenation.—See A., 1942, I, 150.

Mercury-photosensitised reactions of ethylene.—See A., 1942, I, 151.

Photochemistry of *iso*butene.—See A., 1942, I, 151.

Production of heptene [and other olefines].—See B., 1942, II, 2.

Olefines and diolefines from allylic chlorides. A. L. Henne, H. Chanan, and A. Turk (*J. Amer. Chem. Soc.*, 1941, **63**, 3474—3476).—With Mg in Et_2O, CH_2:CH·CHMeCl, b.p. 63°, CHMe:CH·CH_2Cl, b.p. 83°, or the crude mixture (*A*) thereof gives $(CHMe{\cdot}CH{:}CH_2)_2$ (b.p. 101·8°) 7, 4, or 3%, CHMe:CH·CH_2·CHMe·CH:CH_2 (**I**) (b.p. 111·0°) 57, 50, or 60%, and $(CH_2{\cdot}CH{:}CHMe)_2$ (**II**) (b.p. 124·5°) 3%, a little, or 4%, respectively. CH_2:CH·CH_2Cl and (*A*) (1 : 1) with Mg in Et_2O give CH_2:CH·$[CH_2]_2$·CH:CHMe (b.p. 93·7°) 34, (**I**) 21, $(CH_2{\cdot}CH{:}CH_2)_2$ (**III**) (b.p. 59·4°) 10, CH_2:CH·CHMe·CH_2·CH:CH_2 (b.p. 80°) 10, and (**II**) 1%. With MgBuCl in Et_2O, (*A*) gives CHMe:CH·C_5H_{11}-*n* (f.p. −94·04°, b.p. 125·2°) 85, CH_2:CH·CHMeBu$^{\alpha}$ 9, and (**I**) 6%. CH_2:CH·CH_2Cl with Mg gives (**III**) 60%, with CH_2:CHMe·CH_2Cl–Mg–Et_2O gives CH_2:CHMe·$[CH_2]_2$·CH:CH_2 (f.p. −128·88°, b.p. 88·1°) 47, $(CH_2{\cdot}CHMe{:}CH_2)_2$ (**IV**) (f.p. −75·6°, b.p. 114·3°) 30, and (**III**) 12%, with *n*-C_5H_{11}·MgCl gives Δ^{α}-*n*-octene (m.p. −102·11°, b.p. 121·6°) 80%, and with *iso*-C_5H_{11}·MgCl gives Bu$^{\beta}$·$[CH_2]_2$·CH:CH_2 (b.p. 113·19°) 60%. With Mg, CH_2:CHMe·CH_2Cl gives 65% of (**IV**), and with MgBuCl gives *n*-C_5H_{11}·CHMe:CH_2 (f.p. −90·1°, b.p. 119·3°) and some CMe_2:$CHBu^{\alpha}$. Piperylene hydrochloride and MgPrCl give only CHMe:CH·CHMePr$^{\alpha}$. Di*iso*crotyl hydrochloride and MgMeI give CHBu$^{\gamma}$:CHPr$^{\beta}$ (b.p. 114°) and CMe_2:CH·CHMePr$^{\beta}$ (b.p. 128·4°) (1 : 5). The following data are also recorded: CHMeEtPr$^{\alpha}$, b.p. 92·0°; CHMeEtBu$^{\alpha}$, f.p. −120·8°, b.p. 119·1°; $(CH_2Pr^{\beta})_2$, f.p. −91·49°, b.p. 109·3°; $CH_2Bu^{\beta}Bu^{\gamma}$, b.p. 123·0°; CHMePr$^{\beta}Bu^{\beta}$, b.p. 130·3°; n and d of all the compounds above. R. S. C.

Prolycopene, a naturally occurring stereoisomeride of lycopene. L. Zechmeister, A. L. Le Rosen, F. W. Went, and L. Pauling (*Proc. Nat. Acad. Sci.*, 1941, **27**, 468—474).—The pulp of the tangerine tomato was shaken with MeOH and light petroleum and the latter extract was chromatographed on $Ca(OH)_2$. The chromatogram showed about 15 layers which included lycopene (**I**), neolycopene, several other isomerides of (**I**), carotene and its isomerides, and a wide layer containing prolycopene (**II**), which when re-chromatographed yielded nine layers including (**I**). When observed spectroscopically, (**II**) is rapidly converted into (**I**) with I. The change (**II**) → (**I**) occurs more slowly in the presence of S or HBr in light petroleum. The stereochemical configuration of (**II**) is discussed. J. L. D.

Syntheses in the carotenoid series. II. New synthesis of squalene. J. Schmitt (*Annalen*, 1941, **547**, 115—122).—Geraniol is converted by PBr_3 and C_5H_5N in light petroleum into geranyl bromide, b.p. 105—110°/4 mm., which gives Et geranylacetoacetate, b.p. 152—158°/4 mm., hydrolysed by $Ba(OH)_2$ in aq. EtOH to geranylacetone [ζκ-dimethyl-$\Delta^{\epsilon\kappa}$-undecadien-β-one], b.p. 130—133°/13 mm. This is transformed by Mg and $(CH_2{\cdot}CH_2Br)_2$ in Et_2O into squalene, b.p. 225—230°/1·5 mm. (hexachlorides, m.p. 114° and 143°; hexabromides, m.p. 116—118° and 136—138°) (cf. Heilbron *et al.*, A., 1926, 816; Karrer *et al.*, A., 1931, 333). Similarly, ψ-ionone, Mg, and $(CH_2{\cdot}CH_2Br)_2$ in Et_2O yield βζκοτω-*hexamethyl*-$\Delta\beta\zeta\kappa\mu\pi\sigma\phi\psi$-*tetracosaoctadiene*, a pale yellow liquid, b.p. 220—225°/1 mm., which gives intense colour reactions with conc. H_2SO_4 and with $SbCl_3$ but does not appear to give solid adducts with HCl or HBr. It appears to be dehydrogenated by *p*-O:C_6H_4:O at ~100° since a quinhydrone is formed. H. W.

Fluorinated derivatives of propane. IV. A. L. Henne and F. W. Haeckl (*J. Amer. Chem. Soc.*, 1941, **63**, 3476—3478).—The structure of $CHCl_2$·CClF·$CClF_2$ (**I**) is confirmed, but that of other products (A., 1939, II, 491) is corr. Gradually distilling CCl_3·CClF·$CClF_2$ (1) with SbF_3 (0·5) + Cl_2 (0·05 mol.) gives αaβγ-*tetrachloro*-αβγγ-*tetrafluoropropane* (70%), m.p. −58°, b.p. 112·5—112·6°, also obtained

from (I) by successive fluorination (to $CHClF{\cdot}CClF{\cdot}CClF_2$, b.p. 90°) and chlorination. $CCl_2{:}CF{\cdot}CCl_3$ (prep. from $CHCl_2{\cdot}CClF{\cdot}CCl_3$ by NaOH–EtOH) with SbF_3 (1·5 mols.) at 125° gives $CCl_2{:}CF{\cdot}CF_3$ (0·37 mol.) [with $CCl_2{:}CF{\cdot}CClF_2$ (0·27 mol.)], which with Cl_2 in light gives *aaaβ-tetrachloro-βγγγ-tetrafluoropropane*, m.p. 12·1°, b.p. 112·4—112·6°. The following corrections (cf. *loc. cit.*) are made: *aay*-trichloro-*βγγγ*- becomes *aβγ-trichloro-aβγγ-tetrafluoropropane*; *aaaβ*-tetrachloro-*βγγγ*- becomes *aaβγ-tetrachloro-aβγγ-tetrafluoropropane*; *aa*-dichloro-*βγγγ*- becomes ? *aγ-dichloro-aβγγ-tetrafluoro-Δ^a-propene*; *aa*-dichloro-*aβ*-dibromo-*βγγγ*- becomes *aγ-dichloro-aβ-dibromo-aβγγ-tetrafluoropropane*. R. S. C.

Synthesis of organic *aaa*-trifluorides. A. L. Henne, A. M. Whaley, and J. K. Stevenson (*J. Amer. Chem. Soc.*, 1941, **63**, 3478—3479).—Replacement of Cl by F occurs rapidly when compounds containing $C{\cdot}CCl_3$ are heated with SbF_3 (1·5 mols.). $CCl_2{:}CCl{\cdot}CCl_3$ and SbF_3 at 125—140° give *aaβ-trichloro-γγγ-trifluoro-* (I) (43%), f.p. −114·7°, b.p. 88·3°, *aaβγ-tetrachloro-γγ-difluoro-* (28%), f.p. −103·0°, b.p. 128·0°, and *aaβγγ-pentachloro-γ-fluoro-Δ^a-propene* (13%), b.p. 170·2°. *βγ-Dichloro-aaγγ-trifluoro-Δ^a-propene* [prep. from $CCl_2(CClF_2)_2$ by Zn–EtOH], f.p. −121·2°, b.p. 44·7°, and SbF_3 give *β-chloro-aaγγγ-pentafluoro-Δ^a-propene* (47%), f.p. −130·4°, b.p. 6·8°, converted by Cl_2 into *aaβ-trichloro-aβγγγ-pentafluoropropane* (II), f.p. −4·30°, b.p. 72·0°. Cl_2 and (I) give *aaaββ-pentachloro-γγγ-trifluoropropane* (III), f.p. 109·1°, b.p. 153·1°, also obtained from $CEtCl_3$ by way of $CEtF_3$. With SbF_3, $CPhCl_3$ gives $CPhF_3$ (60%; much decomp.), $CHCl{:}CCl{\cdot}CCl_3$ gives *aβ-dichloro-γγγ-trifluoro-Δ^a-propene*, f.p. −109·23°, b.p. 53·7°, $CCl_2{:}CF{\cdot}CCl_3$ gives $CCl_2{:}CF{\cdot}CF_3$, b.p. 46·0° (and thence *aaaβ-tetrachloro-βγγγ-tetrafluoropropane*, m.p. 12·1°, b.p. 112·4°), and $CCl_2{:}CH{\cdot}CCl_3$ gives $CCl_2{:}CH{\cdot}CF_3$. $CEtF_3$ gives (III) and thence (II). R. S. C.

Catalytic conversion of olefines into alcohols.—See B., 1942, II, 3.

Reactions of (+)- and (−)-γ-methyl-α-ethylallyl alcohol and their derivatives. R. S. Airs, M. P. Balfe, and J. Kenyon (*J.C.S.*, 1942, 18—26).—dl-*γ-Methyl-α-ethylallyl H phthalate*, m.p. 52—53°, is resolved via the brucine salt, m.p. 168°, into the (+)- and (−)-*form* (I), m.p. 70·5°, $[\alpha]_{5461}$ ±15° in $CHCl_3$, hydrolysed by 5N-NaOH (more dil. NaOH causes racemisation) to the (+)- (II) and (−)-*alcohol* (III), $[\alpha]_{5461}$ ±14·24° in CS_2. On reduction (H_2, PtO_2), (II) yields (+)-, b.p. 131—133°, $[\alpha]^{20}_{5893}$ +7·09° (homogeneous) (H phthalate, m.p. 48—49°, $[\alpha]^{20}_{5893}$ +9·70° in $CHCl_3$), and the freshly prepared *dl*-alcohol (IV) yields *dl*-CHEtPr^a·OH, b.p. 132·5—133·5° (H phthalate, m.p. 75—76°); a 2-years-old specimen (V) gives a hexanol, b.p. 131—133°. (IV) gives a p-*xenylurethane*, m.p. 102°, and (V) a mixture of this (75%) with the *p*-xenylurethane, m.p. 84—86°, of CHEt:CH·CHMe·OH (VI). dl-*γ-Methyl-α-ethylallyl chloride* ($SOCl_2$), b.p. 123—124° (slight decomp.), is hydrolysed (H_2O, $CaCO_3$) to a mixture of (IV) and (VI), reduced to *dl*-CHEtPr·OH (p-*xenylurethane*, m.p. 132—133°) and *dl*-CHMeBu·OH (p-*xenylurethane*, m.p. 91—92°; *H phthalate*, m.p. 48°). (−)-γ-Methyl-α-ethylallyl chloride [from (II)], a^{19}_{5461} −14·75°, is hydrolysed to a hexenol, a^{20}_{5461} −0·07°, reduced to a hexanol, b.p. 132—137°, a^{20}_{5461} +0·02° (H phthalate, $[\alpha]_{5461}$ +0·07° in $CHCl_3$). (II) and (III) undergo mutarotation at varying rates, increased by a trace of acid. The ratio of $[\alpha]$ to that of the H phthalate shows that (V) has undergone 27% racemisation, and contains 41% of (+)-CHMe:CH·CHEt·OH and 32% of (+)-CHEt:CH·CHMe·OH. It is suggested that this rearrangement is due to a pseudo-cyclic structure of the allylic alcohols, confirmed by parachor vals. of 12 derivatives, including dl-*γ-methyl-α-ethylallyl acetate*, b.p. 54—56°, and *benzoate*, b.p. 144—145°. The p-*nitrobenzoate* has m.p. 35—37°. (I) with boiling MeOH yields *Me γ-methyl-α-ethylallyl ether*, b.p. 110—112°, a^{21}_{5461} −0·18°, also obtained, a^{23}_{5461} + 6·88°, from the alcohol prepared from the same specimen of (I), with K, then MeI. A. Li.

Catalytic dehydrogenation and condensation of aliphatic alcohols. II. V. I. Komarewsky and J. R. Coley (*J. Amer. Chem. Soc.*, 1941, **63**, 3269—3270).—Conversion of alcohols into ketones by Cr_2O_3 at, usually, 400—425° (cf. A., 1941, II, 158) is extended to *n*-C_{3-8}, *n*-C_{10}, and *n*-C_{18} alcohols, yields being 27·8—83·2%. EtOH + *n*-C_8H_{17}·OH and *n*-C_5H_{11}·OH + *n*-$C_{10}H_{21}$·OH give *n*-C_7H_{15}·COMe (41·7%) and *n*-C_9H_{19}·COBu^a (27·2%), respectively, with smaller amounts of *sym.* ketones, except $COMe_2$ which is never obtained. Aldehydes give similarly better, and aldols still better, yields, confirming the mechanism previously proposed (*loc. cit.*). At 760 and 125—135 mm., *n*-C_8H_{17}·OH gives 56 and 73·9%, respectively, of ketone. The following are new: aldol-2 : 4-dinitrophenylhydrazone, m.p. 125·5—126·5°; $CO(C_6H_{13}\text{-}n)_2$, m.p. 39—40°; n-*tetradecan-ε-ol*, m.p. 28·5°, and *-one*, m.p. 25·5—26°; n-*nonadecan-κ-ol*, m.p. 65·5°. R. S. C.

Denatured alcohol containing 1 : 3-dioxolan.—See B., 1942, II, 3.

Separation of *iso*- and *n*-butyl alcohols from hydrocarbons by azeotropic distillation. R. Negishi and C. Isobe (*Bull. Chem. Soc. Japan*, 1941, **16**, 278—284).—Bu^{a}OH and Bu$^\beta$OH may be separated from hydrocarbons (PhMe or gasoline) by extraction with H_2O followed by distillation of the azeotropic mixture. F. J. G.

Mechanism and kinetics of anionotropic change.—See A., 1942, I, 148.

Structure–property relations of isomeric octanols. G. L. Dorough, H. B. Glass, T. L. Gresham, G. B. Malone, and E. E. Reid (*J. Amer. Chem. Soc.*, 1941, **63**, 3100—3110).—Relations are tabulated between structure of the carefully purified 4 octanols and 18 methylheptanols and their b.p. at 20, 100, 300, and 760 mm., the difference between the b.p. and that of the hydrocarbon, latent heat of vaporisation, d^0_4, d^{25}_4, the difference between *d* and that of the hydrocarbon, expansion (0—25° and 80—100°), n^{25}_D, m.p., molal heat capacity, solubility in H_2O, η, total surface energy, parachor, Ramsey and Shields const., dielectric const., fluidity, association at 15°, *X*-ray secondary peak, rate of esterification with AcOH at 136±0·5° (1 and 100—200 hr.) and Ac_2O at 35±0·01° (125 hr.), oxidation by O_2 at 137° (rate and ratio CO_2/CO produced), and toxicity to *Lupinus albus*, goldfish, newts, and tadpoles. Data include the following; those in parentheses refer to α-naphthylurethanes and 3 : 5-dinitrobenzoates, respectively. *n*-Octan-*a*-, m.p. −15·0°, b.p. 195·0° (m.p. 67·0°, 60·8°), -*β*-, m.p. −31·6°, b.p. 180·0° (an oil; m.p. 32·3°), -*γ*-, m.p. −45·0°, b.p. 173·0° (m.p. 54·0°, 69·4°), and -*δ*-ol, m.p. −40·7°, b.p. 176·3° (m.p. 65·5°, 53·9°). *ζ*-Methyl-*n*-heptan-*a*-, m.p. (of glass) −106·0°, b.p. 187·6° (m.p. 68·5°, 58·3°), -*β*-, m.p. (of glass) −105·0°, b.p. 171·8° (an oil; m.p. 34·4°), and -*γ*-ol, m.p. −58·5°, b.p. 158·5° (oils). *β-Methyl*-n-*heptan-a*- (from *n*-C_5H_{11}·CHMe·MgBr and CH_2O), m.p. −112·0°, b.p. 175·4° (an oil; m.p. 50·6°), -*β*-, m.p. −50·4°, b.p. 156·1° (m.p. 57·5°; an oil), -*γ*-, m.p. (of glass) −85·0°, b.p. 167·2° (m.p. 73·0°, 38·5°), and -*δ*-ol, m.p. (of glass) −81·0°, b.p. 166·3° (m.p. 70·0°, 71·7°). *ε-Methyl*-n-*heptan-a*- {from CHMeEt·$[CH_2]_2$·MgBr (I) and $[CH_2]_2O$}, m.p. (of glass) −104·0°, b.p. 186·5° (oils), -*β*- [from (I) and MeCHO], m.p. (of glass) −120·0°, b.p. 171·9° (oils), and -*γ*-ol, m.p. 91·2°, b.p. 153·4° (an oil; m.p. 89·8°). *γ*-Methyl-*n*-heptan-*a*-, m.p. −90·0°, b.p. 185·8° (oils), -*β*- (from CHMeBu^a·MgBr and MeCHO), m.p. (of glass) −114·0°, b.p. 166·1° (oils), -*γ*-, m.p. (of glass) −83·0°, b.p. 159·4° (m.p. 52·0°; an oil), and -*δ-ol* (from CHMeEt·MgBr and Pr^{a}CHO), b.p. 164·7° (an oil; m.p. 91·8°). *δ-Methyl*-n-*heptan-a*- (from CHMePr^a·CH_2·MgBr and $[CH_2]_2O$), b.p. 182·7° (oils), -*β*-, m.p. (of glass) −102·0°, b.p. 171·7° (oils), -*γ*-, m.p. (of glass) −123·0°, b.p. 155·4° (an oil; m.p. 92·4°), and -*δ*-ol, m.p. (of glass) −82·0°, b.p. 160·8° (m.p. 90·0°; an oil). *n*-C_6H_{11}·OH, b.p. 137·8°. CHMePr^a·OH, b.p. 119·5°. CH_2Bu^β·OH, b.p. 130·5°. CHMeEt·CH_2·OH, b.p. 128·0°/752 mm. Bu$^\beta$·$[CH_2]_2$·OH, b.p. 151·7°/758 mm. CHMePr^a·CH_2·OH, b.p. 148·9°/760 mm. CHMeBu^a·OH, b.p. 139·7°/759 mm. *n*-C_5H_{11}·CHMe·OH, b.p. 158·5°/754 mm. CHMePr^a·$[CH_2]_2$·OH, b.p. 94·6°/40 mm. *n*-C_5H_{11}Br, b.p. 127·8°/745 mm. Bu^{a}Br, b.p. 101·3°. Bu$^\beta$·$[CH_2]_2$·Br, b.p. 147·6°. CHMeEt·CH_2Br, b.p. 121·0°. Bu$^\beta$Br, b.p. 91·2°. *n*-C_5H_{11}·CHMeBr, b.p. 81·7°/45 mm. CHMeEt·$[CH_2]_2$·Br, b.p. 146·5°. CH_2Bu^βBr, b.p. 117·5°. CHMeEtBr, b.p. 91·2°/750 mm. CHMePr^{a}Br, b.p. 118·4°. CHMePr^a·$[CH_2]_2$·Br, b.p. 87·5°/50 mm. EtCHO, b.p. 48·8°. CHMeBu^{a}Br, b.p. 143·9°/750 mm. CHMePr^a·CH_2Br, b.p. 83·8°/100 mm. Pr^{a}CHO, b.p. 74·9°. Pr$^\beta$CHO, b.p. 63·5°. COMeEt, b.p. 80·6°. M.p. are corr. R. S. C.

***β*-Methyltetradecan-*a*-ol.** K. Lindblad and E. Stenhagen (*J. Amer. Chem. Soc.*, 1941, **63**, 3539—3540).—*n*-$C_{12}H_{25}$·CHMe·CO_2Et, Na, BuOH, and (later) EtOH in light petroleum give *β-methyl-n-tetradecan-a-ol* (40%), m.p. 32·0—32·2°, b.p. 134°/2 mm. R. S. C.

Amyl nitrite. Determination and decomposition.—See B., 1942, II, 1.

Explosion hazard in the chlorination of alkyl*iso*thiocarbamides to prepare alkanesulphonyl chlorides. K. Folkers, A. Russell, and R. W. Bost (*J. Amer. Chem. Soc.*, 1941, **63**, 3530—3532).—During the prep. of $AlkSO_2Cl$ from aq. SAlk·C(:NH)·NH_2,HCl by Cl_2, a violent explosion may occur if an excess of Cl_2 is used. NCl_3 is probably formed. R. S. C.

Condensation of sulphoxides with *p*-toluenesulphonamide and substituted acetamides. D. S. Tarbell and C. Weaver (*J. Amer. Chem. Soc.*, 1941, **63**, 2939—2942).—Condensation of *p*-$C_6H_4Me{\cdot}SO_2{\cdot}NH_2$ (I) with R_2SO in Ac_2O at 100° or boiling P_2O_5–$CHCl_3$ gives sulphilimines, $R_2S{\rightarrow}N{\cdot}SO_2{\cdot}C_6H_4Me$-*p*, the structure of which is proved by prep. also from R_2S and chloramine-*T* (Mann *et al.*, *J.C.S.*, 1922, **121**, 1052; Clarke *et al.*, A., 1927, 243). The products are unaffected by alkali, dissolve in cold HCl (? salt-formation), and in hot HCl are hydrolysed to R_2SO and (I). Sulphilimines, $R_2S{\rightarrow}NR'$, are similarly obtained by Ac_2O in which $R' = CCl_3{\cdot}CO$ or $CHCl_2{\cdot}CO$, but not if $R' = CH_2Cl{\cdot}CO$ or Bz. Analogous reactions are discussed. Prep. of $[CH_2]_4{>}S$, b.p. 119—120°, from Br·$[CH_2]_4$·Br and Na_2S in aq. EtOH is modified to give 64% yield. *Tetramethylene sulphoxide* (II), b.p. 105—107°/12 mm., is obtained by 30% H_2O_2 at 0° or in $COMe_2$. The following are described: Et_2, 83—85°/12 mm., Me_2, b.p. 85—87°/25 mm., and Ph_2 sulphoxide, b.p. 85—87°/25 mm.; $[CH_2]_4{>}SO_2$, m.p. 10—10·5°; diethyl-, m.p. 145—146°, *tetramethylene*-, m.p. 134—135°, and *diphenyl*- (prep. by P_2O_5 but not Ac_2O), m.p. 108—110°, *-sulphin*-p-*toluenesulphonylimine*; $CCl_3{\cdot}CO{\cdot}NH_2$ (prep. by boiling $CCl_3{\cdot}CO_2H$ with $SOCl_2$ and a little C_5H_5N in Et_2O and later treatment with NH_3), m.p. 139—141°;

tetramethylenesulphintrichloroacetylimine, m.p. 116—117°; *tetramethylene-*, m.p. 149—151°, and *diethyl-sulphindichloroacetylimine*, m.p. 112—113°. The following condensations failed: (OH·$[CH_2]_2$)$_2$SO–(**I**); Et_2SO– or Ph_2SO–CCl_3·CO·NH_2; Et_2SO– or (II)–NH_2Bz–Ac_2O (gives PhCN); fluorene–Me_2SO or –(**II**); 2 : 7-dinitrofluorene–Me_2SO or –(**II**). Sulphoxides do not show "CO" properties; *e.g.*, (**II**) does not react with CH_2N_2 or PhCHO. R. S. C.

Configuration of naturally occurring glycerol esters. H. O. L. Fischer and E. Baer (*Schweiz. med. Wschr.*, 1941, **71**, 321—322).—The Na compounds of *d*(+)- and *l*(−)-*iso*propylideneglycerol with *n*-$C_{16}H_{33}I$ and $C_{18}H_{37}I$ in boiling $(CH_2{\cdot}OMe)_2$ yielded the :CMe_2 compounds of α-hexadecyl- and α-octadecyl-glycerol; hydrolysis with AcOH gave the free alcohols, identical with chimyl alcohol (**I**), m.p. 62—63°, and batyl alcohol (**II**), m.p. 71°. The two enantiomorphic forms of synthetic (**II**) have [α] ±0°. The diacetylated synthetic batyl alcohols had $[\alpha]_{5461}^{20}$ ±8·6° in $CHCl_3$ (c = 11·2). A crude prep. of the glyceryl ethers from the unsaponifiable fraction of *Chimaera monstrosa* liver oil was treated with $COMe_2$, giving a product with $[\alpha]_D$ −14·0° (in substance); the two :CMe_2 compounds of the synthetic (**II**) had $[\alpha]_D^{40}$ ±12·6° in melted substance. (**II**) belongs to the *d*-series, so does selachyl alcohol, as it can be transformed into *d*-batyl alcohol by catalytic reduction. Natural (**I**) is dextrorotatory. A. S.

Preparation of alkane-αω-disulphonic acids. S. Zuffanti and R. Hendrickson (*J. Amer. Chem. Soc.*, 1941, **63**, 2999—3000).—Ethane-αβ-, m.p. 97°, *propane-*αγ-, b.p. 157°/1·4 mm., n-*butane-*αδ-, m.p. 84°, n-*pentane-*αε-, b.p. 198°/1·7 mm., n-*hexane-*αζ-, m.p. 78°, and n-*decane-*ακ-, m.p. 76°, *-disulphonic acid* are obtained by treating the Na_2 salts in MeOH with dry HCl and give m-$C_6H_4Me{\cdot}NH_2$ salts, m.p. 230°, 222°, 214°, 187°, 158°, and 178°, respectively. R. S. C.

Mechanism and kinetics of carboxylic ester hydrolysis and carboxyl esterification.—See A., 1942, I, 148.

Catalytic reduction of esters using nickel alone as a catalyst. C. L. Palfray. **Behaviour of esters over Raney nickel.** P. L. de Benneville, W. R. McClellan, and R. Connor (*J. Amer. Chem. Soc.*, 1941, **63**, 3540—3541, 3541—3542).—Concerning priority. R. S. C.

Identification of organic acids by use of *p*-bromobenzyl-ψ-thiuronium bromide. B. T. Dewey and H. G. Shasky (*J. Amer. Chem. Soc.*, 1941, **63**, 3526—3527).—p-*Bromobenzyl-ψ-thiuronium bromide* [prep. from *p*-$C_6H_4Br{\cdot}CH_2Br$ and $CS(NH_2)_2$ in hot EtOH], m.p. 213°, with the Na or K salt of the acid in hot EtOH gives the *formate*, m.p. 148°, *acetate*, m.p. 149°, *propionate*, m.p. 146°, *butyrate*, m.p. 142°, n-, m.p. 146°, and iso-*valerate*, m.p. 148°, *hexoate*, m.p. 146°, *heptoate*, m.p. 147°, *octoate*, m.p. 145°, α-*ethyl*-n-*butyrate*, m.p. 141°, *dodecoate*, m.p. 142°, *palmitate*, m.p. 135°, *stearate*, m.p. 135°, *oxalate*, m.p. 194°, *malonate*, m.p. 139°, *succinate*, m.p. 167°, *glutarate*, m.p. 149°, *chloroacetate*, m.p. 154°, *trichloroacetate*, m.p. 146°, *oleate*, m.p. 133°, *benzoate*, m.p. 154°, o-, m.p. 163°, m-, m.p. 154°, and p-*bromo-*, m.p. 173°, o-, m.p. 168°, m-, m.p. 150°, and p-*chloro-*, m.p. 163°, o-, m.p. 154°, m-, m.p. 152°, and p-*iodo-benzoate*, m.p. 181°, *cinnamate*, m.p. 170°, *phthalate*, m.p. 166°, *salicylate*, m.p. 168°, o-, m.p. 151°, m-, m.p. 151°, and p-*toluate*, m.p. 165°. The salts are anhyd. and fairly stable. Depression of the m.p. on admixture is 6—12°. M.p. are corr. R. S. C.

Preparation and properties of acetic acid-d_1. H. Linschitz, M. E. Hobbs, and P. M. Gross (*J. Amer. Chem. Soc.*, 1941, **63**, 3234).—Ac_2O and 99·6% D_2O give AcOD (~99% pure), m.p. 15·66±0·05°, d_4^{20} 1·0527, d_4^{25} 1·0588, n_D^{20} 1·37102. R. S. C.

Alcoholysis of polyvinyl acetate.—See A., 1942, I, 150.

Chlorination of propyl trichloroacetates. C. W. Gayler and H. M. Waddle (*J. Amer. Chem. Soc.*, 1941, **63**, 3358—3359).—Contrary to Maxwell (*Thesis*, 1933), $CCl_3{\cdot}CO_2Pr^{\alpha}$ (1), b.p. 69°/10 mm., and Cl_2 (1 mol.) in light at 120° give β- (0·30 mol.), b.p. 94°/8 mm., γ- (0·28 mol.), b.p. 107°/8 mm., and (? α)-*chloro*-n-*propyl trichloroacetate* (0·02 mol.) [hydrolysed to HCl and a substance (2 : 4-dinitrophenylhydrazone, m.p. 162°)]. $CCl_3{\cdot}CO_2Pr^{\beta}$, b.p. 65°/10 mm., gives similarly CMe_2Cl (0·25 mol.), b.p. 72°/8 mm. (with cold aq. KOH rapidly gives $COMe_2$), and $CH_2Cl{\cdot}CHMe$ *trichloroacetate* (0·31 mol.), b.p. 93·5°/8 mm. [hydrolysed by hot (not cold) 25% KOH to $(CH_2{\cdot}OH)_2$]. Cl·$[CH_2]_3{\cdot}$OH, b.p. 165° (α-naphthylurethane, m.p. 76·5°), is described. R. S. C.

Dimethylneopentylacetic [ααγγ-tetramethyl-*n*-valeric] acid, its methyl ester, amide, and anilide. F. C. Whitmore, W. R. Wheeler, J. D. Surmatis (*J. Amer. Chem. Soc.*, 1941, **63**, 3237).—Addition of di*iso*butylene hydrochloride and EtBr–Et_2O to Mg–MgEtBr–Et_2O and subsequent treatment with CO_2 gives 34% of $CH_2Bu^{\gamma}{\cdot}CMe_2{\cdot}CO_2H$, m.p. 45°, b.p. 229·6°/732 mm. (Me ester, b.p. 176·2°/732 mm.; amide, m.p. 71°; *anilide*, m.p. 78°) (cf. A., 1941, II, 345). R. S. C.

Optically active αβ-diglycerides. J. C. Sowden and H. O. L. Fischer (*J. Amer. Chem. Soc.*, 1941, **63**, 3244—3248).—*d*(+)-*iso*-Propylideneglycerol in boiling Et_2O with, first, Na and then CH_2PhBr or, better, in $(CH_2{\cdot}OMe)_2$ with $NaC_{10}H_7$ and then CH_2PhBr gives d(+)-iso*propylideneglycerol α'-CH_2Ph ether* (**I**), b.p. 95—97°/0·3 mm., $[\alpha]_D$ +16·8°. The corresponding α'-Me ether, b.p. 45—47°/10 mm., $[\alpha]_D$ +22·5°, is similarly prepared. In boiling N-H_2SO_4, (**I**) gives l-*glyceryl α-CH_2Ph ether* (**II**), b.p. 138—139°/0·3 mm., $[\alpha]_D$ +5·3°, but in boiling 90% AcOH gives another product. With RCOCl in $CHCl_3$–quinoline at 37°, (**II**) gives d-*glyceryl α-CH_2Ph ether α'β-distearate* (**III**), m.p. 50·5—51°, $[\alpha]_D$ +6·1° in $CHCl_3$, and *-dipalmitate*, m.p. 42—42·5°, $[\alpha]_D$ +6·3° in $CHCl_3$; the *α'β-dibutyrate*, b.p. 140° (bath)/0·005 mm., $[\alpha]_D$ +15·5°, is obtained in C_5H_5N at 0°. With MeI, $CaSO_4$, and Ag_2O, (**II**) gives d-*glyceryl α-CH_2Ph α'β-Me_2 ether* (**IV**), b.p. 147—148°/13 mm., $[\alpha]_D$ +4·1°. Hydrogenation (PtO_2; slightly >1 atm.) of (**III**) in AcOH gives d-*αβ-distearin*, m.p. 74·5—75°, $[\alpha]_D$ −2·7° in $CHCl_3$ (*acetate*, m.p. 56·5—57°, $[\alpha]_D$ ±0° in $CHCl_3$), the p-*nitrobenzoate*, m.p. 67—67·5°, $[\alpha]_D$ −1·4° (−1·3°) in $CHCl_3$, of which is obtained therefrom by *p*-$NO_2{\cdot}C_6H_4{\cdot}COCl$ in C_5H_5N and from *l*-glyceryl α-*p*-nitrobenzoate by stearyl chloride in quinoline at room temp. d-*αβ-Dipalmitin*, m.p. 67—67·5°, $[\alpha]_D$ −2·3° in $CHCl_3$ [p-*nitrobenzoate*, m.p. 60—60·5°, $[\alpha]_D$ −1·6° (−1·4°) in $CHCl_3$], and d-*αβ-dibutyrin*, b.p. 95° (bath)/0·001 mm., $[\alpha]_D$ +0·69° (homogeneous), ±0° in $CHCl_3$, +1·7° in C_5H_5N, are similarly obtained, but (**IV**) gives d-*glyceryl* α-cyclo*hexylmethyl α'β-Me_2 ether*, b.p. 135—138°/14 mm., $[\alpha]_D$ +4·9°. R. S. C.

Isomerisation of polyene acids and carotenoids. Preparation of β-elæostearic and β-licanic acid. H. H. Strain (*J. Amer. Chem. Soc.*, 1941, **63**, 3448—3452).—The isomerisation of oleic acid (**I**) and the readier isomerisation of α-elæostearic acid (**II**) and its esters by various reagents are described. That of (**I**) by $NaNO_2$–30% HNO_3 and of (**II**) or α-licanic acid by a little I in MeOH has preparative val. Dihydroxyxanthophylls are converted by I into more strongly, and then (more I, longer reaction) into less strongly, adsorbed pigments. Absence of OH decreases the ease of isomerisation. Esterification of OH also decreases the ease of change and leads to products which are separable by chromatography only after hydrolysis. Some adsorbents, *e.g.*, synthetic, activated Mg silicate, although neutral in H_2O, change carotenoids into blue substances similar to those obtained by strong acids or very strong bases. Care is thus needed in isolation of naturally occurring pigments, as accompanying acids may cause isomerisation; this may be avoided by adding org. bases, *e.g.*, $NPhMe_2$, C_5H_5N. R. S. C.

Electrolytic preparation of ethyl glyoxylate. W. Oroshnik and P. E. Spoerri (*J. Amer. Chem. Soc.*, 1941, **63**, 3338—3339).—Electrolytic reduction of $Et_2C_2O_4$ at, best, Pd–Hg (53% yield) or Hg (50%) cathodes gives OEt·CH(OH)·CO_2Et, converted by P_2O_5 into CHO·CO_2Et. R. S. C.

Condensations. XVI. Acylations and alkylations of sodium enolates of aliphatic esters. Syntheses of αα-disubstituted β-keto-esters and other compounds. B. E. Hudson, jun., and C. R. Hauser (*J. Amer. Chem. Soc.*, 1941, **63**, 3156—3162; cf. A., 1941, II, 130).—Prep. (large scale) of CPh_3Cl and $NaCPh_3$ is described. For condensations using $NaCPh_3$ it is best to allow it to react completely (disappearance of red colour) or nearly so with the "enolising" compound in, *e.g.*, Et_2O before adding the second reagent. Reactions described below are thus effected. $Bu^{\beta}CO_2Et$ gives $Bu^{\beta}CO{\cdot}CHPr^{\beta}{\cdot}CO_2Et$ (63%). $Bu^{\gamma}CO_2Et$ with $Pr^{\alpha}CO_2Et$ or $Pr^{\beta}CO_2Et$ gives mixed β-CO-esters owing to the formation (and later condensation) of enolates of the latter esters. $Pr^{\beta}CO_2Et$ with $Et_2C_2O_4$ gives 61% of $CO_2Et{\cdot}CO{\cdot}CMe_2{\cdot}CO_2Et$, but with HCO_2Et gives only 16% of $HCO{\cdot}CMe_2{\cdot}CO_2Et$. $CHRR'{\cdot}CO_2Et$ with R″COCl gives 51—74% of $R''CO{\cdot}CRR'{\cdot}CO_2Et$, examples being (*a*) R = R′ = Me, R″ = Me, Pr^{α}, Pr^{β}, and Ph, (*b*) R = Me, R′ = Et, R″ = Et, Bu^{β}, and Ph, and (*c*) R′ = R = Et, R″ = Ph. *Et αα-dimethylacetoacetate semicarbazone*, m.p. 119°, and *Et β-keto-αδ-dimethyl-α-ethyl*-n-*hexoate*, b.p. 116—119°/15 mm., are described. $Pr^{\beta}CO_2Et$ and $ClCO_2Et$ give 75% of $CMe_2(CO_2Me)_2$. Interaction of EtOAc with RCOCl gives mainly $(RCO)_2CH{\cdot}CO_2Et$: thus, with $Pr^{\alpha}COCl$ it gives 49% of $(Pr^{\alpha}CO)_2CH{\cdot}CO_2Et$; addition of $CH_2Na{\cdot}CO_2Et$ to EtCOCl (excess) in Et_2O at 0° gives *Et β-keto-β*-n-*propionyl*-n-*valerate* (39%), b.p. 98—102°/9 mm., and $EtCO{\cdot}CH_2{\cdot}CO_2Et$ (15%); $CHPr^{\beta}Na{\cdot}CO_2Et$ and $ClCO_2Et$ give *Et β-carbethoxy-β-methylglutarate* (29%), b.p. 150—152°/15 mm., and $CHPr^{\beta}(CO_2Et)_2$ (13%). $Pr^{\beta}CO_2Et$ with PhNCO gives $CO_2Et{\cdot}CMe_2{\cdot}CO{\cdot}NHPh$ (33%) (best method of prep.). Alkylation of EtOAc is impossible owing to condensation, but $Bu^{\beta}CO_2Et$ and $PhSO_2Et$ give $CHEtPr^{\beta}{\cdot}CO_2Et$ (33%), and $Pr^{\beta}CO_2Et$ and $CMe_2Br{\cdot}CO_2Et$ give $(CMe_2{\cdot}CO_2Et)_2$ (30%), also obtained (26%) from the enolate by I. $Pr^{\beta}CO_2Et$ with $(CH_2)_2O$ gives αα-dimethyl-γ-butyrolactone (55%), b.p. 195·5—197·5°. R. S. C.

Introduction of substituted vinyl groups. VIII. Acetoacetic ester series. A. C. Cope and C. M. Hofmann (*J. Amer. Chem. Soc.*, 1941, **63**, 3456—3459; cf. A., 1941, II, 161).—Heating RCHO, $CH_2Ac{\cdot}CO_2R'$, piperidine (**I**), AcOH, and C_6H_6 with continuous removal of H_2O gives 71—89% of *Et α-acetyl-* (**II**), b.p. 118—120°/18 mm. [also obtained by adding (**I**) in a little MeOH to $Pr^{\alpha}CHO$ and $CH_2Ac{\cdot}CO_2Et$ at 5—10° and then keeping at 0°], α-acetyl-δ-methyl- (**III**), b.p. 120—121°/15 mm., and *α-acetyl-γ-ethyl-*, b.p. 122—123°/11 mm., -Δ$^{\alpha}$-n-*hexenoate*, *Pr$^{\beta}$ α-acetyl-* (**IV**), b.p. 125—128°/24 mm., and *α-acetyl-δ-methyl-* (**V**), b.p. 135—136°/24 mm.,

-Δ^{α}-n-*hexenoate*, and *Et α-acetyl-γ-ethyl-*Δ^{α}-n-*octenoate*, b.p. 138—141°/11 mm. NaOEt–EtOH at −5° converts (**II**) and (**III**) into the enolates, which with MeI at the b.p. give Et α-methyl-, b.p. 65—66°/13 mm., and *αδ-dimethyl-*Δ^{β}-n-*hexenoate*, b.p. 73—74°/15 mm., respectively. NaOPr$^{\beta}$–Pr$^{\beta}$OH and then MeI similarly convert (**IV**) and (**V**) into *Pr$^{\beta}$ α-methyl-*, b.p. 75—76°/18 mm., and *αδ-dimethyl-*Δ^{β}-n-*hexenoate*, b.p. 89—91°/25 mm., respectively. Failure of the ethylenic linking to migrate is probably due to the rapidity of the alkylation. Alkylation by BuI or PrI gives mixtures, probably because the slower reaction allows migration of the ethylenic linking and partial addition of EtOH to the resulting $\alpha\beta$-unsaturated ester. R. S. C.

Production of aliphatic dicarboxylic acids.—See B., 1942, II, 4.

Biological degradation of fatty acids by methyl oxidation. Preparation and metabolism of deuterodicarboxylic acids. K. Bernhard [with H. Steinhauser and E. Halpern] (*Helv. Chim. Acta*, 1941, **24**, 1412—1425).—Succinic (**I**), muconic, adipic (**II**), suberic, azelaic, and sebacic (**III**) acids are transformed when heated in D_2O containing NaOH into deuterodicarboxylic acids with sufficiently high D content for biological purposes. D enters the α-position in the mol. and is highest in (**I**), least in (**III**). D is firmly united and the isotopic concn. is unchanged when the neutralised acids are heated in much H_2O. Conversely Na salts of dicarboxylic acids do not acquire D appreciably in 5 at.-% D_2O. Administration of large amounts of $(\cdot CH_2 \cdot CO_2NH_4)_2$ to a dog is not followed by the appearance of the acid in the urine. After administration of deuterosuccinic acid to rats there is an appreciable accumulation of D in the body liquids, thus giving a further proof of the rapid and complete combustion of the compound. Conversion into fatty acids does not occur and the liver fatty acids of the animals contain little D. Experiments on dogs and, in one case, on rats show that the [D] of the heavy compounds is unchanged by their passage through the body. (**II**) is little used by rats and its decomp. in the fatty tissue does not appear to occur. Since the animals received fat and did not appreciably alter in wt. during the experiments a normal fat degradation may be assumed. The diet was also rich in carbohydrates. With help of D therefore it is conclusively shown that the difficultly combustible dicarboxylic acids with 6—10 C are not formed in appreciable amount as intermediate products of normal fat degradation. Verkade's hypothesis that all saturated fatty acids burn through dicarboxylic acids cannot be maintained. Apparently it is mainly the acids with 8—11 C which undergo partial Me oxidation to the corresponding dicarboxylic acids. As long as there is no experimental evidence to the contrary Knoop's theory of β-oxidation is the best representation of the degradation of fats *in vivo*. H. W.

***cis–trans* isomerisations. I. Mechanism of a catalysed isomerisation of maleic acid to fumaric acid. II. Mechanism of the amine-catalysed isomerisation of diethyl maleate.**—See A., 1942, I, 149.

Formation of adipic acid by oxidative degradation of the diaminocarboxylic acid derived from biotin. K. Hofmann, D. B. Melville, and V. du Vigneaud (*J. Amer. Chem. Soc.*, 1941, **63**, 3237—3238).—The diamino-acid obtained by degradation of biotin is oxidised by HNO_3 or $KMnO_4$ to adipic acid. R. S. C.

Preparation of *d*-tartaric acid.—See B., 1942, II, 4.

Mechanism of addition and condensation reactions of carbonyl compounds.—See A., 1942, I, 149.

Mechanism of the Cannizzaro reaction and some allied processes. J. Weiss (*Trans. Faraday Soc.*, 1941, **37**, 782—791).—A mechanism of the Cannizzaro reaction, based on the Haber–Willstätter theory, and supported by experimental evidence, assumes the formation of the radicals RCO and RCH·OH, and involves only electron and H atom transfers for which the energy requirements are fulfilled. The action of alkoxides on aldehydes and the benzoin synthesis are discussed from the same point of view. F. L. U.

Statistics of intramolecular aldol condensations in unsaturated ketone polymerides.—See A., 1942, I, 147.

Decomposition of ozonides with Raney nickel. N. C. Cook and F. C. Whitmore (*J. Amer. Chem. Soc.*, 1941, **63**, 3540).—The ozonides from C_9H_{18} (from CH_2Bu^{γ}·CMeEt·OH) with Raney Ni in pentane give exothermally and later at 155—120° 75% of aldehydes + ketones (MeCHO, COMe·CH_2Bu^{γ}, COEt·CH_2Bu^{γ}, and traces of CH_2O and $Bu^{\gamma}CHO$). R. S. C.

Synthesis of ketones, COR·CHR_2, from αα-disubstituted β-keto-esters. Extension of the acetoacetic ester type of ketone synthesis. B. E. Hudson, jun., and C. R. Hauser (*J. Amer. Chem. Soc.*, 1941, **63**, 3163—3164).—Condensation of CHRR′·CO_2Et with R″COCl by $NaCPh_3$ and fission of the product by H_2SO_4–AcOH–H_2O or, for more resistent esters, HI–AcOH gives 69—81% of COR″·CHRR′. *Buβ CHMeEt ketone*, b.p. 165—167°, is described. R. S. C.

Exchange reaction of diacetyl with deuterium oxide.—See A., 1942, I, 147.

Mechanism of elimination reactions. I. Decomposition of quaternary ammonium bases and xanthate esters. P. G. Stevens and J. H. Richmond (*J. Amer. Chem. Soc.*, 1941, **63**, 3132—3136).—The following results are held to confirm the view that decomp. of quaternary NH_4 compounds and xanthates normally proceeds by elimination of a proton from the β-position (or, for xanthates in which no β-H is available, by γ-elimination) (Ingold's E_2 mechanism), but that such elimination is preceded by formation of a linking between the H involved and the anion of quaternary compounds (an " intermol." linking) or the S of xanthates (an intramol. linking). The difference in behaviour between quaternary hydroxides and halides is due to the lower tendency of the halide ion than of OH′ to form H linkings. Pinacolone and HCO_2NH_4 at 125—175° give $CHMeBu^{\gamma}\cdot NH_2$ (66%) [and 5—10% of a *sec.* amine, b.p. 86° (picrate, m.p. 180°; phenylcarbamide, m.p. 175°], converted by MeI–NaOH into dimethylpinacolylamine (**I**), b.p. 129—130°/759 mm. (hydriodide, m.p. 260—261°; *picrate*, m.p. 214°), which with MeI–C_6H_6 gives *trimethylpinacolylammonium iodide*, m.p. 260°. Transformation into the hydroxide and decomp. thereof at 25—30°/15—20 mm. (later 0·01—0·005 mm.) gives only CH_2:$CHBu^{\gamma}$ and NMe_3, but at 100—160° 52% of (**I**) + MeOH is also formed; absence of rearrangement excludes fission by way of a free radical. Formation of methylene-Δ^2-*cyclo*butene from 1 : 1-dimethyl-2-methylenepyrrolidinium hydroxide (von Braun *et al.*, A., 1928, 770) by way of CH_2:C:CH·[CH]$_2$·NMe_3}OH probably proceeds by preliminary rearrangement thereof to CH_2:CH·CH:CH·CH_2·NMe_3}OH.

OH·[CHMe]$_2$·ONa (prep. from the glycol by Na in boiling PhMe) with boiling CS_2 and later MeI at room temp. gives OH·[CHMe]$_2$·O·CS_2Me, which at 200° gives *βγ-butylene thiocarbonate*, $(CHMe\cdot O)_2CS$, b.p. 87°/8 mm. [? with some thiolcarbonate, $\begin{matrix}CHMe\cdot O\\CHMe\cdot S\end{matrix}\!\!>\!CO$], + MeOH with a little COMeEt + COS + MeSH. Contrary to Kursanov (A., 1928, 1372), $CHPh_2$·O·CS_2Me at ~330°/1 atm. gives $(CHPh_2)_2$ (30), CH_2Ph_2 (58%), CS_2, and a little MeSH and COS; in this case no β- or γ-H is available and decomp. probably proceeds by way of $CHPh_2$· and ·O·CS_2Me. R. S. C.

Micro-determination of arginine.—See A., 1942, II, 160.

Methylaspartic acids and their methylation. H. D. Dakin (*J. Biol. Chem.*, 1941, **141**, 945—950).—NHBz·$CH(CO_2Et)_2$ is converted by NaOEt and CHMeBr·CO_2Et in boiling EtOH followed by acid hydrolysis into BzOH and *β-methylaspartic* [*α-amino-β-methylsuccinic*] *acid* (**I**), m.p. 274—275° (decomp.), the *Cu* salt of which is freely sol. in H_2O. (**I**) or α-methylaspartic [α-amino-α-methylsuccinic] acid (**II**) is converted by Me_2SO_4 and 33% NaOH into ~70% of the theoretical amount of mesaconic acid (**III**) with $(NMe_4)_2SO_4$. The betaines of the two acids may be obtained on pptn. with phosphotungstic acid but on decomp. with $Ba(OH)_2$ are decomposed with formation of additional (**III**) (~30% of the theoretical amount) and NMe_3. Hydrolysed casein on methylation gives fumaric acid equiv. to 4·7—4·93% of aspartic acid; (**III**) could not be detected and it is concluded that neither (**I**) nor (**II**) is among the NH_2-acids derived from casein. H. W.

Synthesis of pantothenic acid and [its] derivatives. S. A. Harris, G. A. Boyack, and K. Folkers (*J. Amer. Chem. Soc.*, 1941, **63**, 2662—2667).—OH·CH_2·CMe_2·CH(OH)·CO_2Na (**I**) with Ac_2O–NaOAc gives the acid diacetate, the chloride ($SOCl_2$) of which with warm NH_2·[CH_2]$_2$·CO_2Et (**II**) alone gives *Et pantothenate acetate*, hygroscopic, but with (**II**) in warm C_5H_5N gives also some diacetate. With boiling Ac_2O, (**II**) gives 67% of *α-acetoxy-ββ-dimethylbutyrolactone* (**III**), m.p. 44—45°, $[\alpha]_D^{29}$ −13·1° in 95% EtOH, and 12% of acid diacetate; treatment of the crude product with $SOCl_2$ gives (**III**). *p*-NO_2·C_6H_4·CO_2·CH_2·CMe_2·CO_2H [prep. from (**I**) and *p*-NO_2·C_6H_4·COCl in C_5H_5N] and NH_2·[CH_2]$_2$·CO_2Na (**IV**) at 100° give *pantothenic acid* p-*nitrobenzoate* (**V**), m.p. 137—138°, $[\alpha]_D^{29}$ +4·5° in 95% EtOH. α-Hydroxy-ββ-methylbutyrolactone (**VI**), antipyrine (**VII**), and $COCl_2$ in C_6H_6 with, later, CH_2Ph·OH and additional (**VII**) give the *carbobenzyloxy*-derivative, m.p. 78°, $[\alpha]_D^{29}$ +12·3° in 95% EtOH, of the lactone, which with (**IV**) gives CH_2Ph·O·CO·NH·[CH_2]$_2$·CO_2H, m.p. 103°, and with (**II**) at 100° gives the *carbobenzyloxy*-ester, b.p. 140—150°/4 × 10^{-6} mm., of Et pantothenate. NH_3–H_2O or –EtOH converts (**VI**) into *NH_4 αγ-dihydroxy-ββ-dimethylbutyrate*, m.p. 135—136°, but liquid NH_3 at 25° gives the *amide*, m.p. 92—94°, $[\alpha]_D^{29}$ +30·9° in H_2O [*αγ-diacetate* (**VIII**), $[\alpha]_D^{25}$ +6·8° in Et_2O, −0·7° in $CHCl_3$, −10·3° in H_2O, −3·2° in abs. EtOH, +5·7° in EtOAc, −5·4° in dioxan]. C_5H_{11}·O·NO in AcOH converts (**VIII**) into the *acid diacetate*, $[\alpha]_D^{25}$ −2·6° in MeOH, ±0° in Et_2O, which with $SOCl_2$ at 100° and then (**II**)–C_5H_5N gives *Et pantothenate diacetate*, $[\alpha]_D^{25}$ +24·2° in Et_2O, hydrolysed by 0·5*N*-$Ba(OH)_2$ at 25° to pantothenic acid. Et pantothenate, its acetate, and (**V**) are inactive in microbiological tests, but the first two are active in rats and chicks. R. S. C.

Preparation and properties of sodium *d*-pantothenate. H. C. Parke and E. J. Lawson (*J. Amer. Chem. Soc.*, 1941, **63**, 2869—2871).—*l*- and *dl*-α-Hydroxy-ββ-dimethyl-γ-butyrolactone in boiling aq. $Ba(OH)_2$ give Ba (+)-, m.p. 213—215°, $[\alpha]_D^{34}$ +7·4° in H_2O, and dl-*αγ-dihydroxy-ββ-dimethylbutyrate*, +H_2O, converted by aq. Na_2SO_4 into the (+)- (**I**), dimorphic, m.p. 166—171° (hygroscopic) and 99—101° (not hygroscopic), $[\alpha]_D^{29}$ +8·4° in H_2O, and dl-*Na* (**II**)

salts, respectively. In liquid NH_3 the lactones give dl- (**III**), m.p. 127°, and (+)-*αγ-dihydroxy-ββ-dimethylbutyramide*, m.p. 92—94° (93—94°), $[\alpha]_D^{24}$ +30·8° in H_2O, +52° in MeOH (also obtained by NH_3–MeOH at room temp.). Fusion of (**II**) with β-alanine at 175° (later 150°) (91% yield) or of (**III**) with the Na salt (**IV**) of β-alanine at 100° (70% yield) gives Na *dl*-pantothenate. Fusion of (**I**) with β-alanine at 180° (61% yield) or heating the *l*-lactone with (**IV**) in $Pr^\beta OH$ (91% yield) gives Na *d*-pantothenate, m.p. 122—124°, $[\alpha]_D^{25}$ +27·04° in H_2O, which is less hygroscopic than is the Ca salt and more suitable as a vitamin standard. R. S. C.

Crystalline calcium pantothenate. H. Levy, J. Weijlard, and E. T. Stiller (*J. Amer. Chem. Soc.*, 1941, **63**, 2846—2847; cf. A., 1940, II, 299).—Prep. of macro-cryst. Ca (+)- and Ca (−)-pantothenate from the micro-cryst. forms is described. W. R. A.

Colorimetric test for methionine.—See A., 1942, II, 160.

Condensation reactions. II. Alkylidene-cyanoacetic and -malonic esters. A. C. Cope, C. M. Hofmann, C. Wyckoff, and E. Hardenbergh (*J. Amer. Chem. Soc.*, 1941, **63**, 3452—3456; cf. A., 1938, II, 5).—Heating $CN{\cdot}CH_2{\cdot}CO_2Et$ (0·5), $COR{\cdot}CH_2R'$ (0·55—0·6), NH_4OAc (0·05), AcOH (0·1 mol.), and C_6H_6 with continuous removal of H_2O gives good yields of $CH_2R'{\cdot}CR{:}C(CN){\cdot}CO_2Et$. Branching decreases the yield, the reaction failing with pinacolone, camphor, and anthrone. Piperidine acetate (**I**) and AcOH also effect this condensation but more slowly. AcOH–(**I**), but not AcOH–NH_4OAc, effects condensation of aldehydes with $CH_2(CO_2Et)_2$; yields are good (88—92%) with $Pr^\beta CHO$ or $Bu^\beta CHO$, and less good with other aldehydes owing to aldol condensation, but for EtCHO or $Pr^\alpha CHO$ Ac_2O is the best reagent. Hydrogenation (Pd–C; also Pt, Ni, or Cu chromite) of the alkylidene-esters gives 90—97% yields. Condensation of $COMe{\cdot}CH_2Ph$ with $CN{\cdot}CH_2{\cdot}CO_2Et$ by AcOH–(**I**) gives, as by-product, a little *2-cyano-3-methyl-1-naphthol*, m.p. 200—201°, the structure of which is proved by oxidation ($KMnO_4$) to o-$C_6H_4(CO_2H)_2$, conversion by Zn dust–$ZnCl_2$–NaCl at 300° into 3 : 1-$C_{10}H_5Me{\cdot}OH$, and by prep. in 47% yield by heating $CH_2Ph{\cdot}CMe{:}C(CN){\cdot}CO_2Et$ with NH_2Ac or (**I**) at 200—220°. $Ph{\cdot}[CH_2]_3{\cdot}CO_2Et$, $CH_2Ph{\cdot}CH{:}CH{\cdot}CO_2Et$, and o-$C_6H_4Me{\cdot}CMe{:}C(CN){\cdot}CO_2Et$ are unaffected by heating in NH_2Ac, and $Ph{\cdot}[CH_2]_3{\cdot}CO_2H$ gives the amide. The following are described. Et α-cyano-β-methyl-Δ^α-*n*-pentenoate, b.p. 116—118°/11 mm., -hexenoate, b.p. 138—139°/19 mm., *-heptenoate*, b.p. 149—150°/19 mm., *-octenoate*, b.p. 143—145°/11 mm., and *-nonenoate*, b.p. 124—125°/2 mm. *Pr^β α-cyano-β-methyl-Δ^α-n-hexenoate*, b.p. 143—146°/25 mm. $CEt_2{:}C(CN){\cdot}CO_2Et$, b.p. 116—118°/9 mm. *Et α-cyano-ββ-dimethyl-*, b.p. 130—133°/12 mm., *-β-n*-propyl-, b.p. 136—137°/11 mm., *-n-* and *-β-isobutyl-*, b.p. 116—118°/3 mm., *-Δ^α-n-hexenoate*. Et α-cyano*cyclo*hexylideneacetate, b.p. 150—151°/9 mm. *Et α-cyano-β-n-amyl-Δ^α-n-octenoate*, b.p. 138—139°/1 mm. Et α-cyano-β-phenyl-, b.p. 136—137°/2 mm., *-β-o-tolyl-*, b.p. 141—143°/3 mm., and *-γ-*phenyl-β-methyl-, b.p. 139—140°/1 mm., *-Δ^α-n*-butenoate. Et α-cyano-β-phenyl-Δ^α-*n*-pentenoate, b.p. 136—138°/2 mm., -n-*hexenoate*, b.p. 135—136°/1 mm., and -n-*octenoate*, b.p. 146—148°/1 mm. *Et α-cyano-δ-phenyl-β-methyl-*n-*pentenoate*, b.p. 167—168°/3 mm. *Et α-cyano-βγ-diphenylacrylate*, m.p. 95—96°, b.p. 195—200°/3 mm. $CHR{:}C(CO_2Et)_2$, in which R = Et, b.p. 119—120°/15 mm., Pr^α, b.p. 122—124°/10 mm., Pr^β, b.p. 135—137°/27 mm., Bu^α, b.p. 146—147°/23 mm., and Bu^β, b.p. 149—150°/26 mm. *Et_2 n-hexylidenemalonate*, b.p. 162—164°/27 mm. *Et α-carbethoxy-γ-ethyl-Δ^α-n-hexenoate*, b.p. 146—148°/21 mm. *Et α-cyano-γ-phenyl*isovalerate, b.p. 140—142°/2 mm. R. S. C.

II.—SUGARS AND GLUCOSIDES.

Preparation of maltose monohydrate by deacetylation of maltose octa-acetate with barium methoxide. W. A. Mitchell (*J. Amer. Chem. Soc.*, 1941, **63**, 3534).—Maltose hydrate is best obtained from the octa-acetate by $Ba(OMe)_2$ (prep. described). Its reducing power $[K_3Fe(CN)_6]$ is recorded. R. S. C.

Formation of "*iso*maltose" from glucose by reversion. K. Myrbäck (*Svensk Kem. Tidskr.*, 1941, **53**, 67—77).—Treatment of glucose with cold conc. HCl gives a mixture of "*iso*maltose," (**I**), $[\alpha]_{Hg}$ +110°, and a trisaccharide (**II**), separable by fractional pptn. with EtOH. Reversion to give up to 65% of (**II**) occurs if reaction is prolonged, but the amount of (**I**) present rapidly reaches ~15% and remains const. (**I**), but not (**II**), is slowly fermented by yeast. The *iso*maltose produced by acid hydrolysis of starch is not formed by reversion, but its identity with (**I**) cannot be established, as the osazones of both are difficult to purify. M. H. M. A.

Emulsin. XLV. Glucosides of hydroxy-sulphonic acids and their esters. B. Helferich and H. Schnorr (*Annalen*, 1941, **547**, 201—215).—Hydrolysis of glucosides of $OH{\cdot}[CH_2]_n{\cdot}R$ by emulsin at p_H 5 is relatively little affected by increase of n from 2 to 4 if R = Cl, I, or SO_3Et, but, if R = SO_3H, there is a great increase in the rate of hydrolysis. Further, for R = SO_3H, the glucoside is readily hydrolysed by cold alkali if n = 2 but not if n = 3 or 4. γ-Chloro-*n*-propyl-β-*d*-glucoside tetra-acetate (prep. from $OH{\cdot}[CH_2]_3{\cdot}Cl$, acetobromoglucose, Ag_2O, and $CaSO_4$ in $CHCl_3$ at room temp.), m.p. 74—75°, $[\alpha]_D^{19}$ −2·50° in $CHCl_3$, with NaOMe–MeOH–$CHCl_3$ at −15° gives the free *glucoside*, m.p. 42° after sintering, $[\alpha]_D^{16}$ −29·5° in H_2O, and with NaI in dry $COMe_2$ at 85° gives *γ-iodo-*n*-propyl-β-*d*-glucoside tetra-acetate*, m.p. 61°, $[\alpha]_D^{17}$ +3·47° in $CHCl_3$, and thence (NaOMe–MeOH–$CHCl_3$ at ~−10°) the free *glucoside*, m.p. 89°, $[\alpha]_D^{16}$ −20·0° in H_2O. With aq. Na_2SO_3 at 100°, this gives *Na n-propyl-β-d-glucoside-γ-sulphonate*, m.p. 226° (corr.), $[\alpha]_D^{16}$ −25·8° in H_2O, which with Ac_2O–AcOH–C_5H_5N at 100° gives the *Na sulphonate tetra-acetate*, +2H_2O, m.p. 213—214° (corr.), $[\alpha]_D^{16}$ −22·9° in H_2O, converted by EtOH–$COMe_2$–H_2SO_4–$CHMeN_2$ into *Et n-propyl-β-d-glucoside-γ-sulphonate tetra-acetate*, m.p. 107—108°, $[\alpha]_D^{17}$ −13·2° in $CHCl_3$. NaOMe–MeOH–$CHCl_3$ at −12° then gives *Et n-propyl-β-d-glucoside-γ-sulphonate*, m.p. 96°, $[\alpha]_D^{17}$ −23·5° in H_2O, stable over NaOH–SiO_2 gel but gradually hydrolysed (SO_3Et gives SO_3H; glucoside linking unaffected) in H_2O. Similar reactions, starting from $OH{\cdot}[CH_2]_4{\cdot}OH$, lead to *δ-chloro-*, m.p. 55—57°, $[\alpha]_D^{22}$ −31·4° in H_2O [*tetra-acetate*, m.p. 104—105° (corr.), $[\alpha]_D^{22}$ −20·7° in $CHCl_3$], and *δ-iodo-*n*-butyl-β-d-glucoside*, m.p. 89—90°, $[\alpha]_D^{22}$ −24·8° in H_2O (*tetra-acetate*, m.p. 86—87°, $[\alpha]_D^{22}$ −20·2° in $CHCl_3$), *Na*, +*x*H_2O, m.p. (anhyd.) 111°, $[\alpha]_D^{22}$ (anhyd.) −25·8° in H_2O (amorphous tetra-acetate), and Et *n*-butyl-β-d-glucoside-δ-sulphonate, $[\alpha]_D^{19}$ −24° in H_2O (*tetra-acetate*, m.p. 83°, $[\alpha]_D^{22}$ −18·5° in $CHCl_3$). R. S. C.

Lignin and related compounds. LIV. Synthesis and properties of glucosides related to lignin. J. H. Fisher, W. L. Hawkins, and H. Hibbert (*J. Amer. Chem. Soc.*, 1941, **63**, 3031—3035; cf. A., 1942, II, 42).—The rates of acidic and alkaline hydrolysis of the β-*d*-xyloside of α-hydroxypropiovanillone, α-hydroxypropiovanillone, and acetovanillone, of acetovanillone β-*d*-glucoside and *β-cellobioside*, m.p. 239—240° (decomp.) (*hepta-acetate*, m.p. 208—209°), of guaiacyl and Ph β-*d*-xyloside, of Ph and *α-hydroxypropioveratrone* β-d-*glucoside*, m.p. indefinite (*tetra-acetate*, m.p. 133·6—133·8°), are determined. Presence of CO *p*- to the phenolic OH greatly increases the rate of hydrolysis of the glucoside by acid and the p_H of the phenol. Relative stabilities are: glucosides = cellobioside > xyloside. It is concluded that lignin may contain phenolic glucosides. R. S. C.

Genistin (an *iso*flavone glucoside) and its aglucone, genistein, from soya beans. E. D. Walter (*J. Amer. Chem. Soc.*, 1941, **63**, 3273—3276).—Physical properties, colour tests, crystallo-optical data, photomicrographs, and absorption spectra of genistin (**I**), genistein (isolated from soya beans), and the tri- and hexa-acetate of (**I**) are recorded. Presence of glucose in (**I**) is rigidly proved. Another flavone is also present in soya beans. R. S. C.

Synthesis of β-β′-chloroethyl-gentiobioside and -primoveroside acetates. L. P. Miller (*J. Amer. Chem. Soc.*, 1941, **63**, 3342—3343).—Acetobromogentiobiose, $Cl{\cdot}[CH_2]_2{\cdot}OH$, Ag_2O, I, and $CaSO_4$ in $CHCl_3$ at room temp. give *β-β′-chloroethylgentiobioside hepta-acetate* (**I**), partial melting at 128—129°, complete at 167—168°, $[\alpha]_D^{25}$ −20·2° in $CHCl_3$. β-β′-Chloroethyl-*D*-glucoside with CPh_3Cl in C_5H_5N at room temp. and then Ac_2O at 0° gives *β-β′-chloroethyl-D-glucoside 6-CPh$_3$ ether* 2 : 3 : 4-*triacetate* (47%), m.p. 158—159°, $[\alpha]_D^{25}$ +30·2° in $CHCl_3$, and thence (HBr–AcOH at 0°) *β-β′-chloroethyl-D-glucoside* 2 : 3 : 4-*triacetate* (55%), m.p. 120—121°, $[\alpha]_D^{28}$ −17·6° in $CHCl_3$ (derived tetra-acetate, m.p. 118—119°), which with acetobromo-glucose or *-D*-xylose, Ag_2O, I, and $CaSO_4$ in $CHCl_3$ gives (**I**) or *β-β′-chloroethylprimoveroside hexa-acetate*, m.p. 176·5—177·5°, $[\alpha]_D^{27}$ −39·9° in $CHCl_3$, respectively. M.p. are corr. R. S. C.

Deoxycorticosterone β-glucoside tetra-acetate. W. S. Johnson (*J. Amer. Chem. Soc.*, 1941, **63**, 3238—3239).—Small-scale prep. of cholestanol α- and β-glucoside in 35—40 and 52—54% yield, respectively, is announced. *Deoxycorticosterone β-glucoside tetra-acetate*, m.p. 176—176·5° (corr.), $[\alpha]_D^{23\cdot6}$ +80° in $CHCl_3$, is obtained by the Helferich method. R. S. C.

Constitution of arabogalactan. I. Components and position of linkage. E. V. White (*J. Amer. Chem. Soc.*, 1941, **63**, 2871—2875).—Extraction of larch sawdust with H_2O at room temp. and pptn. by 95% EtOH gives similar fractions of arabogalactan (**I**), which is regenerated unchanged (gives furfuraldehyde equiv. to 14% of arabinose; very slightly reduces Fehling's solution) by hydrolysis of the *acetate* (20 Ac per 6 galactose + 2 arabinose units). With Me_2SO_4–aq. NaOH–N_2 at 25°, (**I**) gives a *Me_{20}* derivative and thence by HCl–MeOH the *Me_{20} ether Me_7 glucoside* and finally Me α- + β-2 : 4-dimethyl-*d*-galactoside (3 mols.; separated by insolubility in light petroleum) and a petroleum-sol. syrup (*A*) containing Me 2 : 3 : 4-tri- (1 mol.) and 2 : 3 : 4 : 6-tetra-methyl-*d*-galactoside (2 mols.) and Me 2 : 3 : 5-trimethyl-*l*-arabinoside (1 mol.). Identification of the components of (*A*) is detailed. (**I**) contains 1 : 3 and 1 : 6 O-linkings and a substantial part of the galactose is engaged at $C_{(3)}$ and $C_{(6)}$. (**I**) has a branched-chain structure, terminated by galactopyranose and arabofuranose units. R. S. C.

Fractionation of waxy and ordinary maize starch. C. G. Caldwell and R. M. Hixon (*J. Amer. Chem. Soc.*, 1941, **63**, 2876—2880).—Fractionation of maize starch by electrodialysis and freezing is described. The relative amounts of sol. and insol. products depend entirely on the extent of peptisation. The rate of crystallisation

during ageing is followed by a modification of the Sallinger process. The limit dextrins (prep. by β-amylase described) from the waxy and ordinary starch are very similar. 0·93 and 0·67% of dimethylglucose is obtained by hydrolysis of the methylated starch and limit dextrins, respectively. R. S. C.

Seed mucilages. II. Seed mucilage of *Plantago arenaria*. W. A. G. Nelson and E. G. V. Percival (*J.C.S.*, 1942, 58—61).—The seed mucilage (I) of *P. arenaria* contains ash, 5·4% (as sulphate) (3·3% after prolonged dialysis), pentosan, 90%, and uronic anhydride, 7·5%. Hydrolysis ($H_2C_2O_4$) yields *l*-arabinose 9·5%, *d*-galactose 3%, *d*-xylose 62·5%, and an aldobionic acid (12%) composed of *d*-xylose and *d*-galacturonic acid. The *Ac* derivative of (I) contains a sol. fraction, $[\alpha]_D^{17}$ −61° in $CHCl_3$. Hydrolysis (MeOH–HCl) of *methylated* (I), $[\alpha]_D^{17}$ −104° in $CHCl_3$, yields trimethylxylopyranose ~30, 2-methylxylose (*anilide*, m.p. 140°, $[\alpha]_D^{18}$ +240° in EtOAc) ~23, tetramethylgalactopyranose ~4, and a mixture, ~40%, of dimethylxylose with (?) methylated arabinoses. It is suggested that (I) has a basic mol. unit with 9 xylo- and 1 galacto-pyranose end-groups, 10 xylopyranose linking units joined by 1 : 2-β-linkings, 3 arabinose linking units, 8 xylose residues at branching points with free OH groups at $C_{(2)}$, and 2 galacturonic acid residues. A. Li.

Constitution of starch synthesised *in vitro* by potato phosphorylase. W. N. Haworth, R. L. Heath, and S. Peat (*J.C.S.*, 1942, 55—58).—The granular starch prepared from glucose 1-phosphate and potato phosphorylase (Hanes, A., 1940, III, 826) with Me_2SO_4 yields a *methylated starch*, $[\alpha]_D^{20}$ +203° in $CHCl_3$, hydrolysed (MeOH–HCl) to 2 : 3 : 6-trimethyl- with >1·5% of tetramethyl-glucose. From these results and measurements of η, a laminated structure is suggested, each unit having 80—90 glucose residues, joined by 1 : 4-α-linkings. A. Li.

Fermentability of corn-starch products : relation to starch structure. R. W. Kerr and N. F. Schink (*Ind. Eng. Chem.*, 1941, **33**, 1418—1421).—Contrary to the usually accepted ideas, starches are heterogeneous and are not composed of a single type of common mol. At least two fundamentally different chemical configurations must exist in maize starch, and although both are built up from α-glucoside linkings, probably only one is composed of 1 : 4-glucoside or maltose-type linkings. Attention is drawn to certain facts that support these principles. The total reducing sugar and fermentability of syrups made by the diastatic conversion of maize starch are not increased by acid pretreatment of the starch or by subsequent acid hydrolysis of the syrup. R. G. W.

Electrodialysis and electrophoresis in starch research. M. Samec [with C. Nučič and V. Pirkmaier] (*Kolloid-Z.*, 1941, **94**, 350—358). —Summary and bibliography. F. L. U.

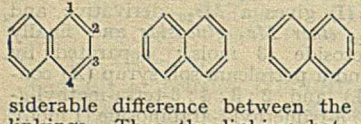
Hydrocolloidal cellulose and cellulose hydrosols.—See A., 1942, I, 143.

III.—HOMOCYCLIC.

Di*cyclo*hexylidene-2 : 2′-sulphone. O. Grummitt and C. Helber (*J. Amer. Chem. Soc.*, 1941, **63**, 3236).—Di-Δ¹-*cyclo*hexenyl (I) and a little quinol in liquid SO_2 at 100° give 50% of *di*cyclo*hexylidene*-2 : 2′-*sulphone* (II), m.p. 76—77°, which at 110—120° regenerates (I) and SO_2. R. S. C.

Production of aromatic hydrocarbons from mixtures of paraffins and *cyclo*paraffins.—See B., 1942, II, 5.

Fixation of aromatic double bonds. S. Rangaswami and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1941, **14**, **A**, 547—571).—Review of the literature leads to the conclusion that there is sufficient justification for concluding in favour of fixation of the double linkings in C_6H_6, $C_{10}H_8$, anthracene (I), phenanthrene (II), hydrindene, tetrahydronaphthalene, fluorene, dibenzfuran, xanthone, and xanthene, and quinoline and *iso*quinoline. This fixation seems to be of varying degrees, being very weak when chelate rings are the cause of fixation, more prominent when heterocyclic rings are involved, and more or less rigid in polynuclear aromatic structures such as $C_{10}H_8$, (I), etc. The objection that C_6H_6 and $C_{10}H_8$ have absolutely plane, symmetrical structures appears to be overcome by an application of the theory of resonance. For $C_{10}H_8$ three stable valency bond structures can be formulated, as a consequence of which there is considerable difference between the characteristics of the different linkings. Thus the linking between $C_{(1)}$ and $C_{(2)}$ has ⅔ double bond character whereas that between $C_{(2)}$ and $C_{(3)}$ has only ⅓ double bond character with the result that the former behaves very much like a double linking whereas the latter has very little such characteristics. The result is a great difference in reactivity giving rise to "fixation." In the cases of (I) and (II) the differences between the linkings are even greater owing to the existence of larger nos. of valency bond structures and it may be expected that the differences between the linkings will be further accentuated by the presence of substituents which can produce powerful electrometric effects (OH, NH_2, Br, NO_2). Similar explanations can be given of the effect of heterocyclic and chelate rings. This fixation can never be absolutely rigid since the other linkings also have very small but nevertheless appreciable double bond characteristics. When the more reactive positions are protected, the feebler reactivity of the others is exhibited particularly with powerful reagents and under favourable conditions. H. W.



So-called Dewar formula for benzene. T. S. Patterson (*Chem. and Ind.*, 1942, 54).—Seven formulæ for C_6H_6 were suggested by Dewar (*Proc. Roy. Soc. Edin.*, 1866—1869, **6**, 82), and the adoption of one particular formula as the "Dewar formula" is questioned. A. T. P.

Kinetics and mechanism of electrophilic benzene substitution reactions.—See A., 1942, I, 148.

Mechanism of the Friedel–Crafts reaction. F. Fairbrother (*Trans. Faraday Soc.*, 1941, **37**, 763—769).—When *cyclo*hexane solutions of $AlBr_3$ and EtBr are mixed there is a large increase in the dielectric polarisability, which is not shown if PhBr is used in place of EtBr. This probably indicates the formation of an ion-pair of high dipole moment. This evidence reinforces that afforded by the radioisotopic exchange of halogen atoms between org. and inorg. halogenides (cf. A., 1937, I, 320; 1941, I, 336) in favour of the conversion of the covalent C–halogen bond into an ionic bond, through complex formation with the catalyst. F. L. U.

Use of amalgamated aluminium as catalyst in the Friedel–Crafts reaction. L. I. Diuguid (*J. Amer Chem. Soc.*, 1941, **63**, 3527—3529).—C_6H_6, RCl, and Al–Hg (activated by a little RCl) at room temp. give the following yields of PhR : PhEt 76; PhPr$^\alpha$ 15·2 + PhBr$^\beta$ 52·2 (from Pr$^\alpha$Cl); PhPr$^\beta$ 83·3 (from Pr$^\beta$Cl); CPhMeEt 36·6 + PhBu$^\alpha$ (from Bu$^\alpha$Cl); CPhMe$_3$ 59·9 (from CHMeEtCl) or 74·5% (from Bu$^\gamma$Cl). α-$C_{10}H_7$·CHMeEt (48%) is similarly obtained from CHMeEtCl. R. S. C.

Vapour-phase nitration of toluene. J. L. Bullock and E. T. Mitchell (*J. Amer. Chem. Soc.*, 1941, **63**, 3230—3231).—PhMe–HNO_3–H_2O (1 : 0·7 : 1) at 150° gives *o*- 55·7—55·9, *m*- 5·0, and *p*-$C_6H_4Me{\cdot}NO_2$ 39·1—39·3%. More HNO_3 (1 : 1·2 : 1) or interaction at 250° gives very similar proportions. R. S. C.

Mechanism and kinetics of aromatic side-chain substitution.—See A., 1942, I, 148.

Identification of organic compounds. IV. Chlorosulphonic acid as reagent for identification of alkylbenzenes. E. H. Huntress and J. S. Autenrieth (*J. Amer. Chem. Soc.*, 1941, **63**, 3446—3448; cf. A., 1940, II, 242).—Alkylbenzenes are converted by $ClSO_3H$ into sulphonyl chlorides, which with $(NH_4)_2CO_3$ give the sulphonamides. Structures of the monoalkyl-amides are proved by oxidation ($KMnO_4$) to *p*-$CO_2H{\cdot}C_6H_4{\cdot}SO_3H$. Sulphones are formed as by-products as follows : Ph_2SO_2 27, (*p*-$C_6H_4Me)_2SO_2$ 1—10, (*p*-$C_6H_4Et)_2SO_2$ 1—6, (*p*-$C_6H_4Pr^\beta)_2SO_2$ 2—3, others 0%. The following are described : $PhSO_2{\cdot}NH_2$, m.p. 150—150·5°; *p*-$C_6H_4Me{\cdot}SO_2{\cdot}NH_2$, m.p. 135·5—136°; p-*ethyl*-, m.p. 109—110°, p-n-, m.p. 107—108°, and p-iso-*propyl*-, m.p. 104·5—105·5°, p-n-, m.p. 94·5—95°, p-sec.-, m.p. 81—82·5°, p-tert.-, m.p. 136—137°, and p-iso-*butyl*-, m.p. 84—85°, p-n-, m.p. 85·5—86·5°, and p-tert.-*amyl*-, m.p. 83—84°, p-n-*hexyl*-, m.p. 85—85·5°, p-n-*nonyl*-, m.p. 94·5—95°, p-n-*undecyl*-, m.p. 95·7—96·2°, p-cyclo*hexyl*-, m.p. 160—160·5°, 3 : 4-, m.p. 143—144°, 2 : 4-, m.p. 136·5—137°, and 2 : 5-*dimethyl*-, m.p. 145·5—146·5°, 2 : 4 : 5-, m.p. 175—176°, and 2 : 4 : 6-*trimethyl*-, m.p. 141·5—142·5°, 2-*methyl*-5-iso*propyl*-, m.p. 114·5—115·5°, ? 2 : 4-*diethyl*-, m.p. 98—99°, ? 2 : 4-*dimethyl*-5-*ethyl*-, m.p. 147—148°, 2 : 3 : 4 : 5-, m.p. 183·5—184°, 2 : 3 : 4 : 6-, m.p. 141·5—142°, and 2 : 3 : 5 : 6-*tetramethyl*-, m.p. 153—154°, ? 2 : 4-*dimethyl*-5-n-*propyl*-, m.p. 90—93°, ? 2 : 4-*dimethyl*-5-iso*propyl*-, m.p. 155·5—156°, 2 : 4 : 6-*trimethyl*-3-*ethyl*-, m.p. 131—132°, *pentamethyl*-, m.p. 182—183°, ? 2 : 4-*dimethyl*-6-tert.-*butyl*-, m.p. 132—133°, 2 : 4 : 6-*triethyl*-, m.p. 118—118·5°, 2 : 5-*di*-tert.-*butyl*-, m.p. 135·5—136·5°, and 2 : 3 : 5 : 6-*tetra*iso*propyl*- [prep. from the chloride by NH_3 in light petroleum, not by $(NH_4)_2CO_3$], m.p. 154·5—155°, -*benzenesulphonamide*; 2 : 3 : 5 : 6 : 1-$C_6HPr^\beta_4{\cdot}CO_2R$, in which R = Me, m.p. 126—126·5°, and Et, m.p. 99—99·5°; *p*-$C_6H_4Me{\cdot}SO_2Cl$, m.p. 64—66°; 3 : 4-*dimethyl*-, m.p. 52°, 2 : 4 : 6-*trimethyl*-, m.p. 50—53°, p-tert.-*butyl*-, m.p. 80—82°, 2 : 3 : 4 : 5-, m.p. 72—73°, and 2 : 3 : 5 : 6-*tetramethyl*-, m.p. 98—99°, *pentamethyl*-, m.p. 77—78·5°, ? 2 : 4-*dimethyl*-6-tert.-*butyl*-, m.p. 65—67°, p-cyclo*hexyl*-, m.p. 51—52·5°, and 2 : 3 : 5 : 6-*tetra*iso*propyl*-, m.p. 141·5—142°, -*benzenesulphonyl chloride*. R. S. C.

Action of aluminium chloride on aromatic hydrocarbons. III. Polyethyl- and tetramethyl-benzenes. (Miss) D. Nightingale and F. Wadsworth (*J. Amer. Chem. Soc.*, 1941, **63**, 3514—3517; cf. A., 1940, II, 160).—*as*- and *s*-$C_6H_3Et_3$ are partly converted into one another by $AlCl_3$ at 70—75°. 1 : 2 : 3 : 4-$C_6H_2Et_4$ gives a 1 : 1 mixture of 1 : 2 : 3 : 5- (I) and 1 : 2 : 4 : 5-isomeride. Prehnitene gives 83% of *iso*durene and 17% of durene. In all cases some higher and lower alkylbenzenes are also formed. C_6HEt_5 and, very readily, C_6Et_6 are dealkylated by $AlCl_3$. *s*- or *as*-$C_6H_3Et_3$ with EtCl–$AlCl_3$ at 20—21° gives $C_6H_2Et_4$ containing mainly (I). R. S. C.

Preparation of the chlorodinitrobenzenes from the corresponding dinitroanilines. L. H. Welsh (*J. Amer. Chem. Soc.*, 1941, **63**, 3276—3278).—Prep. of 2 : 3 : 1- (**I**) (30%), 2 : 5 : 1- (**II**) (12%), and 3 : 4 : 1-$(NO_2)_2C_6H_3$·NHAc (8·8%) and a dark solid from *m*-NO_2·C_6H_4·NHAc by HNO_3 (*d* 1·5) in H_2SO_4 at −5° to 0°, rising to 45°, and hydrolysis of (**I**) and (**II**) by conc. H_2SO_4 at 115° are described. The 6 dinitroanilines are converted into $C_6H_3Cl(NO_2)_2$ in 63—77% yield by NO·SO_3H–H_2SO_4–H_3PO_4 at −2° to 2° and then CuCl–HCl at 10° (later 80°); purification is effected by washing with conc. H_2SO_4 and chromatography (Al_2O_3). R. S. C.

Mechanism and kinetics of reactions involving free radicals.—See A., 1942, I, 147.

Manufacture of styrene derivatives.—See B., 1942, II, 5.

Syntheses in the carotenoid series. I. New preparation of hexatrienes. J. Schmitt (*Annalen*, 1941, **547**, 103—115).—In connexion with the possibility of synthesising β-dihydrocarotene and thence β-carotene, the interaction of the Mg derivative **I**) of Br·$[CH_2]_4$·Br with ketones and aldehydes has been investigated. This leads to αζ-diols, readily dehydrated to hexadienes which are easily transformed into hexatrienes. Gradual addition of $COPh_2$ to a filtered solution of (**I**) in Et_2O gives *aaζζ*-tetraphenylhexane-αζ-diol, m.p. 211°, converted by hot glacial AcOH into *aaζζ*-tetraphenyl-$\Delta^{a\varepsilon}$-hexadiene, m.p 105°, dehydrogenated by SeO_2 in gently boiling AcOH, by *p*-O:C_6H_4:O at 180°, or by Se at 300° to *aaζζ*-tetraphenyl-$\Delta^{a\gamma\varepsilon}$-hexatriene, m.p. 205°. Similarly (**I**) and fluorenone afford the very sparingly sol. *aζ-difluorenylhexane-aζ-diol*, m.p. 260° (decomp.), converted by $PhSO_3H$ in boiling Ac_2O into *aζ-didiphenylene-*$\Delta^{a\varepsilon}$*-hexadiene*, m.p. 211°, which with SeO_2 in boiling PhOMe–AcOH–H_2O yields aζ-didiphenylene-$\Delta^{a\gamma\varepsilon}$-hexatriene, m.p. 336°. COPhMe and (**I**) afford *βη-diphenyl-*n*-octane-βη-diol*, m.p. 160°, transformed by boiling HCO_2H into *βη-diphenyl-*$\Delta^{\beta\zeta}$*-octadiene*, b.p. 158—159°/1·5 mm., and thence by *p*-O·C_6H_4:O at 170—180° into an isomeric *-octadiene*, m.p. 64°. (**I**) and PhCHO give aζ-diphenylhexane-aζ-diol, m.p. 132°. H. W.

Preparation of Δ^8-, $\Delta^{8(14)}$-, and Δ^{14}-cholestenes. J. C. Eck and E. W. Hollingsworth (*J. Amer. Chem. Soc.*, 1941, **63**, 2986—2990).—Dehydration of cholestan-7-ol (best prepared from the ketone by Na–C_5H_{11}·OH) by $CuSO_4$ in boiling xylene containing a little $EtCO_2H$ gives Δ^8-*cholestene* (**I**), m.p. 85—86°, $[\alpha]_D^{18}$ +11·2° in CCl_4; in absence of $EtCO_2H$ some $\Delta^{8(14)}$-*cholestene* (**II**), m.p. 53—54°, $[\alpha]_D^{25}$ +21·2° in CCl_4, is also formed. (**II**) is best obtained by shaking (**I**) with Pd–H_2 in EtOAc. HCl–$CHCl_3$ at 0° converts (**I**) or (**II**) into Δ^{14}-*cholestene* (**III**), m.p. 73—74°, $[\alpha]_D^{21}$ +26·6° in CCl_4, and a small amount of a *cholestanol*, m.p. 119—120°, $[\alpha]_D^{22}$ +37·1° in CCl_4. The structure of (**I**) is deduced from oxidation by CrO_3–aq. H_2SO_4–AcOH–C_6H_6 to Δ^8-*cholesten-7-one*, m.p. 86·5—87·5°, $[\alpha]_D^{21}$ +3·8° in CCl_4 (absorption max. at 251 mμ.) (and a *diketone*, $C_{27}H_{44}O_2$, m.p. 74—75°, $[\alpha]_D^{24}$ −53·8° in CCl_4), reduced by Na–C_5H_{11}·OH to cholestan-7-one. Structures of (**II**) and (**III**) follow by analogy with other series and are confirmed by relationships of [α]. Hydrogenation of (**III**) gives cholestane [for (**I**) and (**II**) cf. above]. >1 mol. of Br is consumed by (**I**), (**II**), or (**III**) owing to liberation of HBr, but the exact amount depends on the solvent. ~2 mols. of BzO_2H are consumed by (**I**), (**II**), or (**III**). R. S. C.

Formation of an azulene on zinc dust distillation of pyrethrosin. M. S. Schechter and H. L. Haller (*J. Amer. Chem. Soc.*, 1941, **63**, 3507—3510).—Pyrethrosin (**I**) and Zn dust at ~300—550° give 1·5% of *pyrethrazulene*, a blue oil, possibly CMe<CH:C·CMe:CH / CH:C·CMe:CH>CH, since its absorption spectrum very closely resembles that of vetivazulene and its *s*-$C_6H_3(NO_2)_3$ *compound*, sinters at 165—166°, m.p. 167—168°, with $KMnO_4$ yields AcOH as sole acidic product. With PtO_2–H_2 in AcOH, (**I**) yields *tetrahydropyrethrosin*, m.p. 231—232°. R. S. C.

Purification of anthracene. O. C. Dermer and J. King (*J. Amer. Chem. Soc.*, 1941, **63**, 3232).—Anthracene is purified by conversion into the (CH·CO)$_2$O adduct and regenerated therefrom by sublimation from soda-lime. R. S. C.

Invert soaps of naphthalene. J. B. Niederl and H. Weingarten (*J. Amer. Chem. Soc.*, 1941, **63**, 3534—3535).—β-$C_{10}H_7$·NH_2 (**I**) and *n*-$C_{16}H_{33}Br$ in hot EtOH give *N-cetyl-β-naphthylamine*, m.p. 64° (*hydrobromide*, m.p. 161°), converted by hot MeI–K_2CO_3–EtOH into *β-naphthyldimethylcetylammonium iodide*, m.p. 106°. Bu^aBr and (**I**) in boiling BuOH give oily β-$C_{10}H_7$·$NHBu^a$, converted by boiling Bu^aBr into oily β-$C_{10}H_7$·NBu^a_2, which with MeI at room temp. gives *β-naphthylmethyldi-*n*-butylammonium iodide*, m.p. 157°. With an excess of Me_2SO_4 at 120°, (**I**) gives *β-naphthyltrimethylammonium methosulphate*, m.p. 288°. The PhOH coeff. of the quaternary salts is >0·2. R. S. C.

Interaction of betaine with primary aromatic amines, organic disulphides, and sodium sulphite. F. Challenger, P. Taylor, and (in part) B. Taylor (*J.C.S.*, 1942, 48—55).—Betaine (**I**) (free from hydrochloride) and NH_2Ph (reflux) give NHPh·CO·CH_2·NHPh, new m.p. 111—112° [*N*-NO-derivative, new m.p. 142—143° (decomp.)], NHPhMe, and NMe_3, but no NH_3, $NHMe_2$, or NH_2Me. (**I**) and *p*-C_6H_4Me·NH_2 similarly yield *p*-toluidinoacet-*p*-toluidide, new m.p. 133—134° [*NO*-derivative, m.p. 156—159° (decomp.)], and *p*-C_6H_4Me·NHMe; in some experiments a *base*, (?) (*p*-C_6H_4Me·NH·CO·CH_2)$_2$NMe, m.p. 143—144°, was also obtained. *p*-NH_2·C_6H_4·OR (R = Me, Et) affords *p*-anisidinoaceto-*p*-anisidide, m.p. 131—132° [*N-NO*-compound, m.p. 155—159° (decomp.) (rapid heating)], or *p*-phenetidinoaceto-*p*-phenetidide, m.p. 137—138°, and *p*-NHMe·C_6H_4·OR. β-$C_{10}H_7$·NH_2 and (**I**) at 200—220° yield β-$C_{10}H_7$·NHMe. (**I**) and Ph_2S_2 (reflux) afford an oil (contains PhSMe), converted by 3% aq. $KMnO_4$ at 100° into $PhSO_2Me$. $(Bu^aS)_2$ yields $MeSBu^a$, and (*n*-C_5H_{11}·S)$_2$ affords similarly MeS·C_5H_{11}-*n*. Oxidation (H_2O_2–AcOH at 100°) of the corresponding pure sulphide gives *methyl-*n*-butyl-*, m.p. 29—30°, or *-*n*-amylsulphone*, m.p. 35—36°, respectively. $^+NEt_3$·CH_2·CO_2^- and NH_2Ph (reflux) afford NHPhEt. No apparent reaction is observed with methionine and NH_2Ph at 190—210°. Only a little NHPhMe is isolated from NH_2Ph and paraformaldehyde (**II**) at 130—210°. (**I**) heated with Na_2SO_3 in CO_2 yields Me_2S, but no odour of Me_2Se or Me_2Te is observed when (**II**) is heated at 270° with Na_2SeO_3 or K_2TeO_3, respectively. Theoretical aspects are discussed. A. T. P.

Restricted rotation in arylamines. II. Preparation and resolution of *N*-β-carboxypropionyl-*N*-ethyl-3-bromomesidine and 4-*N*-β-carboxypropionyl-*N*-alkylamino-5-alkoxy-1 : 3-dimethylbenzenes. R. Adams and H. W. Stewart (*J. Amer. Chem. Soc.*, 1941, **63**, 2859—2864; cf. A., 1940, II, 339).—Mesidine is obtained from the NO_2-compound by Raney Ni–H_2 at 2—3 atm. Heating 1 : 3 : 5 : 4 : 2-C_6HMe_3Br·NH_2 and aq. Et_2SO_4 at ~80° (less well, 95°), conversion into the NO-derivative (*A*) by HCl–$NaNO_2$, and reduction thereof by $SnCl_2$–conc. HCl at 70—75° gives 3-*bromo-*N*-ethylmesidine* (N = 1) (**I**) (49·5%), b.p. 136—137°/4 mm.; the aq. mother-liquors from (*A*) at room temp. yield 1 : 3 : 5 : 4 : 2-C_6HMe_3Br·OH, m.p. 84—84·5° [lit. 81° (uncorr.)]. With $(CH_2$·$CO)_2O$ and a drop of H_3PO_4 in boiling C_6H_6, (**I**) gives N-β-*carboxypropionyl-*N*-ethyl-*3*-bromomesidine*, m.p. 111·5°, resolved by cinchonidine (not other bases) in EtOAc–MeOH into the d- (cinchonidine salt, m.p. 117—118°, [α] −41°) and l- (cinchonidine salt, m.p. 112·5—114·5°, [α] −66°) *-forms*, m.p. 104·5°, [α] ±25°, which in boiling Bu^aOH have a half-life ~28 hr. (cf. 9 hr. for the *N*-Me analogue, *loc. cit.*). *m*-5-Xylenol in Et_2O with aq. HNO_3 gives 36% of the 4- (**II**), m.p. 65—66°, and 25% of the 2-NO_2-compound, m.p. 108·5°. The dry Na salt of (**II**) with boiling Me_2SO_4–C_6H_6 gives 93·5% of the Me ether, m.p. 44—45°, reduced by Raney Ni–H_2 in 95% EtOH at 100°/135 atm. to 5 : 1 : 3 : 4-OMe·$C_6H_2Me_3$·NH_2 (**III**) (98·5%), m.p. 35·5—36·5°, b.p. 120—121°/10 mm. This yields as above 5-*methoxy-*N*-methyl-*m*-4-*xylidine* (60·8%), b.p. 61—62°/1·5 mm., the N-β-*carboxypropionyl* derivative (**IV**), m.p. 153·5°, of which is resolved to the d- (cinchonidine salt, m.p. 133—136°, [α] −56°) and l- (amorphous cinchonidine salt, [α] −46°) *-forms*, m.p. 152—153°, [α] ±13°, half-life in boiling MeOAc 2·7 hr. Addition of (**IV**) to fuming HNO_3 at 0° gives the 2 : 6-$(NO_2)_2$-derivative (99·2%), m.p. 178—178·5°, which, as also the amides described below, could not be resolved although it had p_H 2·92 whereas the other amides have p_H 3·97—4·06 (0·1M. solutions in 70% EtOH). With EtBr–H_2O at room temp., (**III**) gives the *N-Et* derivative (56·1%), b.p. 61—62°/1·5 mm. (N-β-*carboxypropionyl* derivative, m.p. 133·5°). The Na derivative of (**II**) gives, as above, *4-nitro-5-ethoxy-*m*-xylene*, m.p. 78·5°, *5-ethoxy-*m*-4-xylidine*, b.p. 73—74°/1 mm. [*hydrochloride*, sublimes at 190° (decomp.)], *5-ethoxy-*N*-methyl-*, b.p. 65—66°/1 mm. (N-β-*carboxypropionyl* derivative, m.p. 114·5°), and *-N-ethyl-*m*-4-xylidine*, b.p. 69—70°/1 mm. (N-β-*carboxypropionyl* derivative, m.p. 91·5°). M.p. are corr. [α] are $[\alpha]_D^{30}$ in abs. EtOH. R. S. C.

***N*¹-Silver derivatives of sulphanilamide and related compounds.** C. E. Braun and J. T. Towle (*J. Amer. Chem. Soc.*, 1941, **63**, 3523).—Addition of aq. $AgNO_3$ (1 mol.) to the Na derivatives of p-NH_2·C_6H_4·SO_2·NH_2, its *N*⁴-Ac derivative (prep. of the Na salt by conc. aq. NaOH described), or sulphapyridine give the N¹-*Ag* salts. R. S. C.

Derivatives of sulphanilamide and cholic acid.—See A., 1942, II, 146.

Chemotherapeutic studies; preparation of substituted sulphonamides. C. Marchant, C. C. Lucas, and L. McClelland (*Canad. J. Res.*, 1942, **20**, **B**, 5—16).—*p*-Acetamidobenzenesulphonamides, *p*-NHAc·C_6H_4·SO_2·NHR, are obtained by warming equimol. quantities of the reactants with $COMe_2$ containing C_5H_5N or by melting an intimate mixture of the acid chloride (1 mol.) and amine (2 mols.). NH_2-compounds are obtained by catalytic reduction of NO_2-compounds and CO_2Et-compounds by esterifying (HCl + EtOH) the requisite acids. Ac is removed by hydrolysis with boiling acid or alkali. *Sulphanilamides*, *p*-NH_2·C_6H_4·SO_2·NHR, are thus obtained (the m.p. of the N⁴-*Ac* derivatives are recorded in parentheses) in which R = *p*-, m.p. 165° (258°), *m*-, m.p. 169° (244°), and *o*-, m.p. 179° (200°) -NO_2·C_6H_4·; 3 : 6-, m.p. 199° (266·5°), and 3 : 4-, m.p. 189° (239°), -NO_2·C_6H_3Me·; 6 : 3-, m.p. 188° [261·5° (decomp.)], and 4 : 2-, m.p. 117° (175°), -OMe·$C_6H_3(NO_2)$·; *p*-, m.p. 138° (235°), *m*-, m.p. 177°, and *o*-, m.p. 208°, -NH_2·C_6H_4·; 3 : 6-, m.p. 208·5°, and 3 : 4-, m.p. 185°, -NH_2·C_6H_3Me·; 6 : 3-, m.p. 232°, and 4 : 2-, m.p. 195°, -OMe·$C_6H_3(NH_2)$·; *p*-, m.p. 190° (208°), *m*-, m.p. 133·5° (205°),

and *o*-, m.p. 155·5° (244·5°), -C_6H_4Me; *p*-, m.p. 194° (200°), *m*-, m.p. 163·5° (193°), and *o*-, m.p. 199° (212°), -OMe·C_6H_4·; *p*-, m.p. 197°, *m*-, m.p. 196° (274°), and *o*-, m.p. 226° (233°), -$CO_2H·C_6H_4$·; *p*-, m.p. 230°, *m*-, m.p. 105°, and *o*-, m.p. 165·5°, -$CO_2Et·C_6H_4$·; 2 : 6-, m.p. 231° (236·5°), and 2 : 4-, m.p. 149° (214·5°), -$C_6H_3Me_2$; 2 : 5-OMe·C_6H_3Me·, m.p. 161° (206°); 2 : 5-$C_6H_3MePr^\beta$, m.p. 150·5° (160·5°); *p*-C_6H_4Ac, m.p. 211° (254·5°); *p*-C_6H_4Bz, m.p. 181·5° (218·5°); *p*-C_6H_4Br, m.p. 178° (208°); OEt·$[CH_2]_2$·, m.p. 100° (150°); *p*-$AsO_3H_2·C_6H_4$·, m.p. — [275° (decomp.)]. *Disulphanilyl-p-phenylenediamine*, m.p. 263° (decomp.) [Ac_2 derivative, m.p. 316·5° (decomp.)], -m-*toluylenediamine*, m.p. 229° (Ac_2 derivative, m.p. 278°), and -*benzidine*, m.p. 290° (Ac_2 derivative, m.p. 288°), are described. M.p. are corr. H. W.

4-Amino-4′-di-β-hydroxyethylamino-2′-methylazobenzene. G. Shulman (*J. Amer. Chem. Soc.*, 1941, **63**, 3236—3237).—Coupling of *m*-$C_6H_4Me·N([CH_2]_2·OH)_2$ [prep. from *m*-$C_6H_4Me·NH_2$ by $(CH_2)_2O$ at >1 atm.) with *p*-$NO_2·C_6H_4·N_2Cl$ in HCl–NaOAc and reduction of the product by 10% cryst. Na_2S at 90° gives *4-amino-4′-di-β-hydroxyethylamino-2′-methylazobenzene*, orange, m.p. 149°, whence blue to black dyes are obtained by diazotisation and further coupling. R. S. C.

Decomposition of arylazo-β-naphthylamines by sodium nitrite and glacial acetic acid. H. H. Hodgson and C. K. Foster (*J.C.S.*, 1942, 30—33).—Many arylazo-β-naphthylamines are converted by $NaNO_2$–AcOH at 70°, then at room temp., into the unstable diazonium acetates, which are then decomposed to the corresponding arylazo-β-naphthyl acetates. These may be partly or wholly hydrolysed by the H_2O formed in the reaction to the naphthols as with, *e.g.*, *o*-$NO_2·C_6H_4·N_2·C_{10}H_6·NH_2$-*β*. The following are new: m-, m.p. 85°, and p-*fluoro*-, m.p. 120°, m-*chloro*-, m.p. 160°, 2 : 5-*dichloro*-, m.p. 168°, p-*iodo*-, m.p. 170°, 4-*bromo*-3-*nitro*-, m.p. 190°, 3-*nitro*-4-*methyl*-, m.p. 199°, 4-*chloro*-2-*nitro*-, m.p. 255°, 4-*bromo*-2-*nitro*-, m.p. 259°, and 3 : 5-*dinitro*-2-*hydroxy*-*benzeneazo*-β-*naphthylamine*, m.p. 274°; 4-, m.p. 214°, and 5-*nitro*-1-*naphthaleneazo*-β-*naphthylamine*, m.p. 212°; *benzeneazo*-β-*naphthyl acetate*, m.p. 117°; p-*fluoro*-, m.p. 130°, m-, m.p. 81°, and p-*chloro*-, m.p. 134°, p-*bromo*-, m.p. 136°, m-*nitro*-, m.p. 162°, 2-*nitro*-4-, m.p. 133°, and 3-*nitro*-4-*methyl*-, m.p. 157°, 4-*chloro*-2-*nitro*-, m.p. 163—164°, 4-*bromo*-2-, m.p. 160°, and -3-*nitro*-, m.p. 167°, 3 : 5-*dinitro*-2-*hydroxy*-, m.p. 184°, and p-*carboxy*-*benzeneazo*-β-*naphthyl acetate*, m.p. 206°; 4-, m.p. 155°, and 5-*nitronaphthaleneazo*-β-*naphthyl acetate*, m.p. 180°. A. T. P.

Preparation of aromatic sulphuric esters. J. Feigenbaum and C. A. Neuberg (*J. Amer. Chem. Soc.*, 1941, **63**, 3529—3530).—$ArKSO_4$ is best (90%; no distillation) obtained by adding, first, $ClSO_3H$ in the cold and then 50% aq. KOH to ArOH in $NPhMe_2$. For some phenols C_5H_5N is preferable to $NPhMe_2$. R. S. C.

Preparation and properties of three isomeric *n*-hexylcresols and their chlorinated derivatives. P. P. T. Sah and H. H. Anderson (*J. Amer. Chem. Soc.*, 1941, **63**, 3164—3167).—*o*-, *m*-, and *p*-Cresol with SO_2Cl_2 at room temp. (later warm) give 5-chloro-*o*- (~84%), m.p. 48—49°, b.p. 220—225°, 6-chloro-*m*- (~84%), m.p. 66°, b.p. 234—236°, and 3-chloro-*p*-cresol (77%), b.p. 195—197°. o-, b.p. 263—264°, m-, b.p. 280—283°, and p-*tolyl*, b.p. 268—270°, 5-*chloro*-o-, b.p. 280—283°, 6-*chloro*-m-, b.p. 286—288°, and 3-*chloro*-p-*tolyl*, b.p. 283—285°, n-*hexoate* (all prepared in 75—85% yield by *n*-$C_5H_{11}·COCl$ in boiling CCl_4) with $AlCl_3$ at 140° give 3-*n*-hexoyl-*o*- (50·5%), b.p. 131—132°/1 mm., 4-*n*-hexoyl-*m*- (85%), b.p. 135—137°/2 mm., and 3-*n*-hexoyl-*p*- (62%), b.p. 132—133°/2 mm., 5-*chloro*-3-n-*hexoyl*-o- (60%), b.p. 149—151°/1 mm., 6-chloro-4-*n*-hexoyl-*m*- (76%), m.p. 42—44°, b.p. 152—154°/1 mm., and 3-*chloro*-5-n-*hexoyl*-p- (62%), b.p. 150—152°/1 mm., -*cresol*, reduced by Zn–Hg–conc. HCl–EtOH–PhMe to 3-*n*-hexyl-*o*- (70%), b.p. 130—131°/1 mm., 4-*n*-hexyl-*m*- (90%), b.p. 132—133°/1 mm., 3-*n*-hexyl-*p*- (70%), b.p. 134—135°/1 mm., 5-*chloro*-3-n-*hexyl*-o- (90%), b.p. 140—142°/2 mm., 6-chloro-4-*n*-hexyl-*m*- (80%), m.p. 27—29°, b.p. 150—152°/1 mm., and 3-*chloro*-5-n-*hexyl*-p- (75%), b.p. 137—139°/1 mm., -*cresol*. The isomeric *n*-$C_6H_{13}·C_6H_4·OH$ are converted into the appropriate Cl-derivatives by SO_2Cl_2–CCl_4 in 60—65% yield. Chlorination reduces the toxicity of the *n*-hexylcresols to mice. R. S. C.

Synthesis of amyl- and hexyl-α-naphthol. Y. F. Chi and C. T. Jang (*J. Amer. Chem. Soc.*, 1941, **63**, 3155—3156).—α-$C_{10}H_7·OH$, RCO_2H, and $ZnCl_2$ give 2-n-, m.p. 75·5—76·5°, b.p. 160—168°/5 mm. (*oxime*, m.p. 115—117°; *semicarbazone*, m.p. 163—165°), and 2-iso-*valeryl*-, m.p. 65—66·5°, b.p. 150—155°/2 mm. (*oxime*, m.p. 149—151°; *semicarbazone*, m.p. 213—215°), and 2-n-*hexoyl*-, m.p. 62—63°, b.p. 180—186°/5 mm. (*oxime*, m.p. 97—99°; *semicarbazone*, m.p. 183—184°), reduced (Clemmensen) to 2-n-, m.p. 45—46·5°, b.p. 130—135°/5 mm., and 2-iso-*amyl*-, b.p. 135—140°/3 mm., and 2-n-*hexyl*-, m.p. 42—43°, b.p. 155—165°/3 mm., -1-*naphthol*, respectively. R. S. C.

Exchange reactions of 4-nitro-1-naphthyl methyl and ethyl ether with sodium ethoxide and methoxide, respectively, and the reduction of certain 1-nitronaphthalene derivatives. H. H. Hodgson and J. Habeshaw (*J.C.S.*, 1942, 45—47).—1 : 2-, 1 : 4-, or 2 : 1-$C_{10}H_6Cl·NO_2$ and 25% KOH–MeOH at 55° afford 2 : 1- 4 : 1- or 1 : 2-$NO_2·C_{10}H_6·OH$, respectively, in ~90% yield, whereas replacement of Cl in *o*- or *p*-$C_6H_4Cl·NO_2$ requires reaction under pressure. 4 : 1-$NO_2·C_{10}H_6·OMe$ (**I**) in NaOEt–EtOH at 65° yields 4 : 1-$NO_2·C_{10}H_6·OEt$ (**II**), reconverted by NaOMe–MeOH at 65° into (**I**). The use of NaOPr in similar experiments yielded amorphous substances. The mechanism of the exchange is discussed. 4 : 1-$C_{10}H_6Cl·NO_2$ or (**I**) and Zn–EtOH yield 4 : 4′-*dichloro*-, m.p. 262—263°, or 4 : 4′-*dimethoxy*-1 : 1′-*azonaphthalene*, m.p. 105—107°, respectively. Conditions are established for the reduction of (**I**) and (**II**) to the amines. A. T. P.

Carboxylic acid derivatives of 4 : 4′-diaminodiphenylsulphone. W. H. Gray and B. C. Platt (*J.C.S.*, 1942, 42—45).—4 : 4′-Diaminodiphenylsulphone (**I**) and $Et_2C_2O_4$ yield 4 : 4′-*biscarbethoxyformamido-diphenylsulphone*, m.p. 257°, converted by hot 2·5% aq. NaOH (6 min.) into 4-*amido*-4′-*carboxyformamido*-, froths at 195°, or by hot 0·5% KOH–EtOH (15 min.) into 4 : 4′-*biscarboxyformamido-diphenylsulphone*, froths at 188° to a solid, m.p. ~275°. (**I**) and $CO_2H·CH_2·COCl$ (modified prep.) in dioxan at 65° yield 4 : 4′-*biscarboxyacetamidodiphenylsulphone*, $+H_2O$, froths at 183° and loses CO_2 to give the 4 : 4′-$(NHAc)_2$-compound. (**I**) and $(CH_2·CO)_2O$ at 170° or 225° afford 4 : 4′-*bis*-β-*carboxypropionamido*-, m.p. 227° (converted into the imide), or 4 : 4′-*bis*-*succinimido*-*diphenylsulphone*, m.p. 343°, respectively. δ-Carbethoxyvaleryl or η-carbomethoxyoctoyl chloride and (**I**) in $COMe_2$–$CaCO_3$ (reflux) yield 4 : 4′-*bis*-δ-*carbethoxyvalerimido*-, m.p. 139°, or 4 : 4′-*bis*-η-*carbomethoxyoctamido-diphenylsulphone*, m.p. 122° (free *acid*, m.p. 134°), respectively. (**I**) (1 mol.) and *o*-$C_6H_4(CO)_2O$ (1 mol.) at 200°, or in C_5H_5N at 100° (bath), give 4-*amino*-4′-*phthalimidodiphenylsulphone* (**II**), m.p. 256—258°, also obtained from *o*-$CO_2H·C_6H_4·CO_2Me$ with or without $ZnCl_2$; 2 mols. of *o*-$C_6H_4(CO)_2O$ in C_5H_5N give the 4 : 4′-*bisphthalimido*-compound (**III**), m.p. 310°, also obtained from Me H or Et_2 phthalate. (**II**)–5% aq. NaOH at 100°, or (**III**)–0·5% KOH–EtOH, yield 4-*amino*-4′-*o*-*carboxybenzamido*-, froths at 176° [heat → (**II**)], or 4 : 4′-*bis*-*o*-*carboxybenzamido*-*diphenylsulphone*, m.p. 182° (decomp.) [heat → (**III**)], respectively. Camphoric anhydride and (**I**)–C_5H_5N (reflux) yield the 4 : 4′-*biscamphorimido*-compound (+0·5H_2O), m.p. 375°; pimelic, maleic, malic, glutamic, and quinolinic acid act similarly. Toxicity and coccicidal activity of the products are given. A. T. P.

Detoxication. XI. Identification of pyrocatechol-4-sulphonamide as a metabolic product of *p*-hydroxybenzenesulphonamide in the rabbit. Synthesis of derivatives of pyrocatecholsulphonamide. R. T. Williams (*Biochem. J.*, 1941, **35**, 1169—1174; cf. A., 1942, III, 334).—1 : 2 : 4-$(OH)_2C_6H_3·SO_3H$ [from *o*-$C_6H_4(OH)_2$ and conc. H_2SO_4 at 0°] with Ac_2O in C_5H_5N, followed by PCl_5 on the resulting C_5H_5N salt, yields 1 : 2-*diacetoxybenzene*-4-*sulphonyl chloride*, m.p. 116°, which with aq. NH_3, then dil. HCl, gives pyrocatechol-4-sulphonamide (**I**) (a resin), and with NH_2Ar in EtOAc yields the Ac_2 derivatives, m.p. 127—128°, 153°, and 131°, respectively, of *pyrocatechol*-4-*sulphonanilide*, m.p. 225° (decomp.), -m-*chloroanilide*, m.p. 177°, and -β-*naphthylamide*, m.p. 218° (decomp.). With Me_2SO_4, *p*-$OH·C_6H_4·SO_2·NH_2$ (**II**) yields *anisole*-p-*sulphondimethylamide*, m.p. 75. When the urine of rabbits fed with (**II**) is hydrolysed (HCl), extracted with Et_2O, the extracts acetylated, and the H_2O-sol. Ac derivatives hydrolysed and methylated (Me_2SO_4) it yields *veratrole*-4-*sulphondimethylamide*, m.p. 112°, also obtained (m.p. 113° and 115°, respectively) by methylating (**I**) or veratrole-4-sulphonamide. A. Li.

Reactions of hydrazoic acid. I. L. H. Briggs, G. C. de Ath, and (in part) S. R. Ellis (*J.C.S.*, 1942, 61—63).—$CHPh:CH·COMe$ and N_3H–$CHCl_3$–H_2SO_4 at 0°, rising to 60°, afford $CHPh:CH·CO·NHMe$, whereas $CH_2Ph·CH_2·COMe$ (2 : 4-*dinitrophenylhydrazone*, m.p. 131—132°) at 0° similarly yields $CH_2Ph·CH_2·NHAc$. $CH_2Ph·CHMe·COMe$ (2 : 4-*dinitrophenylhydrazone*, m.p. 81°) gives acet-β-phenyl*iso*propylamide. $CH_2Ph·CH(CO_2H)_2$ and N_3H–$CHCl_3$–dioxan–H_2SO_4 at 40° afford *dl*-phenylalanine in 16% yield. Podocarpic acid gives an amine, $C_{16}H_{23}ON$ [*sulphate*, m.p. 279° (decomp.)], in good yield; thus there is little steric hindrance in the Schmidt reaction. Esters also react; *e.g.*, MeOBz or EtOBz and N_3H in $CHCl_3$– or C_6H_6–H_2SO_4 give ~25% of NH_2Ph. *o*-, *m*-, or *p*-Toluic acid (at 40—45°) gives yields of 46, 70, or 24%, respectively, of the corresponding toluidines. Stearic acid (in C_6H_6 at 40°) affords *n*-$C_{17}H_{35}·NH_2$. N_3Me decomposes similarly to N_3H, but ketones and acids are unaffected during the reaction. A. T. P.

Potassium α-naphthyl*iso*propyl. R. D. Kleene (*J. Amer. Chem. Soc.*, 1941, **63**, 3539).—α-$C_{10}H_7·CMe_2·OH$, $NaNH_2$, and MeI in dioxan give the *Me ether*, b.p. 100—101°/3 mm., which with Na–K in Et_2O–N_2 gives α-$C_{10}H_7·CMe_2K$, converted by CO_2 into α-1-*naphthyl*-iso*butyric acid* (32%), m.p. 121—122°. R. S. C.

Factors which greatly increase the activity of the phenolic hydroxyl group of *l*-tyrosine. D. E. Bowman (*J. Biol. Chem.*, 1941, **141**, 877—887).—The rate at which *l*-tyrosine (**I**) reacts with I, $KMnO_4$, or $AgNO_3$ is usually very slow but may be greatly increased by the presence of a PO_4''' buffer, small increases in p_H greatly intensifying the reaction. In the presence of PO_4''' further marked acceleration results from a moderate increase of temp. until the reaction becomes

instantaneous. This reducing action of (I) may be attributed to the phenolic OH. It appears that the normal physiological state should provide the conditions necessary to support the increased activity of this group. This may explain why this group is capable of playing such a dominant rôle in the physiological action of various protein catalysts. H. W.

Derivatives of 1-phenyl*cyclo*alkane-1-carboxylic acids. R. D. Kleene (*J. Amer. Chem. Soc.*, 1941, **63**, 3538—3539).—1-*Phenyl*cyclo*butane*-1-*carboxyl-amide*, m.p. 75—76°, *-anilide*, m.p. 96—96·2°, *-p-toluidide*, m.p. 129—131°, and *-o-bromoanilide*, m.p. 82—83°, 1-*phenyl*cyclo*pentane*-1-*carboxyl-anilide*, m.p. 98—99°, *-p-toluidide*, m.p. 145—146°, and *-o-bromoanilide*, m.p. 75—76°, 1-*phenyl*cyclo*hexane*-1-*carboxyl-anilide*, m.p. 85—86°, *-p-toluidide*, m.p. 165—166°, and *-o-bromoanilide*, m.p. 167—169°, are prepared from the respective acid chlorides. R. S. C.

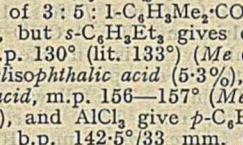
Synthesis and characterisation of *tert.*-naphthenic acids. B. Shive, W. W. Crouch, and H. L. Lochte (*J. Amer. Chem. Soc.*, 1941, **63**, 2979—2984).—*dl*-Camphor (cf. Forster, *J.C.S.*, 1896, **69**, 36, who used *l*-camphor) and Br at 100° give dl-*αα-dibromocamphor*, m.p. 54—55°, oxidised by HNO_3 (*d* 1·6) to dl-*dibromocampholide*, m.p. 138—139°, converted by Zn dust in boiling NH_3–EtOH–H_2O into dl-*bromocamphorenic acid*, m.p. 180—181°, which with Na–Hg in boiling H_2O gives dl-*camphorenic acid*, m.p. 165—166°. H_2–PtO_2 in AcOH then gives dl-*dihydrocamphorenic* [1 : 2 : 2-*trimethyl*cyclo*hexane*-1-*carboxylic*] *acid* (I), m.p. 179—180° (*amide*, m.p. 164—165°). Et 2-*iso*propyl*cyclo*hexanone-2-carboxylate and Zn–Hg–HCl give Et 1-*iso*propyl*cyclo*hexanecarboxylate (crude), b.p. 92—95°/10 mm., hydrolysed by conc. HCl at 140—150° to the *acid* (II), m.p. 104—105° (*anilide*, m.p. 101—102°). Et 2-*iso*propyl*cyclo*pentanone-2-carboxylate, b.p. 248—249°/750 mm., with boiling MgMeI–Et_2O, LiMe–Et_2O, or Mg–MeI–C_6H_6 gives a mixture, whence dehydration by boiling (1 atm.) with $KHSO_4$ gives *Et* 2-*methyl*-1-iso*propyl*-Δ^2-cyclo*pentenecarboxylate*, b.p. 221—222°/753 mm., which by hydrogenation and hydrolysis as above yields 2-*methyl*-1-iso*propyl*cyclo*pentanecarboxylic acid* (III), m.p. 52—53° (*Et* ester, b.p. 225—226°/745 mm.; *anilide*, m.p. 115—116°). Addition of 2-methylcyclopentanone and $CMe_2Br{\cdot}CO_2Et$ in Et_2O to Mg in much Et_2O gives *Et* α-*hydroxy*-α-2-*methyl*cyclo*pentyl*iso*butyrate*, b.p. 122—123°/12 mm., converted as above into *Et* α-2-*methyl*-Δ^1-cyclo*pentenyl*iso*butyrate*, b.p. 224—225°/753 mm., and α-2-*methyl*cyclo*pentyl*iso*butyric acid* (IV), b.p. 256—257°/743 mm. (*Et* ester, b.p. 225—226°/750 mm.; *anilide*, m.p. 102—103°). (I), (II), (III), and (IV) differ from an acid, $C_{10}H_{18}O_2$, obtained from Californian petroleum (Shive *et al.*), by degradation of a base therein (Roberts *et al.*), and ? from Iranian petroleum (Kennedy, B., 1940, 9). R. S. C.

Synthesis of 3 : 5-diethylbenzoic acid. H. R. Snyder, R. R. Adams, and A. V. McIntosh, jun. (*J. Amer. Chem. Soc.*, 1941, **63**, 3280—3282).—20·5% of 3 : 5 : 1-$C_6H_3Me_2{\cdot}CO_2H$ is obtained from *s*-$C_6H_3Me_3$ by HNO_3, but *s*-$C_6H_3Et_3$ gives only a little 3 : 5 : 1-$C_6H_3Et_2{\cdot}CO_2H$ (I), m.p. 130° (lit. 133°) (*Me* ester, b.p. 110—112°/3·5 mm.), with 5-*ethyl*isophthalic *acid* (5·3%), m.p. 265—266°, and 5-*aceto*-3-*ethylbenzoic acid*, m.p. 156—157° (*Me* ester, m.p. 77—78°). PhBr, EtBr (2 mols.), and $AlCl_3$ give *p*-$C_6H_4Br_2$ and *s*-$C_6H_3Et_3$. 2 : 4 : 1-$C_6H_3Et_2{\cdot}NH_2$, b.p. 142·5°/33 mm. (prep. from 2 : 4 : 1-$C_6H_3Et_2{\cdot}NO_2$, b.p. 112—114°/3·8 mm., by Raney Ni–H_2 in EtOH at 40—60°/1000—2000 lb.; 80—90% yield), with Br–AcOH–MeOH at <15° gives 6-*bromo*-2 : 4-*diethylaniline* (55%; ~40% in large-scale runs), b.p. 100—105°/1·5 mm., the diazonium salt from which with H_3PO_2 gives 5-*bromo*-1 : 3-*diethylbenzene* (70%), b.p. 115—119°/17 mm. Prep. of (I) therefrom by Grignard reactions is unsatisfactory, but CuCN in boiling C_5H_5N (bath : 235—240°) gives 3 : 5-*diethylbenzonitrile* (67%), b.p. 147·5—149°/29 mm., whence NaOH in boiling aq. $(CH_2{\cdot}OH)_2$ gives 85% of (I). R. S. C.

Cleavage of the alkyl–oxygen bond in the hydrolysis of esters. *tert.*-Butyl 2 : 4 : 6-trimethylbenzoate. S. G. Cohen and A. Schneider (*J. Amer. Chem. Soc.*, 1941, **63**, 3382—3388).—Cleavage of the O–alkyl linking of esters occurs during methanolysis or acid hydrolysis of *tert.*-alkyl esters. $Bu^{\gamma}OBz$ in boiling MeOH (4 days) gives $MeOBu^{\gamma}$ (60·7%) and BzOH (22·6%) with MeOBz (61·9%; produced from the liberated BzOH and MeOH); the $MeOBu^{\gamma}$ is a direct product, not being formed from $Bu^{\gamma}OH$ and MeOH in presence of BzOH [or (II); cf. below]. With NaOMe (0·1 mol.) in boiling, anhyd. MeOH, $Bu^{\gamma}OBz$ gives MeOBz (71·6%) and $Bu^{\gamma}OH$ (81·7%) and no $MeOBu^{\gamma}$. *Bu*$^{\gamma}$ 2 : 4 : 6-*trimethylbenzoate* (I) (prepared in 79% yield from the acid chloride and $Bu^{\gamma}OH$ in C_5H_5N, but not from the Ag salt and $Bu^{\gamma}Cl$), b.p. 142°/13 mm., in boiling MeOH (7 days) gives $MeOBu^{\gamma}$ (12·5%) and 2 : 4 : 6 : 1-$C_6H_2Me_3{\cdot}CO_2H$ (II) (6·1%) with 82·5% of unchanged (I), but is unaffected by NaOMe–MeOH. Similar cleavage of the O–alkyl linking occurs with esters of primary or *sec.* alcohols and strong acids (*e.g.*, Me_2SO_4), as evidenced by alcoholysis to ROR′. Alkaline hydrolysis occurs by addition of OH^- to give an intermediate $OH{\cdot}CR(:O^-){\cdot}OR'$. Acid hydrolysis (including alcoholysis) occurs by addition of H^+ to give $HO^+{:}CR{\cdot}OR' \rightleftharpoons OH{\cdot}CR^+{:}OR'$. In (I) the C but not the O is sterically hindered; thus, (I) is almost quantitatively converted into (II) by 39·5% HCl–MeOH at 0° or boiling 18% HCl, but boiling 20% NaOH is ineffective. Related results are shown by ROAc: alkaline hydrolysis decreases as R changes from Me to Bu^{γ}, but acid hydrolysis passes through a min. and that of $Bu^{\gamma}OAc$ is ~15% faster than that of MeOAc. R. S. C.

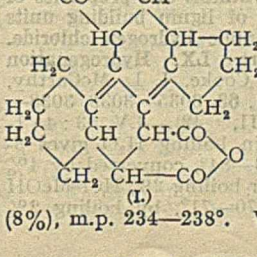
Resonance and the hindered carbonyl–Grignard reaction. I. R. T. Arnold, H. Bank, and R. W. Liggett (*J. Amer. Chem. Soc.*, 1941, **63**, 3444—3446).—Interaction of 2 : 4 : 6 : 1-$C_6H_2Me_3{\cdot}COMe$ with MgRX proceeds by formation of $[C_6H_2Me_3(=CH_2—H)=O—MgX]^+$, and thence of $C_6H_2Me_3{\cdot}C(:CH_2){\cdot}O{\cdot}MgX + H^+$ [gives RH]. If the COMe is replaced by $CO{\cdot}OR$, in which R is a resonating alkyl group, the R may be ejected in the same way as the H above. Thus, *allyl* iso*durylate* (prep. from the Na salt and $CH_2{:}CH{\cdot}CH_2Br$ at 130—160°), b.p. 115—117°/1 mm., with MgPhBr [or *o*-$C_6H_4Me{\cdot}MgBr$] in Et_2O gives $CH_2Ph{\cdot}CH{:}CH_2$ (I) (67—70%) [or *o*-$C_6H_4Me{\cdot}CH_2{\cdot}CH{:}CH_2$] and 2 : 4 : 6 : 1-$C_6H_2Me_3{\cdot}CO_2H$ (II) (95%). This reaction occurs only when the normal reaction is hindered; thus, *allyl αα-dimethyl*-n-*propionate*, b.p. 55—56°/36 mm., with MgPhBr gives $CPh_3Bu^{\gamma}{\cdot}OH$ and $CH_2{:}CH{\cdot}CH_2{\cdot}OBz$ gives $CPh_3{\cdot}OH$ (86%) and a little (I). One *o*-Me has little effect, for *allyl* o-*toluate*, b.p. 148°/45 mm., gives *o*-$C_6H_4Me{\cdot}CPh_2{\cdot}OH$ (68%) and an irresolvable mixture. 84% of (II) is obtained by adding 2 : 4 : 6 : 1-$C_6H_2Me_3{\cdot}MgBr$ in Et_2O to Et_2O through which CO_2 is passed, yields being lower by normal methods. *CH*$_2$*Ph* β-iso*durylate* (prep. from the Na salt and CH_2PhBr in boiling PhMe), b.p. 175—180°/6—8 mm., is also not cleaved by MgPhBr in Et_2O. R. S. C.

Structure of cantharidin and the synthesis of deoxycantharidin. R. B. Woodward and R. B. Loftfield (*J. Amer. Chem. Soc.*, 1941, **63**, 3167—3171).—Formulation of cantharidin (I) as 3 : 6-epoxy-*cis*-1 : 2-dimethyl*cyclo*hexane-1 : 2-dicarboxylic anhydride (A., 1929, 192) is confirmed by synthesis of deoxycantharidin (II). Condensation of $(:CMe{\cdot}CO)_2O$ (III) and $(CH_2{:}CH)_2$ in C_6H_6 at 190—205° (not at lower temp.) (72 hr.) and hydrolysis of the product by 10% aq. NaOH gives cis-1 : 2-*dimethyl*-Δ^4-cyclo*hexene*-1 : 2-*dicarboxylic acid* (IV), m.p. 202·4° (decomp.), converted by boiling AcCl into the *anhydride* (V), m.p. 99·2—99·6° [1 : 1 additive *compound*, m.p. 64—65°, with (III)], hydrogenated (PtO_2; EtOAc) to *cis*-1 : 2-dimethyl*cyclo*hexane-1 : 2-dicarboxylic anhydride, m.p. 129—129·2° [= (II), prep. of which (m.p. 126—128·5°) from (I) is described]. In boiling H_2O, (II) gives deoxycantharidinic acid, but the reverse transformation is also facile and occurs in H_2O, going to completion if the very volatile (II) can sublime away. With Br–AcOH (IV) gives the *bromo-lactone* (VI), m.p. 198·5—199°. With Br–$CHCl_3$, (V) gives a 4 : 5-*dibromide*, m.p. 179—180°, and 4-*bromo*-cis-1 : 2-*dimethyl*-Δ^4-cyclo*hexene*-1 : 2-*dicarboxylic anhydride*, m.p. 89—90° (indifferent to hot $AgNO_3$–EtOH). The evidence now available indicates that in (I) the O- and anhydride rings are probably on the same side of the *cyclo*hexane ring (*exo*-structure). R. S. C.


(VI.)

Isomerisation of naphthalyl chloride. H. E. French and J. E. Kircher (*J. Amer. Chem. Soc.*, 1941, **63**, 3270—3272).—1 : 8-$C_{10}H_6(COCl)_2$ (I) reacts partly in the cyclic form in the Friedel–Crafts reaction (cf. Mason, A., 1925, i, 33, 34). With $AlCl_3$ and C_6H_6 (1 mol.) it gives 50—60% of 1 : 8-$COPh{\cdot}C_{10}H_6{\cdot}CO_2H$ (II), but in one experiment yielded only 13% of (II) and ~40% of a *compound*, m.p. 235—236°, insol. in alkali. With $AlCl_3$ and an excess of C_6H_6, (I) gives (II) (45%), *αα-diphenyl*-1 : 8-*naphthalide* (20%) m.p. 202—203° (corr.) (adds one MgMeI; no active H), and *substances*, m.p. 226—228° (corr.) (7%) and 238—239° (corr.) (3%). Results with PhMe are similar (cf. *loc. cit.*). The structure of *p*-$C_6H_4Me{\cdot}CO{\cdot}C_{10}H_6{\cdot}CO_2H$-1 : 8 is established by decarboxylation to *p*-$C_6H_4Me{\cdot}CO{\cdot}C_{10}H_7$-α and that of *αα*-di-*p*-tolyl-1 : 8-naphthalide (yield ~80%), m.p. 235—236° (corr.), by addition of one MgMeI and absence of active H. The naphthalides are also prepared from 1 : 8-$C_{10}H_6(CO)_2O$ and LiAr. R. S. C.

Synthesis of condensed ring systems. V. Dianhydride of a steradiene-6 : 7 : 11 : 12-tetracarboxylic acid. L. W. Butz and L. M. Joshel. **VI. Dianhydrides of a tetradecahydrochrysene-1 : 2 : 7 : 8-tetracarboxylic acid and a homologue with an angular methyl group.** L. M. Joshel, L. W. Butz, and J. Feldman (*J. Amer. Chem. Soc.*, 1941, **63**, 3344—3347, 3348—3349).—V. Δ^1-*cyclo*Pentenyl-Δ^1-*cyclo*hexenylacetylene and $(:CH{\cdot}CO)_2O$ at 100—150° (not 70°) give 15—17% (in one experiment, 25%) of $\Delta^{8(14):9}$-*steradiene*-6 : 7 : 11 : 12-*tetracarboxylic anhydride* (I), m.p. 252—255° (vac.), 243—249° (air), or (+dioxan) 246—250°, with ~40% of amorphous alkali-sol. material. The C-skeleton of (I) is proved by conversion by Pd–C or Pd–C–$Ca(OH)_2$ at 260—340° and later 340—390° into 1 : 2-trimethylenephenanthrene. Boiling EtOH converts (I) into the 11-*carbethoxy*-12-*carboxy*-6 : 7-*dicarboxylic anhydride* (or an isomeride) (53%), m.p. 223—230° (gas) [at 250° gives (I)], and a *Et*$_4$ *steradiene*-6 : 7 : 11 : 12-*tetracarboxylate* (8%), m.p. 234—238°. With N-KOH at room temp., (I) gives the


(I.)

tetracarboxylic acid, m.p. 231—232° (decomp.), m.p. (+dioxan) 213—214° (decomp.) [Me_4 ester (**II**), m.p. 117·5—120·5°; absorbs Br]. Hydrogenation of (**I**) gives mixtures, but that (PtO_2; AcOH) of (**II**) gives Me_4 $\Delta^{8(9)}$-*sterene*-6 : 7 : 11 : 12-*tetracarboxylate* (**III**), m.p. (from MeOH) 165·4—166°, resolidifies, remelts at 168—174°, or (from $COMe_2$–MeOH) 164·5—170°. The following absorption max. and ε, respectively, in EtOH are recorded: (**I**) 2560 A., 19,000; 1 : 2 : 2*a* : 3 : 4 : 5 : 6 : 7 : 8 : 8*a* : 9 : 10 : 11 : 12-*tetradecahydrochrysene*-1 : 2 : 7 : 8- (**IV**; see below) 2570 A., 23,500, the derived 2*a*-*methyltetradecahydrochrysene*-1 : 2 : 7 : 8- (**V**; see below) 2540 A., 24,000, and 1 : 5-dimethylhexahydronaphthalene-3 : 4 : 7 : 8- 2470 A., 22,000, -tetracarboxylic anhydride; (**II**) 2560 A., 22,000; (**III**) <~2200 A., 5000.

VI. Di-Δ^1-*cyclo*hexenylacetylene and $(CH{\cdot}CO)_2O$ at 150° give the *dianhydride* (**IV**) (see above) (27%; 19% pure), m.p. 251—254° (vac.). Δ^1-*cyclo*Hexenyl-2′-methyl-$\Delta^{1'}$-*cyclo*hexenylacetylene gives similarly 1·9% of (**V**), m.p. 278—280° (vac.). Pd–C converts (**IV**) at 280—350° or (**V**) at 250—330° into chrysene and [from (**IV**)] a small amount of the *lactone*, m.p. 271·8—272·4°, of 2-hydroxymethylchrysene-1-carboxylic acid. M.p. are corr. R. S. C.

Detoxication. XII. Metabolism of vanillin and vanillic acid in the rabbit. Identification of glucurovanillin and structure of glucurovanillic acid. [Colour reaction for *p*-hydroxy- and *p*-methoxy-benzaldehyde.] H. G. Sammons and R. T. Williams (*Biochem. J.*, 1941, **35**, 1175—1189; cf. A., 1942, III, 334).—In the urine of rabbits fed on vanillin (**I**) or vanillic acid (**II**), (**I**) is determined (after hydrolysis) as 2 : 4-dinitrophenylhydrazone, free (**II**) by OMe (Zeisel), and glucurovanillin as the *β-naphthylhydrazone*, m.p. 179°, $[\alpha]_D^{20}$ −78·9° in MeOH, or 2 : 4-*dinitrophenylhydrazone*, decomp. 200° (shrinking at 150°), $[\alpha]_D^{21}$ −68·2° in dioxan, hydrolysed to (**I**). (**II**) is unaffected by dil. HCl under the conditions used for hydrolysing urine. Methylation (Me_2SO_4) of the crude Ba salt of glucurovanillic acid (**III**) from the urine yields veratric acid, its Me ester, and 2 : 3 : 4-*trimethyl*-o-*methoxy*-p-*carbomethoxyphenyl*-β-d-*glucuronide Me ester*, m.p. 137°, $[\alpha]_D^{23}$ −86·05° in $CHCl_3$, hydrolysed (MeOH–HCl) to Me 2 : 3 : 4-trimethyl-αβ-methylglucuronide. (**III**) is therefore a β-pyranuronoside. *p*-OH- and *p*-OMe-aldehydes in urine give an immediate red colour with naphthoresorcinol and conc. HCl in the cold. A. Li.

Normal and abnormal alkylation of 2-methyl*cyclo*pentyl methyl ketone. G. Wash, B. Shive, and H. L. Lochte (*J. Amer. Chem. Soc.*, 1941, **63**, 2975—2979).—1-Benzoyl-2-methyl*cyclo*pentane (**I**) (prep. from *cyclo*hexane by, successively, AcCl–$AlCl_3$, NaOBr, $SOCl_2$, and C_6H_6–$AlCl_3$), b.p. 281°, with $NaNH_2$ and RI in boiling C_6H_6 gives 1-*benzoyl*-1 : 2-*dimethyl*cyclo*pentane* (49%), b.p. 288° (*oxime*, m.p. 161—162°), 1-*benzoyl*-2-*methyl*-1-*ethyl*- (56%), b.p. 304° (*oxime*, m.p. 115—116°), -1-n-*propyl*- (27%), b.p. 312° (no oxime or semicarbazone), and -1-iso*propyl*- (26%), b.p. 315°, -cyclo*pentane*. The 1-Me and 1-Et derivatives with $NaNH_2$ and a little C_6H_6 or xylene, respectively, at room temp. give 1 : 2-*dimethyl*-, m.p. 98·5—99·5°, and 2-*methyl*-1-*ethyl*-cyclo*pentane*-1-*carboxylamide*, m.p. 84·5—85·5°, respectively, but the 1-Pr compounds are unaffected. The latter with O_3 give poor yields of 2-methyl-1-*n*- (*anilide*, m.p. 141—142°) and -1-*iso*-propyl*cyclo*pentane-1-carboxylic acid (*anilide*, m.p. 115—116°). 2-*Methyl*cyclo*pentanecarboxylanilide* has m.p. 107—108°. In xylene at 110—140° *C*-alkylation is replaced by (*a*) formation of 2-methyl*cyclo*pentanecarboxylamide and *N*-alkylation thereof and (*b*) formation of enol *O*-ethers. In boiling PhMe all three reactions occur. 2-*Methyl*cyclo*propanecarboxyl*-*ethyl*-, m.p. 86—87°, and -iso*propyl*-*amide*, m.p. 87—88°, are thus obtained and are also prepared from the acid chloride. 2-α-*iso*Propoxy-, -*n*-propoxy-, and -ethoxy-benzylidene-1-methyl*cyclo*pentane are obtained as oils and identified by ozonolysis. R. S. C.

Comparison of metallic chlorides as catalysts for the Friedel–Crafts ketone synthesis. O. C. Dermer, D. M. Wilson, F. M. Johnson, and V. H. Dermer (*J. Amer. Chem. Soc.*, 1941, **63**, 2881—2883).—Relative efficiencies for prep. of *p*-$C_6H_4Me{\cdot}COMe$ from PhMe and AcCl under optimum conditions are $AlCl_3 > SbCl_5 > FeCl_3 > TeCl_2 > SnCl_4 > TiCl_4 > TeCl_4 > BiCl_3 > ZnCl_2$. 28 other salts have no catalytic power at the b.p. of PhMe. In many cases >1 mol. of catalyst is required for max. yields, *e.g.*, 3 mols. of $TiCl_4$. Yields often decrease after too long contact, *e.g.*, with $SbCl_5$ and $AlCl_3$ activated by HCl (not pure $AlCl_3$). $PbCl_4$ has slight catalytic effect but causes mainly chlorination; this is also the main reaction if $SbCl_5$ is added first to the PhMe and the yield of ketone is then 2% as against a max. possible ~67%. R. S. C.

Lignin and related compounds. LV. Synthesis and properties of β-hydroxypropioveratrone. LVI. Stability of lignin building units and ethanol-lignin fractions towards ethanolic hydrogen chloride. K. A. West, W. L. Hawkins, and H. Hibbert. **LX. Hydrogenation of maple ethanolysis products. I.** L. M. Cooke, J. L. McCarthy, and H. Hibbert (*J. Amer. Chem. Soc.*, 1941, **63**, 3035—3038, 3038—3041, 3052—3056; cf. A., 1942, II, 42).—LV. 3 : 4 : 1-$(OMe)_2C_6H_3{\cdot}CO{\cdot}[CH_2]_2{\cdot}Cl$ (**I**) with Ag_2O in boiling H_2O gives *β-hydroxypropioveratrone* (**II**) (50%), m.p. 83—84°, converted by 4% KOH–MeOH at room temp. (20% yield) or boiling 2% HCl–MeOH (75% yield) into *β-methoxy*- (**III**), m.p. 70—71°, by boiling 2% HCl–EtOH into *β*-ethoxy- (**IV**) (96%), m.p. 50—51° (cf. A., 1939, II, 172), and by AcCl in C_5H_5N–C_6H_6 at 0° (90% yield) into *β-acetoxypropioveratrone* (**V**), m.p. 100—101°. With KOAc–AcOH at 100°, (**I**) gives 70% of (**V**), which with ~3% KOH–MeOH or –EtOH at room temp. gives (**III**) (90%) or (**IV**) (10%), respectively, and with Na_2CO_3 in aq. dioxan at room temp. gives *αβ-epoxypropioveratrone* (60%), m.p. 93—94° (2 : 4-*dinitrophenylhydrazone*, m.p. 182—183°) [not reconvertible into (**V**)]. 72% H_2SO_4 at room temp. converts (**II**) into a lignin-like material. Conversion of (**II**) into (**IV**) under the conditions of ethanolysis of lignin renders it improbable that substances such as (**II**) occur as free lignin-building units in wood.

LVI. Under the conditions of ethanolysis of lignin (boiling 2% HCl–EtOH–CO_2), α-hydroxy- or α-acetoxy-propiovanillone or -propiosyringone is converted into the corresponding α-OEt-ketone but the derived diketones are substantially unaffected. Admixture of OH-ketone and diketone does not affect the result. In all cases some resinification occurs, the amount increasing with rise in concn. of the ketone and being greater in the syringone than in the vanillone series. Interconversion of OH-ketone and diketone during ethanolysis of lignin is thus excluded and these two types must have different origins. Three maple EtOH-lignins are converted by boiling 2% HCl–EtOH into low-boiling oils and products of increased complexity (η), the extent of the conversion decreasing as the complexity of the lignin increases. Thus, the very complex polymerised-condensation products formed during ethanolysis of wood may be derived from less complex polymerides or from monomeric compounds initially present.

LX. With H_2–Cu chromite in dioxan at 250°/3000 lb., 4 : 3 : 1-$OH{\cdot}C_6H_3(OMe){\cdot}CO{\cdot}CHMe{\cdot}OEt$ gives 4-*n*-propyl*cyclo*hexanol (**VI**) and much H_2O with small amounts of MeOH and EtOH. Reaction proceeds by hydrogenolysis of OMe (and OEt) to OH + CH_4 (and C_2H_6), hydrogenolysis of the new OH, and reduction of CO to CH_2. That the yield of (**VI**) is only 78% may be due to hydrogenolysis of C·C linkings. The 4-*n*-propyl*cyclo*hexane-1 : 2-diol obtained by hydrogenolysis of MeOH-lignin from aspen (Harris *et al.*, A., 1938, II, 332) may be derived from syringyl components. Hydrogenation, as above, of 4-γ-hydroxy-*n*-propyl*cyclo*hexanol (**VII**) gives ~60% of (**VI**), so that the amount of γ-OH-compounds existing in lignin may exceed the small figure indicated by the yield of (**VII**) obtained from lignin (Harris *et al.*, *loc. cit.*). (**VII**) is identified by oxidation (improved to give 50% yield) to β-4-keto*cyclo*hexylpropionic acid, m.p. 62—64° (*semicarbazone*, m.p. 201—202°). *p*-$OMe{\cdot}C_6H_4{\cdot}[CH_2]_2{\cdot}CO_2Et$ and HI at 95° give *p*-$OH{\cdot}C_6H_4{\cdot}[CH_2]_2{\cdot}CO_2H$ (93%), m.p. 127—128°, the Et ester of which is hydrogenated (Raney Ni; EtOH; 210°/200 atm.) to Et β-4-hydroxy*cyclo*hexylpropionate, b.p. 114°/0·6 mm. R. S. C.

***cis–trans* Isomerides derived from 3 : 3-diphenyl-1-hydrindone. Synthesis of 3 : 3-diphenylhydrindene and its derivatives.** P. E. Gagnon and L. P. Charette (*Canad. J. Res.*, 1941, **19**, **B**, 275—290).—3 : 3-Diphenyl-1-hydrindone with ArCHO in MeOH–KOH gives the *trans*-isomeride only, which is converted into the *cis*-isomeride by boiling AcOH, with the exception of *o*-$OEt{\cdot}C_6H_4{\cdot}CHO$, where the *cis*-compound is obtained. The following are described: trans-3 : 3-*diphenyl*-2-o-*methyl*-, m.p. 190° (cis-*compound*, m.p. 176°), -m-*methyl*-, m.p. 175° (cis-*compound*, m.p. 104°), -o-*methoxy*-, m.p. 216° (cis-*compound*, m.p. 182°), -p-*methoxy*-, m.p. 163° (cis-*compound*, m.p. 133°), -o-*ethoxy*-, m.p. 161° (cis-*compound*, m.p. 153°), -o-*chloro*-, m.p. 197° (cis-*compound*, m.p. 151°), and -p-*chlorobenzylidene*-1-*hydrindone*, m.p. 201° (cis-*compound*, m.p. 176°). Reduction (Clemmensen) then affords 3 : 3-*diphenyl*-2-o-, m.p. 132°, and -m-*methyl*-, m.p. 149°, -o-, m.p. 176°, and -p-*methoxy*-, m.p. 178°, -o-*ethoxy*-, m.p. 170°, and -o-, m.p. 160°, and -p-*chloro-benzylhydrindene*, m.p. 156°. 3 : 3-*Diphenyl*-2-*benzylhydrindene* has m.p. 179°. F. R. S.

Acylation of the di-enolate of αδ-dimesitylbutane-αδ-dione. R. E. Lutz, W. G. Reveley, and V. R. Mattox (*J. Amer. Chem. Soc.*, 1941, **63**, 3171—3174).—*trans*-αδ-Dimesityl-Δβ-butene-αδ-dione (**I**) with H_2–PtO_2 in Ac_2O containing $ZnCl_2$ and HCl gives *αδ-diacetoxy-αδ-dimesityl-*$\Delta^{\alpha\gamma}$*-butadiene*, dimorphic, m.p. 172° and 162·5° (unaffected by light in I–$CHCl_3$), which with MgMeI shows 0·18 active H, adds 3·3 MgMeI, and gives αδ-dimesityl-*n*-butane-αδ-dione (**II**). The *cis*-isomeride of (**I**) resists hydrogenation, but gives under the above conditions 70—75% of 3-acetoxy-2 : 5-dimesitylfuran. Direct acylation of (**II**) failed, but with MgMeI (MgPhBr) in Et_2O–N_2 (**II**) gives the dienolate, converted by AcCl into $MgI{\cdot}O{\cdot}CX{:}CH{\cdot}CH(COMe){\cdot}COX$ (X = mesityl), which spontaneously yields 3-*mesitoyl*-5-*mesityl*-2-*methylfuran* (**III**), m.p. 204°, and a little ? *β-acetyl-α-acetoxy-αδ-dimesityl-*Δ^{α}*-buten-δ-one* (**IV**), m.p. 193°. In boiling 0·1N-NaOH–EtOH, (**IV**) gives the *enol*, m.p. 109—110° (red $FeCl_3$ colour), of β-acetyl-αδ-dimesitylbutane-αδ-dione, converted by Ac_2O–H_2SO_4 (drop) into (**III**). (**III**) is oxidised by HNO_3 to an enol, whence it is regenerated by Zn dust in boiling AcOH. The dienolate of (**II**) with BzCl–C_6H_6–*iso*amyl ether gives *dibenzoates*, m.p. 186·5° [hydrolysed to (**II**) by alkali] and 181° (hydrolysis leads to resins), respectively. *O*-Acetylation of (**II**) does not occur. R. S. C.

Acylation of the di-enolate of β-phenyl-αδ-dimesitylbutane-αδ-dione. R. E. Lutz and W. G. Reveley (*J. Amer. Chem. Soc.*, 1941,

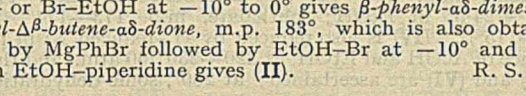
63, 3175—3178).—MgPhBr and (:CH·COMes)$_2$ (Mes = mesityl here and below) give a dienolate (I), MgBr·O·CMes:CH·CPh:CMes·O·MgBr, also formed from COMes·CH$_2$·CHPh·COMes and MgMeI. (I) is obtained similarly, but less well, from MgPhBr and (CHBr·COMes)$_2$. With AcCl in Et$_2$O–N$_2$ at >0°, (I) gives *βγ-diacetyl-β-phenyl-αδ-dimesityl-n-butane-αδ-dione enol acetate* (II), OAc·CMe:C(COMes)·CPhAc·COMes or OAc·CMe:CAc·CPhAc·COMes, m.p. 182°. With MgMeI at 100°, (II) gives 1 CH$_4$; in HCl–AcOH, (II) gives *βγ-diacetyl-β-phenyl-αδ-dimesityl-n-butan-αδ-dione enol* (III), m.p. 181·5° (with MgMeI gives 1 CH$_4$), converted by Ac$_2$O containing a little H$_2$SO$_4$ at room temp. into a *compound*, C$_{32}$H$_{32}$O$_6$S, m.p. 214·5°, and not acetylated by any reagents. Boiling NaOH–EtOH causes *C*-deacetylation of (II) or (III), yielding 3-*mesitoyl*-4-*phenyl*-5-*mesityl*-2-*methylfuran* (IV), m.p. 113° (proof of structure: following abstract). Aq. 25% NaOH and (II) give (IV) and (probably) *β-hydroxy-γ-phenyl-αδ-dimesityl-Δ^β-butene-αδ-dione*, m.p. 162·5°.

R. S. C.

1 : 4-Addition of magnesium methyl iodide to an αδ-unsaturated ketone system involving the ethylenic linking of a 2-aroylfuran, and ring-cleavage of the resulting vinyl allyl ether system. R. E. Lutz and W. G. Reveley (*J. Amer. Chem. Soc.*, 1941, **63**, 3178—3180).—3-Mesitoyl-4-phenyl-5-mesityl-2-methylfuran with MgMeI–Et$_2$O at room temp. (20 min.) and later in boiling Pr$^β_2$O–N$_2$ gives the dienolate (I), MgI·O·CMes:CPh·CBu^γ:CMes·O·MgI (Mes = mesityl), hydrolysed to *β-phenyl-αδ-dimesityl-γ*-tert.-*butyl*-n-*butane-αδ-dione* (II), m.p. 164·5°. Longer interaction in Et$_2$O alone gives, after hydrolysis, a compound, decomp. 125°, m.p. 176° (vac.). (II) is also obtained from COMes·CH:CBu^γ·COMes (III) and MgPhBr, but COMes·CH:CPh·COMes and MgBu^{γ}Cl give only COMes·CH$_2$·CHPh·COMes. With MgMeI, (II) generates 1 CH$_4$ rapidly at room temp. and a second slowly at 100°. Treatment of (I) with I– or Br–EtOH at −10° to 0° gives *β-phenyl-αδ-dimesityl-γ*-tert.-*butyl-Δ^β-butene-αδ-dione*, m.p. 183°, which is also obtained from (III) by MgPhBr followed by EtOH–Br at −10° and with H$_2$–PtO$_2$ in EtOH–piperidine gives (II).

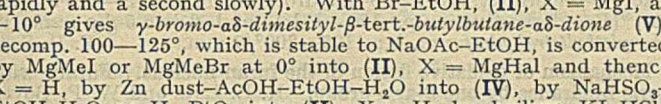
R. S. C.

Stereochemistry of the enols and dienols of αδ-dimesityl-β-tert.-butylbutane-αδ-dione. Proof of 1 : 4-reduction of an α-bromoketone. R. E. Lutz and W. G. Reveley (*J. Amer. Chem. Soc.*, 1941, **63**, 3180—3189).—Structures assigned below (discussed in detail) are proved by the reactions described. Isomeric monoenols are differentiated by letters *a* or *b*, and the position of the OH in the C$_4$-chain by numerals 1—4 (= α—δ), *e.g.*, a_1, b_4, etc. Dienols are differentiated as *A*, *B*, etc., the structure and position of the individual OH being added (when known) in parentheses, *e.g.*, *A* (a_4); when both OH can be described, the *A* etc. may be omitted. Thus, the α- and δ-monoenolates-*A* and -*B* of *αβδ*-trimesitylbutane-αδ-dione (A., 1940, II, 178) become respectively a_1, a_4, b_1, and b_4, and the dienolates-*A* and -*B* become *A* (a_1a_4) and *B* (b_1a_4), respectively. 3-Mesitoyl-5-mesityl-2-methylfuran and MgMeI (6 mols.) in boiling Et$_2$O–Pr$^β_2$O–N$_2$ give the dienolate-*A* (a_4) (I; Mes = mesityl, here and below), hydrolysed by dil. HCl to *αδ-dimesityl-β*-tert.-*butylbutane-αγ-dione enol*-a$_4$ [-Δ^γ-*buten*-δ-*ol*-α-*one*] (II; X = H), m.p. 197° (vac.). (:CH·COMes)$_2$ (III) and MgBu^{γ}Cl (5 mols.) at room temp. to −10° give a mixture of dienol and monoenolate-a_4 [(II), X =

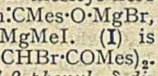


(I.) (II.)

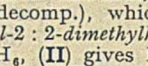
MgCl]. (II), X = H, and unaffected by CH$_2$N$_2$ or FeCl$_3$, yields 1 CH$_4$ with MgMeI at room temp. and is then regenerated by hydrolysis, and is converted by hot 2% KOH–MeOH into *αδ-dimesityl-β*-tert.-*butylbutane-αδ-dione* (IV), m.p. 112° (with MgMeI liberates 1 CH$_4$ rapidly and a second slowly). With Br–EtOH, (II), X = MgI, at −10° gives *γ-bromo-αδ-dimesityl-β*-tert.-*butylbutane-αδ-dione* (V), decomp. 100—125°, which is stable to NaOAc–EtOH, is converted by MgMeI or MgMeBr at 0° into (II), X = MgHal and thence X = H, by Zn dust–AcOH–EtOH–H$_2$O into (IV), by NaHSO$_3$–EtOH–H$_2$O or H$_2$–PtO$_2$ into (II), X = H, by boiling KI–HCl–EtOH (14 hr.) into 2 : 5-*dimesityl*-3-tert.-*butylfuran* (VI), m.p. 132°, by boiling Ac$_2$O-containing a little H$_2$SO$_4$ into 4-*bromo*-2 : 5-*dimesityl*-3-tert.-*butylfuran*, m.p. 189° [also obtained from (VI) by Br–CHCl$_3$], and by boiling KOH–EtOH into *αδ-dimesityl-β*-tert.-*butyl-Δ^β-butene-αδ-dione* (VII), m.p. 115° [reduced to (VI) by Zn dust in AcOH]. (VI) is also obtained from (IV) by boiling HCl–AcOH. The dienolate-*B* (a_4) (VIII) is obtained from (II), X =



(VIII.) (IX.) (X.)

MgHal, by MgMeI or MgMeBr, and characterised by alkaline hydrolysis to (IV), oxidation by I to (VII), and acid hydrolysis to (VI). The monoenolate-b_4 (? IX) is obtained from (IV) by MgMeHal and is reconverted into (IV) by hydrolysis. With MgMeI in boiling Pr$^β_2$O, (IX) gives the dienolate-*C* (b_4) (X), which in I–EtOH gives (VII) and (VI), and with H$_2$O$_2$, KOH–EtOH, or aq. HCl gives (IV). Grignard reactions probably proceed by way of complexes,  steric course of the reactions.

R. S. C.

Reaction between cyclic β-diketones and Grignard reagents. 1 : 3-Diketo-2 : 2-dimethylhydrindene. T. A. Geissman and V. Tulagin (*J. Amer. Chem. Soc.*, 1941, **63**, 3352—3356).—1 : 3-Diketo-2 : 2-dimethylhydrindene (1 mol.) with 0·25 mol. of MgPhBr in C$_6$H$_6$–Et$_2$O gives 75% of 1-*hydroxy*-3-*keto*-1-*phenyl*- (I), m.p. 141—142°, and with 3 mols. of MgPhBr gives 86% of 1 : 3-*dihydroxy*-1 : 3-*diphenyl*- (II), m.p. 141—142° [mixed with (I), 115—125°], -2 : 2-*dimethylhydrindene*; equimol. proportions give approx. equal amounts of (I) and (II). The structures of (I) and (II) are proved by oxidation by K$_2$Cr$_2$O$_7$–AcOH to *o*-COPh·C$_6$H$_4$·CO$_2$H and by HNO$_3$ to *o*-C$_6$H$_4$(COPh)$_2$, respectively. With HCl–ROH, (I) gives 3-keto-1-methoxy- (III), m.p. 160—162°, and 3-*keto*-1-*ethoxy*-, m.p. 135—136° -1-*phenyl*-2 : 2-*dimethylhydrindene*. MgPhBr in C$_6$H$_6$ converts (III) into the Me$_2$ ether (IV), m.p. 171·0—171·3° (lit. 172—174°), of (II). With MeOH–HCl, (II) or (IV) gives a Cl-compound, m.p. 172—174° (decomp.), which in boiling MeOH gives 1 : 3-*epoxy*-1 : 3-*diphenyl*-2 : 2-*dimethylhydrindene* (V), m.p. 70°. With HCl–CaCl$_2$ in C$_6$H$_6$, (II) gives 1 : 3-*dichloro*-1 : 3-*diphenyl*-2 : 2-*dimethylhydrindene*, m.p. 177—178°, converted into (V) by boiling MeOH. Attempts to effect cleavage of (I) by MgPhBr (to give *o*-COPr^β·C$_6$H$_4$·CPh$_2$·OH) failed. The mechanism of cleavage of 1 : 3-diketones by Grignard reagents is discussed; such cleavage is held to necessitate formation of an intermediate, 

R. S. C.

Preparation of 2-methyl-3-*n*-hexadecyl-1 : 4-naphthaquinone. M. Tishler and N. L. Wendler (*J. Amer. Chem. Soc.*, 1941, **63**, 3235—3236).—2-Methyl-5 : 6 : 7 : 8-tetrahydronaphthalene, C$_{15}$H$_{31}$·COCl, and AlCl$_3$ in CS$_2$ give 3-n-*hexadecoyl*-2-*methyl*-, m.p. 53—55°, reduced (Clemmensen) to 2-*methyl*-3-n-*hexadecyl*-5 : 6 : 7 : 8-*tetrahydronaphthalene*, m.p. 45°. S at 205—220° then gives 2-methyl-3-*n*-hexadecylnaphthalene, m.p. 38—40°, oxidised by CrO$_3$–AcOH at room temp. and later 60° to 2-*methyl*-3-n-*hexadecyl*-1 : 4-*naphthaquinone*, m.p. 98—98·5° (*quinol diacetate*, m.p. 78—79°). The curative dose (vitamin-*K*; chicks; 18 hr.) is 0·2—0·3 mg.

R. S. C.

Preparation and properties of phthiocol inner complexes. B. P. Geyer [with G. McP. Smith] (*J. Amer. Chem. Soc.*, 1941, **63**, 3071—3075).—2-Hydroxy-3-methyl-1 : 4-naphthaquinone (I) and a metal salt in MeOH or aq. MeOH give chelated *Co*^{II}, *Cu*^{II}, *Fe*^{II}, *Mg*, *Mn*^{II}, *Ni*^{II}, *UO$_2$*, *Zn*, and *Fe*^{III} derivatives (*A*), some of which separate +MeOH (lost at 150°). The ppts. always contain free (I) which is removed by sublimation. (*A*) are highly coloured, stable up to 200°, insol. in H$_2$O, Et$_2$O, COMe$_2$, *n*-C$_5$H$_{11}$·COMe, or PhCl, somewhat sol. in MeOH, Bu^{α}OH, or PhNO$_2$, decomposed by HCl, NaOH, or dissolution in dioxan. The colour depends on the chelation but the exact position of the absorption max. (recorded) depends on the metal. Catalytic activity for the luminescence of luminol is evinced by (*A*) in the relative order, Co ≫ Cu > Fe^{II} > Fe^{III} > Ni > Mn, the other derivatives being inactive. Details of this effect are studied mainly with the very active Co derivative. EtOH increases the effect but shortens its duration. An inorg. salt of the metal has no catalytic effect and extinguishes the light due to the organo-metallic complex.

R. S. C.

IV.—STEROLS AND STEROID SAPOGENINS.

Preparation of Δ^8-, Δ$^{8(14)}$-, and Δ^{14}-cholestenes.—See A., 1942, II, 137.

Derivatives of sulphanilamide and cholic acid. G. A. D. Haslewood (*Biochem. J.*, 1941, **35**, 1307—1310).—Triformylcholyl chloride and *p*-NH$_2$·C$_6$H$_4$·SO$_2$·NH$_2$–C$_5$H$_5$N at 100° (1 hr.) yield *N-phenylcholamide*-p-*sulphonamide*, m.p. 244—246° (decomp.). Cholylhydrazine (I) and *p*-NHAc·C$_6$H$_4$·SO$_2$Cl (II)–C$_5$H$_5$N at 40° afford a product (III), decomp. >180° (softens ~160°), hydrolysed by boiling 2N-NaOH to (probably) *α-cholyl-β*-p-*aminobenzenesulphonylhydrazine* (IV), m.p. ~150°, decomp. >200°. (I), (III), or (IV) and boiling aq. NaOH give cholic acid, oxidised by CrO$_3$–AcOH to dehydrocholic acid, also obtained by oxidation of (III) or (IV). NHBz·NH$_2$ and (II) in C$_5$H$_5$N yield *α-benzoyl-β*-p-*acetamido*-, m.p. 219—220° (decomp.), and thence (aq. NaOH) *-amino-benzenesulphonylhydrazine*, m.p. 190—192° (decomp.).

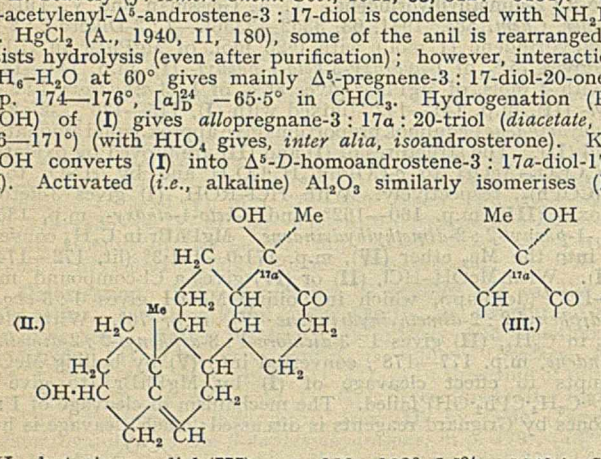
A. T. P.

Preparation of unsaturated steroids from steryl sulphates. A. E. Sobel and M. J. Rosen (*J. Amer. Chem. Soc.*, 1941, **63**, 3536—3537).—K cholesteryl sulphate (I) with RONa–ROH (R = *n*-C$_6$H$_{13}$·CHMe) at the b.p. (177°) gives 88% of pure Δ$^{3:5}$-cholestadiene, m.p. 79·5—80°, [α]$_D^{26}$ −123·2° in CCl$_4$. In absence of a solvent, (I) at 160° or 180° gives impure cholesterylene. With NaOBu^α–Bu^{α}OH at 120°, (I) gives the mixed salt, Na(C$_{27}$H$_{45}$)SO$_4$,2K(C$_{27}$H$_{45}$)SO$_4$, m.p. 174—178° (decomp.). With RONa–ROH (R = *n*-C$_6$H$_{13}$·CHMe) at 169°, K cholestanyl sulphate gives the salt, Na(C$_{27}$H$_{47}$)SO$_4$,K(C$_{27}$H$_{47}$)SO$_4$,

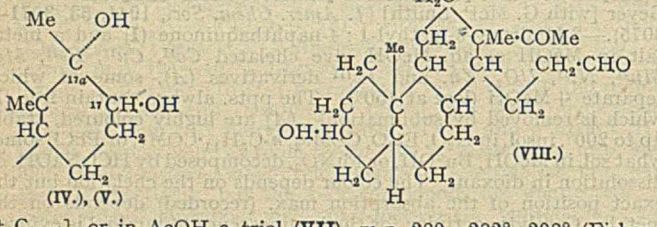
m.p. 234° (decomp.). In absence of NaOAlk hydrolysis is the main reaction. R. S. C.

Deoxycorticosterone β-glucoside tetra-acetate.—See A., 1942, II, 134.

Molecular rearrangement of 17-hydroxypregnane compounds. H. E. Stavely (*J. Amer. Chem. Soc.*, 1941, **63**, 3127—3131).—When 17-acetylenyl-Δ^5-androstene-3 : 17-diol is condensed with NH_2Ph in aq. $HgCl_2$ (A., 1940, II, 180), some of the anil is rearranged and resists hydrolysis (even after purification); however, interaction in C_6H_6–H_2O at 60° gives mainly Δ^5-pregnene-3 : 17-diol-20-one (**I**), m.p. 174—176°, $[\alpha]_D^{24}$ −65·5° in $CHCl_3$. Hydrogenation (PtO_2; EtOH) of (**I**) gives *allo*pregnane-3 : 17*a* : 20-triol (*diacetate*, m.p. 166—171°) (with HIO_4 gives, *inter alia*, *iso*androsterone). KOH–EtOH converts (**I**) into Δ^5-*D*-homoandrostene-3 : 17*a*-diol-17-one (**II**). Activated (*i.e.*, alkaline) Al_2O_3 similarly isomerises (**I**) in



C_6H_6, but gives a *diol* (**III**), m.p. 180—182°, $[\alpha]_D^{24}$ −104° in $CHCl_3$ (*acetate*, m.p. 174—176°, $[\alpha]_D^{25}$ −98° in $CHCl_3$), isomeric at $C_{(17a)}$ with (**II**). Oxidation of (**I**) by boiling Al(OPr$^\beta$)$_3$–*cyclo*hexanone–PhMe and chromatography (Al_2O_3) of the product gives Δ^4-D-*homoandrosten*-17a-*ol*-3 : 17-*dione* [$C_{(17a)}$ as in (**III**)], m.p. 180°, $[\alpha]_D^{23}$ +60° in $CHCl_3$ (*dioxime*, m.p. 255°), stable to boiling 5% KOH–MeOH, which is also obtained from (**III**) by Al(OPr$^\beta$)$_3$–(?)*cyclo*hexanone. Hydrogenation (PtO_2) of (**III**) in EtOH gives D-*homoandrostane*-3 : 17 : 17*a*-*triol* (**IV**), m.p. 259—261° (*mono*-, sinters at 185°, m.p. 190°, and *tri-acetate*, m.p. 247—250°), or in AcOH a *triol* (**V**), m.p. 272—274°, isomeric with (**IV**) only at $C_{(17)}$. Hydrogenation of (**II**) in EtOH gives similarly a *triol* (**VI**), m.p. 256—258° [*di*-, m.p. 220—222°, and *tri-acetate*, m.p. 227°; isomeric with (**IV**)



at $C_{(17a)}$], or in AcOH a triol (**VII**), m.p. 280—282°, 298° (Fisher–Johns apparatus) (lit. 304°) [isomeric with (**V**) at $C_{(17a)}$]. HIO_4 oxidises (**IV**) in aq. MeOH to the *keto-aldehyde* (**VIII**), m.p. 150—152° (*oxime*, m.p. 188—191°, ? of an aldol condensation product; *semicarbazone*, m.p. 187°), which in boiling 5% KOH–MeOH gives a substance, m.p. 181—187°. HIO_4 does not affect (**VI**). CrO_3 oxidises (**V**) or (**VII**) to the same acid, $C_{21}H_{32}O_4$, m.p. 214—216°, 222—225° (Fisher–Johns apparatus) $\alpha \pm 0°$ (Me ester, m.p. 103—105°) (Ruzicka *et al.*, A., 1939, II, 327). R. S. C.

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Complete syntheses of pinocamphone, pinonic acid, and α-pinene. G. Komppa, A. Klami, and A. M. Kuvaja (*Annalen*, 1941, **547**, 185—194).—Successive treatments of verbanone (**I**) with Na and I in Et_2O give a dark brown oil, transformed by NaOH–EtOH into a product which does not afford a cryst. semicarbazone. Gradual addition of Br to (**I**) in $CHCl_3$ gives impure dl-*bromoverbanone*, b.p. 100—115°/3 mm., which regenerates (**I**) when boiled with KOH–EtOH. OBr′ and (**I**) do not give a Br-compound. dl-*Chloroverbanone*, obtained by passing Cl_2 through a solution of (**I**) in $CHCl_3$ containing $CaCO_3$, is converted by NaOEt into (**I**) and by NaOBu into a liquid of ill-defined b.p. from which a semicarbazone could not be obtained; when boiled with $NPhMe_2$ or treated with Zn dust it regenerates (**I**). Oximinoverbanone is reduced (H_2–PtO_2–EtOH) to dl-*aminoverbanol*, m.p. 124° [*hydrochloride* (**II**), m.p. 253°; *platinichloride*, m.p. 255° (decomp.); *Ac* derivative, m.p. (anhyd.) 110—114°]; reduction with Zn dust and AcOH gives much less satisfactory results. Treatment of (**II**) with PCl_5 gives a stereoisomeric *amine*, m.p. 111—114° (*hydrochloride*, m.p. 261°). *l*-Verbanone, $[\alpha]_D$ −36·34° (the substance is optically non-homogeneous), is converted by $NaNH_2$ in Et_2O followed by CO_2 into *verbanonecarboxylic acid* (**III**), m.p. 101—102° (decomp.), which loses CO_2 when preserved or, more rapidly, when warmed, and a cryst. *compound*, $C_{10}H_{17}O_3N$, m.p. 170—172°. With NH_2·CO·NH·NH_2 (**III**) affords verbanonesemicarbazone. Reduction of (**III**) at a K–Hg cathode gives *verbanolcarboxylic acid*, m.p. 144—145°. This loses H_2O when heated with Ac_2O, giving d-δ-*pinenecarboxylic acid*, m.p. 123°, $[\alpha]_D$ +10·56° in $CHCl_3$, converted by $SOCl_2$ into the *chloride* (**IV**), b.p. 112—115°/7 mm., and thence (NH_3) into the *amide*, m.p. 142°. Activated $NaNH_2$ in PhMe at 90° and finally at 130° followed by conc. HCl transforms (**IV**) into *l*-pinocamphone (**V**), b.p. 212—214°, $[\alpha]_D$ −11·12° (semicarbazone, m.p. 226—228°). (**V**) is oxidised by aq. $KMnO_4$ to *dl*-pinonic acid (**VI**), m.p. 103° (semicarbazone, m.p. 203—204°). The transformation of (**V**) and (**VI**) into α-pinene has been described by Ruzicka *et al.* (A., 1921, i, 36, 796; 1924, i, 755). H. W.

Camphor, borneol, and allied substances. S. Yamada (*Bull. Chem. Soc. Japan*, 1941, **16**, 239—251).—Catalytic oxidation of borneol (**I**) using one type of reduced Cu catalyst at 400° for 2 hr., or reduced Ni at 300°, affords 96 or 90% of camphor (**II**), respectively; *iso*borneol (**III**) yields similarly, 86 or 89% of (**II**), respectively. Catalytic (reduced Ni) reduction and rearrangement of (**I**), (**II**), and (**III**) at high temp. and pressures are studied; (**II**) is determined by semicarbazone process, and (**I**) and (**III**) are calc. from vals. of $[\alpha]_D$. (**II**) at 140—160°/80 atm. (initial pressure) yields almost equal amounts of (**I**) and (**III**); (**I**) at 170—190°/71 atm. gives only 1% of (**III**), and (**III**) at 130—150°/53 atm. yields 84% of (**I**), with traces of (**II**). Other experiments are carried out in presence of EtOH, AcOH, C_5H_5N, or *cyclo*hexane. αα′-Dimethylcamphor (**IV**) and Na–EtOH give dimethylborneol (**V**), m.p. 57°, $[\alpha]_D^{26}$ +50·72° in EtOH (phenylurethane, m.p. 112—113°; *p*-nitrobenzoate, m.p. 115—115·8°, $[\alpha]_D^{25}$ +50·94° in EtOH; phthalate, m.p. 177—178°, $[\alpha]_D^{27}$ +16·32° in EtOH; Mg phthalate, m.p. 175—176·2°), and dimethyl*iso*borneol (**VI**), m.p. 47—49°, $[\alpha]_D^{15}$ +36·47° in EtOH [phenylurethane, m.p. 116—117°; *p*-nitrobenzoate, m.p. 114·5—115°, $[\alpha]_D^{19}$ +24·9° in EtOH; phthalate, m.p. 173—174° (formed at 110—115°)]. (**IV**) is also reduced by H_2–reduced Ni in presence or absence of AcOH and EtOH, at 220—230°/60 atm., and the amounts of (**V**) and (**VI**) are ascertained; at 280°, some dehydration occurs. A. T. P.

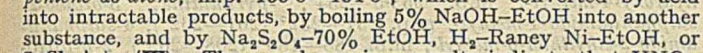
Sapogenins. XII. Position of the carboxyl group in certain triterpene acids. P. Bilham, G. A. R. Kon, and W. C. J. Ross (*J.C.S.*, 1942, 35—42).—Reduction (Clemmensen) of either Me β-boswellenonate or Me β-boswellenedionate gives *Me β-boswellanate*, m.p. 166—167°, $[\alpha]_D$ +131·3° in $CHCl_3$, which could not be saponified. Similar reduction of the Me ester of dihydrobetulonic acid (**I**) affords *Me dihydrobetulanate*, m.p. 166—167°, saponified in very small yield to *dihydrobetulanic acid*, m.p. 293°, more conveniently prepared by reduction of (**I**). The abnormal behaviour of unimol. films of hedraganic acid is not attributable to collapse. Measurements on derivatives of β-boswellic, ursolic, and betulic acid, in which there are no polar groups apart from CO_2H, support the conclusion that in these compounds also the polar group is attached to a terminal ring. The constitution of these triterpenes is discussed. F. R. S.

VI.—HETEROCYCLIC.

Benz*cyclo*octatetraenes. II. Action of acetic anhydride on δ-benzylidenelævulic acids. W. S. Rapson and R. G. Shuttleworth (*J.C.S.*, 1942, 33—35).—δ-Benzylidenelævulic acid and Ac_2O give 2-*keto*-5-*styryl*-2 : 3-*dihydrofuran* (**I**), m.p. 95·5° (cf. Sen and Roy, A., 1930, 1181), which is reduced (Pd–$SrCO_3$–H_2) to 2-*keto*-5-β-*phenylethyltetrahydrofuran*, b.p. 173—175°/7 mm. With the appropriate BzCl derivative (**I**) affords Bz_2, m.p. 177·5—178·5° (lit. 160°), *di*-o-*chloro*-, m.p. 159·5—160°, and *di*-o-*iodo-benzoyl* derivatives, m.p. 192—193°. In the OMe series, the following are described: 2-keto-5-*p*-methoxystyryl-2 : 3-dihydrofuran, m.p. 115—115·5° (lit. 78°) (Bz_2 derivative, m.p. 170—171°), and 2-*keto*-5-β-p-*methoxyphenylethyltetrahydrofuran*, b.p. 195—200°/5 mm. F. R. S.

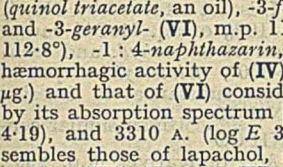
Mechanism of oxidative fission of the furan nucleus. Furans with steric hindrance by one 2-aryl group. R. E. Lutz and W. P. Boyer (*J. Amer. Chem. Soc.*, 1941, **63**, 3189—3192).—*trans*-COMes·CH:CH·CO_2H (Mes = mesityl) [prep. from *s*-$C_6H_3Me_3$, (:CH·CO)$_2O$, and $AlCl_3$ in $(CHCl_2)_2$; 62·5% yield], m.p. 134—137°, with PCl_5 and then $AlCl_3$ in C_6H_6 gives *trans*-COMes·CH:CH·COPh (38—48%), m.p. 60—61°, which does not give the *cis*-isomeride in light, absorbs >1 H_2 (Raney Ni) and after absorption of 1 H_2 gives compounds, m.p. 202·5—203·5° and [? α-*phenyl*-δ-*mesitylbutan*-α(or δ)-*ol*-δ(or α)-*one*], m.p. 86—87°, and with $Na_2S_2O_4$ in boiling 70% EtOH gives α-*phenyl*-δ-*mesitylbutane*-αδ-*dione*, m.p. 52—53°. With warm $SnCl_2$–conc. HCl–AcOH this gives 2-*phenyl*-5-*mesitylfuran*, m.p. 30·5—31°, whence only oils are obtained by HNO_3–AcOH. *p*-C_6H_4Br·CO·CH:CH·COCl, m.p. 100—102°, with *s*-$C_6H_3Me_3$–$AlCl_3$–$(CHCl_2)_2$ gives trans-α-p-*bromophenyl*-δ-*mesityl*-Δ^β-*butene*-αδ-*dione* (79%), m.p. 96—97°, converted by sunlight in C_6H_6 into the cis-*isomeride* (**I**), m.p. 77·5—78°, reduced by $Na_2S_2O_4$–70% EtOH to α-p-*bromophenyl*-δ-*mesitylbutane*-αδ-*dione* (**II**), m.p. 99·5—100°, and reduced and cyclised by $SnCl_2$–conc. HCl–AcOH to 2-p-*bromophenyl*-5-*mesitylfuran* (**III**), m.p. 84° (or, in a preheated bath, 78°, resolidifies, remelts at 84°) [obtained also similarly from (**II**)]. HNO_3–$EtCO_2H$ at −12° to −3° oxidises (**III**) to (**I**). 3-Mesitoyl-4-

phenyl-5-mesityl-2-methylfuran (**IV**) is oxidised by HNO_3–AcOH at 40—45° (cf. A., 1942, II, 144) to *γ-mesitoyl-β-phenyl-α-mesityl-Δβ-n-pentene-αδ-dione*, m.p. 133·5—134·5°, which is converted by acid into intractable products, by boiling 5% NaOH–EtOH into another substance, and by $Na_2S_2O_4$–70% EtOH, H_2–Raney Ni–EtOH, or $SnCl_2$ into (**IV**). These and previous results indicate that HNO_3-oxidation proceeds by the steps



R. S. C.

Condensation of allylic alcohols with hydroxyquinones. L. F. Fieser and M. D. Gates, jun. (*J. Amer. Chem. Soc.*, 1941, **63**, 2948—2953).—2 : 5 : 1 : 4-$(OMe)_2C_6H_2(OH)_2$ [not 1 : 2 : 4 : 5-$C_6H_2(OH)_4$] and phytol (**I**) with anhyd. $H_2C_2O_4$ in dioxan–N_2 at 78° give a mixture, whence 2-*methoxy-5-phytyl*-p-*benzoquinone*, an orange oil, is isolated by chromatography (light petroleum; $MgSO_4$) etc. This gives a pale yellow oily *quinol diacetate* and is formed by elimination of H_2O and MeOH from the primary product. 2 : 1 : 3 : 4-$C_{10}H_4Me(OH)_3$ (**II**), (**I**), and $H_2C_2O_4$ in dioxan at 93° or 81° give similarly vitamin-K_1, identified as quinol diacetate, but the yield is < that from 2 : 1 : 4-$C_{10}H_5Me(OH)_2$ and a mixture is thus probably formed. CHPh:CH·CH_2·OH and (**II**) give similarly the known 3-cinnamyl-2-methyl-1 : 4-naphthaquinone. Reduction of *iso*-naphthazarin (prep. described; 27% yield) by $Na_2S_2O_4$ to the quinol and then condensation as above at 91° with (**I**), farnesol, or geraniol (**III**) gives 2-*hydroxy*-3-*phytyl*- (**IV**), m.p. 56·5—57·7° (*quinol triacetate*, an oil), -3-*farnesyl*- (**V**), an oil (oily *quinol diacetate*), and -3-*geranyl*- (**VI**), m.p. 110—111·5° (*quinol triacetate*, m.p. 111—112·8°), -1 : 4-*naphthazarin*, isolation being tedious. The anti-hæmorrhagic activity of (**IV**) is very great (effective chick dose ~50 μg.) and that of (**VI**) considerable. The structure of (**V**) is proved by its absorption spectrum [max. at 2520 (log *E* 4·26), 2800 (log *E* 4·19), and 3310 A. (log *E* 3·41) in EtOH], which very closely resembles those of lapachol, (**II**), and lomatiol. Cold, conc. H_2SO_4 cyclises (**IV**), (**V**), and (**VI**) to products of β-lapachone type, giving colourless $NaHSO_3$ derivatives: thus are obtained "*β-phytolapachone*" (**VII**), a red oil (nearly colourless *quinol diacetate*), "*β-geranolapachone*," m.p. 232—234° [probably cyclised beyond the stage of (**VII**)], and partly hydrated, impure "*β*-farnesolapachone." 1 : 4 : 5 : 8-$C_{10}H_4(OH)_4$ with (**I**) or (**III**) and $H_2C_2O_4$ as above at 91° give 2-*phytyl*- (**VIII**) and 2-*geranyl-naphthazarin* (**IX**), crimson oils. Et_2O extracts the Na salts of (**IV**), (**VIII**), and (**IX**) completely, mostly, and partly, respectively, from H_2O. M.p. are corr.



(VII.)

R. S. C.

Dibenzfuran derivatives.—See B., 1942, II, 57.

Formation of partly acetylated flavone, flavanone, anthraquinone, and similar compounds. V. Simokoriyama (*Bull. Chem. Soc. Japan*, 1941, **16**, 284—291).—The following derivatives are prepared from the respective OH-compound with Ac_2O (5—10 mols.) and 2—3 drops of C_5H_5N: *phloroglucinaldehyde* 2 : 4-*diacetate*, m.p. 93—94°; *gallacetophenone* 3 : 4-*diacetate*, m.p. 78—81°; iso*sakuranetin* 7-*acetate*, m.p. 173—175°, and 5 : 7-*diacetate*, m.p. 138—140° (formed in 5 or 30 min., respectively); *hesperitin* 7 : 3′-*diacetate*, m.p. 103—105°; *chrysin* 7-*acetate*, m.p. 160—165°; *apigenin* 7 : 4′-*diacetate*, m.p. 192—193°; *acacetin* 7-*acetate*, m.p. 203—208°; *baicalein* 6 : 7-*diacetate*, m.p. 194°; *wogonin* 7-*acetate*, m.p. 159—161°; *kæmpferol* 3 : 7 : 4′-*triacetate*, m.p. 177°; *quercetin* 3 : 7 : 3′ : 4′-*tetra-acetate*, m.p. 160—162°; *myricetin* 3 : 7 : 3′ : 4′ : 5′-*penta-acetate*, m.p. 189—190°; *purpurin* 2 : 4-*diacetate*, m.p. 175—178°. A. T. P.

Action of sulphur on hydrocarbons under high pressure.—See A., 1942, II, 125.

Thionaphthen derivatives.—See B., 1942, II, 56.

αβ-Unsaturated amino-ketones. V. Interaction of pyrrolidine and tetrahydroquinoline with bromine derivatives of benzylideneacetophenone. N. H. Cromwell (*J. Amer. Chem. Soc.*, 1941, **63**, 2984—2986; cf. A., 1941, II, 271).—CHPh:CBr·COPh and pyrrolidine (**I**) (not pyrrole) in light petroleum at −10° give *α-bromo-α-pyrrolidino-β-phenylpropiophenone* (**II**), m.p. 106—107° (decomp.; instantaneous), converted by NaOEt–EtOH under reflux into *α-pyrrolidino-β-phenylacrylophenone* (**III**), m.p. 96—98°. CHPhBr·CHBr·COPh with (**I**) gives *αβ-dipyrrolidino-β-phenylpropiophenone*, m.p. 122—123° (hydrolysed slowly in cold 95% EtOH to PhCHO and some $CH_2Ph·CO·COPh$), and some (**III**). Tetrahydroquinoline with (**II**), α-bromo-α-morpholino- or -α-piperidino-β-phenylpropiophenone (0·5 mol.) in EtOH at room temp. gives *α-pyrrolidino*-, m.p. 148—149° (decomp.), *α-morpholino*-, m.p. 153—154°, and *α-piperidino*-, m.p. 166—167° (hydrolysed by 15% H_2SO_4 at 100° to PhCHO and ω-piperidinoacetophenone), *-β-tetrahydroquinolino-β-phenylpropiophenone*. R. S. C.

Reactions of anils. V. Reversibility of the reaction with acid anhydrides. H. R. Snyder and J. C. Robinson, jun. (*J. Amer. Chem. Soc.*, 1941, **63**, 3279—3280; cf. A., 1940, II, 87).—Maleanilic acid (**I**) and CHPr^a:CEt·CHO (**II**) at 100° give 60—70% of 2-phenyl-5 : 7-diethyl-2-aza[2 : 3 : 1]*dicyclo*-Δ^6-octen-3-one-8-carboxylic acid (**III**), m.p. 143—144°, also obtained (*loc. cit.*) less well from $(CH·CO)_2O$ and CHPr^a:CEt·CH:NPh. The 5 : 7-Me_2 analogue, m.p. 157—158°, of (**III**) is similarly prepared by both methods. It is degraded by conc. NaOH to 3 : 5 : 1-$C_6H_3Me_2·CO_2H$. PhNCO decreases the yield of (**III**) from (**I**) and (**II**) but formation of (**III**) in its presence shows that free H_2O is not an essential intermediate in the reaction. $(CH·CO)_2NPh$ does not condense with (**II**) and (**I**) does not react with $(CH_2:CMe)_2$. R. S. C.

Heterocyclic derivatives related to sulphanilamide. I. Quinoline analogue of sulphanilamide and [its] derivatives. H. Urist and G. L. Jenkins (*J. Amer. Chem. Soc.*, 1941, **63**, 2943—2944).—Di-5-nitro-8-quinolyl disulphide, m.p. 250—252° (decomp.), and conc. HNO_3 at 100° give *5-nitroquinoline-8-sulphonic acid* (**I**), m.p. >211° (decomp.) (*Na* and *benzylisothiocarbamide* salt, m.p. 216·5—217·5°), the *amide*, m.p. 186—187°, of which is reduced by Fe powder in 50% AcOH to *5-aminoquinoline-8-sulphonamide*, m.p. 261—265·5° (decomp.). The chloride, m.p. 104—106°, of (**I**) with 2-amino-pyridine or -thiazole in dry C_5H_5N at 0° gives *5-nitroquinoline-8-sulphon-2′-pyridyl*-, m.p. 249—250° (decomp.), and *-2′-thiazyl-amide*, m.p. 260—261° (decomp.), respectively. M.p. are corr. R. S. C.

Syntheses in the quinoline series. II. Derivatives of 4-methylquinoline. Their structure. III. Nitration of 2-chloro-4-methylquinoline. Preparation of 8-dialkylaminoalkylamino-2-hydroxy-4-methylquinolines. O. H. Johnson and C. S. Hamilton (*J. Amer. Chem. Soc.*, 1941, **63**, 2864—2867, 2867—2869; cf. A., 1938, II, 464).—II. 8-Nitro-4-methylquinoline (**I**) (modified prep.) and Raney Ni–H_2 in EtOH at 75°/45 lb. give *8-amino-4-methylquinoline*, m.p. 84°, the diazonium chloride from which with Cu powder in boiling aq. HCl gives *8-chloro-4-methylquinoline* (20%), m.p. 107°, obtained (54% yield) also from 2 : 8-dichloro-4-methylquinoline by Sn–HCl at 80°. With SeO_2 in boiling EtOH, (**I**) gives 53% of 8-nitro-quinoline-4-aldehyde, converted by $EtNO_2$ and a little $NHEt_2$ in abs. EtOH at room temp. into *8-nitro-4-β-nitro-α-hydroxy-n-propylquinoline* (80%), m.p. 180—190° (decomp.; varies with the rate of heating), which with Raney Ni–H_2 in MeOH at 40 lb. gives *4-amino-4-β-amino-α-hydroxy-n-propylquinoline* (51%), m.p. 82—84°. Quinoline-4-aldehyde reacts normally with MgMeI in Et_2O, giving *α-4-quinolylethyl alcohol* (**II**) (55%), m.p. 125° (picrate, m.p. 181°), which is unaffected by HCO_2H at 150°, is reduced to 4-ethylquinoline at higher temp., and is unaffected by 48% HBr at 100°. $SOCl_2$ converts (**II**) in boiling Et_2O into 4-α-chloroethylquinoline (**III**) (picrate, m.p. 180°), which resists the effect of alkali. 2-Hydroxy-4-bromomethylquinoline with boiling NaOMe–MeOH gives *2-hydroxy-4-methoxy*- (78%), m.p. 171° (converted by $POCl_3$ at 130° into *2-chloro-4-methoxy-methylquinoline*, m.p. 64°), with boiling NH_2Ph gives *2-hydroxy-4-anilino*-, amorphous, m.p. 238—240°, and with *p*-OMe·$C_6H_4·NH_2$ in boiling *n*-$C_5H_{11}·OH$ gives *2-hydroxy-4-p-anisidino*-, m.p. 206—207°, *-methylquinoline*. The abnormal properties of (**II**) and (**III**) may be due to existence in "methylene" forms.

III. 2-Chloro-4-methylquinoline and H_2SO_4–HNO_3 (*d* 1·5) at −5° and later room temp. give *2-chloro*-8- (**IV**) (63%), m.p. 135°, and -6-nitro-4-methylquinoline (**V**) (12%), m.p. 212—213° (lit. 207°), the structure of which is proved by conversion into known compounds and by synthesis of (**V**) from 6-nitro-2-hydroxy-4-methylquinoline by boiling $POCl_3$. With Raney Ni–H_2 in MeOH–dioxan at 50°, (**IV**) and (**V**) give *2-chloro*-8- (**VI**), m.p. 102°, and *-6-amino-4-methylquinoline*, m.p. 154°, respectively. 8-Chloro-2-hydroxy-4-methylquinoline (prep. in 12% yield from $CH_2Ac·CO·NH·C_6H_4Cl$-*o* and H_2SO_4 at 65—70°, later 90°), m.p. 212° (lit. 230°), with $POCl_3$ at 135° gives 60% of 2 : 8-dichloro-4-methylquinoline, m.p. 105° (lit. 87—88°), also obtained in 20% yield from (**VI**) by a diazo-reaction. Boiling 80% AcOH hydrolyses (**IV**) to *8-nitro-2-hydroxy-4-methylquinoline* (92%), m.p. 196°, reduced by Raney Ni–H_2 in $COMe_2$ to *8-amino-2-hydroxy-4-methylquinoline*, m.p. >300° (*Ac* derivative, m.p. 252°). With NaOH, MnO_2, and a little Co_2O_3 in boiling MeOH, (**IV**) gives *8-nitro*-, m.p. 119°, reduced to *8-amino-2-methoxy-4-methylquinoline* (**VII**), m.p. 96° which is also obtained from (**VI**) by boiling NaOMe–MeOH Condensation of (**VII**) with $Br·[CH_2]_x·NH_2,HBr$ (x = 2 or 3) and NaOAc in boiling EtOH, followed by hydrolysis by boiling 20% HCl gives *8-β-diethylaminoethyl-*, m.p. 140°, and *8-γ-diethylamino-n-propyl-amino-2-hydroxy-4-methylquinoline*, m.p. 115°. Quinoline-4-aldehyde hydrate and (**VII**) in boiling abs. EtOH give *8-4′-quinolylmethyleneamino-2-methoxy-4-methylquinoline*, m.p. 144°. R. S. C.

Acid amides as hypnotics. IV. Barbituric acids. F. F. Blicke and M. F. Zienty (*J. Amer. Chem. Soc.*, 1941, **63**, 2991—2993; cf. A., 1942, II, 77).—The following are prepared.
$OPh·[CH_2]_2·CH(CO_2Et)_2$, b.p. 215—218°/30 mm.
$CH_2Ph·CEt(CO_2Et)_2$, b.p. 198—203°/32 mm. Et_2 *β*-phenylethyl-ethyl-, b.p. 222—223°/45 mm., *-n*-, b.p. 220—225°/25 mm., and *-iso*-butyl-, b.p. 158—163°/2 mm., *-α′*-phenylethyl-, b.p. 270—275°/58 mm., -malonate. $OEt·[CH_2]_2·O·[CH_2]_2·CEt(CO_2Et)_2$, b.p. 138—140°/2 mm. $CH_2Ph·C(CH_2·OMe)(CO_2Et)_2$, b.p. 189—192°/14 mm. Et_2 *β*-phenylethyl-methoxymethyl-, b.p. 195—200°/18 mm., -ethoxymethyl-, b.p. 215—218°/23 mm., and *-γ′*-phenoxy-*n*-propyl-, b.p.

298—300°/38 mm., -malonate. Et_2 phenyl-ethoxymethyl-, b.p. 184—187°/14 mm., -butoxymethyl-, b.p. 195—200°/15 mm., -β-methoxyethyl-, b.p. 160—165°/6 mm., and -β-ethoxyethyl-, b.p. 190—193°/14 mm., -malonate. Et_2 β-phenoxyethylethoxymalonate, b.p. 225—230°/29 mm. 5-Benzyl- (*C*), new m.p. 211—212°, 5-α- (*C*), m.p. 207—208°, and 5-β-phenylethyl-, m.p. 168°, 5-γ-phenyl-*n*-propyl-, new m.p. 129—130°, 5-δ-*phenyl*-n-*butyl*-, m.p. 140—141°, 5-ζ-*phenyl*-n-*hexyl*-, m.p. 94—95°, 5-β-cyclo*hexylethyl*-, m.p. 170—171°, 5-*cinnamyl*- (**I**), m.p. 94—95°, 5-methoxymethyl-, new m.p. 185—186°, 5-β-*benzyloxyethyl*-, m.p. 163—164°, 5-β-phenoxyethyl- (*C*), new m.p. 185—186°, and 5-γ-*phenoxy*-n-*propyl*- (**II**), m.p. 123—124°, -5-*ethylbarbituric acid*. 5-β-*Phenylethyl*-5-n-, m.p. 99—100°, and -iso-*propyl*-, m.p. 191—192°, -*allyl*- (*C*), m.p. 151—153°, -n-, m.p. 150—151°, -iso-, m.p. 193—194°, and -sec.-*butyl*-, m.p. 163—164°, -β′-cyclo*hexylethyl*-, m.p. 163—164°, -β′-cyclo*pentylethyl*-, m.p. 166—167°, -α′-*phenylethyl*- (*C*), m.p. 241—242°, -*methoxymethyl*-, m.p. 175—176°, -*ethoxymethyl*-, m.p. 180—181°, -β′-*methoxyethyl*- (*C*), m.p. 164—165°, -β′-*ethoxyethyl*- (*C*), m.p. 169—170°, -β′-*butoxyethyl*-, m.p. 160—161°, -β′-*phenoxyethyl*-, m.p. 210—211°, and -γ′-*propoxy*-n-*propyl*-, m.p. 124—125°, -*barbituric acid*. 5-*Phenyl*-5-*ethoxymethyl*-, m.p. 230—231°, -*butoxymethyl*-, m.p. 182—183°, -β-*methoxyethyl*-, m.p. 210—211°, and -β-*ethoxyethyl*-, m.p. 196—197°, -*barbituric acid*. 5-*Benzyl*-5-*methoxymethylbarbituric acid* (*C*), m.p. 175—176°. 5 : 5-*Di*-β-*phenylethyl*-, m.p. 148—149°, -β-cyclo*hexylethyl*-, m.p. 196—197°, and -γ-*phenoxy*-n-*propyl*-, m.p. 143—144°, -*barbituric acid*. 5-*Ethyl*-5-β′-*methoxy*- (*C*), m.p. 179—180°, -ethoxy- (*C*), new m.p. 179—180°, -*butoxy*- (**III**), m.p. 123—124°, -β′-β″-ethoxyethoxy-, m.p. 96—97°, and -β′-β″-*butoxyethoxy*-, m.p. 83—84°, -*ethylbarbituric acid*. Hypnotic properties of the acids are recorded. The most promising are (**I**), (**II**), and (**III**), which induce very quiet sleep. Compounds marked (*C*) are convulsant.

R. S. C.

Barbiturates containing large radicals. G. S. Skinner and A. P. Stuart (*J. Amer. Chem. Soc.*, 1941, **63**, 2993—2994).—Addition of RBr (1) in $CH_2(CO_2Et)_2$ (1) to $CHNa(CO_2Et)_2$ (1 mol.) in EtOH gives ~85% of Et_2 *n*-do-, b.p. 170—172°/2 mm., *n*-hexa-, b.p. 195—200°/1 mm., and *n*-octa-decylmalonate, b.p. 200—205°/1 mm., converted (method : A., 1937, II, 134) into α-*carbethoxy*-α-n-*dodecyl*-, m.p. 43·5°, b.p. 192—194°/? mm., -*hexadecyl*-, m.p. 49°, b.p. 225—230°/0·3 mm., and -*octadecyl*-, m.p. 55—56°, b.p. 233—238°/0·4 mm., -γ-*butyrolactone*, which, when added with $CO(NH_2)_2$ to NaOEt–EtOH at 10—15° and then gradually heated to 70°, give 81—83% of 5-β-*hydroxyethyl*-5-n-*dodecyl*-, m.p. 145°, -*hexadecyl*-, m.p. 147°, and -*octadecyl*-, m.p. 150°, -*barbituric acid*. Treatment with $CHCl_3$–70% HBr at 50—60° gives 5-β-*bromoethyl*-5-n-*dodecyl*-, m.p. 101·5°, -*hexadecyl*-, m.p. 102·5°, and -*octadecyl*-, m.p. 104·5°, -*barbituric acid*. Hot vapours of the lactones explode in air.

R. S. C.

Pyrimidines. CLXXV. *p*-Sulphamylanilinopyrimidines. G. de Sütö-Nagy and T. B. Johnson (*J. Amer. Chem. Soc.*, 1941, **63**, 3234—3235).—*p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ and the appropriate halogenopyrimidine in EtOH give 2 : 6-*di*-p-*sulphamylanilino*-*pyrimidine*, m.p. 280—282°, and -4-*methylpyrimidine*, m.p. 218—220°, 6-p-*sulphamylanilino*-2-, m.p. 239—240°, and 2-p-*sulphamylanilino*-4-, m.p. 237—239°, -*aminopyrimidine*.

R. S. C.

Sulphonamido-derivatives of pyrimidines. J. M. Sprague, L. W. Kissinger, and R. M. Lincoln (*J. Amer. Chem. Soc.*, 1941, **63**, 3028—3030).—M.p. in parentheses below are, successively, those of the *N*-*p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2$ and *N*-*p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2$ derivatives (prep. as usual) and are in italics if new. $COMe{\cdot}C_6H_{13}$-*n*, HCO_2Et, and Na in Et_2O give *n*-$C_6H_{13}{\cdot}CO{\cdot}CHNa{\cdot}CHO$, which with guanidine carbonate (**I**) in dry EtOH gives 11% of 2-*amino*-4-n-*hexylpyrimidine* (**II**), m.p. 93—94° (*206—207°*, *214—215°*). $COMePr^{\alpha}$, $COMe_2$, COPhMe, and *cyclo*hexanone give similarly 2-amino-4-*n*-propyl- (**III**) (*217—218°*, *253·5—254°*), -4-methyl- (230—231°, 245—246°), -4-phenyl- (*268—269°*, *274—275°*), and -4 : 5-tetrahydrobenz-pyrimidine (252—253°, 255—256°). *n*-$C_6H_{13}{\cdot}CO{\cdot}CH_2{\cdot}CO_2Pr^{\alpha}$ and (**I**) in dry EtOH at 130—150° give 2-*amino*-6-*hydroxy*-4-n-*hexylpyrimidine*, m.p. 199°, converted by $POCl_3$ at 100° into 6-*chloro*-2-*amino*-4-n-*hexylpyrimidine*, m.p. 61—62·5°, which with H_2–Pd–C in EtOH gives (**II**), thus confirming the structure thereof. *n*-$C_5H_{11}{\cdot}CHAc{\cdot}CO_2Et$ and (**I**) at 140—160° give 6-*hydroxy*-2-*amino*-4-*methyl*-5-n-*amylpyrimidine*, m.p. 249—250°, and thence as above 6-*chloro*-2-*amino*-, m.p. 151·5—153°, and 2-*amino*-, m.p. 135—136° (*215—216°*, *182—183°*), -4-*methyl*-5-n-*amylpyrimidine*. $CHEtAc{\cdot}CO_2Et$ gives similarly 2-*amino*-6-*hydroxy*-, m.p. 288—289°, 6-*chloro*-2-*amino*-, m.p. 156—157°, and 2-*amino*-, m.p. 166—167·5°, -5-*ethylpyrimidine*, thus proving the structure of (**III**). $CHBu^{\alpha}(CO_2Et)_2$ gives 2-*amino*-4 : 6-*dihydroxy*-, m.p. 330° (decomp.), and thence 4 : 6-*dichloro*-2-*amino*-, m.p. 170—171°, and 2-*amino*-, m.p. 127—128° (*205—206°*, *241—242°*), -5-n-*butylpyrimidine*. $CHMe(CO_2Et)_2$ gives similarly 2-amino-5-methylpyrimidine (*262—263°*, *271—272°*). 2-*Amino*-4-*ethoxy*-6-*methylpyrimidine*, m.p. 89—90°, 4-*amino*-2-*ethoxypyrimidine*, m.p. 151—152° (*256—257°*, *278—279°*), and 4-*amino*-2-*ethoxy*-6-*methylpyrimidine*, m.p. 109—110° (*186—187°*, *200—201°*), are obtained from the Cl-compounds by NaOEt–EtOH. The following are also described, m.p. in parentheses being those of the N4′-*Ac* derivatives : 2-sulphanilamidopyrimidine, m.p. 251—252° (254—255°); 2-sulphanilamido-4 : 6-dimethyl-, m.p. 175·5—176·5° (240—241·5°), -6-*ethoxy*-4-*methyl*-, m.p. 151—152° (244·5—245°), and -6-*hydroxy*-4-*methyl*-, m.p. 253·5—254°, -*pyrimidine*; 5-*bromo*-2-*sulphanilamido*-4-*methyl*-, m.p. 231—232° (261—262°), 4-*sulphanilamido*-2-*ethylthiol*-6-*methyl*-, m.p. 188—189° (208—209°), 2-*p*-nitrobenzenesulphonamido-4-methyl-, m.p. 230—231°, and 4-p-*nitrobenzenesulphonamido*-2-*ethoxy*-, m.p. 202°, -*pyrimidine*. The above-named sulphonamides are pharmacologically highly active.

R. S. C.

Syntheses in the pyrazine series. IV. 2-Sulphanilamidopyrazine. J. W. Sausville and P. E. Spoerri (*J. Amer. Chem. Soc.*, 1941, **63**, 3153—3154; cf. A., 1940, II, 193).—The prep. of pyrazine-2 : 3-dicarboxylic acid, m.p. (+$2H_2O$) 186° (decomp.), (anhyd.) 190° (decomp.) (first dissociation const. $1{\cdot}7 \pm 0{\cdot}4 \times 10^{-3}$), from quinoxaline is improved (66·8% yield). The 2-carboxylic acid has a first dissociation const. $1{\cdot}2 \pm 0{\cdot}3 \times 10^{-3}$. In boiling $COMe_2$–C_5H_5N 2-aminopyrazine and *p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ give 2-*N*⁴-acetylsulphanilamido- (43%), m.p. 240—242°, and thence (hot 6N-HCl) 2-*sulphanilamido*-*pyrazine* (58%), m.p. 251—251·5°.

R. S. C.

Indazole derivatives.—See B., 1942, II, 131.

Mechanism and kinetics of ring closure.—See A., 1942, I, 148.

Triazines.—See B., 1942, II, 55.

Ammeline derivatives.—See B., 1942, II, 55.

Wing pigment of the butterfly. Methylation and mol. wt. of leucopterin. H. Wieland and P. Decker (*Annalen*, 1941, **547**, 180—184; cf. A., 1933, 1310).—Leucopterin (**I**) is not attacked by CH_2N_2 in anhyd. Et_2O but addition of about 10% of aq. MeOH causes vigorous evolution of N_2 and production of α- (*anhyd.* and *semihydrate*), m.p. >300°, and β-, m.p. >300°, -*trimethyl-leucopterin*. Determinations of the mol. wt. of these substances in freezing PhOH show that (**I**) is $\begin{matrix} NH{\cdot}CO{\cdot}C{\cdot}NH{\cdot}CO \\ \| \\ HN{\cdot}C—NH{\cdot}C{\cdot}NH{\cdot}CO \end{matrix}$. Under similar conditions deiminoleucopterin gives an Me_4 derivative, m.p. 230°. Passage of Cl_2 through (**I**) suspended in H_2O at 60—70° (cf. *loc. cit.*) yields oxalylguanidine, decomp. 245—260° according to the rate of heating in sealed tubes, m.p. >300° in open tubes, hydrolysed by cautious treatment with 2N-NaOH to $H_2C_2O_4$ and guanidine.

H. W.

Chlorophyll. CV. Chlorination and nitration reaction of porphyrins and chlorins. H. Fischer and W. Klendauer (*Annalen*, 1941, **547**, 123—139).—Gradual addition of 3% H_2O_2 to a solution of pyrroporphyrin in AcOH saturated with HCl gives tetrachloropyrroporphyrin (*dihydrochloride*), also obtained by use of conc. HNO_3 in place of H_2O_2; a slight excess of acid causes total decomp. The salt is transformed by $Cu(OAc)_2$ in boiling MeOH into the *Cu* salt of trichloropyrroporphyrin, m.p. >300°. Reaction with CuCN leads to ill-defined products. Treatment of *pyrroporphyrin Me ester hæmin* with HCl and H_2O_2 leads to a *mono*- and a *di*-*chloropyrroporphyrin Me ester*. Attempts to replace Cl by OH by AgOH, NaOH, etc. lead invariably to pyrroporphyrin, indicating that Cl is probably attached to *tert.* C. Cl_1- and Cl_2-compounds of other porphyrins are obtained by chlorination of the corresponding hæmins, the yield depending greatly on the solubility of the latter in AcOH. It is best to use fresh solutions and to moderate the temp. Protracted action leads to extensive oxidation and decomp. Deuterohæmin yields a well-defined *chlorodeuteroporphyrin ester*, m.p. 215°; there is spectroscopic evidence of a Cl_2-compound. Nitrophylloporphyrin (**I**) is brominated in AcOH at 50° to 6-*bromonitrophylloporphyrin ester*, m.p. 211°, identical with the product obtained by treatment of 6-bromophylloporphyrin with cold HNO_3. The successive action of conc. HNO_3 at room temp. and CH_2N_2 on pyrroporphyrin leads to *nitropyrroporphyrin Me ester*, m.p. 209°; the corresponding *hæmin* has m.p. >300°. Spectroscopic comparison of these compounds with (**I**) shows that NO_2 in (**I**) is not carried by γ-Me. Deuteroporphyrin can be nitrated at room temp. and the product is isolated as *nitrodeuteroporphyrin Me ester*, m.p. 163°. Mesoporphyrin requires somewhat more vigorous treatment for its conversion into *nitromesoporphyrin* Me_2 *ester*, m.p. 165°; it does not give a rhodin under the influence of conc. H_2SO_4–oleum. Unexpectedly rhodoporphyrin is transformed by $NaNO_2$ and AcOH at room temp. followed by CH_2N_2 into *nitrorhodoporphyrin* Me_2 *ester*, m.p. 192° after softening at 285° (complex *Cu* salt, m.p. 220°), which could not be converted catalytically into the corresponding NH_2-derivative. Nitrosation of phæoporphyrin a_5 Me_2 ester appears to yield an NO-compound, hydrolysed by the HCl (used in fractionation) to phæoporphyrin a_7 oxime; this is spontaneously hydrolysed under the experimental conditions so that phæoporphyrin a_7 Me_2 ester is isolated after the treatment with CH_2N_2. Mesochlorin e_8 and conc. HNO_2 yield essentially chloroporphyrin e_5. Under milder conditions ($NaNO_2$–AcOH) the main product appears to be dihydroxymesochlorin e_8, m.p. 115°.

H. W.

Phthalocyanines.—See B., 1942, II, 58.

Oxazolines.—See B., 1942, II, 129.

2-Sulphanilamidothiazoline. G. W. Raiziss and LeR. W. Clemence (*J. Amer. Chem. Soc.*, 1941, **63**, 3124—3126).—Cl·$[CH_2]_2{\cdot}NH_2$,HCl

(prep. in 99% yield from the OH-amine in $CHCl_3$ by HCl gas and later $SOCl_2$) or $Br{\cdot}[CH_2]_2{\cdot}NH_2,HBr$ with KCNS gives 2-amino-Δ^2-thiazoline (70%), m.p. 80—82°, which with 1 or 2 mols. of p-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ in C_5H_5N–$COMe_2$ at <60° gives 2-N^4-*acetylsulphanilimido*-3-N^4-*acetylsulphanilamidothiazolidine*, m.p. (+H_2O) 164—165° (gas) or (anhyd.) 205—206°. This is hydrolysed by boiling 10% aq. HCl to 2-*sulphanilamidothiazoline* [*sulphathiazoline*] (**I**) (~50%), shrinks at 207°, m.p. 209—210° (N^4-*Ac* derivative, m.p. 256—258°), 2-sulphanilimido-3-sulphanylthiazolidine, m.p. 259—261° (lit. 265°), and 2-*keto*-3-*sulphamylthiazolidine*, m.p. 206—208°. The effect of (**I**) against types II and III *Pneumococcus* is equal to that of sulphathiazole but is greater against *Staphylococcus aureus*. R. S. C.

Preparation of 2-amino-4-alkylthiazoles from esters of substituted 2-amino-4-thiazylacetic acids. W. M. Ziegler (*J. Amer. Chem. Soc.*, 1941, **63**, 2946—2948).—Addition of Br to $CHRAc{\cdot}CO_2Et$ at <20° (subsequent manipulation at >35—40°) gives $CH_2Br{\cdot}CO{\cdot}CHR{\cdot}CO_2Et$, oils, which with $CS(NH_2)_2$ (slightly >1 mol.) and H_2O at 0° give *Et α-2-amino-4-thiazyl*-n-*butyrate* (**I**) (42%), m.p. 104—105°, -n-*hexoate* (**II**) (33%), m.p. 79—80·5°, and -n-*octoate* (**III**) (45%), m.p. 100—101°. Hydrolysis of (**III**) by NaOH in hot 95% EtOH gives very rapidly the free *acid* (**IV**), m.p. ~125° (decomp.), obtained (70%) by acidification of the alkaline solution at 0° but converted by dil. HCl at 50—60° into 2-*amino*-4-n-*heptylthiazole* (**V**) (85%), b.p. 55—56·5°. 2-*Amino*-4-n-*propyl*- (**VI**) (78%), m.p. 27—27·5°, and -n-*amyl-thiazole* (**VII**) (68%), m.p. 45—46°, are similarly obtained from (**I**) and (**II**), respectively. p-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ does not react with (**I**), (**II**), or (**III**) in $COMe_2$, C_5H_5N at 100°, or quinaldine at 175°, with (**IV**) in NaOH gives (**V**), but with (**V**), (**VI**), or (**VII**) gives 2-p-*acetamidobenzenesulphonamido*-4-n-*heptyl*-, m.p. 166—167°, -n-*propyl*-, m.p. 182—183°, and -n-*amyl-thiazole*, m.p. 163—166°. M.p. are corr. R. S. C.

Thiazoles. XXIV. Exchange reactions between 6-nitro-5-alkoxybenzthiazoles and alcohols. H. H. Fox and M. T. Bogert (*J. Amer. Chem. Soc.*, 1941, **63**, 2996—2999; cf. A., 1939, II, 524).—6-Nitro-5-methoxybenzthiazole (**I**) with KOH–ROH gives 6-*nitro*-5-*ethoxy*- (**II**), m.p. 156°, -n-, m.p. 130—131°, and -iso-*propoxy*-, m.p. 123·5—124°, -n-*butoxy*-, m.p. 126—127°, -β-*phenylethoxy*-, m.p. 117·5—118°, -β-*hydroxyethoxy*-, m.p. 194—195°, and -cyclo*hexyloxy*-, m.p. 114—115°, -*benzthiazole*. Similarly, 6-nitro-5-methoxy-1-phenyl- gives 6-*nitro*-5-*ethoxy*-1-*phenyl*-*benzthiazole*, m.p. 158—159°. The reaction is reversible, for (**II**) with KOH–MeOH regenerates (**I**). $NH_2{\cdot}[CH_2]_2{\cdot}OH$ requires no KOH, for with (**I**) alone at 100° it gives 6-*nitro*-5-β-*aminoethoxybenzthiazole*, m.p. 206°. With boiling 10% aq. NaOH, (**I**) or (**II**) gives 6-*nitro*-5-*hydroxybenzthiazole*, m.p. 156—157° (*K* salt), which could not be alkylated. The lability of the 5-alkoxyl is due to the *vic.* NO_2, since 4-*nitro*-5-*methoxybenzthiazole* [prep. from 2 : 4 : 1-$NO_2{\cdot}C_6H_3(NH_2){\cdot}OMe$], m.p. 184—184·5°, undergoes similar reactions, whereas the 3-NO_2-compound is converted into the disulphide, [2 : 3 : 5 : 1-$NH_2{\cdot}C_6H_2(NO_2)(OMe){\cdot}S]_2$, by rupture of the thiazole ring. M.p. are corr. R. S. C.

5-2′-Thienyl-5-ethylbarbituric acid. F. F. Blicke and M. F. Zienty (*J. Amer. Chem. Soc.*, 1941, **63**, 2945—2946).—Mg 2-thienyl bromide and solid CO_2 in Et_2O–C_6H_6 give thiophen-2-carboxylic acid and thence ($SOCl_2$) the acid chloride, which with CH_2N_2 gives 2-thienyl CHN_2 ketone, m.p. 67—68°, converted by Ag_2O–EtOH into Et 2-thienylacetate (**I**) (68%), b.p. 124—129°/26 mm. [corresponding Me ester, b.p. 115—118°/23 mm., and acid (**II**), m.p. 75—76°]. 2-Thienylmethyl chloride and NaCN in EtOH–H_2O give 2-thienylacetonitrile (60%), b.p. 115—120°/22 mm., hydrolysed by KOH–aq. EtOH to (**II**). Condensation of (**I**) with $Et_2C_2O_4$ by NaOEt–EtOH at 55° and heating the product with glass powder at 155—160°/20 mm. gives 38% of Et_2 2-thienylmalonate, b.p. 145—148°/5 mm., which with NaOEt–EtBr–EtOH gives Et_2 2-thienylethylmalonate (**III**) (64%), b.p. 148—150°/5 mm. Condensation of $CO(NH_2)_2$ and (**III**) by $Mg(OMe)_2$–MeOH gives 5-2′-*thienyl*-5-*ethylbarbituric acid* (58%), m.p. 179—180°, which (as Na salt; rats) has min. lethal and hypnotic doses 200 and 100 mg. per kg. (calc. as acid), respectively. R. S. C.

Thiazole dyes.—See B., 1942, II, 58.

Colour and constitution. II. Absorptions of related vinylene-homologous series. L. G. S. Brooker, F. L. White, G. H. Keyes, C. P. Smyth, and P. F. Oesper. **III. Absorption of 2-*p*-dimethylaminostyrylquinoline and its salts. Effect on absorption of a benzene ring in the chromophoric chain of dyes. IV. Absorption of phenol-blue.** L. G. S. Brooker and R. H. Sprague (*J. Amer. Chem. Soc.*, 1941, **63**, 3192—3203, 3203—3213, 3214—3215; cf. A., 1940, II, 292).—Figures in parentheses below are λ, followed by log ε × 10^4, of the principal absorption max. in MeOH (unless otherwise stated). "Difference" is used for the difference (in A.) between λ of this max. for $X{\cdot}[CH{:}CH]_n{\cdot}Y$ and λ of the max. for $X{\cdot}[CH{:}CH]_{n-1}{\cdot}Y$. λ of the absorption max. of an unsymmetrical substance, X·Z·Y, less the mean λ of the absorption max. of the symmetrical substances, X·Z·X and Y·Z·Y, is termed the "deviation" (expressed in A.). μ are dipole moments × 10^8. M.p. are corr.

II. For a series, $X{\cdot}[CH{:}CH]_n{\cdot}Y$, in which neither X nor Y carries an ionic charge, the "difference" (cf. above) is usually <500 A. and decreases as the series is ascended; thus, λ of the absorption max. increases relatively slowly and blue colours are rare. When X or Y carries an ionic charge, the difference is ~1000 A. even for larger vals. of n and ascent of the series thus soon leads to deep colours. *E.g.*, for cations (**I**),

(*a*) o-C_6H_4<S, N⁺Et>$C{\cdot}[CH{:}CH]_n{\cdot}NHPh \rightleftharpoons$

(*b*) o-C_6H_4<S, NEt>$C{:}[CH{\cdot}CH]_n{:}N^+HPh$, the difference is ~1000 for n = 0—4. For cations (**II**),

(*a*) o-C_6H_4<S, N⁺Et>$C{\cdot}[CH{:}CH]_n{\cdot}NAcPh \rightleftharpoons$

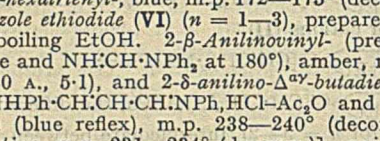
(*b*) o-C_6H_4<S, NEt>$C{:}[CH{\cdot}CH]_n{:}N^+AcPh$, the difference is 620 (n = 2—1) and 350 for n = 3—2), intermediate between the two above-named types; this is due to the wide difference in basicity of the two N, rendering (**IIa**) much more stable than (**IIb**), so that resonance is decreased (*i.e.*, the compound is less degenerate). For (**I**; n = 2), the "deviation" (cf. above) is very small, indicating a degree of resonance approx. equal to that of the symmetrical dyes, *i.e.*, very high. For (**I**) (n = 0 or 1), the deviation is larger, but not abnormally large. Results for deviations in the series o-C_6H_4<CH₂·CH₂, N⁺Et>$C{\cdot}[CH{:}CH]_n{\cdot}NHPh$ (**III**) are similar. The lower degeneracy of (**II**) compared with (**I**) accounts for (**II**) being always less deeply coloured than (**I**) for equal n. Treatment of salts corresponding to (**I**) with alkali gives (**IV**),

(*a*) o-C_6H_4<S, NEt>$C{:}[CH{\cdot}CH]_n{:}NPh \rightleftharpoons$

(*b*) o-C_6H_4<S, N⁺Et>$C{\cdot}[CH{:}CH]_n{\cdot}N^-Ph$. NHPh is not very acidic, so that (**IVb**) is unstable and degeneracy is low; thus, (**IV**) are far less deeply coloured than their salts (**I**). In agreement with these views, deviations for (**IV**) (n = 0—3) are successively 920, 540, and 370. The existence of (**IVb**) is confirmed by μ greatly exceeding the calc. vals. and by conversion at 100° by p-$C_6H_4Me{\cdot}SO_3Me$ etc. into salts (**V**), [o-C_6H_4<S, N⁺Et>$C{\cdot}[CH{:}CH]_n{\cdot}NPhMe$]I⁻, the position of the Me in which is proved by synthesis of the tri-iodide corresponding with (**V**) (n = 3) from $NPhMe{\cdot}CH[{:}CH{\cdot}CH{:}]_2NPhMe\}Cl$ (4490 A.; 8·1) and 1-methylbenzthiazole ethiodide in boiling Ac_2O. In accordance with theory, (i) absorptions of (**V**) closely resemble those of (**I**), except that max. are at slightly shorter λ (reason obscure), and deviation is very small, (ii) cations (**VI**), o-C_6H_4<S, N⁺Et>$C{\cdot}[CH{:}CH]_n{\cdot}N<(CH_2)_5$, are highly degenerate, differences (n = 0—3) being ~1000 and absorptions closely resembling those of (**V**), and (iii) the cation (**VII**),

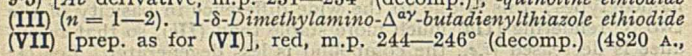
o-C_6H_4<S, N⁺Et>$C{\cdot}[CH{:}CH]_2{\cdot}NMe_2$, is highly degenerate, absorption resembling that of (**VI**) (n = 2) and the deviation being very small. Degeneracy leads to stabilisation by resonance and consequently lower reactivity; thus, (**II**) reacts much faster than the more degenerate (**V**) or (**VI**) with 2-methylbenzthiazole ethiodide in boiling C_5H_5N or with 3-phenylrhodanine in boiling abs. EtOH–NEt_3, and (**II**) reacts faster than (**V**) with (**VI**) (elimination of piperidine). The following are prepared. 1-*Phenylthiolbenzthiazole* [from 1-chlorobenzthiazole (1 mol.), PhSH (2), and NEt_3 (2 mols.) at 100°], b.p. 183—187°/3 mm. [*ethiodide* (**VIII**), m.p. 167—168° (decomp.)]. 1-*Ethylthiolbenzthiazole ethiodide*, m.p. 115—117° (decomp.). 1-*Anilino*- (**I**) (n = 0) [from (**VIII**) by NH_2Ph (2 mols.) in boiling EtOH or, better, from 1-anilinobenzthiazole by EtI], cream-coloured, m.p. 197—198° (decomp.) (2985 A., 1·4), 1-β-anilinovinyl- (**I**) (n = 1) [from (**II**) (n = 1) and NH_2Ph in boiling EtOH], buff, m.p. 265—266° (decomp.) (4140 A., 5·5), 1-δ-*anilino*-$\Delta^{\alpha\gamma}$-*butadienyl*- (similarly prepared) (**I**) (n = 2), brown, m.p. 250—252° (decomp.) (5160 A., 10·7), and 1-ζ-anilino-$\Delta^{\alpha\gamma\epsilon}$-hexatrienyl- (**I**)* ($n$ = 3), m.p. 161—163° (decomp.) (6125 A., 7·6), -benzthiazole ethiodide. 1-β-Acetanilidovinyl- (**II**) (n = 1) [from 1-methylbenzthiazole ethiodide (**IX**) and $NH{:}CH{\cdot}NPh_2$ in boiling Ac_2O or from (**I**) (n = 1) by Ac_2O–C_5H_5N], almost colourless, m.p. 231—233° (decomp.) (3640 A., 1·0), 1-δ-acetanilido-$\Delta^{\alpha\gamma}$-butadienyl- (**II**) (n = 2) [from (**IX**) and $NHPh{\cdot}CH{:}CH{\cdot}CH{:}NPh,HCl$ in boiling Ac_2O or (**I**) (n = 2)], brownish, m.p. 233—234° (decomp.) (4260 A., 3·5) (slowly hydrolysed in MeOH), and 1-ζ-*acetanilido*-$\Delta^{\alpha\gamma\epsilon}$-*hexatrienyl*- (**II**) (n = 3) [from (**VIII**) and $CH_2(CH_2{\cdot}CO{\cdot}NHPh,HCl)_2$ in boiling Ac_2O], reddish-brown, m.p. 203—205° (decomp.) (4610 A., 4·4), -*benzthiazoline ethiodide*. 1-*Anilo*-2-*ethyl*-, colourless, m.p. 64—65° [3020 A., 1·1; μ 2·37±0·03 (calc. 1·6±0·6)], 2-*ethyl*-1-β-*aniloethylidene*-, amber (blue reflex), m.p. 98—99° (decomp.) [3940 A., 3·8; μ 4·17±0·12 (calc. 2·0±0·6)], 2-*ethyl*-1-δ-*anilo*-Δ^{β}-*butenylidene*-, orange-brown, m.p. 109—110° (decomp.) [4480 A., 5·9; μ 5·32±0·10 (calc. 2·0±0·6)], 2-*ethyl*-1-ζ-*anilo*-$\Delta^{\beta\delta}$-*hexadienylidene*-, brown, m.p. 117—119° (decomp.) (4850 A., 6·8), -*benzthiazoline* (**IV**) (n = 0—3), prepared from the appropriate (**I**) by NaOH–$COMe_2$–H_2O. 1-N-*Methylanilino*- (**V**) (n = 0), colourless, m.p. 194—195° (2930 A., 1·3), and 1-δ-*methylanilino*-$\Delta^{\alpha\gamma}$-*butadienyl*- (**V**) (n = 2), orange-brown (green reflex), m.p. 236—238° (decomp.) (4965 A., 10·7)

[corresponding *tri-iodide*, green, m.p. 194—196° (decomp.)], *-benzthiazole ethoperchlorate*. 1-*β-Methylanilinovinyl-*, yellow, m.p. 213—214° (decomp.) (4000 A., 4·6), and 1-*ζ-methylanilino-*$\Delta^{\alpha\gamma\epsilon}$*-hexatrienyl-*, blue, m.p. 157—158° (decomp.) (5975 A., 13·3), *-benzthiazole ethiodide* (**V**). 1-*Piperidinobenzthiazole ethoperchlorate* (**VI**) (n = 0), colourless, m.p. 129—130° (2950 A., 0·8). 1-*β-Piperidinovinyl-*, cream, m.p. 274—277° (decomp.) (3880 A., 5·1), 1-*δ-piperidino-*$\Delta^{\alpha\gamma}$*-butadienyl-*, red, m.p. 205—207° (decomp.) (4830 A., 14·2), and 1-*ζ-piperidino-*$\Delta^{\alpha\gamma\epsilon}$*-hexatrienyl-*, blue, m.p. 172—175° (decomp.) (5840 A., 21·8), *-benzthiazole ethiodide* (**VI**) (n = 1—3), prepared from (**II**) by piperidine in boiling EtOH. 2-*β-Anilinovinyl-* (prep. from quinaldine ethiodide and NH:CH·NPh$_2$ at 180°), amber, m.p. 282—285° (decomp.) (4430 A., 5·1), and 2-*δ-anilino-*$\Delta^{\alpha\gamma}$*-butadienyl-* (prepared similarly by NHPh·CH:CH·CH:NPh,HCl–Ac$_2$O and later NH$_2$Ph–EtOH), brown (blue reflex), m.p. 238—240° (decomp.) (5280 A., 9·5) [*Ac* derivative, m.p. 231—234° (decomp.)], *-quinoline ethiodide* (**III**) (n = 1—2). 1-*δ-Dimethylamino-*$\Delta^{\alpha\gamma}$*-butadienylthiazole ethiodide* (**VII**) [prep. as for (**VI**)], red, m.p. 244—246° (decomp.) (4820 A., 13·4).



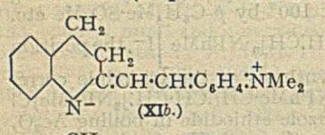
(**X**.) I

3-*Phenyl-5-β-2′-ethyl-1′-benzthiazolinylidenevinylrhodanine*, m.p. 283—285° (decomp.).

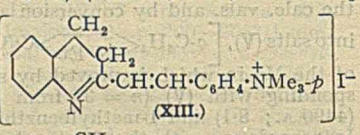


o-C$_6$H$_4$<S, NEt>C:CH·[CH:CH]$_n$·C<S, N$^+$Et>C$_6$H$_4$-o}I$^-$, n = 0 (4230 A., 8·45) and 1 (5575 A., 14·8). {NHPh·CH[:CH·CH:]$_n$NPh}X, n = 1 (3825 A., 5·0) and 2 (4850 A., 6·5). (**X**), n = 0 (5235 A., 7·6) and 1 (6040 A., 19·4). NMe$_2$·[CH:CH]$_2$·CH:NMe$_2$}ClO$_4$ (4130 A., 4·8).

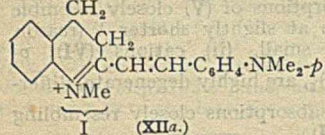
III. The yellow colour of 2-*p*-dimethylaminostyrylquinoline (**XI***a*) (3960 A., 4·02) is due to resonance with the form (**XI***b*). Its red methiodide (Rupe *et al.*, A., 1936, 83) (5520 A., 5·78; in MeNO$_2$



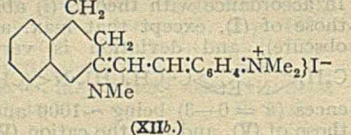
(**XI***b*.)



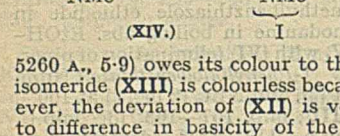
(**XIII**.)



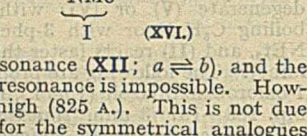
(**XII***a*.)



(**XII***b*.)



(**XIV**.) I



(**XVI**.) I

5260 A., 5·9) owes its colour to the resonance (**XII**; $a \rightleftharpoons b$), and the isomeride (**XIII**) is colourless because resonance is impossible. However, the deviation of (**XII**) is very high (825 A.). This is not due to difference in basicity of the N, for the symmetrical analogues (**XIV**) (6040 A., 18·5; in MeNO$_2$ 6070 A., 13·3) and [*p*-NMe$_2$·C$_6$H$_4$·CH:C$_6$H$_4$:N$^+$Me$_2$]X (**XV**) (in MeNO$_2$ 6100 A., 13·1) are blue and have very similar adsorption. Nor is it due to the aminoalkylidene side-chain, for (**XVI**) shows no deviation. It is due to the stability of (**XII***a*) being enhanced by the Kekulé forms of the C$_6$H$_6$ ring. This effect is not shown with (**XV**) as the resonance forms are equiv., but is operative in a homologue of (**XII**) [difference from (**XI**) 150 and from (**XII**) 360 A.] and in the benzthiazole series. The very slight degeneracy of (**XI**) is due to three causes: the C$_6$H$_6$ effect, the instability of >N$^-$ in the quinoline nucleus of (**XI***b*), and the dipole nature of (**XI**) [μ 3·12 (calc. 2·6)]. The effect of a C$_6$H$_6$ ring on resonance is elaborated also for Michler's ketone, phenol-blue, auramine, and malachite-green. The aldehydic character of *p*-NMe$_2$·C$_6$H$_4$·[CH:CH]$_n$·CHO and non-aldehydic character of NMe$_2$·CHO is similarly due to the C$_6$H$_4$ of the former. A general rule, that the effect on the deviation produced by a change in chemical structure is greater the more degenerate is the compound undergoing change, is postulated and illustrated. Among cyanine dyes in general substitution of 2-quinolyl by 1-benzthiazolyl lessens the colour. This substitution has no effect on very low deviation of the highly degenerate 2 : 2′-carbocyanines, but has an effect on the less degenerate (**XII**). For (**XI**) and its benzthiazole analogue, the lower basicity of benzthiazole renders the (**XI***b*) form more stable and thus reverses the usual effect, deepening the colour; further, replacement of quinoline in (**XI**) by the much less basic 1 : 2-dimethylindole actually leads to a negative deviation (−95 A.; ? interpretation of the negative sign); but for the highly degenerate mixed 2-quinonyl-1-benzthiazolylcarbocyanine the different basicity of the nuclei is without effect and the deviation is negligible. The following are prepared by methods generally similar to those given above. 2-*δ-Anilino-*, brown (blue reflex), m.p. 231—232° (decomp.) (5285 A., 9·50), 2-*δ*-N-*methylanilino-*, dark, m.p. 205—207° (5150 A., 9·9), and 2-*δ-dimethylanilino-*, black (bluish reflex), m.p. 260—261° (decomp.), *-*$\Delta^{\alpha\gamma}$*-butadienylquinoline methiodide* (**XVI**). 2-*δ-Anilo-*Δ^{β}*-butenylidene-1-methyl-1* : *2-dihydroquinoline*, m.p. 101—102°. 2-*δ*-p-*Dimethylamino-*$\Delta^{\alpha\gamma}$*-butadienylquinoline* (from quinaldine and *p*-NMe$_2$·C$_6$H$_4$·CH:CH·CHO in conc. HCl at 100°), orange, m.p. 182—184° (decomp.) (4110 A., 4·0) [*methiodide*, green, m.p. 262—264° (decomp.) (5580 A., 4·9)]. 2-p-*Dimethylaminostyrylbenzthiazole*, yellow, m.p. 206—208° (decomp.) [4000 A., 2·81; μ 3·59 (calc. 2·2)] [ethiodide (5240 A., 6·5; in MeNO$_2$ 5280 A., 6·3)]. 1′-*Methyl*-3-n-*propyl-* (prep. from quinaldine metho-*p*-toluenesulphonate and 1-*β*-acetanilidovinylbenzthiazole *n*-propiodide in boiling C$_5$H$_5$N), m.p. 255—257° (decomp.) (5790 A.), and 3 : 1′-*diethyl-* (prep. similarly using 1-*β-N*-methyl- or 2-*β*-piperidino-vinylbenzthiazole ethiodide), green, m.p. 276—277° (decomp.) (5780 A., 13·6), and 3 : 3′-diethyl- (in MeNO$_2$ 5565 A., 13·1) -thia-2-carbocyanine iodide. 3-p-*Dimethylaminobenzylidene-2-methylindolenine methoperchlorate*, m.p. 183—185° (decomp.) (in MeNO$_2$ 5530 A., 4·35).

NPhR·[CH:CH]$_2$·CH:NPhR}X, in which R = H (4850 A., 6·5) or Me (4490 A., 8·1). 3-1′ : 2′-Dimethylindolenylmethylene-2-methylindolenine methiodide (in MeNO$_2$ 4900 A., 5·3).

IV. Phenol-blue owes its colour to resonance, (*a*) *p*-NMe$_2$·C$_6$H$_4$·N:C$_6$H$_4$:O-*p* $\rightleftharpoons$ (*b*) *p*-N$^+$Me$_2$:C$_6$H$_4$·N·C$_6$H$_4$·O$^-$-*p*, and has very high μ (5·80±0·17 in C$_6$H$_6$; calc. 2·4±0·5). The stability of (*b*) and thus the depth of colour is greatly dependent on the dielectric const. (ϵ) of the solvent; absorption max. are: in *cyclo*hexane (ϵ 2) (reddish-violet solution) 5520, in COMe$_2$ (ϵ 21) 5820, in MeOH (ϵ 31) 6120, and in H$_2$O (ϵ 80) (deep blue solution) 6680 A. This effect is not shown by the symmetrical *p*-NMe$_2$·C$_6$H$_4$·N:C$_6$H$_4$:NMe$_2$-*p*}I and *p*-O:C$_6$H$_4$:N·C$_6$H$_4$·O-*p*}Na, which have absorption max. 7290—7260 and 6280—6420 A., respectively, in COMe$_2$, MeOH, and H$_2$O. R. S. C.

VII.—ALKALOIDS.

Calabash curare. III. H. Wieland, H. J. Pistor, and K. Bähr. **IV.** H. Wieland, K. Bähr, and B. Witkop (*Annalen*, 1941, **547**, 140—155, 156—179; cf. A., 1938, II, 463).—III. The calabash contents are made into a stiff paste with H$_2$O and extracted with MeOH. The dried extract is dissolved in H$_2$O and the solution is completely pptd. with Reinecke acid. The dried ppt. is dissolved in 10 parts of COMe$_2$, the insol. brown matter is centrifuged, and the clear solution treated with 5 vols. of hot H$_2$O. The process is repeated until ~65% of the original material has been removed. The pptd. reineckates are fractionated chromatographically (Al$_2$O$_3$) and the individual fractions are converted into hydrochlorides by successive treatments with Ag$_2$SO$_4$ and BaCl$_2$. Dissolution of *C*-curarine I hydrochloride (**I**) in conc. HCl leads to an intensely violet solution the colour of which is completely discharged by sufficient dilution with H$_2$O. A distinct colour results with 20% HCl. (**I**) is chemically unchanged after several hr. but gradually undergoes decomp. The nature of the halochromism remains unexplained. (**I**) if moistened with Et$_2$O and then dried in a vac. at room temp. has the composition C$_{20}$H$_{23}$ON$_2$Cl, but after remaining in a vac. at room temp. until const. in wt. it is C$_{20}$H$_{21}$N$_2$Cl. It remains uncertain whether H$_2$O of crystallisation is present since although the anhyd. salt acquires H$_2$O when recrystallised the corresponding hydriodide retains its complete H$_2$O content at 150°/vac. At 100° only a small proportion of the Cl in (**I**) remains in ionic union, the greater part becoming attached firmly to C. The colour reactions of (**I**) are described. (**I**) is transformed by KOH–MeOH at 150° into the ether *base* (**II**), C$_{40}$H$_{42}$ON$_4$, m.p. 184°, thus indicating the possible presence of a quinoline or *iso*quinoline ring in (**I**). (**II**) affords a *methiodide*, m.p. 300°, which does not lend itself to the Hofmann degradation. At 200°, (**II**) passes into an isomeric *base*, m.p. >300° after darkening at ~280°. Hydrogenation of (**II**) by Na and boiling C$_5$H$_{11}$·OH yields the H_4-base (**III**), C$_{40}$H$_{46}$ON$_4$, m.p. 105—110° (decomp.) (*methiodide*), also obtained similarly from (**I**), whereas in AcOH containing PtO$_2$ the product is an *octahydride*, m.p. (indef.) 90—95° after softening at 80° (non-cryst. *methiodide*), also obtained similarly from (**II**). (**I**) is immediately converted by Br–H$_2$O (1 mol.) into *C-bromocurarine* I *hydrochloride*, characterised by its great toxicity and converted by Ag$_2$O–Ba(OH)$_2$ into the *brominated ether base*, C$_{40}$H$_{40}$ON$_4$Br$_2$, which is pharmacologically inactive. (**I**) is transformed by HNO$_3$ (*d* 1·2) into *C-nitrocurarine* I *nitrate*, which is 20 times as toxic as the initial curare base. *C*-Curarine II is most conveniently purified through the *picrate*, m.p. 203—204° (corresponding *perchlorate* and *platinichloride*). The hydrochloride is readily brominated and nitrated. The monosubstituted derivatives are much more toxic than the parent base but a (NO$_2$)$_2$-base is less active. *C*-Curarine III is best purified through the cryst. *anthraquinonesulphonate*, decomp. 308—310°, which is converted into the hydrochloride, decomp. 270—274°, $[\alpha]_D^{20}$ −936·9° in H$_2$O (corresponding *picrate*, m.p. 189°). This can also be obtained directly. It has no pharmacological activity.

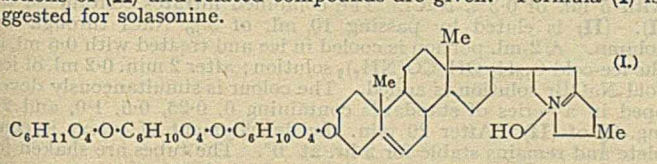
The pptd. reineckates (see above) contain the whole of the biologically active material. The mother-liquors yield curine, m.p. 212° (monohydrate and anhyd.), $[\alpha]_D^{20}$ −328° in C_5H_5N, identical with that described by Boehm.

IV. Application of the modified method of isolation (see above) to calabashes from Urbana and Caracas leads to the isolation of *C-dihydrotoxiferin* I *hydrochloride* (**IV**), $C_{20}H_{23}N_2Cl$, $[\alpha]_D^{20}$ −610·6° in EtOH, −605° in EtOH–H_2O (1 : 1), which has a more rapid and less prolonged physiological action than (**I**), from which it also differs in the absence of halochromism; the corresponding *sulphate*, *hydrobromide*, darkens above 260°, and *picrate* (+H_2O), m.p. 183—185°, are described. *C*-iso*Dihydrotoxiferin* I is present in many calabashes with *C*-curarine I, which it completely resembles in activity; the *hydrochloride*, $C_{20}H_{23}N_2Cl,3H_2O$, $[\alpha]_D^{20}$ −566° in H_2O, which gives a red-brown colour with conc. HNO_3 and does not exhibit halochromism with conc. HCl, the *perchlorate*, and *picrate*, decomp. 242° after softening at 200°, are described. It yields a NO_2-compound. *C-Toxiferin* II *hydrochloride*, $[\alpha]_D^{20}$ +72·1° in H_2O [corresponding *picrate*, m.p. 215° (decomp.) when rapidly heated], is obtained from calabashes from Urbana and Caracas. If the picrate is decomposed in the usual manner with HCl, the product is the much less physiologically active *toxiferin* IIa *hydrochloride* (**V**), decomp. 275° after becoming brown at 250°, $[\alpha]_D^{20}$ +66·3° in H_2O; the corresponding *picrate* has m.p. 210° (decomp.). Contact with Al_2O_3 transforms this hydrochloride into *toxiferin* IIb *hydrochloride* (**VI**), slow carbonisation at >260° after becoming brown at 240°, $[\alpha]_D^{20}$ +78·4° in H_2O [corresponding *picrate*, m.p. 215° (decomp.)], which has lower pharmacological activity. The isolation of (**I**) from the mother-liquors of (**IV**) is described. *Toxiferin* I hydrochloride, $[\alpha]_D^{20}$ −610° in H_2O, activity 0·5 μg. per frog (corresponding *picrate*, m.p. 270° after darkening), which gives a brownish-green, non-characteristic colour with conc. HNO_3 and does not show halochromism with conc. HCl, *toxiferin* II *picrate*, m.p. 216°, (**V**), and (**VI**) are also derived from *Strychnos toxifera*. The alkaloids from the latter source are therefore present in the calabashes of arrow poison but the residues from the aq. extract of the plant are pharmacologically less active than the prepared poison. Apparently the latter material is obtained from a great variety of plants.

H. W.

Solanum **alkaloids. I. Alkaloid from the fruit of** *S. aviculare*. R. C. Bell and L. H. Briggs. **II. Solasonine.** L. H. Briggs, R. P. Newbold, and N. E. Stage. **III. Alkaloids from** *S. auriculatum*. R. C. Bell, L. H. Briggs, and J. J. Carroll. **IV. Glycosidic moiety of solauricine.** L. H. Briggs and J. J. Carroll (*J.C.S.*, 1942, 1—2, 3—12, 12—16, 17—18).—I. The alkaloid, previously regarded as purapurine, is solasonine (**I**).

II. Analyses support formulæ $C_{45}H_{73}O_{16}N$ for (**I**) (from *S. sodomæum*) and $C_{27}H_{43}O_2N$ for solasodine (**II**), and lead to the formulation of (**I**) as a trisaccharide containing rhamnose, galactose, and glucose units with one mol. of (**II**) (cf. Oddo *et al.*, A., 1936, 488). (**II**) contains the steroid nucleus and has one OH in a *cis*-position at $C_{(3)}$ and a double bond at $C_{(5)}$–$C_{(6)}$. It forms an Ac derivative sol. in acids, give *dihydrosolasodine*, m.p. 208·5—210·5°, $[\alpha]_D^{25}$ −63·5° in $CHCl_3$, on catalytic hydrogenation (Pd–C), and with Br–$CHCl_3$ or Br–AcOH followed by crystallisation from H_2O–EtOH–$COMe_2$–HBr gives a *hydrobromide*, $C_{27}H_{43}O_2NBr,HBr$, m.p. 302° (decomp.). Dehydration with HCl–EtOH affords $\Delta^{3:5}$-solasodiene, which is hydrogenated (PtO_2–H_2) to *hexahydrosolasodiene* (*dihydro*chano*solasodan*), m.p. 184—186°, $[\alpha]^{25}$ −18° in $CHCl_3$, formed by saturation of the normal double bonds and further by opening up of the heterocyclic rings. Similar hydrogenation of (**II**) gives tetrahydrosolasodine (dihydro*chano*solasodanol). HNO_2 and (**II**) yield a quaternary *nitrite*, m.p. 260·5—262·5° (decomp.), the " azosolasodine " of Oddo. MeI or EtI with (**II**) gives the hydriodide, and not the methiodide and ethiodide as suggested previously. The colour reactions of (**II**) and related compounds are given. Formula (**I**) is suggested for solasonine.



III. Alcoholic extraction of the dried berries gives a glycoalkaloid, *solauricine* (**III**), $C_{45}H_{73}O_{16}N$, m.p. 269·5—270° (decomp.), hydrolysed to a mixture of sugars and *solauricidine* (**IV**), $C_{27}H_{43}O_2N$, m.p. 220—223°, $[\alpha]_D^{25}$ −89·8° in MeOH [*hydrochloride* (+$2H_2O$), $[\alpha]_D^{25}$ −68·2° in MeOH; *sulphate* (+0·5H_2O); *hydriodide*; *picrate* (+H_2O); and *nitrite*]. Evidence is adduced that (**IV**) is neither identical with nor a dimorphic form of (**II**) but is extremely closely related to it physically and chemically; no structural differences have yet been found. From the juice of the green berries, a product, m.p. 269—270° (decomp.), has been isolated, which is hydrolysed to a mixture consisting mainly of (**II**) with some (**IV**). Both the latter bases occur in dimorphic forms, the respective pairs being indistinguishable.

IV. The glycosidic moiety of (**III**) consists of glucose, rhamnose, and galactose.

F. R. S.

Sinomenine. XLVII. (+)-Dihydrocodeine and (+)-dihydromorphine from sinomenine. K. Goto and T. Arai (*Annalen*, 1941, **547**, 194—200).—(+)-Dihydrocodeinone (demethoxydihydrosinomeneine) is hydrogenated at room temp. in C_5H_5N containing PtO_2 to (+)-*dihydrocodeine* (**I**) (+$2H_2O$), m.p. 87—88°, (anhyd.) m.p. 110°, $[\alpha]_D^{30}$ +146·4° in EtOH (*methiodide*, m.p. 257°, $[\alpha]_D^{30}$ +80·1° in H_2O). Admixture of (**I**) with an equal quantity of its (−)-isomeride gives dl-*dihydrocodeine*, m.p. 105°, $[\alpha]_D$ ±0° (*methiodide*, m.p. 257°). (**I**) is demethylated by boiling HI (*d* 1·7) to (+)-*dihydromorphine*, m.p. 159°, $[\alpha]_D^{30}$ +151·5° in EtOH (*hydriodide*, m.p. 285°, $[\alpha]_D^{29}$ +87·9° in H_2O; *methiodide*, m.p. 245°, $[\alpha]_D^{31}$ +74·9° in H_2O). Similarly, (−)-dihydrocodeine gives (−)-*dihydromorphine*, m.p. 159°, $[\alpha]_D^{30}$ −149·7° in EtOH (*hydriodide*, m.p. 285°, $[\alpha]_D^{28}$ −85·8° in H_2O; *methiodide*, m.p. 245°, $[\alpha]_D^{30}$ −75·1° in H_2O). dl-*Dihydromorphine* has m.p. 154° (*hydriodide*, m.p. 261°; *methiodide*, m.p. 267°). (**I**) and PCl_5 afford (+)-*dihydrochlorocodide* (**II**), m.p. 173°, $[\alpha]_D^{28}$ +177·2° in $CHCl_3$ (*methiodide*, m.p. 248°, $[\alpha]_D^{7}$ +114·8° in EtOH). dl-*Dihydrochlorocodide* has m.p. 146°, $[\alpha]_D$ ±0° (*methiodide*, m.p. 253°). Na in MeOH at 140° converts (**II**) into (+)-*deoxycodeine* C, m.p. 103°, $[\alpha]_D^{20}$ +179·6° in MeOH (*methiodide*, m.p. 238°, $[\alpha]_D^{13}$ +102·4° in 90% MeOH). (−)-Deoxycodeine *C* has m.p. 103°, $[\alpha]_D^{20}$ −177·8° in EtOH (methiodide, m.p. 240°, $[\alpha]_D^{13}$ −102·6° in 90% MeOH). dl-*Deoxycodeine* C, m.p. 85°, $[\alpha]_D$ ±0°, and its *methiodide*, m.p. 218°, are described.

H. W.

VIII.—ORGANO-METALLIC COMPOUNDS.

Sulphophenylarsinic acids and their derivatives. V. 4′-Sulpho- and 4′-sulphamyl-diphenyl-4-arsinic acids. J. F. Oneto and E. L. Way (*J. Amer. Chem. Soc.*, 1941, **63**, 3068—3070; cf. A., 1941, II, 178).—*p*-$C_6H_4Ph{\cdot}AsO_3H_2$ (prep. from the amine by the Scheller reaction or as by-product in the prep. of $AsPhO_3H_2$ by the " Bart " reaction), m.p. >360° (derived di-iodoarsine, m.p. 109—110°), with 96% H_2SO_4 at 110—120° gives 4′-*sulphodiphenyl-4-arsinic acid* (**I**), anhyd. and +H_2O (*Ba* salt), or with $ClSO_3H$ at <20° and later 100° gives 4′-$SO_2Cl{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}AsO_3H_2$-4 (**II**). In boiling H_2O, (**II**) gives (**I**), and with boiling 10% aq. NH_3 gives *NH₄ H* 4′-*sulphamyldiphenyl-4-arsinate* and thence 4′-*sulphamyldiphenyl-4-arsinic acid* (**III**). The *Na* salt of (**I**) with 50% aq. HI and AcOH at room temp. gives *Na* 4-*di-iodoarsinodiphenyl-4′-sulphonate*, decomp. when heated, and thence by 10% aq. NH_3 the derived *arsine oxide Na* salt. In 50% HI and AcOH at 75—80°, (**III**) gives 4′-*sulphamyldiphenyl-4-di-iodoarsine*, m.p. >200°, and thence the *arsine oxide*. Structures are proved by conversion of (**I**) by 50% HI at 100° into *p*-$C_6H_4Ph{\cdot}SO_3H$, identified by conversion of its Cu salt by PCl_5 into the acid chloride.

R. S. C.

IX.—PROTEINS.

New method of fractionation of proteins by electrophoresis convection. J. G. Kirkwood (*J. Chem. Physics*, 1941, **9**, 878—879).—Fractionation of proteins electrophoretically is suggested and the theory of the method is outlined. Preliminary investigations with mixtures of ovalbumin and hæmoglobin indicated significant separation.

W. R. A.

Partial acid hydrolysis of proteins, with reference to mode of linkage of basic amino-acids. A. H. Gordon, A. J. P. Martin, and R. L. M. Synge (*Biochem. J.*, 1941, **35**, 1369—1387).—Wool, edestin, and gelatin are partly hydrolysed by digestion with 10N-HCl at 37° for 139—192 hr., and the products are submitted to electrodialysis. A large proportion of the basic NH_2-acids have thus been isolated as dipeptides, in the case of arginine 80—92%. About ⅓ of the residues are liberated as free NH_2-acids, so that basic NH_2-acids are more resistant. Cystine in edestin is set completely free. The bearing of the results on protein structure is discussed.

P. G. M.

Chemistry of insect cuticle. I. Anthropod cuticles and characterisation of their proteins.—See A., 1942, III, 247.

Supposed occurrence of hydroxyglutamic acid in milk-proteins.—See A., 1942, III, 315.

Methylaspartic acids and their methylation.—See A., 1942, II, 132.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Lignin and related compounds.—LV, LVI, LX.—See A., 1942, II, 143.

Lignin and related compounds. LVII. Mechanism of the ethanolysis reaction. LVIII. Mechanism of the ethanolysis of maple wood at high temperatures. W. B. Hewson, J. L. McCarthy, and H. Hibbert. **LXI. Hydrogenation of ethanolysis fractions from maple wood. II.** L. M. Cooke, J. L. McCarthy, and H. Hibbert. **LXII. High pressure hydrogenation of wood using copper chromite catalyst. I.** H. P. Godard, J. L. McCarthy, and H. Hibbert. **LXIII. Hydrogenation of wood. II.** J. R. Bower, jun., J. L. McCarthy, and H. Hibbert (*J. Amer. Chem. Soc.*, 1941, **63**, 3041—3045, 3045—3048,

3056—3061; 3061—3066, 3066—3068; cf. A., 1942, II, 42).—LVII. Grinding maple wood before or during ethanolysis does not increase above the usual 30% the amount of H_2O-sol., distillable oil (*A*) obtained. Repeated treatment of the wood for short periods with small amounts of HCl–EtOH removes nearly all the lignin. The EtOH-sol. lignin produced by ethanolysis is partly converted by HCl–EtOH into a less sol. lignin. Ethanolysis of lignin thus consists of depolymerisation and subsequent partial polymerisation.

LVIII. Dry EtOH at 150°, 165°, 180°, or 200° extracts the lignin from maple wood only slowly. Addition of small amounts of NaOH or HCl very greatly accelerates the extraction at these temp. as well as at 78°. 1 : 1 aq. EtOH extracts much more than dry EtOH. H_2O at 165° is ineffective, but 2% aq. NaOH is very effective. The yields of (*A*) are less at high than at low temp. Thus, the EtOH-sol. unimol. compounds do not exist in lignin as such but rather combined with each other (*e.g.*, as ethers) and possibly also with carbohydrates. Fission of these aggregates is due to H^+ or OH', the effect of H_2O being to increase the ionisation of EtOH etc., increase of temp. and presence of an appropriate solvent facilitating the process. Formation of EtOH-sol. and -insol. lignins is subsequent to this fission.

LXI. H_2–Cu chromite converts the main maple EtOH-lignin fraction in dioxan at 250°/3400 lb. into H_2O 13·6, MeOH 5·0, EtOH 8·7, 4-*n*-propyl*cyclo*-hexanol (**I**) 8·1, and -hexane-1 : 2-diol 1·9, γ-4-hydroxy*cyclo*hexylpropan-α-ol (**II**) 3·3, a H_2O-insol. *compound* (**III**), b.p. 130—132°/1 mm., 2·1, and high-boiling resins 29·5%. Difference in the yield of (**II**) from that obtained from aspen MeOH-lignin (Harris *et al.*, A., 1938, II, 332) indicates a possible difference in structure. Similar experiments with other fractions indicate that ease of fission to propylphenol units increases with increasing solubility of the fraction. Probably these units are linked by C·O·C in the easily split and by C·C linkings (polymerisation) in the difficultly split portions. The C·O·C linkings may be of acetal type.

LXII. H_2–Cu chromite converts spruce or maple wood in dioxan at 280°/3500 lb. entirely into colourless liquid products, including (**I**) 19·5 and (**II**) 5·8% (calc. on Klason lignin). The recovery of propylphenol units is calc. to be 36%.

LXIII. Maple wood holocellulose is hydrogenated (Cu chromite) at 280°/3500 lb. Comparison of the results with those of the preceding paper indicates that (**I**), (**II**), and (**III**) are derived from the lignin and that a fraction, b.p. 70—125°/20 mm., is derived from the protolignin. R. S. C.

XI.—ANALYSIS.

New form of chromatogram employing two liquid phases. I. Theory of chromatography. II. Application to micro-determination of higher monoamino-acids in proteins.—See A., 1942, I, 160.

Sample carrier for organic liquids.—See A., 1942, I, 159.

Disposal of acid fumes [in micro-Kjeldahl digestions].—See A., 1942, I, 159.

Micro-gasometric determination of nitrogen.—See A., 1942, III, 360.

Determination of total sulphur in organic liquids, using a semi-micro-method. E. B. Lisle (*J.S.C.I.*, 1942, **61**, 20).—The S compound is oxidised to SO_2 by passing the vapour of the compound mixed with O_2 or air over red-hot Pt gauze. The SO_2 is passed over filter-paper impregnated with $Ni(OH)_2$, which is converted into black Ni, the depth of colour being ∝ amount of SO_2 present.

Improved semimicro-determination of sulphur in organic materials. Peroxide–carbon fusion followed by a titration using tetrahydroxy-[benzo]quinone indicator. J. F. Mahoney and J. H. Michell (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 97—98).—The S compound is fused with Na_2O_2–sugar C, and the fused mass dissolved in 12N-HCl, neutralised with aq. 16N-NH_3, an indicator of tetrahydroxybenzoquinone–$AgNO_3$ added, and the mixture titrated with $BaCl_2$. 0·5—5 mg. of S can be determined rapidly and accurately. J. D. R.

Determination of mercury in organic compounds. Iodometric procedure based on the method of Rupp. H. A. Sloviter, W. M. McNabb, and E. C. Wagner (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 890—893).—The sample is digested with $K_2S_2O_8$–H_2SO_4 and the $HgSO_4$ produced is treated with KBr–$KBrO_3$, followed by aq. KI and aq. NaOH. The Hg is now pptd. with aq. N_2H_4 in presence of Na_2CO_3–$MgSO_4$, and the Hg collected and dissolved in known excess of KBr–$KBrO_3$, KI added, and the excess of I titrated with $Na_2S_2O_3$. The high results obtained by Rupp's method, in which CH_2O is the reducing agent, are probably due to reduction of some I by HCO_2H produced from CH_2O during pptn. of Hg or by Cannizzaro reaction. J. D. R.

Colour reaction for sulphurous acid, the thiol group, and formaldehyde. A. Steigmann (*J.S.C.I.*, 1942, **61**, 18—19).—The dye resulting from the action of CH_2O on fuchsin–H_2SO_3 is much more resistant towards strong mineral acids than are plain fuchsin solutions, which are almost decolorised by conc. H_2SO_4. Addition of aq. CH_2O to such a discoloured solution produces but little change; further addition of traces of aq. SO_2 develops an intense pink-violet colour. A diluted fuchsin solution containing much H_2SO_4 and some CH_2O is therefore a delicate and simple reagent for H_2SO_3. Thio-acids can be used in place of H_2SO_3; the new reagent is therefore useful also for the detection of thio-acids. Decolorised fuchsin–H_2SO_4 solution, with $SH·CH_2·CO_2H$ instead of H_2SO_3, is furthermore a selective CH_2O reagent. The new reagents may be used in conjunction with Feigl's I–azide reagent for SH in mercaptans and thio-acids.

Identification of organic acids by use of *p*-bromobenzyl-ψ-thiuronium bromide.—See A., 1942, II, 129.

Determination of citric acid in pure solutions and in milk by the pentabromoacetone method. E. F. Deysner and G. E. Hoem (*Ind. Eng. Chem.* [*Anal.*], 1942, **12**, 4—7; cf. Lampitt and Rooke, B., 1936, 1229).—Citric acid (**I**) is determined by oxidation with $KMnO_4$ in presence of KBr, which converts (**I**) into $CBr_3·CO·CHBr_2$ (**II**), the former method being modified by using an excess of $KMnO_4$ to ensure complete oxidation. Data are presented on the solubility of (**II**) in H_2O, with consequent loss by washing, and on loss in wt. of (**II**) by drying. No abs. method of determining (**I**) can be prescribed, and the method must be standardised for each material analysed. J. D. R.

Determination of citric acid.—See A., 1942, III, 360.

New and highly specified colorimetric test for methionine. T. E. McCarthy and M. X. Sullivan (*J. Biol. Chem.*, 1941, **141**, 871—876).—To 5 c.c. of the solution under examination are added successively 1 c.c. of 14·5N-NaOH, 1 c.c. of 1% glycine (**I**), and 0·3 c.c. of 10% aq. Na nitroprusside with mixing after each addition. The mixture is heated at 35—40° for 5—10 min., cooled in ice-water for 2 min., and treated with shaking with 5 c.c. of HCl–H_3PO_4 mixture (9 vols. of conc. HCl + 1 vol. of 85% H_3PO_4). Shaking is continued for 1 mm., after which the solution is cooled in H_2O at room temp. for 5—10 min. and the colour is matched against a standard solution of methionine (**II**) similarly treated. The use of conc. NaOH + (**I**) inhibits the colour due to histidine and HCl + H_3PO_4 gives a clearer colour than HCl alone. The reaction is highly sp. for (**II**) and is negative for all other NH_2-acids found in the acid hydrolysates of protein. Methionine sulphoxide is negative, as are homocystine, cystine, and cysteine, but glycylmethionine is positive. If the solution is kept cold at the time of addition of the acid no colour reaction is given by tryptophan even if present in considerable amount. The application of the test to the determination of the content of (**II**) in casein and edestin is described. H. W.

Determination of choline. Photometric modification of Beattie's method. M. H. Thornton and F. K. Broome (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 39—41).—The solution of choline (**I**) is pptd. with $NH_4[Cr(NH_3)_2(CNS)_4]$ and the ppt. dissolved in $COMe_2$. The concn. of the salt of (**I**) in the solution is determined photocolorimetrically. Concns. of (**I**) of 0·3—6·5 mg. per c.c. can be determined with a max. error of 2%. J. D. R.

Micro-determination of arginine. J. B. Dubnoff (*J. Biol. Chem.*, 1941, **141**, 711—716).—For complete separation of glycocyamine (**I**) and arginine (**II**) the salt concn. of the solution should be ≯ 0·5%. If neither compound is present in amount >2 mg.-%, the salt concn. may be as high as 1%. Urine is usually diluted 5—10 times with H_2O. Blood filtrates may be prepared by deproteinising according to Folin and Wu or by heat-coagulation at p_H 6 after 1 : 10 dilution with H_2O. Tissue extracts are diluted to contain 1 g. of fresh tissue in 40 ml. of suspension. The p_H is adjusted to 6·0 and the suspension immersed in boiling H_2O for 10 min., cooled, and filtered. Analyses are carried out on the filtrates. 5 ml. of the solution to be analysed are passed through the permutit column and the small amount of (**I**) remaining in the column is removed with 5 ml. of 0·3% NaCl. The combined filtrates contain all the (**I**). (**II**) is eluted by passing 10 ml. of 3% NaCl through the column. A 2-ml. portion is cooled in ice and treated with 0·5 ml. of the ice-cold $C_{10}H_7·OH–CO(NH_2)_2$ solution; after 2 min. 0·2 ml. of ice-cold NaOBr solution is added. The colour is simultaneously developed in a series of standards containing 0, 0·25, 0·5, 1·0, and 2·0 mg.-% of (**II**). After 20 min. the development of colour is complete and remains stable for 2 hr. at 0°. The tubes are shaken for a few sec. to remove excess of gas, warmed to room temp., and the intensity of the colour is measured in a spectrophotometer or colorimeter with light of ~0·525 μ. (yellow-green). H. W.

Determination of adenine. G. H. Hitchings and C. H. Fiske (*J. Biol. Chem.*, 1941, **141**, 827—835).—Adenine and, under certain conditions, guanine can be determined by pptn. with Na picrate and titration of the ppts. with standard NaOH. H. W.

Chlorosulphonic and as reagent for identification of alkylbenzenes.—See A., 1942, II, 136.

Photo-electric determination of nicotinic acid.—See A., 1942, III, 254.

Determination of adenosine-5′-phosphoric acid and its homologues.—See A., 1942, III, 183.

INDEX OF AUTHORS' NAMES, A., II.

APRIL, 1942.