BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

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A., II.—Organic Chemistry

JULY, 1943.

I.—ALIPHATIC.

Isomerisation of *n*-paraffins.—See B., 1943, II, 142.

Co-ordination of silver ion with unsaturated compounds. II. *cis*- and *trans*-Δ$^{\beta}$-Pentene. H. J. Lucas, R. S. Moore, and D. Pressman. **III. Mixtures of trimethylethylene and *cyclo*hexene.** H. J. Lucas, F. W. Billmeyer, jun., and D. Pressman (*J. Amer. Chem. Soc.*, 1943, **65**, 227—229, 230—231; cf. A., 1938, II, 224).—II. Distribution consts. K_W and K_D for *cis*- (**I**) and *trans*-Δ$^{\beta}$-pentene (**II**) and mixtures thereof between CCl_4 and (i) H_2O and (ii) N-KNO_3 and argentation consts. K_O and K_E are determined. *cis*-Configuration favours solubility in H_2O and co-ordination. Since (**I**) and (**II**) have distinguishable K_O and K_E, isomerisation does not occur in the Ag complex. For mixtures of (**I**) and (**II**), K_W and K_O, but not K_D and K_E, agree with the calc. vals.

III. Similar data are recorded for *cyclo*hexene and CHMe:CMe$_2$. The lower vals. of K_D and K_E for mixtures are due to the effect of one olefine on the solubility of the other in the aq. layer. Mixed olefines may be analysed by means of the above-named consts.

R. S. C.

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Oil of lavender. I. Lavandulol, a new monoterpene alcohol from oil of lavender. H. Schinz and C. F. Seidel. **II. Constitution of lavandulol.** H. Schinz and J. P. Bourquin (*Helv. Chim. Acta*, 1942, **25**, 1572—1591, 1591—1611).—I. *Lavandulol* (**I**), b.p. 94—95°/13 mm., α_D^{16} −10·20°, is most easily isolated from the esters of oil of lavender, which are hydrolysed and then treated with *o*-$C_6H_4(CO)_2O$ to separate linalool from the primary and *sec.* alcohols. From the latter mixture (**I**) is isolated by fractional distillation and finally purified through the *allophanate* (**II**), m.p. 117—118°, $[\alpha]_D^{20}$ −8·5° in MeOH. Isolation of (**I**) from the free alcohols which contain geraniol (**III**), nerol, and citronellol is rendered difficult by the presence of much borneol; it may be effected through the allophanate, the m.p. of which as thus prepared is >113—115°. In odour (**I**) closely resembles (**III**). Their physical properties are closely similar but (**I**), unlike (**III**), does not give a compound with $CaCl_2$ and is not dehydrated by *o*-$C_6H_4(CO)_2O$ at 200°. (**II**) usually has m.p. 117—118°; if large quantities of material are available this can be raised to 119—120° but products of m.p. 110—112° are then also obtained. All specimens give very closely similar (**I**) on hydrolysis. Alcohols obtained from the specimens of lower m.p. give the same product (allophanate, m.p. 119—120°) when warmed with AcOH, probably owing to a transformation of admixed limonene forms into more stable terpinolene forms. (**I**) gives an *acetate*, b.p. 61—63°/0·3 mm., which resembles linalyl acetate in odour, a 3 : 5-*dinitrobenzoate*, m.p. 59—60°, which darkens superficially on exposure to light, a non-cryst. phenylurethane, and an *anthraquinone*-2-*carboxylate*, m.p. 62—63°. Hydrogenation (PtO_2 in EtOAc) of (**I**) gives a H_4-derivative, b.p. 93—94°/12 mm., α_D^{20} +12·84° (*allophanate*, m.p. 101—102°), which is saturated towards $C(NO_3)_4$; in an individual, unrepeatable experiment with an inefficient catalyst a H_2-compound was obtained. With $SOCl_2$ (**I**) gives a sulphite, hydrolysable to unchanged (**I**). Attempted degradation of (**I**) by O_3 or $KMnO_4$ gives only $COMe_2$, CH_2O, $H_2C_2O_4$, and an inseparable mixture of more complex fragments. (**I**) resembles closely the alcohol (**IV**) obtained by Ruzicka *et al.* (A., 1935, 605) by the condensation of methylheptenone with CH_2O in presence of $Ba(OH)_2$, followed by treatment of the product with MgMeI and oxidation of the resultant glycol. (**IV**) gives an *allophanate*, m.p. 113—114°, and a 3 : 5-dinitrobenzoate, m.p. 65—67°, which do not depress the m.p. of the corresponding derivatives of (**I**). The *anthraquinone*-2-*carboxylate* of (**IV**) has m.p. 99—100° and the *allophanate* of the H_4-derivative of (**IV**) has m.p. 91—92°. A direct comparison of (**I**) and (**IV**) or their derivatives is difficult since (**I**) is optically active whereas (**IV**) is racemic. The identity in structure of (**I**) and (**IV**) is established in another manner.

II. Treatment of lavandulyl acetate with HBr–AcOH at 0° followed by elimination of HBr by C_5H_5N, hydrolysis, and purification of the product through the H phthalate leads to a partly inactive material from which the homogeneous *allophanate* (**V**), m.p. 139—140°, of *iso*lavandulol [βζ-dimethyl-ε-hydroxymethyl-Δ$^{\beta\epsilon}$-heptadiene] is isolated. *β-Methyl-ε-methylene-*Δ$^{\beta}$*-hepten-ζ-one* (**VI**), b.p. 67—68°/11 mm., is obtained in very small yield by condensing methylheptenone (**VII**) with H_2O–EtOH–CH_2O containing NaOAc and better from the ketone and paraformaldehyde in boiling C_6H_6–Et_2O containing $NaNH_2$ (0·33 mol.) and Na_2SO_4; it is freed from unchanged (**VII**) by taking advantage of its inability to react with $NaHSO_3$ and purified through the *semicarbazone*, m.p. 163—165°. The position of its double linkings is established by its absorption spectrum. It is reduced by $Al(OPr^{\beta})_3$ in $Pr^{\beta}OH$ to *ζ-methyl-γ-methylene-*Δ$^{\epsilon}$*-hepten-β-ol*, b.p. 84°/13 mm., which closely resembles linalool (**VIII**) and borneol in odour; it gives an *allophanate*, m.p. 97°, *acetate*, b.p. 81—83°/12 mm., and non-cryst. 3 : 5-dinitrobenzoate. Under defined conditions (**VI**) is transformed by MgMeI into *βζ-dimethyl-γ-methylene-*Δ$^{\epsilon}$*-hepten-β-ol* (**IX**), b.p. 80—82°/12 mm., which is purified through the borate and characterised as the *phenylurethane*, m.p. 81—82°; it is very similar to (**VIII**). Allyl isomerisation of (**IX**) is effected through the bromide, which after treatment with KOAc in $COMe_2$ and hydrolysis affords an alcohol mixture in which the primary material greatly predominates; after purification through the H phthalate the products gives an *allophanate*, m.p. 143—144°, which does not depress the m.p. of (**V**). The incomplete identity of the m.p. is attributed to the presence of terpinolene and limonene forms in differing proportions. (**I**) is therefore *βζ-dimethyl-ε-hydroxymethyl-*Δ$^{\beta\zeta}$*-heptadiene*, of which Ruzicka's alcohol is a not quite homogeneous form. *Tetrahydroisolavandulyl allophanate* has m.p. 99—100°, and *isolavandulyl* 3 : 5-*dinitrobenzoate* has m.p. 74—75°. The differences between αβ- and βγ-unsaturated terpene alcohols and the occurrence of irregular isoprene chains are discussed.

H. W.

Production of methyl alcohol.—See B., 1943, II, 142.

***ψ*-Saccharin chloride, reagent for identifying alcohols.**—See A., 1943, II, 211.

Purification of aliphatic acids and anhydrides.—See B., 1943, II, 143.

Manufacture of esters of chlorine-containing organic acids.—See B., 1943, II, 143.

Essential unsaturated fatty acids. P. Karrer and H. Koenig (*Helv. Chim. Acta*, 1943, **26**, 619—626).—Linoleic acid is converted by boiling $SOCl_2$ into its *chloride*, b.p. 159°/0·09 mm., and thence by CH_2N_2 in Et_2O into the corresponding CHN_2 ketone. This is directly treated with Ag_2O in EtOH at 60° and the product is hydrolysed to Δ$^{\iota\mu}$-*nonadecadienoic* [*homolinoleic*] *acid* (**I**), b.p. 177—178°/0·2 mm. (**I**) is converted by ozonisation in CCl_4 followed by oxidation with H_2O_2 into sebacic acid. Similarly (**I**) is transformed into the *chloride*, b.p. 173°/0·1 mm., CHN_2 ketone, and Δ$^{\kappa\gamma}$-*eicosadienoic acid* (**II**), b.p. 198°/0·08 mm. Phytenic or phytadienoic acid, (**I**), or (**II**) cannot replace linoleic acid as essential fatty acid and in the organism of the rat there is no appreciable formation of linoleic acid by β oxidation of (**II**).

H. W.

Jasmine perfumes. II. Synthesis of lactones with jasmone-like structure. L. Ruzicka, F. Lardon, and P. Treadwell (*Helv. Chim. Acta*, 1943, **26**, 673—679; cf. A., 1934, 75).—The prep. and purification of COMe·[CH$_2$]$_3$·OAc from CH_2O and $COMe_2$ is very difficult. Hydrogenation (Pd–$CaCO_3$ in EtOAc) of CHAc:CH·OBz gives *γ-keto-n-butyl benzoate* (**I**) (*semicarbazone*, m.p. 156°; *p-nitrophenylhydrazone*, m.p. 128—128·5°), which gives BzOH and COMe·CH:CH$_2$ when distilled in a high vac. but can be purified by mol. distillation. It is hydrolysed with exceptional ease. (**I**) is transformed by *n*-C_5H_{11}·CHBr·CO_2Et and Zn in dioxan into *β-methyl-α-n-amyl-*Δ$^{\kappa}$*-pentenolactone* [*dihydrojasmone lactone*] (**II**), b.p. 105—108°/0·5 mm., and BzOH. Similarly (**I**) and Et αγδ-tribromo-*n*-heptoate yield *β-methyl-α-n-*Δ$^{\beta'}$*-pentenyl-*Δ$^{\alpha}$*-pentenolactone* [*jasmone lactone*] (**III**), which absorbs 2 H_2 (Adams). The odour of (**III**) resembles that of jasmone and of (**II**) dihydrojasmone.

H. W.

Electrolysis of mixtures of nitrate with malonic acid, the hydrogen ester of malonic acid, ethyl- and dimethyl-malonic acid, and succinic acid. F. Fichter and W. Steinbuch (*Helv. Chim. Acta*, 1943, **26**, 695—704).—Electrolysis of the mixtures gives the nitrates of esters of monobasic OH-acids but the greater part of the material is used in the Kolbe synthesis. Mixtures of KNO_3 and $CH_2(CO_2K)_2$ give small amounts of $(CH_2{\cdot}O{\cdot}NO_2)_2$ and $([CH_2]_2{\cdot}ONO_2)_2$. Under similar conditions $CO_2Et{\cdot}CH_2{\cdot}CO_2K$ gives $NO_2{\cdot}O{\cdot}CH_2{\cdot}CO_2Et$, $(CH_2{\cdot}CO_2Et)_2$, EtOAc, and some $CHO{\cdot}CO_2Et$. $CO_2Et{\cdot}CHEt{\cdot}CO_2K$ yields $NO_2{\cdot}O{\cdot}CHEt{\cdot}CO_2Et$ with the two isomeric Et_2 diethylsuccinates. and $CHMe{:}CH{\cdot}CO_2Et$, $CHEt(CO_2Et)_2$, and possibly $COEt{\cdot}CO_2Et$, $CO_2Et{\cdot}CMe_2{\cdot}CO_2K$ affords Et *α-hydroxyisobutyrate nitrate*, b.p. 89—91°/10 mm. [converted by reductive hydrolysis with $Ba(SH)_2$ into $OH{\cdot}CMe_2{\cdot}CO_2H$ and by heating with *p*-toluidine at 140° into $OH{\cdot}CMe_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4Me$-*p*, m.p. 132—133°], with $(CMe_2{\cdot}CO_2H)_2$, $CH_2{:}CMe{\cdot}CO_2Et$, and $CMe_2(CO_2Et)_2$. $CO_2Et{\cdot}[CH_2]_2{\cdot}CO_2K$ yields $([CH_2]_2{\cdot}CO_2Et)_2$, $NO_2{\cdot}O{\cdot}[CH_2]_2{\cdot}CO_2Et$, and $CH_2{:}CH{\cdot}CO_2Et$.

H. W.

Stereochemical studies. XXIII. Optically active dibromosuccinic acids. B. Holmberg (*Arkiv Kemi, Min., Geol.*, 1941, **14**, **B**, No. 33, 7 pp.).—$CHPhMe{\cdot}NH_2$ is no better than morphine or cinchonine for resolving *r*-$(CHBr{\cdot}CO_2H)_2$ (**I**), but is suitable for final optical purification of the stereoisomerides. (I) is shown by its *X*-ray spectrum to be a racemate and not a *dl*-mixture. Vals. of $[\alpha]_D^{18}$ for optically active (**I**) in EtOAc, EtOH, and H_2O are given. The decomp. of (**I**) in neutral solution takes place via a lactone with α of opposite sign, and is inhibited by Br′.

M. H. M. A.

Unsaturated acids and thioacetic acid. B. Holmberg and E. Schjånberg (*Arkiv Kemi, Min., Geol.*, 1940, **14**, **A**, No. 7, 22 pp.; cf. A., 1939, II, 155).—AcSH reacts with unsaturated acids, including *cis*-$CO_2H{\cdot}CMe{:}CH{\cdot}CO_2H$ (**I**) and $(:CH{\cdot}CO)_2O$ (**II**), but not *trans*-(**I**), citraconic anhydride, or aconitic acid, to give (room temp. or 100°) SAc derivatives of saturated acids in good yield, the direction of addition being the same as for HCl, except with $CH_2{:}CH{\cdot}CH_2{\cdot}CO_2H$ and (**I**). The SH-acids (deacetylation with cold aq. NaOH) are oxidised (I–AcOH) to disulphidodiacids, and their CH_2Ph thioethers with neutral H_2O_2 to sulphoxides and thence ($KMnO_4$) to sulphones. The following are prepared as above: *β-acetylthiolpropionic*, m.p. 52—54°, *β-acetylthiol-*, b.p. 129—130°/3 mm., *β-benzylsulphinyl-*, m.p. 70—75°, clear at 78° (also from $CHMeBr{\cdot}CH_2{\cdot}CO_2H$) (+$H_2O$, m.p. 66—68°), *β-benzylsulphonyl-*, m.p. 132—133°, *γ-acetylthiol-*, b.p. 138·5—139°/3 mm., *γ-thiol-*, b.p. 85—87°/0·05 mm. (*thiolactone*, b.p. 55—56°/3·5 mm., formed on distillation), *γγ′-disulphido-di-*, m.p. 109—110°, and *γ-benzylsulphonyl-butyric*, m.p. 148—149°, *acetylthiolsuccinic*, m.p. 125—126°) [much slower from *trans-* than from *cis*-$(:CH{\cdot}CO_2H)_2$] [*anhydride*, m.p. 71—73°, from (**II**)], *β-acetylthiol-β-phenylpropionic*, m.p. 95—96°, *acetylthiomethylol-*, m.p. 90·5—91·5°, and *thiomethylolsuccinic*, m.p. 107·5—108·5° (*γ-thiolactone*, m.p. 109—110°, on heating), *acids*. (I) gives slowly the diastereoisomeric *α-acetylthiol-β-methylsuccinic acids* (**III**), *A*, m.p. 151—153°, *B* (impure), m.p. 108—112° (decomp.), and thence *α-thiol-β-methylsuccinic acids* (**IV**), *A*, m.p. 108—110°, *B*, m.p. 189—190° (decomp.), and CH_2Ph *thioethers*, *A*, m.p. 141—142°, *B*, m.p. 156—157°. Ac_2O and (**IV**) *B* give (**III**) *A*. $SH{\cdot}CMe(CO_2H){\cdot}CH_2{\cdot}CO_2H$ (*Ac* derivative, m.p. 122—123·5°; CH_2Ph *thioether*, m.p. 153—154·5°) gives with $CH_2Cl{\cdot}CO_2H$ *α-carboxymethylthiol-α-methylsuccinic acid*, m.p. 132—133°.

M. H. M. A.

Configurative relationship between optically active malic and thiomalic acids.—See A., 1943, I, 154.

Photometric determination of ascorbic acid.—See A., 1943, III, 502.

Production of γ-keto-β-methylbutanol and methyl *iso*propenyl ketone.—See B., 1943, II, 144.

Manufacture of polyalkylenepolyamines.—See B., 1943, II, 144.

Stereochemistry of labile compounds of tervalent nitrogen.—See A., 1943, I, 175.

Structural characteristics of amino-acids.—See A., 1943, I, 177.

Occurrence of *d*-glutamic acid in protein of tumours and healthy organs.—See A., 1943, III, 402.

Synthesis of peptides by transamination. R. M. Herbst and D. Shemin (*J. Biol. Chem.*, 1943, **147**, 541—547).—Alternate additions of N-NaOH and $ClCO_2CH_2Ph$ to an ice-cold solution of *dl*-alanylalanine gives two modifications of dl-*carbobenzyloxyalanylalanine*, m.p. 144·5—145·5° (**I**) and 168—169° (**II**) (softens at 165°) respectively, with considerable proportions of material of m.p. 133·5—135° (**III**), which may be a mol. compound, a solid solution, or a fortuitous mixture of (**I**) and (**II**). When an aq. solution of pyruvylalanine and *dl*-$NH_2{\cdot}CHPh{\cdot}CO_2H$ is boiled under N_2 transamination occurs accompanied by formation of CO_2 and PhCHO. The product is converted by $ClCO_2CH_2Ph$ into a mixture of (**II**) and (**III**). A scheme is suggested for the biological synthesis of peptide chains from non-amino-acid precursors involving two simple reactions, amination and acylation.

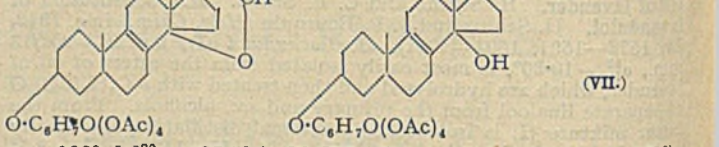
H. W.

Preparation of urea nitrate.—See B., 1943, II, 143.

II.—SUGARS AND GLUCOSIDES.

Raman spectra of sugars.—See A., 1943, I, 176.

Heart glycosides. XX. Structure of scilliroside. A. Stoll, J. Renz, and A. Helfenstein (*Helv. Chim. Acta*, 1943, **26**, 648—672; cf. A., 1942, II, 218, 279).—The structure (*A*; R = H) is assigned to scilliroside (**I**). (I) is oxidised by CrO_3 or $Pb(OAc)_4$ to a substance (**II**) very freely sol. in H_2O or EtOH which could not be caused to crystallise whereas its tetra-acetate (**III**) affords *dehydroscilliroside tetra-acetate* (**IV**) (*A*; R = Ac. 12-CH·OH to 12-CO), m.p. 228—230°, $[\alpha]_D^{20}$ −81·8° in $CHCl_3$, −82·5° in MeOH (*semicarbazone*, decomp. 220°), also obtained by acetylation of (**II**). The absorption curves of (**II**) and (**IV**) are very closely similar. (**IV**) is readily dehydrated by mineral acids in aq. EtOH to *anhydrodehydroscilliroside tetra-acetate*, m.p. 228°, $[\alpha]_D^{20}$ −100° in MeOH, the absorption spectrum of which indicates a constitution (*A*) but with double linkings $C_{(8:14)}$ and $C_{(9:11)}$; the CO group appears to facilitate the formation of a conjugated system. (**IV**) is converted by treatment with NaOH–MeOH followed by dil. acid and then by acetylation into *Me deacetyldehydroisoscillirosidate penta-acetate* (**V**), m.p. 174°, $[\alpha]_D^{20}$ +55° in MeOH. (**IV**) is hydrogenated (PtO_2 in MeOH; Pd or Raney Ni does not offer any advantage) to a mixture of neutral isomerides from which a *compound* (**VI**), $C_{36}H_{56}O_{14}$, m.p. 216—217°, $[\alpha]_D^{20}$ −52·5° in MeOH, is isolated and an acid mixture which yields a *substance*, $C_{38}H_{38}O_{14}$, m.p. 196—198°, $[\alpha]_D^{20}$ −54·5° in MeOH. The corresponding Me ester has m.p. ~155° and does not appear to be homogeneous; it is oxidised to a diketone (*disemicarbazone*, $C_{27}H_{44}O_4N_6$). Tetrahydrodeacetyldeoxyscilliroside is transformed by Ac_2O–C_5H_5N into a mixture of *tetra-acetates*, m.p. 240°, $[\alpha]_D^{20}$ +35° in MeOH, and m.p. 219°, $[\alpha]_D^{20}$ +36° in MeOH, the former of which is oxidised by $Pb(OAc)_4$ to *tetrahydrodeacetyldeoxydehydroscilliroside tetra-acetate*, m.p. 176—177°, hydrogenated (PtO_2 in MeOH) to a substance which appears to be identical with (**VI**). Me deacetyl*iso*scillirosidate penta-acetate is resistant towards $Pb(OAc)_4$ but is slowly oxidised by CrO_3 to the *compound* (**VII**),



m.p. 192°, $[\alpha]_D^{20}$ −37·5° in MeOH (*disemicarbazone*, decomp. 172°). Me tetrahydrodeacetyldeoxy*iso*scillirosidate (*loc. cit.*, new m.p. 240—242°, $[\alpha]_D^{20}$ −24·6° in MeOH) is hydrolysed by acid to glucose and a doubly unsaturated *acid*, $C_{24}H_{34}O_4$, m.p. 185° (decomp.) after softening, $[\alpha]_D^{20}$ −13·5° in MeOH, hydrogenated (PtO_2 or Pd-C) to the saturated *acid*, $C_{24}H_{38}O_4$, m.p. 168°, $[\alpha]_D^{20}$ +15° in MeOH. The presence of a difficultly-reactive, nuclear double linking in (**I**) is established by the oxidation of (**I**) by BzO_2H to the corresponding *oxide*, m.p. 228—230°, softens at 215°, $[\alpha]_D^{20}$ −34·5° in MeOH. The structure of (**I**) is based on the following considerations. Acid hydrolysis removes from (**I**) a mol. of glucose which in analogy with the other heart glucosides is supposed to be attached at $C_{(3)}$. The *sec.* nature of OH united to sugar is experimentally established. The aglycon has not been isolated but all the evidence indicates a steroid structure. Absorption spectrum and behaviour towards alcoholic alkali show that (**I**) like scillaren-*A* has a doubly unsaturated, six-membered lactone ring; this contains OAc assumed to be α- to CO. (**I**) contains a free *sec.* OH which can be oxidised to CO but not acylated; its position at $C_{(12)}$ is established. The presence of *tert.* OH, readily removable as H_2O, at $C_{(14)}$ is proved. The resistant nuclear double linking in (**I**) can be hydrogenated after oxidation of OH at $C_{(12)}$ or elimination of OH at $C_{(14)}$ with production of a second nuclear double linking; this observation and the absorption spectrum of (**I**) indicate the presence of the linking at $C_{(8:9)}$.

H. W.

Configuration of starch and its crystalline degradation products.—See A., 1943, I, 177.

Non-carbohydrate substances in the cereal starches.—See A., 1943, III, 446.

III.—HOMOCYCLIC.

Highly hindered stilbenes. R. C. Fuson, J. J. Denton, and C. E. Best (*J. Org. Chem.*, 1943, **8**, 64—72).—Three hindered stilbenes

are shown to react with H_2, $KMnO_4$, O_3, BzO_2H, Na, K–Na, and a AgOBz–I complex normally but frequently much more slowly than do the unhindered stilbenes. *αβ*-Dimesitylethylene (I), m.p. 132·5—133·5°, is obtained by the action of MgMeI, Mg–MgI_2, or Mg alone on $C_6H_2Me_3$·$CHCl_2$. The yields are nearly the same with the three reagents but the use of Grignard reagent is preferable because it gives a product which is easily purified. *αβ-Dimesitylethanol* (II), m.p. 128—129° (*acetate*, m.p. 117·5—118°), is obtained by the action of H_2 at 125°/2000 lb. on deoxymesitoin in abs. EtOH containing Cu chromite or from 2 : 4 : 6 : 1-$C_6H_2Me_3$·CHO and 2 : 4 : 6 : 1-C_6H_2Me·CH_2·MgCl but a tedious separation from $(CH_2·C_6H_2Me_3)_2$ is required in the latter method. (II) is transformed by H_2SO_4–H_2O (1 : 1 by vol.) at 100° into (?) *di-(αβ-dimesityl)ethyl ether*, m.p. 177—180°, and by P_2O_5 in boiling C_6H_6 or boiling Ac_2O containing conc. HCl into (I). $C_6H_2Me_3$·CHO and CH_2Ph·MgCl give *β-phenyl-α-mesitylethanol*, m.p. 65—66°, also obtained by the action of H_2 at 150°/1550 lb. on CH_2Ph mesityl ketone in MeOH containing Cu chromite and converted by H_2SO_4–H_2O (1 : 1 by vol.) at 100° into *α-phenyl-β-mesitylethylene* (III), m.p. 55—56°. *α-Phenyl-β*-2 : 4 : 6-*tri*iso*propylphenylethanol* is derived from $C_6H_2Pr^{\beta}_3$·CHO and CH_2Ph·MgCl and is transformed by H_2SO_4–H_2O at 100° into *α-phenyl-β-tri*iso*phenylethylene* (IV), m.p. 82·5—83·5°. Treatment of (I) with H_2 at 100°/ and then at 150°/200 lb. in methyl*cyclo*hexane containing Raney Ni gives $(CH_2·C_6H_2Me_3)$, m.p. 114—117°; (III) and (IV) are transformed by similar treatment into *α-phenyl-β-mesitylethane*, m.p. 38—39°, and *α-phenyl-β*-2 : 4 : 6-*tri*iso*propylphenylethane*, b.p. 155—161°/4 mm., m.p. 33—34°. Ozonisation of (I) followed by treatment of the resulting product with alkaline H_2O_2 gives mesitol (V) and mesitoic acid (VI); analogously (III) yields (V), (VI), and BzOH and (IV) yields BzOH and 2 : 4 : 6 : 1-$C_6H_2Pr^{\beta}$·CO_2H and BzOH. (III) and BzO_2H in $CHCl_3$ afford *α-phenyl-β-mesitylethylene oxide*, m.p. 67—68°, reduced by HI to (III); 1 : 3 : 5-$C_6H_3Me_3$ and BzO_2H in $CHCl_3$ give (V) in 18·6% yield. Successive treatments of (III) with powdered Na and solid CO_2 in Et_2O lead to *α-phenyl-β-mesitylsuccinic acid*, m.p. 217—219°, converted by boiling AcCl into the *anhydride*, m.p. 129—130°. *αβ-Dimesitylsuccinic acid*, m.p. 283—285°, and *α-phenyl-β*-2 : 4 : 6-*tri*iso*propylphenylsuccinic acid*, m.p. 195—198°, are obtained similarly. Under identical conditions the colour of a solution of $KMnO_4$ is discharged by stilbene in 1 min., by (III) in 4·5 hr., by (IV) in 30 hr., and by (I) in 60 hr. (I) is converted by the I–AgOBz complex in boiling C_6H_6 followed by alkaline hydrolysis into hydromesitoins, m.p. 212—213° and 158—159°. (III) appears to give a mixture of the expected glycols. H. W.

Synthesis of 1-methylnaphthalene. O. Grummitt and A. C. Buck (*J. Amer. Chem. Soc.*, 1943, **65**, 295—296).—$C_{10}H_8$, paraformaldehyde, and conc. H_3PO_4 in AcOH at 80—85° give 1-$C_{10}H_7$·CH_2Cl (70—72%), b.p. 128—133°/5 mm., the Grignard reagent from which gives *Hg α-naphthylmethyl chloride*, m.p. 126—128°, *α-α′-naphthylacetonaphthalide*, m.p. 175—177°, and 1-$C_{10}H_7$Me (80%), b.p. 238—240° (picrate, m.p. 140—141°). R. S. C.

Nitration of naphthalene. H. E. Fierz-David and R. Sponagel (*Helv. Chim. Acta*, 1943, **26**, 98—111).—Very finely-divided $C_{10}H_8$ is added gradually to a mixture of 62% HNO_3 and 80% H_2SO_4 at 30—40°, after which the temp. is kept for 6 hr. at 50° and 1 hr. at 60°. The crude product yields 2 : 4 : 1-$(NO_2)_2C_{10}H_5$·OH (I), m.p. 137° (yield 0·43%), to aq. NaOH. Distillation of the thus-purified product under 12 mm. gives a mixture (II) of mononitronaphthalenes containing 4·6% of 2-$C_{10}H_7$·NO_2 and a residue in which 1 : 5- and 1 : 8-$C_{10}H_6(NO_2)_2$ are identified. Pure 1-$C_{10}H_7$·NO_2, m.p. 57·8° (block), is best obtained by several crystallisations of (II) from EtOH and from light petroleum. It is distinguished from 2-$C_{10}H_7$·NO_2, which has an odour of cinnamon, by absence of odour and capability of sublimation in a vac. The nitration of $C_{10}H_8$ by 95·5% HNO_3 in AcOH–Ac_2O is described. With ~21% HNO_3 at 95—98° oxidation of $C_{10}H_8$ is not more marked than with other methods of nitration and the yield of crude nitronaphthalenes is ~94·5%. The detection of 2-$C_{10}H_7$·NO_2 in (II) is best effected by reduction and acetylation followed by the separation of *β*-$C_{10}H_7$·NHAc by crystallisation from EtOH. The m.p. diagram of 1- and 2-$C_{10}H_7$·NO_2 is given. Unsuccessful attempts to increase the yield of (I) from $C_{10}H_8$ by use of dil. HNO_3 in presence of $NaNO_2$ and by the use of mixed acids with $NaNO_2$ are described. (I) is primarily formed from $C_{10}H_8$ and not through 1-$C_{10}H_7$·NO_2. Nitration of $C_{10}H_8$ at −60° does not give a trace of 1 : 3-$C_{10}H_6(NO_2)_2$, which therefore is unobtainable by direct nitration of $C_{10}H_8$. H. W.

Butylnaphthalenes and their derivatives. I. 2-*tert.*-Butylnaphthalene. N. G. Bromby, A. T. Peters, and F. M. Rowe (*J.C.S.*, 1943, 144—146).—$C_{10}H_8$, $Bu^{\gamma}Cl$, and $ZnCl_2$ at 70—105° afford 2-$C_{10}H_7Bu^{\gamma}$ (I), b.p. 125°/4 mm. (picrate, m.p. 100—101·5°), and two $C_{10}H_6Bu^{\gamma}_2$, m.p. 146—147°, and 90—95° (picrate, m.p. 157—158°); no 1-$C_{10}H_7Bu^{\gamma}$ is isolated. (I) is similarly obtained using $Bu^{\gamma}Br$ or by dehydrogenating 2-*tert.*-butyl-5 : 6 : 7 : 8-tetrahydronaphthalene (II) (from tetrahydronaphthalene, $Bu^{\gamma}Cl$, and $ZnCl_2$) with S at 215—230°. *p*-$C_6H_4Bu^{\gamma}$·CO·$[CH_2]_2$·CO_2H [*semicarbazone*, m.p. 204—205° (decomp.)] is reduced (Clemmensen) to *p*-$C_6H_4Bu^{\gamma}$·$[CH_2]_3$·CO_2H (*amide*, m.p. 132—134°), the chloride, b.p. 152—154°/14 mm., of which with $AlCl_3$ in light petroleum (b.p. 60—80°) gives 1-*keto*-7-tert.-*butyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 101—102·5° (*semicarbazone*, m.p. 225—226°). Clemmensen reduction then affords (II), whence (I). (II) is oxidised by aq. $KMnO_4$–Na_2CO_3 at 95°, followed by H_2O_2–aq. NaOH at room temp., to 4-tert.-*butylphthalic acid*, m.p. 160—161° (*anhydride*, m.p. 75·5—76·5°). 2-tert.-*Butyl*-1 : 4-*naphthaquinone*, m.p. 76—77° [*phenylhydrazone*, m.p. 190—191°; *p-nitrophenylhydrazone*, m.p. 264—265° (decomp.)], is obtained from (I) and CrO_3–50% aq. AcOH at 65—70°. A. T. P.

Nuclear alkylated anilines.—See B., 1943, II, 171.

Sulphonation of aniline.—See B., 1943, II, 166.

Sulphanilamide derivatives.—See B., 1943, III, 134, 135.

Sulphilimines derived from sulphanilamide. C. W. Todd, J. H. Fletcher, and D. S. Tarbell (*J. Amer. Chem. Soc.*, 1943, **65**, 350—354).—No product was obtained by heating *p*-NH_2·C_6H_4·SO_2·NH_2 (I), Ph_2SO or Et_2SO, and a dehydrating agent. $AsPh_3$ and $AsBu_3$ also do not react. However, the *salts*, *p*-NHAc·C_6H_4·SO_2·NMX [M = Na, X = Cl (II), decomp. 195—205°, or Br, decomp. 250—260°; M = K, X = Cl (III) (best), decomp. 190—200°, or Br, decomp. 210—220°] (prep. described), with SRR′ in boiling 60% EtOH or H_2O at room temp. give 55—85% of N^4-*acetyl*-S-*dimethyl*-, m.p. 141—142° (decomp.), *-diethyl-*, m.p. 181—182° (decomp.), *-di-*n-*propyl-* (IV), m.p. 166—167° (decomp.), *-di-*n-*butyl-* (V), m.p. 160—160·5° (decomp.), *-di-*n-*amyl-*, m.p. 158·5—160° (decomp.), *-diphenyl-* (VI), m.p. 204—204·5°, *-dibenzyl-*, m.p. 192·5—193°, -p-*tolyl*-S-*methyl-* (VII), m.p. 180—180·5°, and *-di-*p-*acetamidophenylsulphanilylsulphilimine* (VIII), m.p. 163·5—164·5° (decomp.), *p*-NHAc·C_6H_4·SO_2·NSRR′. In HCl–dioxan–H_2O, (VI) gives *sulphanilyldiphenylsulphilimine* (IX), m.p. 183—184°, which is diazotised in quinoline–H_2SO_4–H_2O at <10° and then coupled with *β*-$C_{10}H_7$·OH to a product, m.p. 210—211° [(VI) does not thus react], and in conc. HCl at 100° gives (I) and Ph_2SO. In 1% aq. NaOH–PhMe, (V) gives (I) (56%), Bu^{α}_2S, and Bu^{α}_2SO; (IV) gives similarly Pr^{α}_2S. 2-*Acetamidothiazoline* (prep. from the amine by Ac_2O–C_6H_6), m.p. 194·5—195°, with (II) in aq. dioxan gives the S-*oxide*, m.p. 199—200°. SMe·C(:NH)·NH_2,H_2SO_4, OEt·CH:C$(CO_2Et)_2$, and KOH in H_2 at 10° (later 100°) give 6-*hydroxy*-2-*methylthiol*-5-*carbethoxypyrimidine* (34%), m.p. 132—133°, which does not condense with (III), but with boiling $SOCl_2$ gives 6-*chloro*-2-*methylthiol*-5-*carbethoxypyrimidine*, m.p. 58—59·5°. 2-Methylthiolquinoline does not condense with (III) but with chloramine-*T* (X) gives the *sulphilimine*, m.p. 128—129°. R_2S and (X) give p-*toluenesulphonyl*-S-*di-methyl-*, m.p. 154—155°, -n-*propyl-*, m.p. 110—110·5°, and -n-*butyl-sulphilimine*, m.p. 77·5—78·5°. Of the sulphilimines, only (VII) is active [≪ (I)] against *Streptococcus hæmolyticus*. (VIII) and (IX) are inactive. (II) and (III) are inferior to (X) as disinfectants. R. S. C.

Synthesis of sulphanilylamidines. C. E. Kwartler and P. Lucas (*J. Amer. Chem. Soc.*, 1943, **65**, 354—355).—*p*-NHAc·C_6H_4·SO_2Cl and the appropriate amidine in neutral or slightly alkaline aq. $COMe_2$ at 0—5° give N^4-*acetylsulphanilyl-acet-* (51%), m.p. 241—243°, *-propion-*, m.p. 192—195°, *-butyr-*, m.p. 149—151°, *-tridec-*, m.p. 114—116°, *-benz-*, m.p. 211—212°, and *-phenylacet-amidine*, m.p. 193—195°, which in 15—25% HCl–EtOH at room temp. (not other conditions) give 52—75% of the *sulphanilyl-amidines*, m.p. 150—152°, 149—151°, 79—82°, 94—95°, 207—209°, and 173—175°, respectively (cf. B.P. 538,822, B., 1941, III, 344; A., 1943, II, 128). *n*-$C_{12}H_{25}$·CN with HCl–Et_2O–EtOH at 5° gives *tridecimino Et ether hydrochloride*, m.p. 99—102° (decomp.), which with 9·5% NH_3–EtOH at room temp. gives *tridecamidine hydrochloride*, m.p. 135—136°. R. S. C.

Thermal decomposition of quaternary ammonium phenoxides, with reference to the Claisen rearrangement. D. S. Tarbell and J. R. Vaughan, jun. (*J. Amer. Chem. Soc.*, 1943, **65**, 231—233).—CH_2:CH·CH_2·NPhMe$_2$Br (I) (prep. from CH_2:CH·CH_2Br and $NPhMe_2$ in EtOAc), m.p. 125—126°, with Ag_2O–H_2O gives a solution of the hydroxide, which, when distilled with *m*-2-xylenol (II) and NaOH at 1 atm., gives $NPhMe_2$ (92%) and 2 : 6 : 1-$C_6H_3Me_2$·O·CH_2·CH:CH_2 (III) (77%). Use of PhOH or *p*-cresol in place of (II) gives CH_2:CH·CH_2·OPh (IV) (58%) or *p*-C_6H_4Me·O·CH_2·CH:CH_2 (80%), respectively. KOPr$^{\alpha}$, (I), and (II) in Pr$^{\alpha}$OH give *phenyldimethylallylammonium* 2 : 6-*dimethylphenoxide*, +H_2O, m.p. 85—87°, and +3H_2O, m.p. 68—70°, which at 60—85°/2 mm. gives $NPhMe_2$ (74%) and (III) (69%). Treating (I) in H_2O with AgOPh, filtering, and distilling gives $NPhMe_2$ (81%) and (IV) (59%). It is concluded that the rearrangement of phenol allyl ethers does not occur by cleavage into allyl and phenoxide ions. R. S. C.

Condensation of aryldiazonium salts and/or hydroxides with secondary nitroalkanes. C. F. Feasley [with E. F. Degering] (*J. Org. Chem.*, 1943, **8**, 12—16).—ArN_2Cl is neutralised with NaOH and immediately treated with a solution of the *sec.* NO_2-alkane in NaOH; as soon as the reaction is complete the product should be isolated from the ice-cold solution but in the case of alkali-sol. products

sufficient time must be allowed for the coupling before addition of acids. In stability of the chromophoric azo-linking and ease of purification, these products are superior to those derived from the primary NO_2-alkanes. If the original amine contains acidic auxochromic groups, the condensation product dyes silk and wool directly; coupling may be made on the fibre. The following are described: *β-nitro-β-benzeneazo-*, b.p. 98·0°/7 mm., *-β-o-*, m.p. 56·9°, and *-β-m-*, m.p. 71·2—72·2°, *-nitrobenzeneazo-*, *-β-4-nitro-o-toluene-azo-*, m.p. 70·1°, *-β-p-acetamidobenzeneazo-*, m.p. 125·3—125·8°, *-β-p-chlorobenzeneazo-*, m.p. 67·8°; *-β-p-bromobenzeneazo-*, m.p. 90—91°, *-β-2 : 5-dichlorobenzeneazo-*, m.p. 57—58°, *-β-2 : 4 : 6-tribromobenzeneazo-*, m.p. 58·1°, *-β-p-tolueneazo-*, m.p. 20±1°; *-β-o-*, m.p. 93·2—93·6°, and *β-p-carboxybenzeneazo-*, m.p. 167—169°, and *-β-2-naphthaleneazo-propane*, m.p. 67°; *β-nitro-β-m-nitrobenzeneazo-*, m.p. 63·3—63·7°, *-β-4-nitro-o-tolueneazo-*, m.p. 48·9°, *-β-2 : 5-dichlorobenzeneazo-*, m.p. 40—40·3°, *-β-2 : 4 : 6-tribromobenzeneazo-*, m.p. 57·4—58°, and *-β-p-carboxybenzeneazo-butane*, m.p. 129—130°. *β-Nitro-β-phenyl-1 : 4-phenylenedisazo-propane*, m.p. 107—108°, and *-butane*, m.p. 80·9—81·4°, are described. pp'-*Di-β-(β-nitropropaneazo)diphenyl* has m.p. 162—163·6°. H. W.

Products of the action of azobenzene-*p*-carboxyl chloride on α-aminocarboxylic acids and their esters. P. Karrer, R. Keller, and G. Szönyl (*Helv. Chim. Acta*, 1943, **26**, 38—50).—Attempts are described to obtain *N*-acyl derivatives of NH_2-acids suitable for chromatographic separations. Agitation of *p*-$PhN_2{\cdot}C_6H_4{\cdot}COCl$ (**I**) in Et_2O with *l*-valine in 2N-NaOH at room temp. affords 2-p-*benzeneazophenyl*-4-iso*propyloxazol*-5-*one* [N-p-*benzeneazobenzoylvaline lactone*] (**II**), m.p. 115°, (which gives dark violet alkali salts), l- (**III**), m.p. 157—159°, $[\alpha]_D^{15}$ −44·85° in EtOH, and r-, m.p. 229—230°, -N-p-*benzeneazobenzoylvaline*, the latter arising from the hydrolysis of (**II**). Under similar conditions (**I**) and *l*-leucine yield 2-p-*benzeneazophenyl*-4-iso*butyloxazol*-5-*one*, m.p. 147°, and r-N-p-*benzeneazobenzoyl-leucine* (**IV**), m.p. 173°. Glycine yields N-p-*benzeneazobenzoylglycine* (**V**), m.p. 225°, apparently without the corresponding lactone. l(+)-N-p-*Benzeneazobenzoylalanine* (**VI**), m.p. 220°, $[\alpha]_D^{15}$ +55·07° in $COMe_2$, but no lactone is derived from *l*(+)-alanine. The *Me* esters of (**III**), m.p. 138°, $[\alpha]_D^{15}$ −38·4° in $COMe_2$, (**IV**), m.p. 133°, (**V**), m.p. 118°, and (**VI**), m.p. 148°, $[\alpha]_D^{15}$ +38·4° in $COMe_2$, are obtained by means of CH_2N_2. Gradual addition of (**I**) to the appropriate NH_2-acid ester hydrochloride in C_5H_5N at 40—60° leads to the *Me* esters of N-p-*benzeneazobenzoyl*-l-*leucine* (**VIII**), m.p. 104°, $[\alpha]_D^{15}$ +22·6° in $COMe_2$, -l-*glutamic acid*, m.p. 126—128°, $[\alpha]_{608}^{15}$ −11·6° in $COMe_2$, -l-*phenylalanine*, m.p. 145—146°, $[\alpha]_{608}^{15}$ −99·2° in $COMe_2$, -l-*aspartic acid*, m.p. 148—150°, $[\alpha]_{608}^{14}$ −17·3° in $COMe_2$, -l-*methionine*, m.p. 118—119°, $[\alpha]_{608}^{12}$ −27·32° in $COMe_2$, and -l-*proline*, m.p. 125—126°, $[\alpha]_{627}^{12}$ −36·27° in $COMe_2$. The chromatographic separation of mixtures of the Me esters of (**V**), (**VI**), and (**III**) with (**VII**) on basic Zn carbonate is described; $Ca(OH)_2$ and Al_2O_3 are less suitable. H. W.

Nuclear methylation of α-naphthol. A correction. J. W. Cornforth, (Mrs.) R. H. Cornforth, and (Sir) R. Robinson (*J.C.S.*, 1943, 168; cf. A., 1943, II, 28).—The substance obtained from "4-piperidinomethyl-1-naphthol" (**I**) and NaOMe–MeOH is not 4 : 1-$C_{10}H_6Me{\cdot}OH$, but 2 : 4-*dimethyl*-1-*naphthol*, m.p. 84—85° (*picrate*, m.p. 143—144°). That (**I**) is actually the 2 : 1-derivative (cf. Feldman *et al.*, A., 1942, II, 205) is confirmed by hydrogenation (Cu chromite in EtOH at 165°/100 atm.) to 2 : 1-$C_{10}H_6Me{\cdot}OH$ (*picrate*, m.p. 133—134°). A. T. P.

Colour reactions for stilbœstrol.—See A., 1943, II, 212.

Mixed β-naphthyl thioethers. F. E. Ray and G. L. Bowden, jun. (*J. Amer. Chem. Soc.*, 1943, **65**, 297).—β-$C_{10}H_7{\cdot}SH$, AlkBr, and NaOEt in EtOH give β-$C_{10}H_7$·n-*hexyl*, b.p. 160°/20 mm., and n-*heptyl sulphide*, m.p. 34°. *p*-$C_6H_4Ph{\cdot}CHPhCl$ and β-$C_{10}H_7{\cdot}SH$ in C_6H_6 give β-$C_{10}H_7$·*phenyl*-p-*xenylmethyl sulphide*, m.p. 155° (*sulphoxide*, m.p. 220°), which with Me_2SO_4 gives *p*-$C_6H_4Ph{\cdot}C^-Ph{\cdot}S^+Me{\cdot}C_{10}H_7$-$\beta$, whence it is regenerated by H_2O. R. S. C.

Aryl hydroxyalkyl ethers.—See B., 1943, II, 172.

Ethers of duroquinol.—See B., 1943, III, 135.

Synthesis of *cis*- and *trans*-3-Δ⁰-pentadecenylveratrole, a dihydro-derivative of urushiol dimethyl ether. D. Wasserman and C. R. Dawson (*J. Org. Chem.*, 1943, **8**, 73—82).—Et_2 adipate is reduced (H_2 at 255°/1750 lb. in presence of Cu–Cr oxide) to $[CH_2]_6(OH)_2$, b.p. 128—130°/6 mm. (yield 84%), converted by the successive actions of Na and CH_2PhCl in xylene at 120—130° and then at 120° into *ζ-benzyloxyhexanol*, b.p. 154°/2·5 mm. This with $SOCl_2$ in $NPhMe_2$ at 30—45° gives *ζ-benzyloxy*-n-*hexyl chloride*, b.p. 138°/1 mm., the Mg derivative of which with 2 : 3 : 1-$(OMe)_2C_6H_3{\cdot}CHO$ affords the expected *sec.* alcohol, converted (without purification) by $KHSO_4$ at 210° into H_2O and 3-*η-benzyloxy-*Δ$^{\alpha}$-*heptenylveratrole*, b.p. 229°/1 mm.; this is reduced (H_2 at 2—3 atm., Pd-black, AcOH) to 3-*η-hydroxyheptylveratrole*, b.p. 169°/2·7 mm. (together with a little α*μ-dihydroxydodecane*, m.p. 82—82·5°), which with HBr at 140—150° followed by re-methylation yields 3-*η-bromoheptylveratrole*, b.p. 174°/1 mm. With CH_2CN in liquid NH_3 this affords 3-Δ$^{\theta}$-*noninenylveratrole*, b.p. 146°/2 mm., transformed by $NaNH_2$ and *n*-$C_6H_{13}Br$ in liquid NH_3–light petroleum into 3-Δ$^{\theta}$-*pentadecinenylveratrole* (**I**), b.p. 192°/1·4 mm. (**I**) is hydrogenated (Raney Ni in 95% EtOH at 31°) to cis-3-Δ$^{\theta}$-*pentadecenylveratrole* (**II**), b.p. 198°/2 mm., but is reduced by $NaNH_2$ in liquid NH_3 to the trans-*isomeride* (**III**), b.p. 212°/3·2 mm., of (**II**). Complete hydrogenation (Raney Ni) gives 3-*pentadecylveratrole* [*tetrahydrourushiol Me₂ ether*], m.p. 36·8—37°. (**III**) is oxidised by powdered $KMnO_4$ in $COMe_2$ to *n*-$C_6H_{13}{\cdot}CO_2H$ and 2 : 3 : 1-$(OMe)_2C_6H_3{\cdot}CO_2H$. 2 : 3 : 1-$(OMe)_2C_6H_3{\cdot}CHO$ is reduced (Clemmensen) to 2 : 3-*dimethoxytoluene*, b.p. 103°/22·5 mm. H.W.

2 : 4-Dinitro-5-arylaminophenols.—See B., 1943, II, 172.

4-Nitro-3-ethoxytoluene-6-sulphonic acid. C. Buchanan, J. D. Loudon, and J. Robertson (*J.C.S.*, 1943, 168—169).—*m*-$C_6H_4Me{\cdot}OEt$ (**I**) and conc. H_2SO_4 at <30° give 3 : 1 : 6-$OEt{\cdot}C_6H_3Me{\cdot}SO_3H$ (**II**) (p-*toluidine* salt, m.p. 100—120°; *chloride*, b.p. 176—177°/10 mm.; amide, new m.p. 113—114°). (**I**) and conc. H_2SO_4 at 30—35° for 12 hr. followed by HNO_3 (*d* 1·42)–H_2SO_4 at 15—18°, then at room temp., yield 4 : 1 : 3 : 6-$NO_2{\cdot}C_6H_2Me(OEt){\cdot}SO_3H$ (**III**) (p-*toluidine* salt, m.p. 232—233°; *chloride*, m.p. 110—111°) and some 2-NO_2-isomeride (gelatinous *p*-toluidine salt; *chloride*, m.p. 97°). (**III**) is also formed from 4 : 1 : 3-$NO_2{\cdot}C_6H_3Me{\cdot}OEt$ and $ClSO_3H$ at 20°. When HNO_3 is added to (**I**)–H_2SO_4 at 10—15°, then at 15—20°, 6 : 1 : 3-$NO_2{\cdot}C_6H_3Me{\cdot}OEt$ is obtained. 2 : 4 : 1 : 3 : 6-$(NO_2)_2C_6HMe(OEt){\cdot}SO_3H$ (p-*toluidine* salt, m.p. 225—227°; *chloride*, m.p. 104°) is obtained from (**II**) (Na salt) and HNO_3 (*d* 1·5)–H_2SO_4 at <30°, or [with some (**III**) and 4 : 6 : 1 : 3-$(NO_2)_2C_6H_2Me{\cdot}OEt$] from (**II**) and HNO_3 (*d* 1·5). (**III**) (Na salt) and aq. NaOCl–NaOH at 50—55° afford a trace of stilbene derivative [*p*-toluidine salt, m.p. ~285° (decomp.); *sulphonyl chloride*, $C_{18}H_{16}O_{10}N_2Cl_2S_2$, m.p. 212—215°], whereas at 85°, then at room temp., similar treatment yields a substance (p-*toluidine* salt, $C_{18}H_{16}O_{12}N_2S_2,2C_7H_9N$, decomp. 310—311°), converted by Fe–HCl at 100° into a *substance*, $C_{18}H_{22}O_8N_2S_2,2H_2O$, m.p. >350°. A. T. P.

1-Nitro-1-α-hydroxyethyl*cyclo*hexane.—See B., 1943, II, 172.

***iso*Phorone and its derivatives.** A. A. Dodge and E. Kremers (*J. Amer. Pharm. Assoc.*, 1942, **31**, 527—529).—*iso*Phorone (**I**) (oxime, m.p. 77—78°; semicarbazone, m.p. 190—191°) is hydrogenated (Pt; 2 H_2 absorbed) to 3 : 3 : 5-trimethyl*cyclo*hexanol, m.p. 58·5—59° (3 : 5-dinitrobenzoate, m.p. 98·5—99°; acetate, an oil), dehydrated to an oil from which is separated (?) 1 : 3 : 3-trimethyl*cyclo*hexene, b.p. 139—141°. The liquid (3 : 5-dinitrobenzoate, m.p. 61·5—63°) and cryst. "*iso*phoronyl alcohol," m.p. 38° (3 : 5-dinitrobenzoate, m.p. 71·5—72·5°), are probably *cis*- and *trans*-dihydro*iso*phorol. F. O. H.

Phenol–formaldehyde resins. II. Condensation of dihydroxybenzenes with formaldehyde. H. von Euler, E. Adler, and G. J. Gie (*Arkiv Kemi, Min., Geol.*, 1940, **14**, **B**, No. 9, 7 pp.; cf. B., 1942, II, 25).—Quinol (**I**) (1 mol.), CH_2O (2 mols.), and 10% NaOH (2 mols.) give (36 hr.; room temp.) exclusively 2 : 5-*di(hydroxymethyl)quinol* (**II**), m.p. (rapid heating) 190—191° (decomp.) [with Me_2SO_4 gives the 1 : 4-Me_2 *ether*, m.p. 163—164°, and thence ($KMnO_4$–NaOH) 2 : 5 : 1 : 4-$(OMe)_2C_6H_2(CO_2H)_2$], which yields ($FeCl_3$) the *quinone*, m.p. 138°, and the *quinhydrone*, m.p. 160° (decomp.), deep blue. With 4 mols. of CH_2O and 4% NaOH (1 mol.) (**I**) (1 mol.) gives (72 hr.; room temp.) *tetra(hydroxymethyl)-quinol* (**III**), m.p. (rapid heating) 212—213° (decomp.). On slow heating (**II**) and (**III**) give dark resols without melting. *o*-$C_6H_4(OH)_2$ (1 mol.), CH_2O (2 mols.), and 10% NaOH (2 mols.) give (36 hr.; room temp.) exclusively a *di(hydroxymethyl)pyrocatechol* (**IV**), m.p. 116—117° (*Me₂ ether*, m.p. 92°). (**II**) and (**IV**), but not (**III**), are converted into amorphous insol. products very rapidly by hot dil. acids, probably by condensation involving elimination of H_2O between nuclear H of one mol. and $CH_2{\cdot}OH$ of a second mol. etc. M. H. M. A.

Phenol–formaldehyde resins. VIII. Mechanism of the hardening of resols; formation of dibenzyl ethers. H. von Euler, E. Adler, and J. O. Cedwall (*Arkiv Kemi, Min., Geol.*, 1941, **14**, **A**, No. 14, 20 pp.).—Evidence is adduced in favour of the view that the action of heat on *o*-hydroxybenzyl alcohols consists mainly in the formation of di-*o*-hydroxybenzyl ethers with minor quantities of diphenylmethanes. 2 : 3 : 5 : 1-$OH{\cdot}C_6H_2Me_2{\cdot}CH_2{\cdot}OH$ (**I**) at 140° gives an alkali-insol. substance (**II**), m.p. 200°, *di*-2-*hydroxy*-3 : 5-*dimethylbenzyl ether* (**III**), m.p. 99—100°, di-(2-hydroxy-3 : 5-dimethylphenyl)methane (**IV**), m.p. 146°, and a non-cryst. residue (34% of the original material) from which NaOH separates an alkali-insol. portion (**V**). (**II**) does not give a colour with $FeCl_3$, is extraordinarily stable towards acids and bases, cannot be acetylated or methylated, and does not react with ketonic reagents. It is identical with the "polymeric xylo-*o*-methylenequinone" of Fries *et al.* (A., 1907, i, 603) but is probably $C_6H_2Me_2{<}^{O{\cdot}CH_2{\cdot}C_6H_2Me_2{\cdot}O}_{CH_2{\cdot}O{\cdot}C_6H_2Me_2{\cdot}CH_2}$. The yield is 4—8% at 140° increasing to 30% at 180°. (**III**) gives an intense violet colour with $FeCl_3$, yields a *dibenzoate* (**VI**), m.p. 108—108·5°, and reacts vigorously with CH_2N_2 giving a *Me₁ ether* (**VII**), b.p. 155—160°/0·1 mm., which is insol. in NaOH but contains OH since it yields a p-*nitrobenzoate*, m.p. 120—121°. (**VII**) is

oxidised by $KMnO_4$ to *2-methoxy-3 : 5-dimethylbenzoic acid*, m.p. 97—98°. Treatment of (III) or (VII) with Me_2SO_4–2*N*-NaOH–MeOH gives the *Me*$_2$ *ether* (VIII), m.p. 73—74°. The constitution of (III) is further established by its production when the *p*-toluenesulphonate of (I) is heated at 195—200° and the product hydrolysed. (I) or (III) and HBr in light petroleum at room temp. give *2-hydroxy-3 : 5-dimethylbenzyl bromide* (IX), m.p. 73—74°. (VII) similarly gives (IX) and non-cryst. 2 : 3 : 5 : 1-OMe-$C_6H_2Me_2$·CH_2Br. When treated with Na_2CO_3 (IX) passes through the quinonemethide into (II). (VIII) and (VI) are likewise cleaved by HBr. (V) is converted by HBr in cold light petroleum into (IX) in 30% yield. Determinations of mol. wt. (Rast) indicate that (V) at any rate to a considerable extent consists of chain or cyclic mols. composed of 4—5 units of (I) joined to one another by Ph·O·CH_2Ph linkings or alternatingly with CH_2Ph·O·CH_2Ph and Ph·O·CH_2Ph linkings. The elimination of CH_2O from (I) is not entirely accounted for by the production of (IV). In presence of xylenol (X) the yield of (III) is < from (I) alone but its formation remains the fastest reaction and added (X) is not involved to > a limited extent. H. W.

Phenol–formaldehyde resins. IX. Mechanism of the hardening of resols : hardening of tri-*p*-cresol dialcohols. S. Kyrning (*Arkiv Kemi, Min., Geol.*, 1941, **15**, **A**, No. 2, 9 pp.; cf. A., 1940, II, 216).—3 : 5-Di-(2′-hydroxy-5′-methylbenzyl)-*p*-cresol and CH_2O–aq. alkali give 3 : 5-di-(2′-hydroxy-5′-methyl-3′-hydroxymethylbenzyl)-*p*-cresol (I), m.p. 203° (preheated bath), converted by HBr–EtOH into the corresponding *dibromide* (II), m.p. 172° (decomp.). Hardening of (I) at 130°, 200°, 220°, or 240° is accompanied by loss of H_2O and CH_2O; the rate of elimination is examined. Mechanisms of the hardening process involving formation of larger mols. by junction of nuclei through ·CH_2·O·CH_2· is outlined. (II) is also obtained when the product (insol. in $CHCl_3$) formed from (I) at 130° is treated with HBr–$CHCl_3$. A. T. P.

Phenol–formaldehyde resins. XIII. Mechanism of the hardening of resols. Reaction phases of the hardening of dinuclear dialcohols. H. von Euler, E. Adler, and S. Tingstam (*Arkiv Kemi, Min., Geol.*, 1942, **15**, **A**, No. 10, 11 pp.).—The course of the hardening of 1 : 5 : 2 : 3- (I) and 1 : 3 : 4 : 5-CH_2·C_6H_2Me(OH)·CH_2·OH_2 (II) is best represented as a consequence of ether condensation and quinonemethide formation with subsequent polymerisation and oxido-reduction of the quinonemethide groups. The evolution of H_2O and CH_2O from (I) and (II) is measured at definite intervals at 150°, 170°, 190°, and 210°. Loss of CH_2O is small and >0·2 mol. per mol. of (I) or (II) even at 210°. The amount of H_2O evolved increases rapidly to a max. reached at lower temp. in ~1 hr. and at higher temp. in ~30 min., after which it remains const. The loss of H_2O amounts to 1 mol. per mol. of (I) or (II) at 150° increasing to 1·5—1·6 per mol. at the higher temp. At lower temp. therefore the essential consequence of loss of H_2O is the formation of ether chains; at higher temp. this is accompanied by an almost equally rapid production of quinonemethide. At 150° with max. loss of 1·1 mol. of H_2O per mol. of (I) the resultant resin is completely sol. in $CHCl_3$; at higher temp. in proportion as this ratio is exceeded the proportion of resin insol. in $CHCl_3$ increases. Apparently the " ether-chained " resin is sol. in $CHCl_3$ but as methide formation and polymerisation cause mol. enlargement and complexity the solubility diminishes more and more. With (II) a much more rapid diminution of solubility in $CHCl_3$ is observed. At 150° (0·5 mol. of H_2O lost) the product is completely sol. whereas at 160° (0·95 mol. lost) 56% of the residue is insol. At higher temp. complete insolubility is rapidly attained. Probably quinonemethide formation occurs sooner with (II) than with (I) and overlaps ether production to a greater extent. (Cf. A., 1943, II, 161.) H. W.

Phenol–formaldehyde resins. XIV. Mechanism of the hardening of resols. Hardening of di- and tetra-alcohols of dihydric phenols. S. Kyrning (*Arkiv Kemi, Min., Geol.*, 1942, **15**, **B**, No. 11, 8 pp.).—Investigation of the loss of H_2O on heating OH·CH_2 derivatives of dihydric phenols confirms the reaction mechanism advanced for the resol hardening of the products from mono- and di-alcohols of monohydric phenols. The loss of H_2O from 1 : 4 : 2 : 5- and 1 : 2 : 3 : 6-$(OH)_2C_6H_2(CH_2·OH)_2$ is in agreement with the simultaneous production of ether, diphenylmethane (I), and quinonemethide (II) derivatives. With 1 : 4 : 2 : 3 : 5 : 6-$(OH)_2C_6(CH_2·OH)_4$ formation of (I) is excluded and the quantity of H_2O evolved suggests that ether formation is accompanied by production of (II) as second main action. This assumption is largely confirmed by the behaviour of the corresponding quinone-tetra-alcohol (III) from which the formation of (I) or (II) is impossible; the elimination of H_2O is within the limits required for an exclusive ether condensation. The ready hardening of (III) shows that quinone CO activates CH_2·OH in the same manner as does phenolic OH. Etherification of CH_2·OH greatly diminishes the reactivity. H. W.

Phenol–formaldehyde resins. XV. Mechanism of the hardening of resols; reaction sequence in the hardening of *o*- and *p*-phenolalcohols. H. von Euler, E. Adler, J. O. Cedwall, and O. Törngren (*Arkiv Kemi, Min., Geol.*, 1942, **15**, **A**, No. 11, 19 pp.).—Examination of observations made with 2 : 3 : 5 : 1-OH·$C_6H_2R′R″$·CH_2·OH (R′ = R″ = Me; R′ = H; R″ = Me; R, = Br, R″ = Me) and 4 : 3 : 5 : 1-OH·$C_6H_2Me_2$·CH_2·OH indicates that hardening is due to a concurrence of reactions mainly controlled by the structure of the reacting mols., reaction temp., and duration. Although quant. differentiations cannot yet be made, the *o*-quinonemethides derived from *o*-hydroxybenzyl alcohols and their ethers can react to give dihydroxystilbenes (I) [and thence stilbenequinones (II)], dihydroxydiphenylethanes (III), dimeric quinonemethides [and thence (III)], and trimeric quinonemethides with succeeding phenolaldehydes and nuclear-methylated phenols, whereas the similarly derived *p*-quinonemethides for structural reasons can give only (I), (II), and (III). Resitols formed at low temp. contain mainly ether bridges with some CH_2 bridges. To a small extent there is also loss of H_2O with production of quinonemethides and loss of CH_2O leading to diphenylmethanes and possibly " cracking " with production of OH-aldehydes. At higher temp. these reactions occur to an increased extent and are interlocked. In the final stages of the reaction polymerisation of the quinonemethides and stilbenequinones plays a decisive part in the mol. enlargement. The temp. is the decisive factor for the extent to which the ether bridges participate in the secondary reactions. The duration of reaction is of importance only within a certain initial period. Subsequently a condition characteristic for each temp. is reached which then undergoes little further alteration. 4 : 3 : 5 : 1-OH·$C_6H_2Me_2$·CH_2·OH loses H_2O and CH_2O in a sealed tube at 155° giving *di-4-hydroxy-3 : 5-dimethylbenzyl ether* (IV), m.p. 173—173·5°, converted by boiling AcOH into *4-hydroxy-3 : 5-dimethylbenzyl acetate* (V), m.p. 77°. (IV) is largely unchanged at 175° and at 200° still evolves little CH_2O but gives a small amount of a sublimate of 4 : 3 : 5 : 1-OH·$C_6H_2Me_2$·CHO (oxime, m.p. 166·5—168°). The residue contains unchanged (IV), (:CH·$C_6H_2Me_2$·OH-1 : 3 : 5 : 6)$_2$, and (CH_2·$C_6H_2Me_2$·OH)$_2$. (IV) in $CHCl_3$ is converted by HBr into *4-hydroxy-3 : 5-dimethylbenzyl bromide*, m.p. 115—116° (decomp.) [with AcOH–NaOAc gives (V)], which in Et_2O is converted by saturated aq. $NaHCO_3$ into 3 : 5 : 3′ : 5′-*tetramethylstilbene*-4 : 4′-*quinone*, softens and blackens at 215—217°. This with $SnCl_2$ in $COMe_2$ or H_2–PtO_2 in EtOAc gives 4 : 4′-dihydroxy-3 : 5 : 3′ : 5′-tetramethylstilbene, m.p. 237—238° (diacetate, m.p. 236—237°). H. W.

Quinoidation of triaryl compounds. Diphenylbromonaphthylmethyl chlorides. L. C. Anderson and D. Johnston (*J. Amer. Chem. Soc.*, 1943, **65**, 239—242).—MgPhBr and 5 : 1-$C_{10}H_6Br$·CO_2Me (less well, the acid or acid chloride) in boiling PhMe give an impure *carbinol* (I), converted by AcCl into *diphenyl-5-bromo-1-naphthylmethyl chloride* (II) (62%), m.p. 172—174°, which with $NPhMe_2$ in aq. $COMe_2$ gives (I), m.p. 150—151° [with HCl–Et_2O gives only a little (II)]. Attempts to prepare 8 : 2-$C_{10}H_6Br$·CO_2H failed. 5 : 8 : 2-$C_{10}H_5Br_2$·CO_2Et gives *diphenyl-5 : 8-dibromo-2-naphthylcarbinol* (77%), m.p. 127—128° (the acid chloride gives only an oil), and thence (AcCl) the *chloride* (III), m.p. 163—164°. 2-$C_{10}H_7Br$, AcCl, and $AlCl_3$ in $PhNO_2$ give a 1 : 1 mixture (1 : 10 in CS_2) of 6 : 2- and 2 : 1-$C_{10}H_6Br$·COMe, oxidised by KOCl to acids, which yield *Me 6-bromo-2-naphthoate* (IV) (42%), m.p. 123—124·5°. The derived acid, m.p. 280° (decomp.) (other methods of prep. give poor yields), and *Et* ester, m.p. 67—68°, are also described. MgPhBr (100% excess) (LiPh gives an oil) and (IV) in PhMe give *diphenyl-6-bromo-2-naphthylcarbinol*, + AcOH, m.p. 99—101°, and thence the *chloride* (V), m.p. 118—119°. 2 : 1-$C_{10}H_6Br$·CO_2Me, a liquid, gives similarly *diphenyl-2-bromo-1-naphthylmethyl chloride* (VI), m.p. 203—204°, and thence the *carbinol*, m.p. 129—131°. 4 : 1-$C_{10}H_6Br$·CPh_2Cl or *-p*-C_4H_4Br·CPhCl·$C_{10}H_7$-*α* with AgCl in SO_2 at room temp. rapidly gives AgBr (55—65% in 2·5 days), but none is formed from (II), (III), (V), or (VI) by AgCl or Ag_2SO_4 in SO_2, Me_2SO_4, PhCN, or $PhNO_2$ in 6—30 days, indicating little tendency to form transannular quinonoid compounds. All these halides give red, amorphous products, except (III) which is unchanged in SO_2. R. S. C.

Quinoidation of triaryl compounds. Diphenylhydroxynaphthylcarbinols. L. C. Anderson and D. G. Thomas (*J. Amer. Chem. Soc.*, 1943, **65**, 234—238).—Unsuccessful attempts are recorded to prepare naphthofuchsones having CO and :CPh_2 in different rings of the $C_{10}H_8$ nucleus. OH·$C_{10}H_6$·CPh_2·OH give coloured liquids at or above the m.p. when naphthofuchsone formation is theoretically possible but not when it is impossible. *p*-OH·C_6H_4·CPh_2·OH in 6% H_2SO_4–AcOH gives the same colour (absorption spectrum) as does *p*-O:C_6H_4:CPh_2. $C_{10}H_8$ derivatives which can give a naphthofuchsone with CO and :CPh_2 in one ring are stabilised in 6% H_2SO_4–AcOH; those which can give no naphthofuchsone rapidly decompose, probably by fluorene formation; stability is intermediate when formation of the naphthofuchsone involves both rings. 1 : 6 : 2-$C_{10}H_5Br_2$·OH with Sn, conc. HCl, and EtOH gives 6 : 2-$C_{10}H_6Br$·OH and some 6 : 2-$C_{10}H_6Br$·OEt (I). 2 : 1-OAlk-$C_{10}H_6$·MgBr and PhCN in C_6H_6–Et_2O give *2-ethoxy-* (30%), m.p 88—89°, and *2-methoxy-6-benzoylnaphthalene* (45%), m.p. 81—82°, both hydrolysed by aq. HBr–AcOH to *2-hydroxy-6-benzoylnaphthalene* (70—80%), m.p. 158—159°. With MgPhBr in Et_2O–C_6H_6 this gives *diphenyl-6-hydroxy-2-naphthylcarbinol* (II) (75%), m.p. 170—171° (sealed tube; reddish-purple liquid), also obtained less well from

6 : 2-OH·$C_{10}H_6$·CO_2Et by MgPhBr. β-$C_{10}H_7$·OMe, AcCl, and $AlCl_3$ in $PhNO_2$ give 6 : 2-OMe·$C_{10}H_6$·COMe and thence, successively, (NaOCl) 6 : 2-OMe·$C_{10}H_6$·CO_2H, (HBr–AcOH) -OH·$C_{10}H_6$·CO_2H, -OH·$C_{10}H_6$·CO_2Me, and (MgPhBr) (**II**). Zn in AcOH reduces (**II**) to 6-*benzhydryl*-2-*naphthol*, m.p. (anhyd.) 52° or (+*x*MeOH) 101·5—103°. The *Me* ester, m.p. 130—131·5°, of 5 : 1-OH·$C_{10}H_6$·CO_2H (prep. from 1 : 5-NH_2·$C_{10}H_6$·SO_3H modified), *Me* 8-*hydroxy*-2-, m.p. 151—152·5°, 7-*hydroxy*-1-, m.p. 124—126°, and 6-*hydroxy*-1-*naphthoate*, m.p. 112—113°, with MgPhBr in Et_2O–C_6H_6 give *diphenyl*-5-*hydroxy*-1- (63%), m.p. 199—200° (red liquid), -8-*hydroxy*-2- (67%), m.p. 162—163° (pale liquid), -7-*hydroxy*-1- (67%), m.p. 231·5—232·5° (pre-heated bath; orange-red liquid), and -6-*hydroxy*-1-*naphthylcarbinol*, m.p. 188—190° (pale liquid). α-$C_{10}H_7$·OBz and $AlCl_3$ at 150—165° give 1 : 2-, m.p. 64—65°, but at 100° give 1 : 4-OH·$C_{10}H_6$·COPh, m.p. 164—165°. R. S. C.

Fluorine-substituted aromatic acids. G. P. Hager and E. B. Starkey (*J. Amer. Pharm. Assoc.*, 1943, **32**, 44—49).—*o*-, decomp. 106°, *m*-, decomp. 108°, and *p*-C_6H_4Me·N_2BF_4, decomp. 107°, are converted into *o*-, b.p. 114°/763 mm., *m*-, b.p. 123°/766 mm., and *p*-C_6H_4MeF, b.p. 110°/767 mm., respectively, from which are obtained: *o*-, *m*-, and *p*-C_6H_4F·CH_2Br, -C_6H_4F·CHO, and *o*-, m.p. 124°, *m*-, m.p. 124·5—125·5°, and *p*-C_6H_4F·CO_2H, m.p. 186°. *o*-, b.p. 110—115°/15 mm., *m*-, b.p. 229°/766 mm., and *p*-C_6H_4F·CH_2·CN, b.p. 100—103°/3 mm., and boiling 60% H_2SO_4–AcOH give *o*-, m.p. 61—62°, *m*- (not cryst.), and *p*-C_6H_4F·CH_2·CO_2H, m.p. 82°, respectively. *o*-, m.p. 180—181°, *m*-, m.p. 166·5°, and *p*-fluorocinnamic acid, m.p. 209·5°, and o-, m.p. 116·5°, m-, m.p. 101°, and p-*fluoromandelic acid*, m.p. 133°, are prepared from C_6H_4F·CHO. The antibacterial activity of the above F-acids is determined. Although introduction of *p*-Cl, -Br, or -I doubles the toxicity (white rats) of BzOH, *p*-F has little effect. A. T. P.

Optically active nitro- and amino-mandelic acids. II. A. Fredga and E. Andersson (*Arkiv Kemi, Min., Geol.*, 1941, **14**, **B**, No. 38, 7 pp.).—*p*-NO_2·C_6H_4·CHBr·COCl with warm aq. $NaHCO_3$ gives *r*-*p*-NO_2·C_6H_4·CH(OH)·CO_2H (**I**), m.p. 126—127°, in 65% yield. It is resolved by quinidine in boiling aq. EtOH into (+)-p-*nitromandelic acid*, (**II**) m.p. 93—94°, $[\alpha]^{25}_{3893}$ +128·9°, $[\alpha]^{25}_{5461}$ +151·8° in H_2O [*quinidine* and *Pb* (+$1H_2O$) salts]. The acid remaining in the mother-liquors after removal of (**II**) is resolved by strychnine in boiling 30% EtOH into (−)-p-*nitromandelic acid* (**III**), m.p. 93—94°, $[\alpha]^{25}_{D}$ −129·2°, $[\alpha]^{25}_{5461}$ −152·1° in H_2O [*strychnine* (+$2H_2O$) salt]. (**I**) as Na salt in H_2O is reduced (H_2–Pd–C) to *r*-*p*-NH_2·C_6H_4·CH(OH)·CO_2H (**IV**), decomp. 205—210° after becoming discoloured. Similarly (**II**) gives (+)- (**V**), decomp. >200°, becomes yellow at ~140° and brown at 200°, $[\alpha]^{25}_{D}$ +106·9°, $[\alpha]^{25}_{5461}$ +128·7° in 0·1N-NaOH, $[\alpha]^{25}_{D}$ +133·0°, $[\alpha]^{25}_{5461}$ +157·3° in N-HCl, and (**III**) gives (−)-p-*aminomandelic acid* (**VI**), $[\alpha]^{25}_{D}$ −106·5° in 0·1N-NaOH. (**IV**) is transformed through the diazo-compound into *r*-OH·CHPh·CO_2H, and (**V**) into (+)-OH·CHPh·CO_2H, $[\alpha]^{25}_{D}$ +153° in H_2O. (**II**) and (**V**) have therefore the same configuration as *l*-(+)-mandelic acid whereas (**III**) and (**VI**) are related to the *d*-(−)-acid. H. W.

Lactones related to the cardiac aglycones. XI. Synthesis of β-substituted $\Delta^{\alpha\beta}$-butenolides from methyl ketones. E. R. Blout and R. C. Elderfield (*J. Org. Chem.*, 1943, **8**, 29—36).—The possibility of preparing these compounds by methods involving the removal of a substituent in the α-position of the requisite butyrolactones has been explored. Addition of *cyclo*hexyl Me ketone (**I**) and $CHCl_2$·CO_2Et in Et_2O to Mg–Hg gives *Et α-chloro-β-hydroxy-β-cyclohexylbutyrate*, b.p. 110—135°/1·8 mm., converted by HBr in boiling glacial AcOH into *α-chloro-β-cyclohexylbutyrolactone* (**II**), b.p. 131—135°/0·9 mm., m.p. 131—131·5°. (**II**) is largely resinified by boiling quinoline whilst boiling $NPhMe_2$ causes only partial removal of HCl with formation of obscure condensation products; C_5H_5N is without action. Boiling 4% aq. NaOH partly converts (**II**) into *α-hydroxy-β-cyclohexylbutyrolactone*, m.p. 144° (p-*nitrobenzoate*, m.p. 154—154·5°), whilst anhyd. KOAc in boiling AcOH gives *β-cyclohexyl-*$\Delta^{\alpha\beta}$*-butenolide* [*β-cyclohexyl-*Δ^{α}*-butenolactone*] (**III**), b.p. 115—117°/0·1 mm., further identified by conversion into Me *β*-formyl-*β-cyclohexylpropionate* (semicarbazone, m.p. 118—119°). Addition of (**I**) and CH_2Cl·CO_2Et to NaOEt–EtOH at −80° gives *Et αβ-oxido-β-cyclohexylbutyrate*, b.p. 86—90°/0·3 mm., converted by boiling HBr–AcOH into a material with an odour of (**III**) but contaminated with other substances of approx. the same b.p. COPhMe, $CHCl_2$·CO_2Et, and Mg–Hg afford OH·CPhMe·CHCl·CO_2Et (**IV**), b.p. 124—126°/1·5 mm., with some $(CPhMe·OH)_2$. (**IV**) and boiling HBr–AcOH yield COPhMe, *Et-α-chloro-β-phenylcrotonate*, b.p. 103°/5 mm., and *β*-phenyl-$\Delta^{\alpha\beta}$-butenolide, m.p. 93°. Et *β*-hydroxy-*β-cyclohexylbutyrate* is converted by boiling HBr–AcOH into *β-cyclohexylbutyrolactone*, b.p. 124—126°/1·2 mm. (yield 79%), also obtained in 78% yield by use of boiling H_2SO_4–AcOH–H_2O. It is brominated in boiling glacial AcOH to *β-x-bromocyclohexylbutyrolactone* (**V**), b.p. 130—135°/1 mm., m.p. 63—63·5°, converted by 2N-NaOH and subsequent acidification into *β-x-hydroxycyclohexylbutyrolactone* (**VI**), b.p. 140—152°/0·7 mm. (p-*nitrobenzoate*, m.p. 163—164·5°). (**VI**) is oxidised by CrO_3 in 90% AcOH at <30° to *β-x-ketocyclohexylbutyrolactone*, m.p. 82—83·5° [p-*nitrophenylhydrazone*, m.p. 187—188° (decomp.) (softens at 184°); :*N·OH*-derivative, m.p. 160—161° (decomp.)]. Anhyd. KOAc, boiling AcOH, and (**V**) appear to give a mixture of acetoxy*cyclo*hexyl- and *cyclo*hexenylbutyrolactone, b.p. 110—114°/0·2 mm. M.p. and b.p. are corr. H. W.

Lactones related to the cardiac aglycones. XII. Condensation of ethyl oxalate with ethyl γ-*cyclo*hexylcrotonate and a method for predicting the products from such condensations. E. R. Blout, J. Fried, and R. C. Elderfield (*J. Org. Chem.*, 1943, **8**, 37—42).—Past (A., 1942, II, 28, 29) and present experiences of the authors with those of Kuhn *et al.* (A., 1937, II, 438) and Boese *et al.* (A., 1934, 632) show that in condensations involving $Et_2C_2O_4$ and γ-substituted Δ^{α}- and Δ^{β}-crotonic esters and their vinylogues, the position originally occupied by the double linking is of little importance and the controlling factor is the electronic nature of the substituent at $C_{(\gamma)}$. Condensation occurs in the γ-position if this is H. If the γ-substituent is a *n*-alkyl, condensation takes place at $C_{(\gamma)}$ with progressively poorer yields as the inductive effect of the substituent increases. When the electron-donating capacity of the γ-substituent is still further enhanced, as in the case of the *cyclo*hexyl group, condensation occurs at $C_{(\alpha)}$; aryl substituents lead to condensation in this position. C_5H_5N, used as solvent, has no effect on the course of the condensation. Gradual addition of $Et_2C_2O_4$ in dry Et_2O to KOEt in EtOH–Et_2O at 0° and subsequent addition of Et *γ-cyclohexylcrotonate* in dry C_5H_5N to the mixture at 0° gives Et *γ*-keto-*β*-carbethoxy-*δ-cyclohexyl-*Δ^{γ}-pentenoate (**I**) as a heavy yellow oil which could not be cryst. or distilled without decomp. (2 : 4-*dinitrophenylhydrazone*, m.p. 76—77°). It is hydrolysed by conc. HCl–AcOH at room temp. to *α-keto-β-carbethoxy-δ-cyclohexyl-*Δ^{γ}*-pentenoic acid*, m.p. 83·5—84° (p-*bromophenacyl* ester, m.p. 108—109°), and the corresponding *β-carboxy-acid*, m.p. 217° after decomp. from 135°. Boiling conc. HCl–AcOH converts either ester into *α-keto-δ-cyclohexyl-*Δ^{γ}*-pentenoic acid*, m.p. 93—94°, which gives a red colour with $FeCl_3$ in EtOH, and is transformed by boiling Ac_2O into the corresponding *lactone acetate*, C_6H_{11}·CH<$^{CH_2·CH}_{O—CO}$>C·OAc, m.p. 87—88°. (**I**) is reduced (H_2–PtO_2 in abs. EtOH) and then hydrolysed (KOH) to *α-hydroxy-β-carboxy-δ-cyclohexyl-n-valeric acid* (**III**), m.p. 126—127° (*di*-p-*bromophenacyl* ester, m.p. 143—144°). *Et γ-cyclohexylbutyrate*, b.p. 86—87°/0·6 mm., is condensed with $Et_2C_2O_4$ to Et α-keto-*β*-carbethoxy-*δ-cyclohexyl-n*-valerate (2 : 4-*dinitrophenylhydrazone*, m.p. 81—82·5°), reduced and hydrolysed to (**II**). H. W.

Addition of sodium triphenylmethyl and lithium phenyl to cinnamic ester and benzylideneacetophenone. A. Michael and C. M. Saffer, jun. (*J. Org. Chem.*, 1943, **8**, 60—63).—*Me βγγγ-tetraphenylbutyrate* (**I**), m.p. 170·5—171° (*acid*, m.p. 227—228°), is obtained in modest yield by addition of CPh_3Na in anhyd. Et_2O to CHPh:CH·CO_2Me (**II**) in Et_2O and N_2 at −20°. Considerable polymerisation and formation of tar seem to occur and reactions of this type are only successful in the complete absence of moisture and enolisable H. *Et βγγγ-tetraphenylbutyrate*, m.p. 127—127·5°, is obtained similarly from CHPh:CH·CO_2Et. Pyrolysis of (**I**) gives $CHPh_3$ and CHPh:CH·CO_2H. CHMe:CH·CO_2Et does not appear to give an additive compound with CPh_3Na. *αaβγγ-Pentaphenylpropanol* (**III**), m.p. 160·5—161°, obtained by addition of LiPh in Et_2O to (**II**) in Et_2O and N_2 at −20°, passes at 180—200°/4 mm. into *αaβγγ-pentaphenylpropene*, m.p. 214—215°. *Li cinnamate* has m.p. 303—305° (decomp.). With COPh·CH:CHPh, LiPh affords CHPh:CH·CPh_2·OH, m.p. 110—111°, and (**III**). M.p. are corr. H. W.

3 : 4-Dinitrobenzoic acid. H. Goldstein and R. Voegeli (*Helv. Chim. Acta*, 1943, **26**, 475—481).—In compounds 3 : 4 : 1-$(NO_2)_2C_6H_3X$ when X is a substituent of the first order (Cl, Br, Me, OMe) the NO_2 at $C_{(3)}$ is mobile but when X is a substituent of the second order (NO_2, CO_2H) the mobility is shown by NO_2 at $C_{(4)}$. 3 : 4 : 1-$(NO_2)_2C_6H_3$·CO_2H (**I**) [prep. from 1 : 3 : 4-$C_6H_3Me(NO_2)_2$ described] is converted into the *chloride*, b.p. 204—205°/17 mm., 188°/11 mm., m.p. 50—51°, *Me* ester, m.p. 87°, *amide*, m.p. 165—166°, and *anilide*, m.p. 188—189°. With the appropriate reagent it affords 3-nitro-4-hydroxy-, -4-methoxy-, -4-amino-, -4-dimethylamino-, and -4-anilino-benzoic acid. (**I**) and N_2H_4,H_2O in boiling EtOH afford 4 : 3 : 1-NH_2·NH·$C_6H_3(NO_2)$·CO_2H, which could not be purified by itself or as N_2H_4 salt (**II**) but is characterised by its *Ac*, m.p. 276—278° (decomp.), and *CMe_2*:, m.p. 243°, derivatives. (**II**) is transformed by 10% Na_2CO_3 at 100° into 1-*hydroxy*-1 : 2 : 3-*benztriazole*-6-*carboxylic acid*, decomp. without melting at ~225°, deflagrates at 245—247°. 3-*Nitro*-4-*phenylhydrazinobenzoic acid*, m.p. 241°, changes at ~205°, is transformed by boiling glacial AcOH into 6-*carboxy*-2-*phenyl*-2 : 1 : 3-*benztriazole* 1-*oxide*, m.p. 250°. M.p. are corr. H. W.

2-Bromo-4 : 5-dinitrobenzoic acid. H. Goldstein and G. Gianola (*Helv. Chim. Acta*, 1943, **26**, 173—181).—4 : 2 : 1-NO_2·C_6H_3Br·CO_2H (prep. from *o*-toluidine described) is converted by HNO_3 (*d* 1·54) and conc. H_2SO_4 at room temp. and finally at 100° into 2-*bromo*-4 : 5-*dinitrobenzoic acid* (**I**), m.p. 184°. Its constitution is established by its conversion by conc. aq. NH_3 at room temp. into 2-*bromo*-5-*nitro*-4-*aminobenzoic acid*, m.p. 264° (*Ac* derivative, m.p. 205°), deaminated to 5 : 2 : 1-NO_2·C_6H_3Br·CO_2H (**II**) anhyd. K CO_3

and NH_2Ph at 100° yield 2-*bromo*-5-*nitro*-4-*anilinobenzoic acid*, m.p. 253·5°, transformed by boiling NH_2Ph, K_2CO_3, and Cu powder into 5 : 2 : 4 : 1-NO_2·C_6H_2($NHPh$)$_2$·CO_2H and [C_6H_2(NO_2)($NHPh$)·CO_2H-4 : 5 : 2]$_2$. (**I**) and boiling 2N-NaOH or MeOH–KOH at 50° yield 2-*bromo*-5-*nitro*-4-*hydroxy*-, m.p. 221°, or -4-*methoxy-benzoic acid*, m.p. 250°, respectively. 2-*Bromo*-5-*nitro*-4-*dimethylaminobenzoic acid*, m.p. 232° (decomp.), is obtained from (**I**) and aq. $NHMe_2$ at 100°. N_2H_4,H_2O and (**I**) readily yield 2-bromo-5-nitro-4-hydrazinobenzoic acid, m.p. 167° (decomp.) [*Ac*, m.p. 263·5°, and :*CMe*$_2$, m.p. 244° (decomp.), derivatives], transformed by boiling 2N-Na_2CO_3 into 6-*bromo*-3-*hydroxybenztriazole*-5-*carboxylic acid*, deflagrates without melting at 211°. 2-*Bromo*-5-*nitro*-4-*phenylhydrazinobenzoic acid*, m.p. ~180° when heated very rapidly or 231° (becomes yellow-brown at 170—175°) when heated slowly, is converted by boiling AcOH into 6-*bromo*-3-*oxido*-2-*phenylbenztriazole*-5-*carboxylic acid*, orange or yellow needles, m.p. 236°. (**I**) is reduced by $SnCl_2$ and conc. HCl to 2-bromo-4 : 5-diaminobenzoic acid dihydrochloride (**II**); the free acid blackens almost immediately on contact with air and is characterised as its *Ac*$_2$ derivative, m.p. 257°. (**II**) is transformed by more prolonged treatment with NaOAc and boiling Ac_2O into 6-*bromo*-2-*methylbenziminazole*-5-*carboxylic acid*, m.p. 323°, and by HNO_2 into 6-*bromobenztriazole*-5-*carboxylic acid*, m.p. ~325° (decomp.). (**II**) is converted by Ac_2 in boiling H_2O into 7-*bromo*-2 : 3-*dimethyl*-, m.p. 278° (decomp.), and by NaOAc and Bz_2 in boiling abs. EtOH into 7-*bromo*-2 : 3-*diphenyl*-, m.p. 234·5°, -*quinoxaline*-6-*carboxylic acid*. M.p are corr.. H. W.

Nitration of β-polyalkylphenyl*iso*valeric acids. II. β-*m*-**5-Xylyl-*iso*valeric acid.** L. I. Smith and L. J. Spillane (*J. Amer. Chem. Soc.*, 1943, **65**, 282—289).—The structure of 2 : 6 : 3 : 4 : 5 : 1-$(NO_2)_2C_6Me_3$·CMe_2·CH_2·CO_2Me (A., 1940, II, 230) is confirmed by the behaviour of related compounds. Adding KNO_3–H_2SO_4 to 3 : 5 : 1-$C_6H_3Me_2$·CMe_2·CH_2·CO_2Me (**I**) in $CHCl_3$–H_2SO_4 at −15° to 5° gives a small amount of *Me* β-2 : 4-*dinitro*-m-5-*xylyl*iso*valerate* (**II**), m.p. 73·5—74°, and a larger amount of an oily nitrosulphonic acid. 65% of (**II**) is obtained in $CHCl_3$ alone at <5—10°. Boiling Ac_2O–H_2SO_4 or HCl at 100° does not affect (**II**). H_2–PtO_2 reduces (**II**) in MeOH at 38 lb. to an amine, m.p. 86·5—90° (*Ac* derivative, m.p. 138·5—139·5°), of unknown structure. Dil. HNO_3–H_2O_2–AcOH, $KMnO_4$–AcOH, or NaOH–MeOH with (**I**) yields indefinite products. H_2SO_4 at room temp. hydrolyses (**II**) to the *acid*, m.p. 153—154·5° [with H_2SO_4–MeOH regenerates (**II**)], which with Cu chromite in quinoline at 225—235° yields an oil and gives indefinite products (no HNO_2) with NaOMe–MeOH. With HNO_3 (*d* 1·5) and H_2SO_4 at 3° room temp., (**I**) or (**II**) gives *Me* β-2 : 4 : 6-*trinitro*-m-5-*xylyl*iso*valerate* (**III**), m.p. 127—127·5°, converted by NaOH–aq. MeOH into a *substance*, m.p. 234—244° (decomp.), and by conc. H_2SO_4 into the *acid*, m.p. 194—198·5° (decomp.). With Cu chromite in quinoline–N_2 at 170—175°, this acid gives 5 : 7-*dinitro*-4 : 4 : 6 : 8-*tetramethyl*-3 : 4-*dihydrocoumarin* (**IV**), m.p. 163·5—164°, slowly sol. in 4N-NaOH, reduced by Zn–80% AcOH to a phenol and by H_2S–NH_3–aq. EtOH at 100° to impure 5-nitro-7-amino-4 : 4 : 6 : 8-tetramethyl-3 : 4-dihydrocoumarin, softens 188°, m.p. 192—197°. *m*-4-xylenol, CMe_2:CH·CO_2H (**V**), $AlCl_3$, and HCl in light petroleum at <0° (later the b.p.) give 4 : 4 : 6 : 8-*tetramethyl*-3 : 4-*dihydrocoumarin* (45%), m.p. 104·5—105°, which with HNO_3 (*d* 1·5) in H_2SO_4 gives (**IV**) (proof of structure). H_2S–NH_3–aq. MeOH at 100° reduces (**II**) to *Me* β-4-*nitro*-2-*amino*-m-5-*xylyl*iso*valerate*, m.p. 91—92° (*Ac* derivative, m.p. 138·5—139°), hydrolysed by boiling 6N-HCl to the *acid*, m.p. 176·5—179° (decomp.) (Ac derivative, m.p. 187·5—180°, resists ring-closure). 2 : 6 : 1-$C_6H_3Me_2$·$NHAc$ (**VI**), m.p. 179—180° (lit. 177°), (**V**), HCl, and $AlCl_3$ in $C_2H_2Cl_4$ at 5° give only an oil. $Bu^{\beta}CO_2H$ with SO_2Cl_2–Bz_2O_2 in boiling CCl_4 and then H_2SO_4–MeOH gives *Me* β-*chloro*iso*valerate* (28%), b.p. 69—72°/17 mm., which with NaOH gives (**V**) but cannot be condensed with (**VI**). HNO_3 (*d* 1·5) in AcOH–Ac_2O at <20° (later 50°) converts (**I**) into *Me* 4-*nitro*-m-5-*xylyl*iso*valerate* (**VII**) (87%), b.p. 153—155°/5 mm., hydrolysed by alkali to the *acid* (**VIII**), m.p. 134—136°, which is also obtained (m.p. 135—136°) by similarly nitrating the corresponding acid. The structure of (**VII**) is proved by reduction by Zn–80% AcOH to 4 : 4 : 6 : 8-*tetramethylhydrocarbostyril*, m.p. 150—151° [also obtained from (**VIII**)]. HNO_3 (*d* 1·5) in H_2SO_4 at 0° converts (**VII**) into (**III**); under other conditions some (**II**) can be isolated from mixed products. R. S. C.

Polyalkylbenzenes. XXXII. Reaction between dimethylacrylic acid and *m*-xylene. L. I. Smith and L. J. Spillane (*J. Amer. Chem. Soc.*, 1943, **65**, 202—208; cf. A., 1941, II, 6).—*m*-Xylene, CMe_2:CH·CO_2H, and $AlCl_3$ at −8° to room temp. give β-m-5-*xylyl*iso*valeric acid* (**I**) (97%), m.p. 111—112° [*Me* ester (**II**), b.p. 134—137°/11 mm.], cyclised in H_2SO_4 at room temp. to 3 : 3 : 5 : 7-*tetramethylhydrindone* (**III**), m.p. 57·5—58° (*oxime*, m.p. 154·5—155°), which is probably the same as the hydrindone, m.p. 62—63°, of Smith *et al.* (A., 1940, II, 224). *m*-Xylene, CMe_2:CH·$COCl$, and $AlCl_3$ in CS_2 at 0—35° give 4-β-*methylcrotonyl*-m-*xylene* (61%), b.p. 137—139°/15 mm., converted by O_3 in AcOH or $KMnO_4$ in $COMe_2$ into 2 : 4 : 1-$C_6H_3Me_2$·CO_2H and by treating with HCl–$AlCl_3$ (excess)–CS_2 and evaporating (not other conditions) into (**III**) (48%) and tar. This proves the structure of (**III**) and probably also of (**I**). 2 · 4 : 1-$C_6H_3Me_2$·$COMe$ and MgMeBr in boiling Et_2O give β-m-4-*xylylpropan*-β-*ol* (**IV**) (88%), b.p. 88—90°/2 mm., the bromide (prep. by PBr_3–Et_2O) from which with $CHNa(CO_2Et)_2$–EtOH gives (?) 2 : 4 : 1-$C_6H_3Me_2$·CMe:CH_2, b.p. 82—82·5°/18 mm.; the corresponding chloride (prep. by HCl in light petroleum at 0°) with anhyd. K_2CO_3–MeOH at room temp. gives the *Me ether*, b.p. 62·5—65°/2 mm., of (**IV**), which with K etc. and then CO_2 gives only oils. Only oils are obtained from 1 : 3 : 5-$C_6H_3Me_2Pr^{\beta}$ by KCH_2Ph and then CO_2. 3 : 5 : 1-$C_6H_3Me_2$·CH_2·CN with $NaNH_2$ and then MeI in Et_2O gives α-m-5-*xylyl*iso*butyronitrile* (impure), b.p. 131°/25 mm. (in liquid NH_3 much *s*-$C_6H_3Me_3$ is formed), which in 85% H_2SO_4 at 100° gives the *amide* (33%), m.p. 109·5—110·5°. Boiling 25% H_2SO_4 then gives the *acid* (**V**), m.p. 116·5—117·5°, the chloride (prep. by $SOCl_2$ and C_5H_5N) of which with CH_2N_2–C_6H_6–Et_2O at 0°, Ag_2O–MeOH, and then NaOH–aq. MeOH gives only traces of acid. MgMeI and (**II**) in Et_2O give a product, converted by boiling AcOH + a trace of H_2SO_4 into 1 : 1 : 3 : 3 : 4 : 6-*hexamethylindane*, b.p. 114—117°/13 mm., indifferent to $KMnO_4$ and O_3–EtBr. Decarboxylation of (**I**) gives a mixture. Boiling $KMnO_4$–NaOH–H_2O oxidises (**V**) and (**I**) to α-3 : 5-*dicarboxyphenyl*-iso-*butyric* (**VI**), m.p. 298—300° (Me_3 ester, m.p. 73·5—76·5°), and -*valeric acid*, m.p. 247—250° (also formed with HNO_3–H_2O at 198—200°; Me_3 ester, m.p. 68·5—69·5°), respectively. R. S. C.

Rearrangement of phenyl allyl ethers. VII. Isomeric ethyl *p*-α- and -γ-methylallyloxybenzoates. W. M. Lauer and P. A. Sanders (*J. Amer. Chem. Soc.*, 1943, **65**, 198—201; cf. A., 1940, II, 15).—*p*-OH·C_6H_4·CO_2Et (**I**) and $CHMe$:CH·CH_2Cl in boiling NaOEt–EtOH give *Et* p-Δβ-*butenoxybenzoate* (**II**), m.p. 51—51·5°, and thence (KOH–MeOH) the derived *acid*, m.p. 176·5—178°, hydrogenated to *p*-OBu^{α}·C_6H_4·CO_2H, also obtained from (**I**) by $Bu^{\alpha}Br$–NaOEt–EtOH. Ozonolysis of (**II**) gives MeCHO (proof of structure). At 210—227°, (**II**) gives *Et* 4-*hydroxy*-3-α-*methylallylbenzoate* (**III**), m.p. 76—78°, converted by boiling NaOMe–MeOH–Me_2SO_4 and then hot 20% aq. NaOH into 4-*methoxy*-3-α-*methylallylbenzoic acid*, m.p. 159—160°, which with O_3 in EtBr gives CH_2O (proof of structure). With KOH–MeOH, (**III**) gives the derived *acid*, m.p. 113—114°, which by heating in quinoline and then treating with CH_2Br·CO_2Et–NaOH yields, after hydrolysis, *o*-CH_2:CH·$CHMe$·C_6H_4·O·CH_2·CO_2H, m.p. 125° (lit. 120—120·5°). CH_2:CH·$CHMeCl$ and (**I**) give similarly *Et* p-α-*methylallyloxybenzoate* (**IV**) and (**III**), separated by way of the acids; p-α-*methylallyloxybenzoic acid*, m.p. 155—156°, gives (**IV**) by way of the Ag salt and with H_2–Pd–$CaCO_3$ yields p-sec.-*butoxybenzoic acid*, m.p. 119—120°, also obtained from (**I**) by $CHMeEtBr$–NaOEt–EtOH etc. With O_3 in EtBr, (**IV**) gives CH_2O. At 222—240° (**IV**) gives 3 : 4 : 1-$CHMe$:CH·CH_2·C_6H_3(OH)·CO_2Et (**V**), m.p. (crude) 69—75°, and a little $(CH_2$:$CH)_2$. Hydrolysis of (**V**) gives 4-*hydroxy*-3-Δβ-*butenylbenzoic acid* (**VI**), m.p. 115—116°. Me_2SO_4–NaOMe–MeOH and then hot 25% KOH–MeOH convert (**V**) into 4-*methoxy*-3-Δβ-*butenylbenzoic acid* (**VII**), m.p. 150—151·5°, and (?) an impure isomeride. Ozonolysis of (**VII**) gives MeCHO and a little CH_2O; hydrogenation gives 4-*methoxy*-3-n-*butylbenzoic acid*, m.p. 131·5—132·5°. *Me* 2-*methoxy*-5-*carbomethoxyphenylacetate*, m.p. 79—80°, is obtained from (**VII**) or 3 : 4 : 1-CH_2:CH·CH_2·C_6H_3(OMe)·CO_2H by $KMnO_4$–$COMe_2$ at room temp. and esterification of the products by way of the Ag salts. (See A., 1943, II, 205.) R. S. C.

[Attempted] synthesis of aldehydes from acyl hydrazides. C. Niemann and J. T. Hays (*J. Amer. Chem. Soc.*, 1943, **65**, 482—484).—*Benzenesulphon*-o-*nitrobenzhydrazide* (prep. from $PhSO_2Cl$ and *o*-NO_2·C_6H_4·CO·NH·NH_2 in C_5H_5N at 10°), m.p. 184—184·5°, with Na_2CO_3 in $(CH_2$·$OH)_2$ at 160° gives no *o*-NO_2·C_6H_4·CHO. *Benzenesulphon*-p-*nitrobenzhydrazide*, m.p. 201—202°, under these conditions gives *p*-NO_2·C_6H_4·CO_2H and $PhSO_2Na$. R. S. C.

Production of amidines.—See B., 1943, II, 172.

Addition of dienes to di-*o*-methoxycinnamic acids. II. R. Adams and R. B. Carlin (*J. Amer. Chem. Soc.*, 1943, **65**, 360—363).—1 : 3 : 5-C_6H_3Me(OMe)$_2$ with Li–$Bu^{\alpha}Cl$ and then $NPhMe$·CHO–Et_2O at room temp. and later the b.p. gives 3 : 5 : 1 : 4-$(OMe)_2C_6H_2Me$·CHO, m.p. 91—92° (lit. 90—91°), which with $CH_2(CO_2H)_2$–C_5H_5N–piperidine at 100° gives 2 : 6-*dimethoxy*-4-*methylcinnamic acid* (98%), m.p. 202° (decomp.), converted by $(CH_2$:$CMe)_2$ in xylene at 170° into 2′ : 6′-*dimethoxy*-4 : 5 : 4′-*trimethyl*-1 : 2 : 3 : 6-*tetrahydrodiphenyl*-2-*carboxylic acid*, m.p. 178—180°. 1 : 3 : 5-*n*-C_5H_{11}·C_6H_3(OMe)$_2$ gives similarly 2 : 6-*dimethoxy*-4-n-*amyl*-*benzaldehyde*, b.p. 148—152°/0·3 mm., and -*cinnamic acid*, m.p. 179° (decomp.), which with isoprene in xylene at 185° gives 2′ : 6′-*dimethoxy*-5-*methyl*-4′-n-*amyl*-1 : 2 : 3 : 6-*tetrahydrodiphenyl*-2-*carboxylic acid* (**I**), m.p. 115—115·5° (or, in one experiment, an *isomeride*, m.p. 133—134°). The *Me* ester, b.p. 170°/0·1 mm., thereof with S at 240—250° followed by hydrolysis gives 2′ : 6′-*dimethoxy*-5-*methyl*-4′-n-*amyldiphenyl*-2-*carboxylic acid*, m.p. 146°, converted by 48% HBr–AcOH–Ac_2O into the known 3′-hydroxy-4′′-methyl-5′-*n*-amyldibenz-2-pyrone, whence follows the orientation of (**I**). M.p. are corr. R. S. C.

Symmetrical diaryls from diazotised amines. Reducing agents. II. E. R. Atkinson, D. Holm-Hansen, A. D. Nevers, and S. A. Marino (*J. Amer. Chem. Soc.*, 1943, **65**, 476—477; cf. A., 1941, II, 170).—*o*-CO_2H·C_6H_4·N_2Cl with activated Cu powder (**I**) in H_2O at

5—10° gives *o*-$C_6H_4Cl{\cdot}CO_2H$ (**II**) (54%) and diphenic acid (**III**) (32%), with (**I**) in dil. aq. NH_3 gives (**III**) (67—71%) and $NH(C_6H_4{\cdot}CO_2H\text{-}o)_2$ (10%), in warm 23N-HCO_2H gives *o*-$OH{\cdot}C_6H_4{\cdot}CO_2H$ (**IV**) (<70%), with (**I**) in HCO_2H gives BzOH (40%), (**III**) (10%), and tar, in warm EtOH gives (**IV**) (50—75%) and a little MeCHO, and with (**I**) in EtOH at 0° gives BzOH (50%), (**II**) (a little), and (*o*-$CO_2H{\cdot}C_6H_4{\cdot}N{:})_2$ (very little). R. S. C.

Tetracyanodimethyl*cyclo*propane. L. Ramberg and S. Wideqvist (*Arkiv Kemi, Min. Geol.*, 1941, **14**, **B**, No. 37, 13 pp.).—$CHBr(CN)_2$ and aq. $COMe_2$–KI afford 1 : 1 : 2 : 2-*tetracyano*-3 : 3-*dimethyl*cyclo*propane* (**I**), m.p. 209·5—210° (corr.). It is converted by boiling N-KOH into 1-*carboxy*-2-*carbamyl*-3 : 3-*dimethyl*cyclo*propane*-1 : 2-*dicarboxylimide* (**II**), m.p. 197° (decomp.), also obtained by the action of alkali on 1 : 2-dicyano-3 : 3-dimethyl*cyclo*propane-1 : 2-dicarboxylimide (**III**), m.p. 242°, prepared from *αα′*-dicyano-*ββ*-dimethylglutarimide and its *αα′*-Br_2-derivative in boiling 40% AcOH. (**II**) is probably transformed by $NaNO_2$ in 25% H_2SO_4 into the corresponding dicarboxylic acid. (**I**) is converted by KOH and conc. NH_3 in a sealed tube at 115° into a compound, m.p. 165°, which could not be obtained quite pure but is very probably caronic acid. Conc. HCl converts (**I**) or (**III**) into a *compound*, m.p. 265°, probably $CMe_2<^{CH(CO_2H){\cdot}CO}_{CCl(CN)—CO}>NH$. (**III**) is also obtained from (**I**) and KOBr. H. W.

Preparation of *αβ*-unsaturated aldehydes. P. A. Plattner and L. M. Jampolsky (*Helv. Chim. Acta*, 1943, **26**, 687—694; cf. A., 1942, II, 102).—*cyclo*Hexanone-2-oxalic [2-ketohexahydrophenylglyoxylic] acid is converted by boiling Ac_2O containing a little HBr–AcOH into the unstable 3 : 4 : 5 : 8-*tetrahydrocoumaran*-1 : 2-*dione* 3-*enol acetate* (**I**), m.p. 89—92°, which gives a yellow colour with $C(NO_2)_4$ but no reaction with $FeCl_3$. Hydrogenation (PtO_2 in EtOH) of (**I**) causes the uniform absorption of 3 H_2 and gives non-cryst. products. Partial hydrogenation (Pt in EtOH at 20°; H_2 ≡ 1 mol.) of (**I**) gives *hexahydrocoumaran*-1 : 2-*dione* 3-*enol acetate* (**II**), m.p. 100—101°, or (H_2 ≡ 2 mols.) 2-*acetoxyhexahydrocoumaran*-1-*one*, m.p. 64—66°. (**II**) is hydrolysed (KOH–MeOH) to *hexahydrocoumaran*-1 : 2-*dione*, m.p. 99—101°, which when distilled in CO_2 under atm. pressure passes into Δ^1-tetrahydrobenzaldehyde (*oxime*, m.p. 98—99°; *semicarbazone*, m.p. 213—216°). 2-Methyl*cyclo*hexanone is converted into 6-methyl-3 : 4 : 5 : 8-tetrahydrocoumaran-1 : 2-dione 2-enol acetate, m.p. 77—78°, hydrogenated and hydrolysed to 6-*methylhexahydrocoumaran*-1 : 2-*dione*, m.p. 107—108°, which when distilled over a free flame gives Δ^2-tetrahydro-*m*-tolualdehyde (*semicarbazone*, m.p. 205—206°). M.p. are corr. H. W.

Aromatic aldehydes.—See B., 1943, II, 174.

Stabilisation of aldehydes.—See B., 1943, II, 174.

Condensation of chloroacetophenone with ethanol- and diethanolamine and of chloroacetopyrocatechol with *β*-methoxyethylamine. K. W. Brighton and E. E. Reid (*J. Amer. Chem. Soc.*, 1943, **65**, 479).—$COPh{\cdot}CH_2Cl$ with $NH_2{\cdot}[CH_2]_2{\cdot}OH$ gives *ω-β-hydroxyethyl*-, m.p. 144°, and with $NH([CH_2]_2{\cdot}OH)_2$ slowly gives *ω-di-(β-hydroxyethyl)-aminoacetophenone*, m.p. 44° (hydrochloride). 3 : 4 : 1-$(OH)_2C_6H_3{\cdot}CO{\cdot}CH_2Cl$ with $OMe{\cdot}[CH_2]_2{\cdot}NH_2$ gives *ω-β-methoxyethylaminoacetopyrocatechol*, m.p. 93° (*hydrochloride*, m.p. 186°). R. S. C.

Preparation of phenylglyoxal. B. Holmberg (*Arkiv Kemi, Min., Geol.*, 1940, **14**, **A**, No. 9, 9 pp.).—$CH_2Bz{\cdot}S{\cdot}CH_2R$ (R = CO_2H, $CH_2{\cdot}CO_2H$, or Ph) (cf. A., 1943, II, 183) with alkaline H_2O_2 gives $CH_2Bz{\cdot}SO{\cdot}CH_2R$, which when distilled from dil. HCl + $HgCl_2$ yields BzCHO (**I**) and $CH_2R{\cdot}S{\cdot}HgCl$. In absence of $HgCl_2$ mercaptals and additive products of (**I**) and the mercaptan are formed, The following are prepared: *β-phenacylthiolpropionic*, m.p. 46—49° (+H_2O, m.p. 59—61°), and *β-phenacylsulphinylpropionic*, m.p. 121·5—122·5°, *acids*; *compound* $2(I),2CH_2Ph{\cdot}SH,H_2O$, m.p. 69—70° (opaque; clear at 82°), volatile in steam; *mercaptal*, m.p. 150—151·5°, and *semi-mercaptal*, m.p. 106—108°, of (**I**) and $SH{\cdot}[CH_2]_2{\cdot}CO_2H$. *β-Benzylsulphinylpropionic acid*, m.p. 149—149·5° (decomp.), does not yield (**I**) with dil. HCl + $HgCl_2$. M. H. M. A.

Phenyl 2 : 4 : 6-trimethylbenzyl diketone. R. P. Barnes and R. J. Brown (*J. Amer. Chem. Soc.*, 1943, **65**, 412—415).—*Ph* 2 : 4 : 6-*trimethylbenzyl diketone* (**I**), m.p. 55°, resembles $CHPh_2{\cdot}CO{\cdot}COPh$ rather than $CH_2Ph{\cdot}CO{\cdot}COMes$ (Mes = mesityl here and below) (cf. A., 1934, 410; 1935, 979), although the nuclear H are unusually reactive. MesCHO and $COPh{\cdot}CH_2Br$ give a substance (poor yield), m.p. 137°, containing Br, but $CHMes{:}CH{\cdot}COPh$ and H_2O_2 in MeOH–NaOH–H_2O give *βγ-epoxy-α-phenyl-γ-mesitylpropan-α-one* (80%), m.p. 73°, which with NaOH in hot MeOH gives (**I**). (**I**) gives no colour with $FeCl_3$ and is 100% ketonic (Kurt Meyer) in EtOH. With *o*-$C_6H_4(NH_2)_2$ it gives 2-*phenyl*-3-2′ : 4′ : 6′-*trimethylbenzylquinoxaline*, m.p. 118°. The structure of (**I**) is proved by cleavage by H_2O_2–aq. MeOH to BzOH and $CH_2Mes{\cdot}CO_2H$. With Br in $CHCl_3$, (**I**) gives *Ph* 3-*bromo*-2 : 4 : 6-*trimethylbenzyl diketone* (**II**), m.p. 72° [derived *quinoxaline* (**III**), m.p. 161°], converted by H_2O_2 etc. into BzOH and 2 : 4 : 6 : 3 : 1-$C_6HMe_3Br{\cdot}CO_2H$ and giving with boiling Ac_2O–KOAc (not AcOH–KOAc) the *enol acetate* (**IV**), m.p. 107°, stable to Br–$CHCl_3$. Cold, conc. H_2SO_4 hydrolyses (**IV**) to the enolic *form* (**V**), m.p. 147°, of (**II**) [which also yields (**IV**) and (**III**)]; in boiling EtOH, (**V**) yields (**II**) and it reacts with H_2O_2 as does (**II**). Dissolving (**II**) in H_2SO_4 and pouring the solution on to ice gives (**V**). In Et_2O, (**V**) and Br yield an oily *compound*, $C_{18}H_{16}O_2Br_2$, which with KI–$COMe_2$ gives I and (**II**). R. S. C.

Synthesis of 2-keto*cyclo*hexylsuccinic acid and related substances. II. Syntheses involving *cyclo*hexanone. E. H. Charlesworth, J. A. McRae, and H. M. MacFarlane (*Canad. J. Res.*, 1943, **21**, **B**, 55—64).—Et *cyclo*hexanone-2-carboxylate (**I**) is converted by the successive actions of Na and $CH_2Br{\cdot}CO_2Et$ in boiling C_6H_6 into the 2-carboxylate-2-acetate, b.p. 195—210°/45 mm., hydrolysed and decarboxylated by boiling conc. HCl to 2-keto*cyclo*hexylacetic acid, m.p. 75—78° (phenylhydrazone, m.p. 162—163°). (**I**), $CHMeBr{\cdot}CO_2Et$, and NaOEt in boiling EtOH afford *Et α-2-keto-1-carbethoxy*cyclo*hexylpropionate*, b.p. 180—190°/17 mm., whence (boiling conc. HCl) *α*-2-keto*cyclo*hexylpropionic acid. Similar condensation of (**I**) with $CH_2Ph{\cdot}CHBr{\cdot}CO_2Et$ leads to $CH_2Ph{\cdot}CH(OH){\cdot}CO_2Et$, converted by conc. HCl into $CHPh{:}CH{\cdot}CO_2H$. Attempts to condense (**I**) with $CHBr(CO_2Et)_2$ and Na in C_6H_6 lead to $[CH(CO_2Et)_2]_2$ whereas with NaOEt in EtOH the product appears to be $[{:}C(CO_2Et)_2]_2$, m.p. 54—55°. (**I**) and $CO_2Et{\cdot}CHBr{\cdot}CH_2{\cdot}CO_2Et$ (**II**) in EtOH–NaOEt give a product, b.p. 237°/10 mm., hydrolysed to an acid, m.p. 102—103° (not 2-keto*cyclo*hexylsuccinic acid). *cyclo*Hexanone (**III**), $CH_2Br{\cdot}CO_2Et$, and Zn in boiling C_6H_6 give Et 1-hydroxy*cyclo*hexylacetate, b.p. 143—146°/37 mm., transformed by boiling conc. HCl into cyclo*hexanolaceto-γ-lactone*, b.p. 152—156°/28 mm. *cyclo*Hexanol-*α*-propio-*γ*-lactone, b.p. 150°/21 mm., is obtained similarly. The Reformatsky reaction could not be achieved with (**III**) and $CHBr(CO_2Et)_2$ or (**II**). H. W.

Indanone ring-closure of unsymmetrical *ββ*-diarylpropionic acids. C. F. H. Allen and J. W. Gates, jun. (*J. Amer. Chem. Soc.*, 1943, **65**, 422—424).—$CHPh{:}CH{\cdot}CO_2H$, PhBr, and $AlCl_3$ at 20° give, after esterification, *Me β-phenyl-β-*p*-bromophenylpropionate*, b.p. 220—225°/24 mm., and thence the acid, m.p. 107—108°, which with PCl_5–CS_2 (later warm) and then $AlCl_3$–CS_2 at 10—15° (later room temp.) gives 3-*p*-bromophenylindanone (**I**), m.p. 59—60°. With CrO_3 this gives *o*-$CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_4Br$-*p*, m.p. 172—173°, proving the structure of (**I**) (cf. Kohler *et al.*, A., 1910, i, 562; Waldmann *et al.*, A., 1930, 600). The dibromo-3-phenylindanone of Kohler *et al.* (*loc. cit.*) is the 2 : 4′-Br_2-compound, since it is reduced to (**I**) by MgMeI in boiling Et_2O. R. S. C.

Apparently anomalous bromination in the polyphenylindene series. C. F. H. Allen and J. W. Gates, jun. (*J. Amer. Chem. Soc.*, 1943, **65**, 419—422).—2 : 3-Diphenylindenone (**I**) and Br (1 mol.) in AcOH containing (very slowly without) a little HBr give 3-*phenyl*-2-p-*bromophenylindenone* (**II**), m.p. 145—146°, the structure of which is proved by oxidation (CrO_3) to *p*-$C_6H_4Br{\cdot}CO_2H$ (**III**) and *o*-$C_6H_4Bz{\cdot}CO_2H$ and by the following synthesis: *o*-$C_6H_4(CO)_2O$ with *p*-$C_6H_4Br{\cdot}CH_2{\cdot}CO_2H$ (**IV**) gives *α*-p-*bromobenzylidenephthalide*, m.p. 154—155°, which with MgPhBr gives (**II**). Similarly, the compound, m.p. 200—201°, obtained from 2 : 3 : 5 : 6-tetraphenylindenone (**V**) (A., 1943, II, 35) is 3 : 5 : 6-*triphenyl*-2-p-*bromophenylindenone*, since with CrO_3 it yields (**III**) and 4 : 5 : 2 : 1-$C_6H_2Ph_2Bz{\cdot}CO_2H$. With an excess of Br, (**I**) gives 6-*bromo*-3-*phenyl*-2-p-*bromophenylindenone*, m.p. 201—202°, which with $KMnO_4$ in $COMe_2$ gives 4 : 5′-*dibromo*-2′-*benzoylbenzil*, m.p. 140—141°, and thence (H_2O_2–alkali) (**III**) and 2 : 5 : 1-$C_6H_3BzBr{\cdot}CO_2H$. 2 : 3 : 4 : 7-*Tetraphenylindenone* (**VI**), m.p. 204—205°, and Br give a mixture, including 6- (or 5-)*bromo*-3 : 4 : 7-*triphenyl*-2-p-*bromophenylindenone* (**VII**), m.p. 254—255°, the location of one Br being proved as follows: 3 : 6 : 1 : 2-$C_6H_2Ph_2(CO)_2O$ and (**IV**) give 3 : 6-*diphenyl-α*-p-*bromobenzylidenephthalide*, m.p. 213—214°, converted by MgPhBr into 3 : 4 : 7-*triphenyl*-2-p-*bromophenylindenone*, m.p. 257—258°, which with Br gives (**VII**) and with CrO_3 gives (**III**). The appropriate substituted *o*-$C_6H_4(CO)_2O$ with $CH_2Ph{\cdot}CO_2H$ gives 4 : 5-, m.p. 212—213°, and 3 : 6-*diphenyl*-, m.p. 166—167°, 4 : 5-*diphenyl*-3 : 6-*dimethyl*-, m.p. 232—233° (also obtained from the H_2-anhydride at >290°), and 3 : 4 : 5 : 6-*tetraphenyl*-, m.p. 338—340°, *α-benzylidenephthalide* and thence (MgPhBr) (**V**), (**VI**), 2 : 3 : 4 : 7-*tetraphenyl*-5 : 6-*dimethyl*-, m.p. 234—235°, and 2 : 3 : 4 : 5 : 6 : 7-*hexaphenyl-indenone*, m.p. 279—280°, respectively. Identity of (**V**) is confirmed by conversion by MgPhBr into the known carbinol. The need for HBr during the brominations is explained by a mechanism involving quinonoid ions, which involves location of a Br at $C_{(6)}$ of (**VII**). R. S. C.

Modification of the Ullmann synthesis of fluorene derivatives. W. C. Lothrop and P. A. Goodwin (*J. Amer. Chem. Soc.*, 1943, **65**, 363—367).—Adding 2-methyl-4 : 5-benz-1 : 3-oxaz-6-one (**I**) in C_6H_6 to Et_2O–MgPhBr gives *o*-$NHAc{\cdot}C_6H_4{\cdot}CPh_2{\cdot}OH$ (23%), m.p. 197—198° (lit. 192°), identified by hydrolysis by HCl–EtOH to *o*-$NH_2{\cdot}C_6H_4{\cdot}CPh_2{\cdot}OH$, m.p. 119° (lit. 121·5°), converted by Ac_2O–NaOAc into 6 : 6-diphenyl-2-methyl-4 : 5-benz-1 : 3-oxazine, m.p. 137—139° (lit. 135—137°). The reverse addition gives *o*-$NHAc{\cdot}C_6H_4{\cdot}COPh$ (33%), m.p. 88° (lit. 89°), and thence (conc. HCl–EtOH) *o*-$NH_2{\cdot}C_6H_4{\cdot}COPh$. Adding *o*-$C_6H_4Me{\cdot}MgBr$ to (**I**) gives similarly 2′-*acetamido*- (43%), m.p. 104°, and thence 2′-*amino*-

2-*methylbenzophenone*, m.p. 84°, which with $NaNO_2$–5N-HCl gives 1-*methylfluoren*-9-*one* (**II**) (49%), m.p. 98° (identified by oxidation by $KMnO_4$ to the 1-carboxylic acid), and a little 2′-*hydroxy*-2-*methylbenzophenone*, m.p. 65—67°. Boiling 47% HI and red P reduce (**II**) slowly to 1-*methylfluorene*, m.p. 87°. *m*-C_6H_4Me·MgBr gives an oil, hydrolysed to 2′-*amino*-3-*methylbenzophenone* (10% over-all), m.p. 57°, which yields a trace of 2-methylfluorenone. Adding 1-$C_{10}H_7$·MgBr to (**I**) gives *o*-*NHAc*·C_6H_4 *α*-$C_{10}H_7$ *ketone* (**III**) (47%), m.p. 125°; the reverse addition gives less (**III**) and some *o*-*acetamido*-, m.p. 209—211°, hydrolysed to *o*-*amino*-*phenyldi*-*α*-*naphthylcarbinol*, m.p. 206° (decomp.). (**III**) yields, as above, *o*-NH_2·C_6H_4·CO·$C_{10}H_7$-*α*, 1 : 2-benzfluoren-9-one, and chrysofluorene. Adding 2 : 1-$C_{10}H_6Me$·MgBr to (**I**) gives *o*-*acetamido*- (34%), m.p. 132°, and thence *o*-NH_2·C_6H_4 2-*methyl*-1-*naphthyl ketone*, m.p. 114°, and 6-methyl-7-benzanthrone. 2-$C_{10}H_7$·MgBr leads to an oil, which yields *o*-NH_2·C_6H_4 *β*-$C_{10}H_7$ *ketone* (8·3%), m.p. 106°, and thence traces of 3 : 4-benzfluorenone. CH_2Ph·MgCl and 1 : 3 : 4-$C_6H_3Me_2$·MgI with (**I**) give only oils. Adding MgPhBr to 2-methyl-4 : 5-2′ : 3′-naphth-1 : 3-oxaz-6-one (**IV**) gives Ph 2-acetamido (39%), m.p. 141—145°, and thence *Ph* 2-*amino*-3-*naphthyl ketone* (**V**), m.p. 114°; some *diphenyl*-2-*acetamido*-3-*naphthylcarbinol*, m.p. 226° (decomp.), is also formed. Ring-closure of (**V**) as above yields 2 : 3-benzfluorenone (13%) and a little *Ph* 2-*hydroxy*-3-*naphthyl ketone*, m.p. 156°. CH_2Ph·MgCl and (**IV**) give only a small yield of *αγ*-*diphenyl*-*β*-2-*acetamido*-3-*naphthylpropan*-*β*-*ol*, m.p. 181°. 2-$C_{10}H_7$·MgBr and (**IV**) give *β*-$C_{10}H_7$ 2-*acetamido*-, m.p. 169°, and thence 2-*amino*-3-*naphthyl ketone* (4% over-all), m.p. 154—156°, which by diazotisation etc. yields 2 : 3 : 5 : 6-*dibenzfluoren*-9-*one*, m.p. 185° (resists reduction), and a little *β*-$C_{10}H_7$ 2-*hydroxy*-3-*naphthyl ketone*, m.p. 139°.

R. S. C.

Polynitro-compounds of fluorene. F. E. Ray and W. C. Francis (*J. Org. Chem.*, 1943, **8**, 52—59).—2 : 2′-Dinitrodiphenyl-6-carboxylic acid is converted by conc. H_2SO_4 at 190°±5° into 4 : 5-dinitrofluorenone (**I**), m.p. 273·5°. The substance, m.p. 243° [*oxime*, m.p. 265°; phenylhydrazone, new m.p. 252—253° (decomp.)], thus described by Schmidt *et al.* (A., 1906, i, 27), is the 2 : 5-$(NO_2)_2$-compound; it is formed with 4 : 6′-dinitrodiphenic acid, new m.p 306—307°, by the oxidation of 2 : 5-dinitrophenanthraquinone by $KMnO_4$ in the presence of alkali. 2 : 4 : 7-Trinitrofluorenone (**II**), m.p. 175·5°, is obtained by nitration of 2 : 5- and 2 : 7-dinitrofluorenone (cf. Bell, A., 1928, 1010); the compound is identical with the "2 : 6 : 7- (or 2 : 3 : 7-)trinitrofluorenone" of Schmidt *et al.* (*loc. cit.*). It is very resistant to oxidation by acid $KMnO_4$. 2 : 4 : 5 : 7-Tetranitrofluorenone, m.p. 252—253°, is obtained from (**I**) or (**II**) and a mixture of boiling fuming HNO_3 (*d* 1·59—1·60) and conc. H_2SO_4.

H. W.

1 : 2 : 5 : 6-Dibenzfluorenone.—See B., 1943, II, 174.

Preparation of derivatives of chrysene by the Robinson–Mannich base synthesis of unsaturated ketones. A. L. Wilds and C. H. Shunk (*J. Amer. Chem. Soc.*, 1943, **65**, 469—475).—The hygroscopic methiodide from pure NEt_2·[CH_2]$_2$·COMe (**I**) (modified prep. from paraformaldehyde, $COMe_2$, and $NHEt_2$,HCl in EtOH) with Me 1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene-2-carboxylate (**II**) and NaOMe (1 mol.) in MeOH–C_6H_6 gives 92% of *Me* 1-*keto*-2-*γ*-*keto*-n-*butyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-2-*carboxylate* (**III**), m.p. 145—145·5°; owing to its content of *δ*-*diethylamino*-*γ*-*diethylamino*-*methylbutan*-*β*-*one* (**IV**), b.p. 92—92·5°/0·4 mm. (prep. described), crude (**I**) gives much lower yields of (**III**). The dimethiodide of (**IV**) with (**II**) gives *Me* 1-*keto*-2-*γ*-*keto*-*β*-*methylene*-n-*butyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-2-*carboxylate* (**V**) (72%), m.p. 157·5—158·5°. In boiling KOH–MeOH–N_2 or conc. HCl–AcOH–N_2, (**III**) gives 5-*keto*-1 : 2 : 2a : 3 : 4 : 5-*hexahydrochrysene* (**VI**) (90 or 84%), m.p. 188—188·5° [*oxime*, sinters 218°, m.p. 220—222° (decomp.)] [and a trace of an acid, m.p. 232—234° (gas)], but in boiling NaOMe–MeOH–N_2 gives *Me* 5-*keto*-1 : 2 : 2a : 3 : 4 : 5-*hexahydrochrysene*-2a-*carboxylate* (79%), m.p. 178·5—179·5°, which is indifferent to hot HCl–AcOH but in KOH–MeOH yields (**VI**). Pd–C–N_2 dehydrogenates (**VI**) at 280—300° to chrysene (78%) and 5-*hydroxychrysene* (18%), m.p. 271—273° (*acetate*, m.p. 201—202°; *Me ether*, m.p. 147·5—148·5°; no $FeCl_3$ colour), the latter being the main product (83% + a trace of a neutral substance, m.p. 135—155°) obtained by Pd–C in xylene–N_2. When treated with MgMeI–Et_2O–C_6H_6 and then aq. NH_4Cl and finally Pd–C at 300–320°, (**VI**) gives 5-methylchrysene (76%). In conc. HCl–AcOH–N_2, (**V**) gives 5-*acetoxy*- (**VII**) (76—83%), m.p. 167—168°, and thence (conc. HCl–EtOH–N_2) 5-*hydroxy*-4-*methyl*-1 : 2-*dihydrochrysene* (**VIII**), m.p. 159—160°; KOH–MeOH yields >43%. With Pd–C–N_2 at 200—250° and then boiling Ac_2O, (**VII**) gives 5-*acetoxy*-, di- (? tri-)morphic, m.p. 185—187°, and thence 5-*hydroxy*-4-*methylchrysene*, m.p. 287—288° (vac.). H_2–Pd–C in dioxan converts (**V**) into mixed *Me* 1-*keto*-2-*γ*-*keto*-*β*-*methyl*-n-*butyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-2-*carboxylates*, *form*, m.p. 123·5—124·5°, and thence (KOH–MeOH) mixed 5-*keto*-4-*methyl*-1 : 2 : 2a : 3 : 4 : 5-*hexahydrochrysenes* (**IX**), *form*, m.p. 189—189·5° [*oxime*, m.p. ~252—254° (decomp.)], which is dehydrogenated as above to (**VIII**) and with Zn–Hg–HCl and then Pd–C yields 4-methylchrysene, m.p. 229·5—230°.

R. S. C.

Oximation of juglone. H. Goldstein and P. Grandjean (*Helv. Chim. Acta*, 1943, **26**, 181—185).—Oximation of 5-hydroxy-1 : 4-naphthaquinone (juglone) (**I**) occurs in position 1. 5-Hydroxy-1 : 4-naphthaquinone-1-oxime, decomp. 203° [lit. m.p. 187° (decomp.)], is reduced and then benzoylated to 4 : 1 : 8-NHBz·$C_{10}H_5$(OBz)$_2$, m.p. 247°, prepared for comparison from 4-benzeneazo-1 : 8-dihydroxynaphthalene. 4-Benzamido-, m.p. 233°, and 2-*benzamido*-, m.p. 213°, -1 : 5-*dibenzoyloxynaphthalene* are described. (**I**) is obtained by oxidation of 1 : 5 : 4-$(OH)_2C_{10}H_5$·NH_2. M.p. are corr.

H. W.

Naphthazarin. H. E. Fierz-David and W. Stockar (*Helv. Chim. Acta*, 1943, **26**, 92—98).—Naphthazarin (**I**) is obtained in 59% yield by the addition of a solution of S (7 g.) in 66% oleum (120 g.) to 1 : 5-$C_{10}H_6(NO_2)_2$ in H_2SO_4,H_2O (400 g.) at >40° and is purified by sublimation at 170—180°/vac. Addition of H_3BO_3 does not improve the yield. Reduction of 1 : 5- or 1 : 8-$C_{10}H_6(NO_2)_2$ by NH_2Ph in conc. H_2SO_4 gives (**I**) in only 22% or 11·5% yield respectively. (**I**) condenses with NH_2Ar usually at room temp. to 2-arylamino-5 : 8-dihydroxy-1 : 4-naphthaquinones; *products* are described from NH_2Ph, *o*-NH_2·C_6H_4·OMe, *o*- and *m*-toluidine, *m*- and *p*-xylidine, and *m*- and *o*-C_6H_4Cl·NH_2. *p*-OEt·C_6H_4·NH_2, *α*- and *β*-$C_{10}H_7$·NH_2, *m*- and *p*-OMe·C_6H_4·NH_2 also condense. 2-Anilino-5 : 8-dihydroxy-1 : 4-naphthaquinone is sulphonated to a marine-blue dye. A second arylamino-residue is introduced if (**I**) is heated for some time with an excess of base but the products are sol. with great difficulty.

H. W.

Oximation of 2-hydroxy- and 2-anilino-1 : 4-naphthaquinone. H. Goldstein and P. Grandjean (*Helv. Chim. Acta*, 1943, **26**, 468—475).—Oximation of 2-hydroxy-1 : 4-naphthaquinone in acid or alkaline medium gives 2-hydroxy-1 : 4-naphthaquinone-1-oxime (**I**), m.p. ~195° (decomp.) (lit. decomp 180°). It is reduced to 1 : 2 : 4-NH_2·$C_{10}H_5(OH)_2$ [Ac_3 derivative (**II**), m.p. 155·5°]. 1 : 3-$C_{10}H_6(OH)_2$ is converted by $CH_2Bu\beta$·O·NO in EtOH–KOH at 0° into 4 : 1 : 3-NO·$C_{10}H_5(OH)_2$ identical with (**I**) and yielding (**II**) when reduced and acetylated, thus proving the structure of (**I**). 2-Methoxy-1 : 4-naphthaquinone can be obtained directly by heating 1 : 2-NO·$C_{10}H_6$·OH with MeOH–conc. H_2SO_4. 2-Anilino-1 : 4-naphthaquinone does not react with NH_2OH in acid solution but in alkaline medium affords the 1-*oxime* (**III**), m.p. 222° (decomp.). This is reduced to 3 : 4 : 1-NHPh·$C_{10}H_5(NH_2)$·OH, the ON-Bz_2 derivative, m.p. 235°, of which with boiling AcOH gives 5-*benzoyloxy*-2 : 3-*diphenyl*-*α*-*naphthiminazole* (**IV**), m.p. 181°, thus establishing the vicinal position of NHPh and :N·OH in (**III**). (**IV**) is converted by successive treatments with KOH–EtOH and Me_2SO_4 into 5-*methoxy*-2 : 3-*diphenyl*-*α*-*naphthiminazole* (**V**), m.p. 162°. 1 : 4-OMe·$C_{10}H_6$·N_2Ph is converted by the successive action of $SnCl_2$ and aq. HCl into 4-*amino*-3-*anilino*-1-*methoxynaphthalene*, m.p. 182° (decomp.); the *Bz* derivative, m.p. 195°, of this is converted into (**V**) by boiling glacial AcOH, thus confirming the structure of (**IV**). M.p. are corr.

H. W.

2-Methyl-3-phytyl-1 : 4-naphthaquinone.—See B., 1943, III, 136.

Celastrol. IV. O. Gisvold (*J. Amer. Pharm. Assoc.*, 1942, **31**, 529—532; cf. A., 1941, II, 18).—Celastrol (**I**) with AcOH–O_3 is degraded to a CO-acid, m.p. 166—167°, [α] +22·1° in EtOH (2 : 4-*dinitrophenylhydrazone*, $C_{25}H_{32}O_7N_4$, m.p. 192°). Acetylation (Thiele) of (**I**) and methylcelastrol gives colourless, abnormal *triacetates*, $C_{28}H_{38}O_7$, m.p. 100—101°, and $C_{29}H_{40}O_7$, respectively. (**I**) is reduced (Pt–H_2) to dihydrocelastrol, m.p. 177°, which readily oxidises to (**I**). (**I**) is 8-hydroxy-3-methyl-4-homohydrogeranyl- (or -hydrogeranyl-)1 : 2-naphthaquinone.

F. O. H.

IV.—STEROLS AND STEROID SAPOGENINS.

Sensitive colour reaction for steroids. M. C. Nath (*Ann. Biochem. Exp. Med.*, 1942, **2**, 83—86).—When conc. H_2SO_4 is poured down the side of a test-tube containing a solution of a steroid in glacial AcOH containing a drop of 1% $Hg(OAc)_2$ in glacial AcOH, a brown, red, or violet ring develops at the junction of the two layers with a blue or green ring above it. Variations observed with different concns. of the reagents are described.

P. C. W.

Colour reaction of steroids in relation to their structures. M. C. Nath and M. K. Chakraborty (*Ann. Biochem. Exp. Med.*, 1942, **2**, 73—82).—An attempt is made to correlate the location of double linkings in steroids with the colours developed by particular reagents. It is suggested that a $\Delta^{4:5}$ linking (actual or potential) is responsible for the development of red or carmine and a $\Delta^{7:8}$ linking for the blue colour in Rosenheim's, Kohlenberg's, and Rosenheim and Callow's reactions. The relation between structure and the absorption bands found during the colour development is discussed.

P. C. W.

Preparation of cholesteryl *p*-aminobenzoate. D. Kritchevsky (*J. Amer. Chem. Soc.*, 1943, **65**, 480).—Cholesteryl *p*-nitrobenzoate, m.p. 190·5—191·5°, $[\alpha]_D^{20}$ −6·97° in $CHCl_3$, with Fe filings in boiling AcOH gives the *p*-aminobenzoate, m.p. 237·8—238·8°, $[\alpha]_D^{20}$ +3·68° in $CHCl_3$, hydrolysed by hot NaOH–EtOH.

R. S. C.

Scymnol. W. Bergmann and W. T. Pace (*J. Amer. Chem. Soc.* 1943, **65**, 477—478).—Location of OH at $C_{(3)}$ (cf. Ashikari, A. 1939, III, 692) is confirmed. Scymnol tetra-acetate, m.p. 145·5—

147°, with CrO_3–AcOH at 90° gives (after hydrolysis) cholic and then 3 : 7 : 12-triketocholanic acid (**I**). Tschesche's products (A., 1932, 268) were impure. Scymnoltriketo-acid (Windaus, A., 1930, 1039) with conc. HCl–AcOH gives the *chlorohydrin*, $C_{27}H_{39}O_6Cl$, m.p. 225—227°, which with CrO_3–AcOH at 80° yields (**I**). R. S. C.

Oxidative degradation of *i*-stigmasteryl methyl ether. B. Riegel, E. W. Meyer, and J. Beiswanger (*J. Amer. Chem. Soc.*, 1943, **65**, 325—328).—Formation of *i*-ethers is used to protect the OH at $C_{(3)}$ of sterols. *i*-Stigmasteryl Me ether (from stigmasterol in 77% yield) wih O_3 in $CHCl_3$ at 0° and then H_2O_2 gives 6-*methoxy*-i-*bisnorcholenic acid* (**I**), $+H_2O$ and anhyd., m.p. 174·8—176·3°, $[\alpha]_D^{25}$ +17° in $CHCl_3$, which gives gums when rearranged. *Me* 3-p-*toluenesulphonyloxy*-Δ^5-*bisnorcholenate* (**II**), m.p. 133—134°, and KOAc in boiling MeOH give *Me* 6-*methoxy*-i-*bisnorcholenate* (**III**) (98%), m.p. 72·0—72·8°, $[\alpha]_D^{25}$ +37·3° in $CHCl_3$, converted by KOH–MeOH into (**I**) having m.p. 168—171° and $[\alpha]_D^{23}$ +33° in $CHCl_3$. With a little H_2SO_4 in boiling MeOH, (**III**) gives *Me* 3-*methoxy*-Δ^5-*bisnorcholenate* (**IV**), m.p. 117—118°, $[\alpha]_D^{25}$ −63·3° in $CHCl_3$, which is also obtained by boiling (**II**) in MeOH and by rearranging the crude Me ester from either " form " of (**I**). Boiling KOH–MeOH hydrolyses (**IV**) to the *acid*, m.p. 199—202°, $[\alpha]_D^{25}$ −77·8° in $CHCl_3$. With boiling $Zn(OAc)_2$–Ac_2O–AcOH, (**III**) gives Me 3-acetoxy-Δ^5-bisnorcholenate. M.p. are corr. R. S. C.

Preparation of deoxycholic acid from cholic acid. G. A. D. Haslewood (*Biochem. J.*, 1943, **37**, 109—112).—A more detailed account of work previously abstracted (A., 1942, II, 365). 3 : 12-*Dihydroxy*-7-*ketocholanic acid*, m.p. ~83°, and its *Et* ester, m.p. 160—161°, are new. R. L. E.

Preparation of deoxycholic acid from cholic acid. A. W. Schneider and W. M. Hoehn (*J. Amer. Chem. Soc.*, 1943, **65**, 485).—Oxidation of cholic acid or its Me ester by CrO_3 in AcOH or AcOH–C_6H_6 and heating (170—200°) the semicarbazones or hydrazones of the products with KOH– or NaOH–MeOH gives deoxycholic acid, $[\alpha]_D^{26}$ +57°±1° in MeOH, which is similarly obtained from Me 7 : 12-dihydroxy-3-benzoyloxycholanate when the sol. (MeOH) semicarbazone of the oxidation product is used. R. S. C.

Constitution of cafestol. A. Wettstein and K. Miescher (*Helv. Chim. Acta*, 1943, **26**, 631—641; see also A., 1943, II, 203).—*t*-Dehydroandrosterone with piperonal and *m*-NO_2·C_6H_4·CHO in an alkaline medium gives 16-*piperonylidene*-, m.p. 242—243°, and 16-m-*nitrobenzylidene*-Δ^5-*androsten*-3t-*ol*-17-*one*, m.p. 248·5—250°, respectively. 16-m-*Nitrobenzylidene-androsterone*, m.p. 189—190°, and -*œstrone Me ether*, m.p. 187—188°, are similarly prepared. M.p. are corr. H. W.

Saccharides of deoxycorticosterone.—See A., 1943, II, 156.

Alengol.—See A., 1943, II, 211.

Steroids. VII. Compounds related to 6-methyl-11-deoxycorticosterone. M. Ehrenstein (*J. Org. Chem.*, 1943, **8**, 83—94).—Δ^5-Pregnene-3(β) : 21-diol-20-one 21-acetate is converted by $Al(OPr^{\beta})_3$ in boiling $Pr^{\beta}OH$ followed by hydrolysis and treatment with $COMe_2$ and anhyd. $CuSO_4$ into Δ^5-pregnene-3(β) : 20 : 21-triol 20 : 21-CMe_2 ether, m.p. 175°, $[\alpha]_D^{29·5}$ −46·5° in $COMe_2$, which is hydrolysed by EtOH–aq. AcOH to Δ^5-pregnene-3(β) : 20 : 21-triol, m.p. 222—229°, $[\alpha]_D^{31}$ −54·0° in MeOH. This with BzO_2H in $CHCl_3$ gives 5 : 6-*oxido*-*pregnane*-3(β) : 20 : 21-*triol* (**I**), m.p. 221—223°, $[\alpha]_D^{30}$ −63·5° in $COMe_2$. (**I**) is converted by MgMeBr in Et_2O–PhOMe ultimately at 130° into 6-*methylpregnane*-3(β) : 5 : 20 : 21-*tetraol*, m.p. 229—230° (decomp.), $[\alpha]_D^{28·5}$ −24·0° in MeOH, partly acetylated by Ac_2O in cold C_5H_5N to the 21-*monoacetate* (**II**), m.p. 177·5—180°, $[\alpha]_D^{30}$ +15·0° in MeOH, with some 3 : 21-*diacetate* (**III**), m.p. 185—187°. (**II**) is oxidised by CrO_3 in AcOH to 6-*methylpregnane*-5 : 20 : 21-*triol*-3-*one* 20 : 21-*diacetate*, m.p. 205—210°, converted by HCl in $CHCl_3$ into resinous 6-*methyl*-Δ^4-*pregnene*-20 : 21-*diol*-3-*one diacetate*. (**III**) is oxidised by CrO_3 in AcOH to the non-cryst. 6-methylpregnane-3(β) : 5 : 21-triol-20-one 3 : 21-diacetate. H. W.

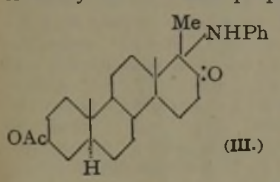
Steroids and sex hormones. LXXXIV. 17(α)-Hydroxy-20-keto-compounds of the pregnene and *allo*pregnane series. M. W. Goldberg, R. Aeschbacher, and E. Hardegger (*Helv. Chim. Acta*, 1943, **26**, 680—686; cf. Stavely, A., 1942, II, 147).—17-Acetylenyl-Δ^5-androstene-3(β) : 17(α)-diol is converted by (*p*-C_6H_4Me·SO_2·$NH)_2Hg$ in boiling 96% EtOH with subsequent treatment of the product with H_2S and then 2N-KOH into Δ^5-pregnene-3(β) : 17(α)-diol-20-one (**I**), hexagonal leaflets or long needles, m.p. 190—191°, $[\alpha]_D$ −83·6°±3° and −87·9°±3° in dioxan, respectively [*oxime*, m.p. ~255—260°; 3-monoacetate, m.p. 186—188°, and its oxime, m.p. 235—240° (decomp.)]. 17-Acetylenyl-Δ^5-androstene-3(β) : 17(α)-diol diacetate is transformed similarly into the diacetate, m.p. 194—195°, $[\alpha]_D$ −54·4°±3° in dioxan, of (**I**), also obtained by protracted treatment of (**I**) with Ac_2O–C_5H_5N at 105°. (**I**) is apparently transformed by $Al(OBu^{\nu})_3$ in C_6H_6–$COMe_2$ into (mainly) 3(β) : 17*a*(β)-dihydroxy-17*a*-methyl-Δ^5-*D*-homoandrosten-17-one, m.p. 176—178°. 17-Acetylenyltestosterone is converted [as for (**I**)] into Δ^4-*pregnen*-17(α)-*ol*-3 : 20-*dione*, m.p. 192—193°, $[\alpha]_D$ +64·4°±3° in dioxan, almost quantitatively isomerised by activated Al_2O_3 to 17*a*(β)-hydroxy-17*a*-methyl-Δ^4-*D*-homoandrostene-3 : 17-dione, m.p. 181—184°, and converted by KOH–MeOH into 17*a*(α)-hydroxy-17*a*-methyl-Δ^4-*D*-homoandrostene-3 : 17-dione with (predominatingly) non-investigated acidic products. 17-Acetylenylandrostane-3(β) : 17(α)-diol yields 3(β) : 17(α)-dihydroxy*allo*pregnan-20-one, m.p. 208—210°, $[\alpha]_D$ −22·9°±2° in dioxan [3-monoacetate, m.p. 139—142° (lit. 190—192°)]. M.p. are corr. H. W.

Constituents of the adrenal cortex and related substances. LIX. Δ^4-Pregnen-21-ol-3 : 12 : 20-trione and -12(β) : 21-diol-3 : 20-dione. H. G. Fuchs and T. Reichstein (*Helv. Chim. Acta*, 1943, **26**, 511—530).—Diacetylætiodeoxycholic acid is converted by successive treatment with $SOCl_2$ and CH_2N_2 into non-cryst. 21-diazopregnane-3(α) : 12(β)-diol-20-one diacetate (**I**), hydrolysed by KOH–MeOH at room temp. to the corresponding diol (**II**). In AcOH at 100° (**II**) passes into *pregnane*-3(α) : 12(β) : 21-*triol*-20-*one* 21-*monoacetate* (**III**), m.p. 149·5—150·5°, $[\alpha]_D^{18}$ +139·7°±4° in $COMe_2$ (also $+1H_2O$), which with Ac_2O and C_5H_5N at 90° gives the *triacetate* (**IV**), m.p. 114—115°. (**I**) is hydrolysed by K_2CO_3–$KHCO_3$ in aq. MeOH at room temp. into 21-diazopregnane-3(α) : 12(β)-diol-20-one 12-monoacetate, which in anhyd. AcOH at 105° passes into *pregnane*-3(α) : 12(β) : 21-*triol*-20-*one* 12 : 21-*diacetate* (**V**), two forms, m.p. ~72—95° and 156—158°, $[\alpha]_D^{19}$ +150·7°±2° in $COMe_2$, with some (**III**). (**V**) is acetylated to (**IV**). Excess of CrO_3 oxidises (**III**) to *pregnan*-21-*ol*-3 : 12 : 20-*trione acetate* (**VI**), m.p. 189—191°, $[\alpha]_D^{17}$ +153·0°±3° in $COMe_2$, whereas 1 equiv. of CrO_3 affords a mixture from which (?) *pregnane*-3(α) : 21-*diol*-12 : 20-*dione* 21-*monoacetate*, m.p. 149—151°, $[\alpha]_D^{19}$ +157·6°±3° in $COMe_2$, is isolated; it is further oxidised to (**VI**). In boiling C_6H_6–$COMe_2$, (**III**) and $Al(OPh)_3$ yield *pregnane*-12(β) : 21-*diol*-3 : 20-*dione* 21-*monoacetate* (**VII**), m.p. 190—192°, $[\alpha]_D^{14}$ +146·3°±3° in $COMe_2$; this is oxidised by CrO_3 in AcOH at room temp. to (**VI**). (**V**) is oxidised by CrO_3 to *pregnane*-12(β) : 21-*diol*-3 : 20-*dione diacetate* (**VIII**), m.p. 120—122°, $[\alpha]_D^{17}$ +142·4°±4° in $CHCl_3$, also obtained from (**VII**) and Ac_2O in C_5H_5N at 20° and then 90°. Bromination followed by treatment with boiling C_5H_5N converts (**VI**), (**VII**), and (**VIII**) into Δ^4-*pregnen*-21-*ol*-3 : 12 : 20-*trione acetate*, m.p. 182—184°, $[\alpha]_D^{14}$ +228·6°±3° in $COMe_2$, Δ^4-*pregnene*-12(β) : 21-*diol*-3 : 20-*dione* 21-*monoacetate* (**IX**), m.p. 182—184°, $[\alpha]_D^{21}$ +203·7°±2°, $[\alpha]_{5461}^{21}$ +251·6°±2° in $COMe_2$, and Δ^4-*pregnene*-12(β) : 21-*diol*-3 : 20-*dione diacetate* (**X**), m.p. 158—159°, $[\alpha]_D^{17}$ +197·7°±5° in $COMe_2$, respectively. These show the ultraviolet absorption spectrum characteristic of $\alpha\beta$-unsaturated ketones. Acidic or cautious alkaline hydrolysis converts them respectively into Δ^4-*pregnen*-21-*ol*-3 : 12 : 20-*trione*, m.p. 180—183°, $[\alpha]_D^{23}$ +238·9°±3°, $[\alpha]_{5461}^{23}$ +298°±3° in dioxan, $[\alpha]_D^{23}$ +215·1°±2°, $[\alpha]_{5461}^{23}$ +265·8°±2° in $COMe_2$, Δ^4-*pregnene*-12(β) : 21-*diol*-3 : 20-*dione*, m.p. 98—124° (decomp.), $[\alpha]_D^{21}$ +186·1°±2°, $[\alpha]_{5461}^{21}$ +221·1°±2° in dioxan, and its 12-*monoacetate*, m.p. 188—192°, $[\alpha]_D^{19}$ +185·3°±2°, $[\alpha]_{5461}^{19}$ +226·3°±3° in $COMe_2$. Preliminary experiments appear to show that (**IX**) and (**X**) are at any rate less potent than corticosterone in the Everse–de Fremery test and that (**X**) is inactive in 4-mg. doses in the anti-insulin test. M.p. are corr. (block); limit of error ±2°. H. W.

Steroids and sex hormones. LXXXIII. *A*-Homocholestanone and *A*-homodihydrotestosterone. M. W. Goldberg and H. Kirchensteiner (*Helv. Chim. Acta*, 1943, **26**, 288—301).—The methods used for the enlargement of ring D have been extended to that of ring A. Catalytic reduction (PtO_2 in AcOH at room temp.) of *cyclo*hexanone cyanohydrin gives 1-aminomethyl*cyclo*hexanol (**I**) (*hydrochloride*, m.p. 210—212°; N-*Bz* derivative, m.p. 142—143°) and di-1-hydroxyhexahydrobenzylamine (*hydrochloride*, m.p. 250—252°; N-*NO*-compound, m.p. 133—134°); the yield of (**I**) is greatly increased if HCl is added to the reaction mixture. Similar hydrogenation of *cyclo*hexanone cyanohydrin acetate leads to dihexahydrobenzylamine, isolated as the *NO*-derivative, m.p. 100—101°. Cholestanone cyanohydrin is hydrogenated (PtO_2 in AcOH at room temp.) to 3-*hydroxy*-3-*aminomethylcholestane*, m.p. 194—197° [*hydrochloride*; N-*Ac* (**II**), m.p. 227—228°, and *Ac*$_2$, m.p. 176—178°, derivatives], transformed by HNO_2 into A-*homocholestanone*, m.p. 85—87°, $[\alpha]_D$ +50° in $CHCl_3$ (*semicarbazone*, m.p. 239—242°; *oxime*, m.p. 197—199°). Hydrogenation of *cholestanone cyanohydrin acetate*, m.p. 123—126°, yields (**II**), Ac wandering from O to N. 17-Acetoxydihydrotestosterone gives a very unstable cyanohydrin, m.p. 175—187° (characterised as the 3 : 17-*diacetate*, m.p. 198—200°), hydrogenated to 17-*acetoxy*-3-*aminomethylandrostan*-3-*ol hydrochloride*, m.p. 295—297° (decomp.) [17-*acetoxy*-3-*acetamidomethylandrostan*-3-*ol* has m.p. 224—226°], converted by HNO_2 and subsequent hydrolysis (N-MeOH–KOH) into A-*homodihydrotestosterone* (**III**), m.p. 197—199°, $[\alpha]_D$ +108·5° in $CHCl_3$ [*oxime*, m.p. 225—227°; *acetate*, m.p. 146—148° (*semicarbazone*, m.p. 239—241°)]; (**III**) is devoid of pharmacological activity. Cholestanone is converted by NaOEt and *iso*amyl formate in Et_2O at room temp. into the *OH·CH:* compound, m.p. 176—178°, and by PhCHO in EtOH containing a little aq. NaOH into two *CHPh:* derivatives, m.p. 145—146° and 126—128°, and a *OH·CHPh·* compound, m.p. 184—186°. *Benzylidene*- and *bromo*-, m.p. 113—115°, -A-*homocholestanone* are described. *Androstanedione dicyanohydrin diacetate* has m.p. 171—172°. M.p. are corr. H. W.

Constituents of the adrenal cortex and related compounds. LVII. 17-Hydroxy-20-ketosteroids and the mechanism of their rearrangement into polyhydrochrysene derivatives. C. W. Shoppee and D. A.

Prins (*Helv. Chim. Acta*, 1943, **26**, 185—200).—It is deduced from theoretical considerations that the hydration of acetylenylandrostane derivatives is most likely to occur without ring enlargement if OH at $C_{(17)}$ is etherified or esterified, if an amine instead of H_2O is added at the triple linking and if the experiment is performed in neutral solution. Thus 3(*β*) : 17(*α*)-diacetoxy-17-acetylenylandrostane is converted by aq. $HgCl_2$ and NH_2Ph in C_6H_6 at 60—62° (cf. Stavely, A., 1940, II, 180; 1942, II, 147) into 3(*β*) : 17(*α*)-diacetoxy*allo*pregnan-20-one (**I**), m.p. 227—229°, $[\alpha]_D^{20}$ +2·5°±2° in $COMe_2$ (cf. Ruzicka *et al.*, A., 1939, II, 327), converted by boiling 4% KOH–MeOH into 3(*β*) : 17(*α*)-dihydroxy-17*a*-methyl-*D*-homoandrostan-17-one (**II**), m.p. 295—300° (3-acetate, m.p. 243—244°). (**I**) is converted by N_2H_4,H_2O–NaOEt–EtOH at 180° into 3(*β*)-*hydroxy*-17a-*methyl*-Δ^{17}-*D*-*homoandrostene*, m.p. 159—160°, also obtained similarly from (**II**); this is hydrogenated (PtO_2 in AcOH) and then oxidised to 17*a*-methyl-*D*-homoandrostan-3-one, m.p. 180—182° (Ruzicka *et al.*, A., 1940, II, 180, 218), which is converted by N_2H_4,H_2O and NaOEt–EtOH at 175° into 17*a*-methyl-*D*-homoandrostane. (**I**) is not hydrogenated in presence of PtO_2 in AcOH at 20° or 100° or in presence of Raney Ni in MeOH at 100° or 120°. 17(*α*)-Hydroxy-3(*β*)-acetoxy-17-acetylenylandrostane is transformed similarly into a small proportion of a substance, m.p. 176—177°, which has not been investigated further,



(III.)

the *compound* (**III**), m.p. 232—233°, $[\alpha]_D^{23}$ −103·3°±6° in dioxan [*NO*-derivative, m.p. 194° (decomp.)] (obtained by rearrangement of the anil), and 17(*α*)-*hydroxy*-3(*β*)-*acetoxy*allo*pregnan*-20-*one* (**IV**), apparently two forms, m.p. 184—186° and 190—192°, $[\alpha]_D^{23}$ −24·3°±3°, $[\alpha]_{5461}^{23}$ −29·4°±3° in dioxan. (**IV**) is oxidised (CrO_3 in AcOH at room temp.) and then hydrolysed (K_2CO_3–aq. MeOH) to *t*-androsterone and 17*a*(*β*)-hydroxy-3(*β*)-acetoxy-17*a*-methylandrostan-17-one, m.p. 158—159°. (**IV**) is hydrogenated (PtO_2 in EtOH) and then acetylated (Ac_2O–C_5H_5N at room temp.) to 17(*α*)-hydroxy-3(*β*) : 20(*β*)-diacetoxy*allo*pregnane, flat platelets which are transformed at ~185° into rectangular prisms, m.p. 200—202°; this appears to be the sole product. (**IV**), Ac_2O, and C_5H_5N at 100° yield 3(*β*) : 17(*α*)-diacetoxy*allo*pregnan-20-one, m.p. 227—229°. M.p. are corr. (block); limit of error ±2°.

H. W.

Constituents of the adrenal cortex and related compounds. LVIII. Rearrangement of 17-hydroxy-20-ketosteroids into polyhydrochrysene derivatives. Acetylations in the presence of boron fluoride. C. W. Shoppee and D. A. Prins (*Helv. Chim. Acta*, 1943, **26**, 201—223).—Hydration of 3(*β*) : 17(*α*)-dihydroxy-17-acetylenyl-Δ^5-androstene by the method of Stavely (A., 1940, II, 180; 1942, II, 147) affords 3(*β*) : 17(*α*)-dihydroxy-Δ^5-pregnen-20-one (**I**), m.p. 176—179°, $[\alpha]_D^{21}$ −60°±3° in $CHCl_3$ (acetate, m.p. 187—188°, $[\alpha]_D^{18}$ −61·3°±5° in $CHCl_3$), and 17*a*-*anilino*-3(*β*)-*hydroxy*-17a-*methyl*-Δ^5-D-*homoandrosten*-17-*one*, m.p. 150°, $[\alpha]_D^{18}$ −186·6°±7° in $CHCl_3$ [*acetate*, m.p. 236—238°; *NO*-derivative, m.p. 140° and 170—174° (decomp.) after resolidification], identical with the " anil " of Stavely (*loc. cit.*) and Goldberg *et al.* (A., 1939, II, 553). (**I**) is converted by Ac_2O and C_5H_5N at 120° into the diacetate (**II**), m.p. 193—195°, $[\alpha]_D^{22}$ −55·9°±2° in dioxan, with a compound, m.p. 177—178°, $[\alpha]_D^{18}$ −79°±2° in $CHCl_3$, which may be identical with it. Hydration (Stavely) of 3(*β*) : 17(*α*)-diacetoxy-20-acetylenyl-Δ^5-androstene yields (**II**), also obtained by the BF_3 method. Filtration of (**I**) in dry C_6H_6 through Al_2O_3 followed by immediate elution causes partial conversion into 3(*β*) : 17*a*(*β*)-dihydroxy-17*a*-methyl-Δ^5-*D*-homoandrosten-17-one (**III**), m.p. 176—178°, $[\alpha]_D^{18}$ −105·6°±3° in $CHCl_3$; if undried solvents are used and longer contact with the column is permitted the change becomes more complete. 17*a*(*β*)-Hydroxy-3(*β*)-acetoxy-17*a*-methyl-Δ^5-*D*-homoandrosten-17-one, m.p. 176° (change at 160°), $[\alpha]_D^{17}$ −91·1°±4° in $CHCl_3$, is obtained similarly or by acetylation of (**III**). (**III**) is converted by Al(OBu$^\gamma$)$_3$ in abs. C_6H_6–$COMe_2$ at 100° into 17*a*(*β*)-hydroxy-17*a*-methyl-Δ^4-*D*-homoandrostene-3 : 17-dione, m.p. 178—180°, $[\alpha]_D^{17}$ +60·8°±3° in $CHCl_3$. (**II**) is hydrolysed by boiling KOH–MeOH to 3(*β*) : 17*a*(*α*)-dihydroxy-17*a*-methyl-Δ^5-*D*-homoandrosten-17-one, prisms which pass into hexagonal prisms at ~260° and at 290° into rodlets which melt at 302—305° (*acetate*, m.p. 277—278°, $[\alpha]_D^{19}$ −100·9°±4° in dioxan). (**I**) is hydrogenated (PtO_2 in AcOH) and then acetylated to 17(*α*)-hydroxy-3(*β*) : 20(*β*)-diacetoxy*allo*pregnane, m.p. 202—204°, $[\alpha]_D^{21}$ −7·9°±3° in $CHCl_3$. Nieuwland's mixture (BF_3, Ac_2O, AcOH, and HgO) (cf. A., 1930, 745) causes hydration of the triple linking through an unknown series of intermediates whereby the presence of Hg" is essential, and causes acetylation of free OH. The prep. of the following compounds proves it to be a very powerful acetylating agent: 3(*β*) : 17a(*β*)-*diacetoxy*-17a-*methyl*-Δ^5-D-*homoandrosten*-17-*one*, m.p. 238—240°, $[\alpha]_D^{22}$ −68·4°±3° in dioxan, from (**I**) or (**III**) [reduced (H_2, PtO_2, AcOH) to 3(*β*) : 17*a*(*β*)-diacetoxy-17*a*-methyl-*D*-homoandrostan-17-one (**IV**), m.p. 221—222°, $[\alpha]_D^{18}$ −6·1°±3° in $COMe_2$]; (**IV**), from its 3-*monoacetate*, m.p. 159—160°, $[\alpha]_D^{15}$ −34·8°±4° in dioxan, obtained by rearrangement (Al_2O_3) of 17(*α*)-hydroxy-3(*β*)-acetoxy*allo*pregnan-20-one (**V**); (**IV**) from (**V**); 3(*β*) : 17a(*α*)-*diacetoxy*-17a-*methyl*-Δ^5-D-*homoandrosten*-17-*one*, m.p. ~248° after changing at ~240, $[\alpha]_{Hg}^{19}$ −32·8°±4° in $CHCl_3$, reduced to the -D-*homoandrostan*-7-*one*, m.p. 232—235° (change at 228°), $[\alpha]_D^{15}$ 0°±4° in $COMe_2$. M.p. are corr. (block); limit of error ±2°.

H. W.

ψ-**Sapogenin compounds.**—See B., 1943, III, 135.

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Inversion of menthone with trichloroacetic acid in aprotic solvents. A. Weissberger (*J. Amer. Chem. Soc.*, 1943, **65**, 102—110).—The equilibrium, *l*- (**I**) ⇌ *d*-*iso*-menthone, in presence of CCl_3·CO_2H (**II**) in C_6H_6, C_6H_{14}, and $CHCl_3$ at 20° is investigated polarimetrically and cryoscopically. The catalytic activity per mol. of acid is a max. when the molar ratio (**I**) : (**II**) = 1 : 2 for the range (**I**) = 0·1—1·0 mol. per l. At const. [(**II**)], the reaction rate falls with increasing [(**I**)], the effect being greater if the (**II**) is in excess. The temp. coeff. from 20° to 50° gives a heat of activation = 6200 g.-cal. [*α*] of the equilibrium mixture depends on the [(**II**)], since (i) (**II**) affects the [*α*] and (ii) higher [(**II**)] decreases the proportion of (**I**). Inversion occurs by interaction of a (**I**)–(**II**) complex with another mol. of (**II**) or by rearrangement of a complex, 1(**I**)–2(**II**). Tubandt's view (A., 1911, ii, 28) of the nature of " Rechtsmenthon " is confirmed. R. S. C.

Effect of solvents in chemical reactions. III. Influence of addenda on the inversion of *l*-menthone with acids in benzene. A. Weissberger (*J. Amer. Chem. Soc.*, 1943, **65**, 242—245; cf. A., 1932, 22).—PhOH, PhOMe, $COPh_2$, *l*-menthol, COPhMe, $COMe_2$, *l*-menthone, and Et_2O reduce the rate of inversion of *l*-menthone (**I**) by CCl_3·CO_2H in C_6H_6 at 20±0·1°. The quant. results, given as % acid eliminated (order of efficiency as above), parallel those for salt-formation of *p*-NMe_2·C_6H_4·N_2Ph and interaction of CHN_2·CO_2Et with CCl_3·CO_2H (A., 1931, 1375). Inversion of (**I**) by HCl in C_6H_6 is retarded by Et_2O but accelerated by PhOH. R. S. C.

Inversion of *l*-menthone and reaction of diazoacetic ester with chloroacetic acids. A. Weissberger (*J. Amer. Chem. Soc.*, 1943, **65**, 245—246).—Decomp. of CHN_2·CO_2Et and inversion of *l*-menthone by CCl_3·CO_2H, $CHCl_2$·CO_2H, or CH_2Cl·CO_2H in C_6H_6 all agree with the Brönsted relation. R. S. C.

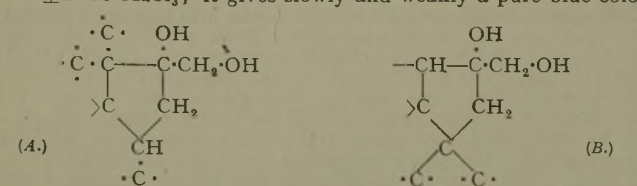
Isomeric Δ^1-menthenes (carvomenthenes). A. A. Dodge and E. Kremers (*J. Amer. Pharm. Assoc.*, 1942, **31**, 525—527).—*l*- and *d*-Carvoxime are reduced (H_2; Raney Ni) to *d*- (**I**), b.p. 77—78°/7 mm., $[\alpha]_D^{23}$ +5·92° [hydrochloride, m.p. 192—195°; *picrate*, m.p. 184—185° (decomp.)] (cf. Read and Johnston, A., 1934, 413), and *l*-carvomenthylamine (**II**), b.p. 81·5—82·0°/9 mm., $[\alpha]_D^{23}$ −8·34° [hydrochloride, m.p. 197—198°; *picrate*, m.p. 184—185° (decomp.)], respectively. (**I**), treated with HNO_2, refluxed, steam-distilled, and fractionated in vac., affords two fractions, (*a*), b.p. 43·8—45·5°/0·02—0·03 mm., $[\alpha]_D^{25}$ −1·22° (3 : 5-dinitrobenzoate, m.p. 105—106°), and (*b*), b.p. 44·0—45·5°/0·02 mm., $[\alpha]_D^{25}$ +1·62°; similarly, (**II**) gives (*a*), b.p. 40·5—42·5°/0·025 mm., $[\alpha]_D^{20}$ +0·88° (3 : 5-dinitrobenzoate, m.p. 108·5—109·5°), and (*b*), b.p. 42·5—44·5°/0·025 mm., $[\alpha]_D^{20}$ −2·18°. These carvomenthol preps. readily lose H_2O during fractionation, giving a menthene fraction, the carvomenthol from (**I**) giving a product of $[\alpha]_D^{20}$ +19·54° [nitrosochloride (impure), m.p. 81·5—83°, and its nitrolbenzylamine base, m.p. 107—107·5°], and that from (**II**) a product of $[\alpha]_D^{20}$ −10·98° (nitrosochloride, m.p. 98—99°). When dehydrated by refluxing with anhyd. $CuSO_4$ at 180—200° for 9 hr., the carvomenthol from (**I**) yields a carvomenthene fraction, $[\alpha]_D^{23}$ +11·44° (nitrosochloride, m.p. 90—91°, and its nitrolbenzylamine, m.p. 106—107°, and nitrolmorpholine base, m.p. 159—160°), and that from (**II**) a carvomenthene fraction, $[\alpha]_D^{28}$ −8·65° (nitrosochloride, m.p. 90—91°, and its nitrolbenzylamine, m.p. 107—107·5°, and nitrolmorpholine base, m.p. 159—160°) (cf. Johnston and Read, A., 1935, 1245). Vals. of *d* and *n* are also given. F. O. H.

Lavandulol, a new monoterpene alcohol from oil of lavender.—See A., 1943, II, 181.

Volatile vegetable compounds. XXII. Composition of " natural " cedrene and constitution of " synthetic " cedrene. Y. R. Naves, G. Papazian, and E. Perrottet (*Helv. Chim. Acta*, 1943, **26**, 302—337).—" Synthetic " cedrene (termed *α*-cedrene) (**I**), b.p. 100°/3·5 mm., $[\alpha]_D^{20}$ −91·22° to −91·33°, obtained by dehydration of cedrol, m.p. 86—86·5°, $[\alpha]_D^{18}$ +13·06° in abs. EtOH, +8·76° in CH_2Ph·OH, +14·26° in dioxan, is a well-defined sesquiterpene with an endocyclic ethylenic linking. It is possibly a 2 : 8-dimethyl-2 : 5-*endoiso*propylidene-[0 : 3 : 5]-di*cyclo*-Δ^8-decene (2 : 8-dimethyl-2 : 5-*endoiso*propylidene-1 : 2 : 3 : 4 : 5 : 6 : 7 : 10-octahydroazulene). " Natural " cedrene, obtained by fractional distillation from American oil of red cedar, is a mixture containing a considerable proportion of (**I**), its isomeride with an exocyclic CH_2 (*β*-cedrene), and a mixture of tricyclic sesquiterpenes which appear to be allied closely in structure to the cedrenes. (**I**) with H_2O_2 in presence of H_2SO_4 and AcOH gives an excellent yield of *cedranone*, b.p. 134°/4 mm., α_D −84·70° (*oxime*, m.p. 103·5—104°, $[\alpha]_D$ −78·59° in $CHCl_3$, −69·14° in MeOH). The material, sol. in acid, obtained by Treibs (A., 1935, 983) by the action of conc. H_2SO_4 on the cedrenes is a dehydrosesquiterpene or mixture of dehydrosesquiterpenes.

H. W.

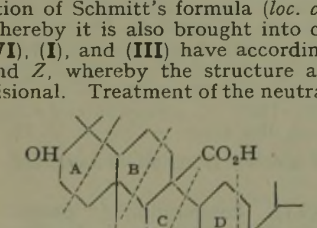
Constitution of cafesterol. III. Constitution of cafestol. A. Wettstein and K. Miescher (*Helv. Chim. Acta*, 1943, **26**, 631—641; cf. A., 1942, II, 371).—Since cafesterol has been shown not to belong to the sterol group its name is modified to "cafestol" (**I**). The union of the *cyclo*pentane ring in (**I**) is probably in accordance with (*A*) or (*B*). Floridin has proved very useful in the chromatographic purification of cafestyl acetate (**II**), m.p. 173—175°, $[\alpha]_D^{20}$ −91°±2° in $CHCl_3$; it gives slowly and weakly a pure blue colour



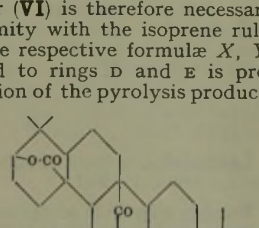
(*A.*) (*B.*)

with mineral acids but the intense blue fluorescence under the Hg-vapour lamp is no longer observed. The residues from (**II**) yield a (non-homogeneous) kahweyl acetate, m.p. ~146°, $[\alpha]_D^{24}$ −234° in $CHCl_3$, characterised by high extinction, intense green-blue colour with mineral acids, reaction with $(CH{\cdot}CO)_2O$, and non-fluorescence in ultra-violet light; it is possibly identical with the compound of Bengis *et al.* (A., 1932, 975). Alkaline hydrolysis of the Me_2 ester (A., 1942, II, 198) from epoxycafestanediol gives a *Me H* ester, $C_{20}H_{30}O_5$, m.p. 150·5—152°, and ultimately a non-cryst. product; hydrolysis resembles that of Me_2 3*t*-acetoxy-Δ^5-ætiobilienate. Probably, therefore, $C_{(5)}$ or $C_{(3)}$ closely resembles $C_{(13)}$ of the steroid skeleton and is quaternary or at any rate *tert.* Differences, however, are found between the *cyclo*pentane ring of (**I**) and ring D of the steroid mol. The colour reactions of *m*-$C_6H_4(NO_2)_2$ with (**I**) and its derivatives are less intense and develop much more slowly than those of 17-ketosteroids. Further, epoxynorcafestanone *A* and epoxynorcafestadienone do not condense with ArCHO (see A., 1943, II, 199). M.p. are corr. H. W.

Triterpenes. LXXIII. Pyrolysis of a product of the transformation of quinovic acid. L. Ruzicka and G. Anner (*Helv. Chim. Acta*, 1943, **26**, 129—142).—The dilactonic dicarboxylic anhydride (**I**), m.p. 260° (decomp.) (cf. Schmitt *et al.*, A., 1940, II, 88), obtained by the oxidation of novaquinone with H_2O_2 (improved prep.) is pyrolysed at ordinary pressure. The acidic products of pyrolysis consist of a solid and a liquid portion, the former of which is separated by fractional crystallisation into two isomeric dicarboxylic *acids*, $C_{14}H_{20}O_4$, m.p. 183—184°, $[\alpha]_D$ −155° in EtOH (**II**) [Me_2 ester, a liquid which gives a distinct yellow colour with $C(NO_2)_4$], and m.p. 200—202°, $[\alpha]_D$ −170° in EtOH, either of which is transformed by boiling Ac_2O into the *anhydride* (**III**), $C_{14}H_{18}O_3$, m.p. 80—80·5°, which passes into (**II**) when hydrolysed by 0·1N-KOH. Dehydrogenation of (**III**) under varied conditions in presence of Pd–C or Se gives 1 : 2-$C_{10}H_6Me_2$ [identified by the m.p. and mixed m.p. of its picrate, styphnate, and additive compound with $C_6H_3(NO_2)_3$] and 1 : 2-*dimethylnaphthalene*-5 : 6-*dicarboxylic anhydride* (**IV**), m.p. 164·5—165·5°. The established formation of 1 : 8-dimethyl- and 1 : 2 : 8-trimethyl-picene (**V**) by the dehydrogenation of quinovic acid (**VI**) and of pure (**V**) by the similar treatment of norquinovenol proves that 1 : 2-$C_{10}H_6Me_2$ and (**IV**) can arise only from rings A and B of the pentacyclic skeleton of (**VI**). A modification of Schmitt's formula (*loc. cit.*) for (**VI**) is therefore necessary whereby it is also brought into conformity with the isoprene rule. (**VI**), (**I**), and (**III**) have accordingly the respective formulæ *X*, *Y*, and *Z*, whereby the structure assigned to rings D and E is provisional. Treatment of the neutral portion of the pyrolysis products

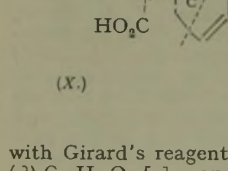


(*X.*)



(*Y.*)

with Girard's reagent *T* gives two portions which in composition, (?) $C_{14}H_{22}O$, $[\alpha]_D$, and n_D^{19} are very closely similar but are distinguished from one another in ultra-violet absorption spectrum. The reacting portion thus appears to be a mixture of ketones a fraction of which is $\alpha\beta$-unsaturated. This portion gives in small yield a 2 : 4-*dinitrophenylhydrazone*, m.p. (indef.) 125—130°, corresponding in composition to $C_{14}H_{22}O$. This fraction is treated with MgMeI, dehydrated by $KHSO_4$ at 185—190°, and then dehydrogenated with Pd–C or Se at 340—420°, whereby a liquid $C_{13}H_{18}$±CH_2 is ultimately obtained which does not combine with picric acid or $C_6H_3(NO_2)_3$ and in



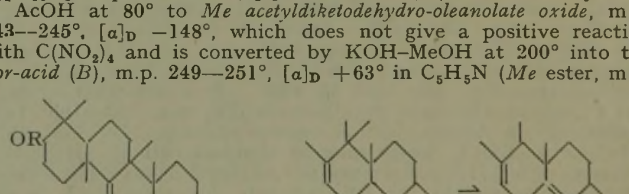
(*Z.*)

which the presence of a C_6H_6 ring is established spectroscopically. This may possibly be explained by the assumption that ring E is five-membered. M.p. are corr. H. W.

Triterpenes. LXXIV. Dehydrogenation of quinovic acid to chrysene hydrocarbons. L. Ruzicka, A. Grob, and G. Anner [with V. Prelog and K. Huber] (*Helv. Chim. Acta*, 1943, **26**, 254—264; cf. Wieland *et al.*, A., 1936, 849).—Quinovic acid (**I**) is dehydrogenated by Se at 360° and the product is extracted successively with light petroleum, b.p. 40—70°, and C_6H_6; from the last solvent 1 : 8-dimethylpicene (**II**) is isolated. The portion sparingly sol. in light petroleum after being purified chromatographically gives a hydrocarbon, C_nH_n, m.p. 193—195°, softens slightly at 190° (additive *compound* with 2 : 7-dinitroanthraquinone, $C_{24}H_{24}$,$C_{14}H_6O_6N_2$, m.p. 220—230°). The same hydrocarbons are obtained by the dehydrogenation of pyroquinovatrienic acid (Wieland *et al.*, A., 1939, II, 425). (**I**) is converted by Se at 330—340° into (**II**) anhydropyroquinovic acid, and two *hydrocarbons*, C_nH_n, m.p. 239—240° (additive *compound* with 2 : 7-dinitroanthraquinone) and 233·5—234·5° respectively. Spectroscopically they very closely resemble alkylchrysenes, thus indicating that ring E of (**I**) is five-membered.

The action of the Mg compound from *β-o*-tolylethyl bromide on 1-keto-5 : 6-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene followed by elimination of H_2O from the product affords *α-o-tolyl-β*-5 : 6-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthylethane*, m.p. 53—54°, dehydrogenated by Pd–C at 320° to *α-o-tolyl-β*-5 : 6-*dimethylnaphthylethane*, m.p. 60°, which is converted by $AlCl_3$ in CS_2 into 1 : 7 : 8-*trimethylchrysene*, m.p. 281—282°. Similarly, *α*-2 : 3-*dimethylphenyl-β*-5 : 6-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthylethane*, b.p. 165°/1 mm., is transformed successively into *α*-2 : 3-*dimethylphenyl-β*-5 : 6-*dimethylnaphthylethane*, m.p. 90·5—91·5°, and 1 : 2 : 7 : 8-*tetramethylchrysene*, m.p. 298—299°. M.p. are corr. H. W.

Triterpenes. LXXV. Position of the carboxyl group in oleanolic and glycyrrhetic acid. L. Ruzicka, O. Jeger, and M. Winter (*Helv. Chim. Acta*, 1942, **26**, 265—279).—Oxidation of Me acetyloleanolate (**I**) by SeO_2 in dioxan at 200° gives Me diketoacetyldehydro-oleanolate (**II**), m.p. 251—252° (cf. A., 1939, II, 331), converted by mild alkaline hydrolysis into *Me diketodehydro-oleanolate*, m.p. 263—265° (high vac.), which does not give a yellow colour with $C(NO_2)_4$ and is reconverted by Ac_2O–C_5H_5N into (**II**) and the corresponding acid, which passes in boiling xylene into *nor-β-amyradienedionol acetate* (**III**) (*A*; R = Ac), m.p. 323—324° (high vac.), $[\alpha]_D$ +227°. Energetic hydrolysis of (**II**) leads to nor-*β*-amyradienedionol (*A*; R = H) (**IV**), m.p. 295° (high vac.), $[\alpha]_D$ +233°, acetylated to (**III**), which is also obtained directly from (**I**). (**III**) is transformed by N_2H_4,H_2O in EtOH at 200° into the *pyridazine* derivative, $C_{29}H_{42}ON_2$, m.p. 304—306° (vac.), $[\alpha]_D$ +275°, and is hydrogenated (PtO_2 in AcOH at 90°) to the *substances*, $C_{31}H_{48}O_3$, m.p. 218—219°, and $C_{31}H_{46}O_4$, m.p. 271—273°, $[\alpha]_D$ +139·4°. (**II**) is oxidised by CrO_3 in AcOH at 80° to *Me acetyldiketodehydro-oleanolate oxide*, m.p. 243—245°, $[\alpha]_D$ −148°, which does not give a positive reaction with $C(NO_2)_4$ and is converted by KOH–MeOH at 200° into the *nor-acid* (*B*), m.p. 249—251°, $[\alpha]_D$ +63° in C_5H_5N (*Me* ester, m.p.

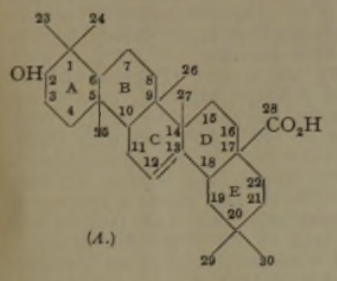


(*A.*) (*B.*)

203—204°), which gives a yellow colour with $C(NO_2)_4$, and (**IV**). Ketoacetyloleanolic acid (**V**) is transformed by Br in AcOH into *ketoacetyldehydro-oleanolic acid*, m.p. 288—289°, $[\alpha]_D$ +233°, which can be sublimed unchanged at 260—270°/high vac. and gives a pale yellow colour with $C(NO_2)_4$. (**V**) is decarboxylated in quinoline (cf. A., 1939, II, 29) to *acetylnor-β-amyrenolone*, m.p. 237—238° (high vac.), $[\alpha]_D$ +52°, and *acetylnor-β-amyradienolone*, m.p. 202°, $[\alpha]_D$ +150°. The acetylnor-*β*-amyradienolone obtained by the oxidation of glycyrrhetic acid is oxidised by CrO_3 in AcOH to *bisnor-β-amyrenoltrione acetate*, m.p. 246—248° [*semicarbazone*, m.p. 222—224° (decomp.)]. These observations are not compatible with the constitution assigned to oleanolic and other triterpenic acids by Bilham *et al.* (A., 1942, II, 148) but are consistent with Haworth's variant of the formulation of the *β*-amyrin–oleanolic acid group. M.p. are corr. and $[\alpha]_D$ are in $CHCl_3$ unless otherwise stated. H. W.

Triterpenes. LXXVI. Pyrolysis of methyl hydrogen *iso*oleanonelactonedicarboxylate. L. Ruzicka, F. C. van der Sluys-Veer, and O. Jeger (*Helv. Chim. Acta*, 1943, **26**, 280—288; cf. A., 1939, II, 220).—Pyrolysis of Me H *iso*oleanonelactonedicarboxylate gives a product separated by Girard's reagent *T* into a ketonic (**I**) and a non-ketonic (**II**) portion. The semicarbazone, m.p. 203—204°, from (**I**) is converted by N_2H_4,H_2O and NaOEt–EtOH at 200° into a *hydrocarbon*, b.p. ~120°/12 mm., dehydrogenated by Se at 340—350° to 1 : 6-$C_{10}H_6Me_2$, identified by its compounds, m.p. 132—133° and

114—115°, respectively with $C_6H_3(NO_2)_3$ and picric acid. (**II**) is converted by KOH–MeOH into neutral and acidic portions, the former giving a *hydrocarbon*, $C_{13}H_{22}$, b.p. ~115°/12 mm., dehydrogenated by Se at 340—350° to 2 : 7-$C_{10}H_6Me_2$, m.p. 96—97° [picrate, m.p. 135—136°; additive compound with $C_6H_3(NO_2)_3$, m.p. 151—152°]. The acidic portions contain 2 : 7 : 7-trimethyl-3 : 4 : 5 : 6 : 7 : 8-hexahydronaphthalene-1-carboxylic acid, dehydrogenated to 2 : 7-$C_{10}H_6Me_2$. The results confirm the position of the double linking and the disposition of Me groups in oleanolic acid (*A* but are not reconcilable with the formula of Bilham *et al.* (A., 1942, II, 148). A suggested scheme for numbering the β-amyrin residue (see *A*) is given. M.p. are corr. H. W.



(*A.*)

VI.—HETEROCYCLIC.

Production of furfuraldehyde from *D*-lyxose and *D*-ribose. R. C. Hockett, A. Guttag, and M. E. Smith (*J. Amer. Chem. Soc.*, 1943, **65**, 1—3).—The amounts and rates of production of furfuraldehyde produced from *D*-lyxose (**I**) and *D*-ribose (**II**) by 12% HCl under standard conditions are recorded. Yields are *D*-xylose > (**II**) > *L*-arabinose > (**I**). Rates are (**II**) > (**I**). R. S. C.

Furyl ketones.—See B., 1943, II, 146.

Rearrangement of phenyl allyl ethers. VIII. Ethyl *p*-γγ-dimethylallyloxybenzoate. W. M. Lauer and O. Moe (*J. Amer. Chem. Soc.*, 1943, **65**, 289—293; cf. A., 1943, II, 194).—*p*-OH·C_6H_4·CO_2Et (**I**), CMe_2:CH·CH_2Br, and K_2CO_3 in boiling $COMe_2$ give an ester (76%), hydrolysed by KOH–MeOH to p-*γ-methyl-Δβ-butenoxybenzoic acid* (**II**), m.p. 150—151°. With aq. $KMnO_4$ this gives *p*-CO_2H·C_6H_4·O·CH_2·CO_2H and with H_2–Pd–$CaCO_3$ gives *p*-CH_2Bu^{β}·C_6H_4·CO_2H, m.p. 141—142°, also obtained from (**I**) by $CH_2Bu^{\beta}Br$–K_2CO_3–$COMe_2$ and then KOH–MeOH. The *Et* ester (prep. by way of the Ag salt), b.p. 92·5—93°/0·1 mm., of (**II**) at 197—224°/50 mm. gives CMe_2:CH_2, (**I**), and, by "abnormal" rearrangement, after hydrolysis, 1 : 1 : 2-*trimethyl*-1 : 2-*dihydrobenzfuran*-4-*carboxylic acid* (**III**), m.p. 180—182° (p-*bromophenacyl* ester, m.p. 105—106°). *o*-OMe·C_6H_4·COMe (**IV**), b.p. 115—117°/10—12 mm., with $MgPr^{\beta}Br$ gives β-o-*anisyl*-γ-*methyl*-n-*butan*-β-*ol*, b.p. 90—91°/1 mm., dehydrated by H_2SO_4 in AcOH at room temp. to β-o-*anisyl*-γ-*methyl*-Δ^{β}-*butene*, b.p. 77—78°/1 mm. [with CrO_3–AcOH gives (**IV**) and $COMe_2$], which with 48% HBr in boiling AcOH yields 1 : 1 : 2-*trimethyl*-1 : 2-*dihydrobenzfuran*, b.p. 62—63°/1 mm. With Ac_2O–$AlCl_3$ in $PhNO_2$ at <10° this gives 4-*acetyl*-1 : 1 : 2-*trimethyl*-1 : 2-*dihydrobenzfuran*, b.p. 140—142°/4—5 mm. (*semicarbazone*, m.p. 186—187°; with PhCHO–alkali gives the 4-*CHPh*:*CH*·*CO* derivative, m.p. 108—109°), oxidised by NaOCl–aq. MeOH at ≯48° to (**III**) (proof of structure), m.p. 182—183°. Replacement of K_2CO_3–$COMe_2$ in the prep. of (**II**) by NaOEt–EtOH leads to 1 : 1-*dimethylchroman*-5-*carboxylic acid*, m.p. 176—177° (p-*bromophenacyl* ester, m.p. 147—148°), also obtained from (**I**) by CMe_2:CH_2 and $ZnCl_2$ in AcOH at room temp. and later ~40°. R. S. C.

Preparation of αβ-unsaturated aldehydes.—See A., 1943, II, 195.

Addition of dienes to coumarin and substituted cinnamic acids. I. R. Adams, W. D. McPhee, R. B. Carlin, and Z. W. Wicks (*J. Amer. Chem. Soc.*, 1943, **65**, 356—360).—$(CH_2$:$CMe)_2$ (**I**), but not $(CH_2$:$CH)_2$ (**II**) or isoprene (**III**), adds to coumarin in xylene at 260° to give 4′ : 5′-*dimethyl*-1′ : 2′ : 3′ : 6′-*tetrahydro*-3 : 4 : 5 : 6-*dibenz*-2-*pyrone* (22%), m.p. 181—181·5°, also obtained from *trans*-*o*-OH·C_6H_4·CH:CH·CO_2H in xylene at 185° and dehydrogenated by Pd–C–CO_2 at 280—320° to 4′ : 5′-*dimethyl*-3 : 4 : 5 : 6-*dibenz*-2-*pyrone* (**IV**) (71%), m.p. 175—175·5°. *cis*-*o*-OMe·C_6H_4·CH:CH·CO_2H (**V**) (modified prep.; 93% yield) and (**I**) in xylene at 170° give 2′-*methoxy*-4 : 5-*dimethyl*-1 : 2 : 3 : 6-*tetrahydrodiphenyl*-2-*carboxylic acid*, m.p. 191°; an *isomeride* (**VI**), m.p. 159—159·5°, is obtained from *trans*-*o*-OMe·C_6H_4·CH:CH·CO_2H (**VII**) at 180°; both products with boiling 48% HBr–AcOH give the same 2′-*OH-acid*, m.p. 183—185°, which could not be dehydrated and which loses CO_2 when dehydrogenated and thus has the CO_2 and *o*-OH·C_6H_4 in the *trans* configuration. With 48% HBr–AcOH at 180° or KOH–EtOH at 225°, (**VI**) gives a diastereoisomeric 4′ : 5′-*dimethyl*-1′ : 2′ : 3′ : 6′-*tetrahydro*-3 : 4 : 5 : 6-*dibenz*-2-*pyrone*, m.p. 154—155°, and thence (**IV**). Commercial or pure (**III**) in xylene with (**V**) at 170° or (**VII**) at 185° gives rather poorly 2′-*methoxy*-5-(or 4-)*methyl*-1 : 2 : 3 : 6-*tetrahydrodiphenyl*-2-*carboxylic acid*, *forms*, m.p. 199—199·5° or 147—147·5°, respectively. (**II**) does not add to (**V**) or (**VII**). 4 : 6-*Dimethoxy*-2-*methylcinnamic acid*, m.p. 190°, is obtained from 7-hydroxy-5-methylcoumarin by boiling NaOH–Me_2SO_4 in 18% yield or from 3 : 5 : 1 : 2-$(OMe)_2C_6H_2Me$·CHO by $CH_2(CO_2H)_2$–C_5H_5N–piperidine at 100° in 100% yield; with (**I**) or (**II**) in xylene at 170° it gives 2′ : 4′-*dimethoxy*-4 : 5 : 6′-*trimethyl*-, m.p. 174—175°, or -6′-*methyl*-, m.p. 140—141°, -1 : 2 : 3 : 6-*tetrahydrodiphenyl*-2-*carboxylic acid*, respectively. M.p. are corr. R. S. C.

Identity of laguncurin, kino-yellow, and maclurin. M. Nierenstein (*Quart. J. Pharm.*, 1943, **16**, 11—12).—Laguncurin and kino-yellow (obtained by heating aromodendrin above its m.p.) when acetylated (Ac_2O + NaOAc) both yield 5 : 7-diacetoxy-4-(3′ : 4′-diacetoxyphenyl)coumarin, thus identifying both as maclurin. J. N. A.

Pyrrolidines and piperidines.—See B., 1943, II, 145, 174.

Reaction of glutarimides with phosphorus pentachloride. New pyridine synthesis. W. W. Crouch and H. L. Lochte (*J. Amer. Chem. Soc.*, 1943, **65**, 270—272).—$[CH_2]_5NH$ and PCl_5 at 50° give 2 : 3 : 6-*trichloropyridine*, m.p. 66—67° (cf. Bernheimer, A., 1882, 1189), hydrogenated (Pd–C; MeOH–HCl) to C_5H_5N and probably identical with a substance prepared by Sell *et al.* (*J.C.S.*, 1898, **73**, 439). CH_2:CMe·CO_2Me (**I**), CN·CH_2·CO_2Et (**II**), and NaOEt in boiling EtOH give CO_2H·CH(CN)·CH_2·CHMe·CO_2Me, which at 220° gives CO_2 and CN·$[CH_2]_2$·CHMe·CO_2Me, b.p. 157—160°/58 mm., converted by boiling 50% H_2SO_4 and then 25% NaOH into CO_2H·$[CH_2]_2$·CHMe·CO_2H, m.p. 75—76°. The derived anhydride (prep. by AcCl) with NH_3 at 120° and then 200° gives *α-methylglutarimide*, m.p. 91°, converted by PCl_5 (3 mols.) into 2 : 5 : 6-*trichloro*-2-*methylpyridine*, m.p. 94—95°. Condensation of (**I**) and (**II**), methylation, hydrolysis, etc. as above give *αα′-dimethylglutarimide*, m.p. 172—174°, and thence by PCl_6 2 : 6-*dichloro*-3 : 5-*dimethylpyridine*, m.p. 97—98°. R. S. C.

Simplified synthesis of nicotinamide and the reaction of hydrogen peroxide with nitriles. A. Georg and P. Bachmann (*Helv. Chim. Acta*, 1943, **26**, 358—362).—A very poor yield of nicotinamide (**I**) is obtained by the action of 90% H_2SO_4 on 3-cyanopyridine (**II**) at 125°. Treatment of (**I**) with H_2O_2 in feebly alkaline solution at 65° gives (**II**) in max. yield ~19%. The yield of (**II**) increases with $[H_2O_2]$ to ~6%, after which it declines. H. W.

Derivatives of pyridine acids. I. *N*-β-Acylaminoethylnicotinamides. E. M. Hodnett and V. E. Stewart (*J. Amer. Chem. Soc.*, 1943, **65**, 254—255).—Et nicotinate and NH_2·$[CH_2]_2$·NHAcyl at 100° give *nicotin*-β-*acet*-, m.p. 170—171°, -*propion*-, m.p. 126—127°, -n-*butyr*-, m.p. 157—159°, -n-*valer*-, m.p. 141—142°, and -n-*hexamidoethylamide*, m.p. 124—125°. The products are convulsant stimulants, less toxic than nikethamide but deficient in potency. R. S. C.

Synthesis of nicotinuric acid. S. W. Fox and H. Field, jun. (*J. Biol. Chem.*, 1943, **147**, 651—652).—Nicotinamide is converted by N_2H_4,H_2O in boiling, conc. aq. solution into *nicotinhydrazide*, m.p. 158—159°, converted into the *azide*, m.p. 48—49°, which with aq. NH_2·CH_2·CO_2Na affords nicotinuric acid (nicotinylglycine), m.p. 238—241° (decomp.). H. W.

Vitamin *B* group. II. H. von Euler, L. Ahlström, and H. Hasselquist (*Arkiv Kemi, Min., Geol.*, 1942, **15**, **B**, No. 21, 8 pp.).—Nicotinyl chloride (**I**) (hydrochloride used) (1 mol.) and $CO(NH_2)_2$ (2 mols.) in C_5H_5N give *nicotinylcarbamide*, m.p. 229° (decomp.). Acetylsulphanilhydrazide and (**I**) in C_5H_5N at 90—110° afford N^1-*nicotinyl*-N^4- (**II**), m.p. 197° (+H_2O), or (6 days at 100°/12 mm.) anhyd., m.p. 235° [*hydrochloride*, m.p. 239°; Ac_2O gives the N^1-*Ac* derivative, $C_{16}H_{16}O_5N_4S$, m.p. 208° (decomp.)], and N^1-*dinicotinyl*-N^4-*acetylsulphanilhydrazide* (**III**), +H_2O, m.p. 197°, or (2 days at 110°/12 mm.) anhyd., m.p. 208° (*dihydrochloride*, m.p. 220°). (**II**) is also obtained from nicotinhydrazide and *p*-NHAc·C_6H_4·SO_2Cl–C_5H_5N at 90—110°, whilst (**I**) and (**II**) in C_5H_5N at 100° afford (**III**). (**II**) and 10% HCl–EtOH give N^1-*nicotinylsulphanilhydrazide*, m.p. 209°. A. T. P.

Nicotinamide-nucleoside. F. Schlenk and H. von Euler (*Arkiv Kemi, Min., Geol.*, 1941, **14**, **A**, No. 13, 12 pp.; cf. A., 1935, 1024).—The isolation of *nicotinamide-nucleoside*, $C_{11}H_{15}O_5N_2Cl$, +H_2O (*hydrochloride*) (nicotinamide : pentose : : 1·03 : 1), from phosphatase and cozymase in H_2O + 0·1N-NaOH at pH 4—5 at 30° for 3—4 days is described. A. T. P.

Pyridines.—See B., 1943, II, 146.

Mesityl oxide and diacetone alcohol in the Bucherer synthesis of hydantoins. H. R. Henze, T. R. Thompson, and R. J. Speer (*J. Org. Chem.*, 1943, **8**, 17—28; cf. A., 1942, II, 271; Marsh *et al.*, A., 1940, II, 289).—In consequence of divergent results the behaviour of mesityl oxide (**I**) and diacetone alcohol (**II**) towards a solution of KCN and $(NH_4)_2CO_3$ in 50% EtOH (Bucherer procedure for hydantoin formation) has been re-examined. Under these conditions (**I**) passes at 58° into 5-methyl-5-β-methylpropenylhydantoin (**III**), m.p. 194° (corr.), and 5-hydroxy-3 : 5 : 5-trimethylpyrrolid-2-one (**IV**), m.p. 209—210° (corr.) (acetate, m.p. 138°). (**IV**) is obtained in 7% yield from diacetoneamine and HCN at 0° followed by treatment of the product with boiling HCl or in 28% yield from diacetoneamine H oxalate and KCN in H_2O at room temp. with subsequent boiling of the product with HCl. The structure of (**III**) is established by its hydrogenation to 5-*methyl*-5-*isobutylhydantoin*, m.p. 144·5° (corr.), also obtained by treating $COMeBu^{\beta}$ with KCN

and $(NH_4)_2CO_3$ in 50% EtOH at 58°. Gradual addition of Br in AcOH to a cold solution of (**III**) in AcOH gives the *dibromide*, m.p. 185° (decomp.). (**III**) and HBr in AcOH give *5-methyl-5-β-bromo-β-methylpropylhydantoin* (**V**), m.p. 193° (decomp.), which is converted into (**III**) by treatment with 0·24N-NaOH at 100°, with AgOH in C_6H_6 at 100°, or with aq. NaOAc at room temp. for 3 days. (**II**) is transformed by prolonged warming with KCN and $(NH_4)_2CO_3$ in 50% EtOH at 58° into 5 : 5-dimethylhydantoin (**VI**), m.p. 175—176° (corr.), and α-hydroxy-αγ-dimethyl-γ-valerolactone (**VII**), m.p. 65° (corr.), converted into (**IV**) by treatment $NaNO_2$–HCl followed by NaOH; removal of unchanged (**VII**), and boiling the filtrate with acid. The yields depend considerably on the duration of the heating. Diacetone alcohol cyanohydrin and $(NH_4)_2CO_3$ in EtOH at 58° yield (**VI**) and *α-ureido-αγ-dimethyl-γ-valerolactone* (**VIII**), m.p. 209—210° (corr.), also obtained by the Bucherer synthesis from (**II**). (**VIII**) is converted by boiling H_2SO_4 or HCl into *α-carbamido-αγ-dimethyl-γ-valerolactone*, m.p. 203° (decomp.), but is unchanged by $SOCl_2$ at 100°. α-Amino-αγ-dimethyl-γ-valerolactone, HCl, and KCNO at 0° give *5-methyl-5-β-hydroxy-β-methylpropylhydantoin* (**IX**), m.p. 147° (corr.), also obtained from (**VIII**). (**IX**) and HBr in AcOH afford (**V**). $SOCl_2$ transforms (**IX**) into (**III**). H. W.

Configuration of tervalent nitrogen. A dicyclic hydrazine derivative. E. L. Buhle, A. M. Moore, and F. Y. Wiselogle (*J. Amer. Chem. Soc.*, 1943, **65**, 29—32).—Adding Br·$[CH_2]_3$·Br (or Cl·$[CH_2]_3$·Cl : no details) (1 mol.) slowly to N_2H_4 (2 mols.) in boiling 95% EtOH gives bases, separated by fractionation into *pyrazolidine* (**I**), m.p. 10—12°, b.p. 54—56°/26 mm., 138°/760 mm. (*oxalate*, *B*,$H_2C_2O_4$, m.p. 114—115°; *Bz*$_2$ derivative, m.p. 146—147°), 1 : 2-*trimethylenepyrazolidine* (**II**), m.p. 1·5—2·5°, b.p. 74—75°/26 mm., 173°/760 mm. (hygroscopic hydrochloride and methiodide; *picrate*, m.p. 159—159·5°), bistrimethylenedi-imine, b.p. 70—73°/15 mm. [7%; *picrate*, m.p. 220—230° (decomp.); *Bz*$_2$ derivative, m.p. 185—186°; *dioxalate*, m.p. 170—170·5°; *dihydrobromide*, m.p. 240—250° (decomp.) (varies with rate of heating)] (cf. Howard *et al.*, A., 1899, i, 750), and 50% of quaternary salts; the proportions of (**I**) and (**II**) formed vary but their combined yield is constantly 30%. (**I**) reduces Fehling's and Tollens' solutions rapidly at room temp. (**II**) reduces warm Fehling's solution and cold Tollens' reagent, decolorises Br in CCl_4, is indifferent to H_2–catalyst, and titrates as a monoacidic base in H_2O ($K = 1·0 \times 10^{-6}$). R. S. C.

Sulphilimines derived from sulphanilamide.—See A., 1943, II, 186.

Pyrazolones.—See B., 1943, II, 176.

Action of aliphatic diazo-compounds on αβ-unsaturated ketones. II. *cis*- and *trans*-Dibenzoylethylene. III. Benzylideneacetone and diazomethane. L. I. Smith and K. L. Howard (*J. Amer. Chem. Soc.*, 1943, **65**, 159—164, 165—166; cf. A., 1937, II, 380).—II. *trans*-(CHBz·)$_2$ and CH_2N_2 in Et_2O–$CHCl_3$ at −10° give 99·6% of 3 : 4-dibenzoyl-Δ^1-pyrazoline (**I**), m.p. 108°, but *cis*-(CHBz·)$_2$ gives 3 : 4-*dibenzoyl-Δ*^{2}*-pyrazoline* (**II**) (79·5%), m.p. 129—129·5°. Melting (**I**) or recrystallising it from aq. EtOH gives (**II**), which is differentiated from (**I**) by yielding with PhNCO the 1-*carbanilido*-derivative, m.p. 156—156·5°. No CO· derivatives, NO-derivatives, or reduction products could be obtained from (**II**). Slow addition of Br in $CHCl_3$ to (**II**) in $CHCl_3$ at >12° and then evaporation in air yields HBr and 3 : 4-*dibenzoylpyrazole* (69·3%), m.p. 169°, also obtained from (**II**) in poor yield by pyrolysis (best at 138—141°/20—24 mm.) or (25%; m.p. 169—170°) by oxidation ($KMnO_4$; boiling $COMe_2$). CPh_2N_2 and *trans*-(CHBz·)$_2$ in $CHCl_3$–light petroleum give 4 : 5-*dibenzoyl*-3 : 3-*diphenyl-Δ*^{1}*-pyrazoline* (**III**) (47·3%), softens 147°, m.p. 157°, 2 : 3-*dibenzoyl*-1 : 1-*diphenylcyclopropane* (**IV**) (20·3%), m.p. 179°, and tars; *cis*-(CHBz·)$_2$ reacts more slowly, giving traces of (**III**) and a *substance*, m.p. 151—152°, with mainly orange gums. PhNCO, Br, and chloranil do not yield definite products from (**III**), but $KMnO_4$ in $COMe_2$ at room temp. yields (**IV**); pyrolysis, best at 175°/20—21 mm., gives (**IV**) and (?) 3 : 4-*dibenzoyl*-5 : 5-*diphenyl-Δ*^{2}*-pyrazoline*, m.p. 173—173·5°. Adding $NaNH_2$ to $COPh_2$ + COPhMe in Et_2O at 0° gives $CPh_2(CH_2Bz)_2$, converted by Br in CS_2 at 0° into $CPh_2(CHBrBz)_2$ (30%), m.p. 132—133° (and a high-melting by-product), which with KI–EtOH gives (**IV**). Reduction of (**IV**) gave gums; the expected products could not be obtained by HBr–AcOH or H_2SO_4–AcOH, and boiling alkaline $KMnO_4$, $CHNa(CO_2Et)_2$, and *l*-menthyl *N*-aminocarbamate are without action. $CHPhN_2$ and *trans*-(CHBz·)$_2$ give oils.

III. CHPh·CH·COPh and CH_2N_2 in dry Et_2O at −5° to 0° give 3-acetyl-4-phenyl-Δ^2-pyrazoline (**V**) (98·8%), m.p. 101° (oxime, m.p. 181°) (cf. Azzarello, A., 1905, i, 941), but in one experiment a small amount of a very unstable substance, m.p. 90—92°, resolidifies, remelts 98—100°, possibly the Δ^1-pyrazoline, was obtained. At 190—205°/16—20 mm., (**III**) gives *β-phenyl-Δ*^{α}*-n-propenyl Me ketone* (46%; 7·5% formed at 230—235°/1 atm.), b.p. 132—138°/17 mm. (*semicarbazone*, m.p. 183·5—184°), which is unstable in air and with O_3 in $CHCl_3$ and then Zn dust–$AgNO_3$–quinol yields COPhMe. R. S. C.

Pyrazole compounds. II. Synthesis of 3-hydroxy-1-phenyl-5-pyrazoloneimide. A. Weissberger and H. D. Porter (*J. Amer. Chem. Soc.*, 1943, **65**, 52—54; cf. A., 1943, II, 72).—Adding CN·CH_2·COCl (unstable; prep. by PCl_3–Cl_2; 54% yield), b.p. 56—58°/0·5 mm., to NHPh·NH_2 (**I**) in Et_2O at 0° gives *cyanoacet-β-phenylhydrazide* (**II**) (33%), m.p. 105—106°. Diazotising CN·CH_2·CO·NH·NH_2 gives the explosive hydrazide (and, by slow reaction, also 16% of *s-dicyanoacethydrazide*, m.p. 194—196°), which with (**I**) gives 52% of (**II**). Adding $K_2S_2O_8$ to (**II**) and *p*-NH_2·C_6H_4·NMe_2 in 3% aq. Na_2CO_3 gives a yellow-orange colour, discharged by acid. With Ac_2O at 100°, (**II**) gives *α-acet-*, m.p. 149—150°, and with BzCl–dioxan at 100° gives *α-benz-*, m.p. 155—156°, *-β-cyanoacet-α-phenylhydrazide*, both stable to cold 2% NaOH. In boiling NaOMe–MeOH or, less well, cold 2% aq. NaOH, (**II**) yields 3-*hydroxy-5-imino*-1-*phenylpyrazoline* (74%), *forms*, m.p. 142—143° (stable) and 160·5—161·5°, converted by dil. HCl at 100° into 3-hydroxy-1-phenyl-5-pyrazolone (~20%), also obtained (71%) from 3-amino-1-phenyl-5-pyrazolone by hot HCl–EtOH–H_2O. R. S. C.

Pyrazoles.—See B., 1941, II, 203.

Influence of peptide bond glycine in formation of new peptide linkings. G. Ågren (*Arkiv Kemi, Min., Geol.*, 1941, **14**, **B**, No. 21, 6 pp.).—The property of NH_2·CH_2·CO_2Et to form anhydrides (diketopiperazines) is transferred to the alanine ester by coupling the latter in peptide linkings with glycine. A comparison is made between rate of anhydride formation of the Et esters of glycine, glycylglycine, diglycylglycine, glycylalanine (**I**), and alanylglycine (**II**) in aq. solutions at 37°. Rate of anhydride formation is independent of the initial concn. of the ester and is probably a first-order reaction. In 2 hr., 85% of ester (**I**) and 64% of (**II**) are converted into anhydride. A. T. P.

Reactions of phenanthraquinone and retenequinone with amines under pressure. G. M. Jaffe and A. R. Day (*J. Org. Chem.*, 1943, **8**, 43—51).—Phenanthrenequinone (**I**) and NH_2Me in C_6H_6 at 100° afford small amounts of phenanthroxazine (**II**), m.p. >360°, and of a quinhydrone *compound*, $C_{28}H_{19}O_3N$, m.p. 150—214° (decomp.), from (**I**) and 9 : 10-aminophenanthrol, oxidised entirely to (**I**) by CrO_3, and mainly (63% yield) 1-methylphenanthriminazole, m.p. 196° (picrate, m.p. 288—289°). Under similar conditions (**I**) and NH_2Et afford (**II**), a *quinhydrone*, and 2-*methyl*-1-*ethylphenanthriminazole*, m.p. 193·5—194·5° [*picrate*, m.p. 222—242° (decomp.)]. $NH_2Bu^α$ similarly gives (**II**), a *quinhydrone*, and 2-n-*propyl*-1-n-*butylphenanthriminazole*, m.p. 199—200° (*picrate*, m.p. 59—62°). CH_2Ph·NH_2 gives (**II**), a *quinhydrone*, m.p. 150—192° (decomp.), and 2-phenylphenanthroxazole, m.p. 206·5—207°. Mechanisms are suggested. Retenequinone and the primary amine in C_6H_6 at 100° give exclusively 2-*methyl*-, m.p. 108°, 2-*ethyl*-, m.p. 127·5—128·5°, 2-propyl-, m.p. 100—101·5°, and 2-phenyl-, m.p. 172°, -retenoxazole. Aminolysis and simultaneous aminolysis and hydrolysis of 2-arylphenanthroxazoles does not yield iminazoles, thus eliminating the possibility of intermediate oxazole formation in the prep. of iminazoles. H. W.

Reactions of phenanthraquinone and retenequinone with aldehydes and ammonium acetate in acetic acid solution. E. A. Steck and A. R. Day (*J. Amer. Chem. Soc.*, 1943, **65**, 452—456).—Formation of iminazoles from phenanthra- (**I**) or retene-quinone (**II**) by RCHO–NH_4OAc–AcOH occurs by way of the quinonedi-imines. (**I**) does not react with NH_2Ac or $CHPh(NHAc)_2$, m.p. 254° (lit. 238°), in boiling AcOH, and $(CHPh)_3N_2$ is unstable in AcOH. With NH_4OAc in boiling AcOH, (**I**) gives *phenanthraquinonedi-imine*, +4AcOH, m.p. 243—244°, +3AcOH (retained at 120°), m.p. 240—250°, and solvent-free, m.p. 290—292° (*Ac*$_2$ derivative, m.p. 259—260°, prepared by Ac_2O–AcOH), which with PhCHO in boiling AcOH, boiling NaOH–EtOH, or hot piperidine gives 2-phenylphenanthriminazole, m.p. 314° (picrate, m.p. 289—290°), also obtained directly from (**I**) by PhCHO–NH_4OAc–AcOH. With RCHO–NH_4OAc–AcOH, (**I**) gives *phenanthriminazole* [4 : 5-oo′-*diphenyleneglyoxaline*] [prepared by using $(CH_2)_6N_4$ in place of RCHO], m.p. 292°, and its 2-*Pr*^{β}, m.p. 228—229°, 2-2′-*furyl*, +H_2O, m.p. 279·5—280·5°, 2-*o*-(+0·5H_2O), m.p. (anhyd.) 287—287·5° (lit. 270—276°), 2-*m*-, m.p. 343—344°, and 2-p-*OH*·C_6H_4, m.p. >360°, 2-*o*-, m.p. 214—215° (lit. 207—208·5°), and 2-p-*anisyl*, m.p. 254—255°, 2-*m*-, m.p. 271·5—272° (lit. 240°), and 2-p-NO_2·C_6H_4, m.p. 341°, 2-o-C_6H_4Cl, m.p. 235—235·5°, 2-p-NMe_2·C_6H_4, m.p. 259—260°, and 2-3′ : 4′-CH_2O_2·C_6H_3 derivative, m.p. 257—257·5°. Similarly, (**II**) gives *reteneiminazole*, +H_2O, m.p. 128—132°, resolidifies, remelts 167—168°, and its 2-*Ph* derivative, +AcOH, m.p. 93—100°, but with *o*-OH·C_6H_4·CHO–NH_4OAc–AcOH gives 2-o-*hydroxyphenylreten-oxazole* (65%), m.p. 243—244°, and *-iminazole* (32%), m.p. 216—217°; the di-imine, which could not be isolated, was probably an intermediate, although (**II**) and NH_4OAc in boiling AcOH give a *substance*, $C_{18}H_{19}ON$, m.p. 211—220° (*picrate*, m.p. 226—227°), unchanged by PhCHO. M.p. are corr. R. S. C.

2-Bromo-4 : 5-dinitrobenzoic acid.—See A., 1943, II, 192.

Ultra-violet absorption spectra of nitrogenous heterocycles. V. Blocking effect of methyl groups on the ultra-violet absorption spectra of hydroxypurines and pyrimidines. J. R. Loofbourow

(Srs.) M. M. Stimson, and M. J. Hart. **VI. Effect of pH on the spectrum of uracil-5-carboxylic acid. VII. Effect of hydroxy-substitutions on the ultra-violet absorption of the series : hypoxanthine, xanthine, and uric acid.** (Srs.) M. M. Stimson and M. A. Reuter (*J. Amer. Chem. Soc.*, 1943, **65**, 148—151, 151—152, 153—155; cf. A., 1931, 1308).—V. Comparison of the absorption spectra of the pairs uracil–1 : 3-dimethyluracil and xanthine–caffeine shows that the unmethylated compounds exist as ketones until the pH becomes high. Results of Levene *et al.* (A., 1926, 1260) for uracil (**I**) are confirmed for pH 3—11. pH has a slight effect on the spectra of the methylated compounds, "resonance" (tautomerism), ·C⁺(:O):C⁻·CH₂· ⇌ ·CO·CH:CH· ⇌ ·C(OH):C:CH· and ·NMe·CH:N· ⇌ ·NMe·C⁻:N⁺H·, being suggested as the cause.

VI. Introduction of CO_2H at $C_{(5)}$ of (**I**) shifts the weakest absorption of the band at 2700—2900 A. from pH 11 to pH 7. Absorption at 2170 A. is due to the CO_2H.

VII. Absorption spectra of the hypoxanthine (**II**), xanthine (**III**), and uric acid (**IV**) are reported for pH 3, 7, and 11. At pH 7 each OH shifts the max. 200 A. towards the red and increases the mol. extinction by 1000 units. (**II**) shows a drop at pH 7 preliminary to enolisation. (**III**) resembles (**I**) in showing enolisation only at pH 11. Since the absorption of (**IV**) resembles the alkaline absorption of (**III**), (**IV**) is probably monoenolic even in acid. R. S. C.

Protoporphyrin. I. Purification of protoporphyrin IX as obtained from hæmoglobin. II. Improved micro-method for converting protoporphyrin into mesoporphyrin. M. Grinstein and C. J. Watson (*J. Biol. Chem.*, 1943, **147**, 667—669, 671—673).—I. Crude protoporphyrin is purified by dissolution in C_5H_5N and addition of light petroleum (**I**), b.p. 30—60°, to incipient pptn.; separation is nearly quant. if sufficient (**I**) is used at 0°. Protoporphyrin Me ester, m.p. 223—224°, is obtained by chromatography on Al_2O_3 with $CHCl_3$–(**I**) as eluent. It is best hydrolysed by overnight contact with 25% HCl at 0°.

II. Modifications in the method of Fischer *et al.* (A., 1924, i, 230) and Schultze (A., 1942, III, 394) improve the yield of mesoporphyrin to ~60%. H. W.

Reactions of morpholinomethanol with compounds containing active hydrogen atoms. M. Zief and J. P. Mason (*J. Org. Chem.*, 1943, **8**, 1—6).—Addition of the requisite nitroparaffin to a mixture of 37% CH_2O and morpholine at 0° gives *β-nitro-αγ-dimorpholino-*, m.p. 119—120°, and *β-nitro-αγ-dimorpholino-β-methyl-*, m.p. 124—125°, *-propane* and *β-nitro-α-morpholinobutane* (**I**), b.p. 134—136°/15 mm. (*picrate*, m.p. 120—122°). These substances are reduced readily in a Parr hydrogenation apparatus of the low-pressure type using a Raney Ni catalyst activated by the method of Covert and Adkins and 96% EtOH, thus giving *β-amino-αγ-dimorpholino-*, m.p. 67—68° (*phenylcarbamide*, m.p. 233—234°), and *β-amino-αγ-dimorpholino-β-methyl-*, b.p. 148—150°/1 mm. (*phenylcarbamide*, m.p. 177—178°), *-propane* and *β-amino-α-morpholinobutane*, b.p. 102—104°/14 mm. (3 : 5-*dinitrobenzoate*, m.p. 162—163°; gummy products with PhNCO and α-$C_{10}H_7$·NCO; waxy Bz derivative; does not give Ac or *p*-C_6H_4Br·SO_2 derivatives). Of these NO_2-derivatives only (**I**) appears to be reducible by Sn and HCl. Morpholinomethanol (**II**) does not appear to react with *o*- or *p*-C_6H_4Me·NO_2 and the product of its reaction with 1 : 2 : 4-$C_6H_3Me(NO_2)_2$ explodes when distillation is attempted. (**II**) is transformed by the necessary primary or *sec.* amine and anhyd. K_2CO_3 at room temp. into *morpholinomethylbutylamine*, b.p. 58—62°/13 mm., *-aniline*, b.p. 108—112°/10 mm., *-o-toluidine*, b.p. 107—109°/10 mm., *-diethylamine*, b.p. 86—89°/13 mm., *-dibutylamine*, b.p. 134—136°/14 mm., *-dicyclohexylamine*, b.p. 112—116°/8 mm., *-piperidine*, b.p. 111—113°/12 mm., and *-morpholine*, b.p. 122—124°/12 mm. NHPhMe and (**II**) gave a mixture from which no homogeneous compound other than dimorpholinomethane could be isolated. $NPhMe_2$ and (**II**) do not appear to react. Picrates of these methylenediamines could not be obtained owing to the hydrolysis caused by 96% EtOH. (**II**) does not appear to react with MeCN, EtCN, or PrCN but with CH_2Ph·CN yields *α-morpholinomethyl-α-tolunitrile*, b.p. 103—105°/7 mm., in 51% yield. CH_2Ph·COMe and (**II**) give the *compound*, $C_{19}H_{28}O_3N_2$, b.p. 109—111°/11 mm., which does not give a picrate. *Phenyldimorpholinomethane*, m.p. 101—101·5°, is formed from (**II**) and PhCHO at room temp. H. W.

Sulphanilamide compounds. VII. Thiazoline derivatives. J. H. Hunter and H. G. Kolloff (*J. Amer. Chem. Soc.*, 1943, **65**, 156—159; cf. A., 1941, II, 147).—*p*-NHAcyl·C_6H_4·SO_2Cl and 2-amino-Δ^2-thiazoline hydrobromide (**I**) in aq. Na_2CO_3–Et_2O give 2-*imino*-3-N⁴-*acetyl-*, m.p. 183°, and -3-N⁴-n-*hexoyl-*, m.p. 160—160·5°, *-sulphanilylthiazolidine*, hydrolysed by dil. H_2SO_4 at 100° to NH_3 and 3-*sulphanilylthiazolid-2-one* (**II**), m.p. 209—210°. Similarly are prepared 2-*imino*-3-N⁴-*acetylsulphanilyl-4-methyl-*, m.p. 178—179°, -5-*methyl-*, m.p. 162—163°, and -5-*phenyl-thiazolidine*, m.p. 181—183°, 2-*imino*-3-N⁴-n-*hexoylsulphanilyl-4-methyl-*, m.p. 145—146°, -5-*methyl-*, m.p. 164—165°, and -5-*phenyl-thiazolidine*, +EtOH, m.p. 203—204°, and thence by hydrolysis 3-*sulphanilyl-4-methyl-* (**III**), m.p. 134·5—135·5°, -5-*methyl-* (**IV**), m.p. 190·5—191·5°, and -5-*phenyl-thiazolid-2-one* (**V**), m.p. 168—170°. *p*-NO_2·C_6H_4·SO_2Cl with (**I**) etc. yields 2-*imino*-3-p-*nitrobenzenesulphonyl-thiazolidine* (**VI**), m.p. 135—137°, -4-, m.p. 133—134·5°, and -5-*methylthiazolidine*, m.p. 114—114·5°, and -5-*phenylthiazolidine*, m.p. 139·5—140·5°, with smaller amounts of 2-p-*nitrobenzenesulphonimido*-3-p-*nitrobenzenesulphonyl-thiazolidine*, m.p. 268·5—270·5°, -4-, m.p. 242—242·5°, and -5-*methylthiazolidine*, m.p. 219·5—220·5°, and -5-*phenylthiazolidine*, m.p. 215·5—218°. Sn–HCl–aq. EtOH at 45—47° reduces (**VI**) etc. to 2-*imino*-3-*sulphanilyl-thiazolidine* (**VII**), m.p. 144—145°, -4-, m.p. 137—138°, and -5-*methylthiazolidine*, m.p. 153—153·5°. Dil. H_2SO_4 at 100° hydrolyses (**VI**) etc. to 3-p-*nitrobenzenesulphonyl-thiazolid-2-one* (**VIII**), m.p. 182—183°, -4-, m.p. 139—141°, and -5-*methylthiazolid-2-one*, m.p. 177°, and -5-*phenylthiazolid-2-one*, m.p. 165·5—168°, respectively. Acid hydrolysis of (**VII**) etc. also affords (**II**), (**III**), and (**IV**). Preliminary results show the compounds (**VIII**) etc. to be the most effective of these products against β-hæmolytic streptococci, although ineffective against type I pneumococci. R. S. C.

Thiazoles.—See B., 1943, II, 174, 175, 178, 199.

Cyanine dyes.—See B., 1943, II, 174.

Isosteric and structurally similar compounds. XVII. Derivatives of pyrimidinothiazole. H. Erlenmeyer and H. P. Furger (*Helv. Chim. Acta*, 1943, **26**, 366—368).—Monobromobarbituric acid and HCS·NH_2 in boiling Et_2O give 2′ : 6′-*diketo*-1′ : 2′ : 3′ : 6′-*tetrahydropyrimidino*-5′ : 4′-5 : 4-*thiazole*, NH·CO·C·S / CO·NH·C·N >CR [(**I**), R = H], decomp. 305—310°. 2′ : 6′-*Diketo-2-methyl*-1′ : 2′ : 3′ : 6′-*tetrahydropyrimidino*-5′ : 4′-5 : 4-*thiazole* [(**I**), R = Me], decomp. 247°, is obtained similarly from MeCS·NH_2 in boiling EtOH. H. W.

VII.—ALKALOIDS.

Spectroscopic detection of the opium alkaloids. P. Csokán (*Z. anal. Chem.*, 1942, **124**, 344—351).—Extinction curves are reproduced, and band max. tabulated. L. S. T.

Aconite alkaloids. XI. Action of methyl-alcoholic sodium hydroxide on atisine, *iso*atisine, and dihydroatisine. W. A. Jacobs and L. C. Craig (*J. Biol. Chem.*, 1943, **147**, 567—569; cf. A., 1942, II, 335).—The conversion of atisine (**I**) into dihydroatisine (**II**), m.p. 149—151° softens at 142°, $[\alpha]_D^{27}$ −44° in PhMe, is confirmed by analysis of the hydrochloride (**III**), m.p. 259° (decomp.) after softening, and by the observation that (**II**) or (**III**) absorbs 1 H_2 (PtO_2 in MeOH) with production of a mixture of isomerides from which tetrahydroatisine (**IV**), m.p. 172—173°, $[\alpha]_D^{29}$ −10° in C_5H_5N, can be isolated. Milder treatment of (**I**) with NaOH–MeOH leads to iso*atisine* (**V**), $C_{22}H_{33}O_2N$, m.p. 150—151°, $[\alpha]_D^{25}$ −16·5° in PhMe [*hydrochloride* (**VI**), m.p. 295—299° (decomp.) after softening, $[\alpha]_D^{25}$ −4° in H_2O]. (**V**) or (**VI**) absorbs 2 H_2, giving a mixture from which (**IV**) is obtained. H. W.

Aconite alkaloids. XII. Benzoylheteratisine, a new alkaloid from *Aconitum heterophyllum*. W. A. Jacobs and L. C. Craig (*J. Biol. Chem.*, 1943, **147**, 571—572; cf. A., 1942, II, 335).—Extraction of atis root with dil. H_2SO_4 and treatment of the neutralised (Na_2CO_3) extract with C_6H_6 removes *benzoylheteratisine* (**I**), $C_{29}H_{37}O_6N$, m.p. 213—214° after softening, $[\alpha]_D^{25}$ +73° in EtOH [*hydrochloride*, m.p. 218—221° (decomp.) after darkening and softening], hydrolysed to BzOH and heteratisine, m.p. 265—267° (slow decomp.), $[\alpha]_D^{25}$ +40° in MeOH, which possibly does not occur as such in *A. heterophyllum* but is an artefact produced from (**I**) during the isolation process. H. W.

VIII.—ORGANO-METALLIC COMPOUNDS.

Relative reactivities of organo-metallic compounds. XLVI. Addition of metals to phenylated olefines in liquid ammonia solution. H. Gilman and J. C. Bailie. **XLVII. Organo-strontium compounds.** H. Gilman, R. N. Meals, G. O'Donnell, and L. Woods (*J. Amer. Chem. Soc.*, 1943, **65**, 267—268, 268—270).—XLVI. CPh_2:CH_2 with Na in NH_3 and then NH_4Cl gives $CHPh_2Me$ (67%) and $(CH_2\cdot CHPh_2)_2$ (17%) (cf. Wooster *et al.*, A., 1934, 762); with Ca 45—70 and 14%, with Sr 20 and 14%, and with Ba 70 and 35%, respectively, were obtained. CPh_2:CHPh with Ca, Sr, and Ba in NH_3 gives 40, 61, and 48%, respectively, of $CHPh_2\cdot CH_2Ph$. $CHPh_3$ with Ba in NH_3 and then CO_2 gives only a trace of $CPh_3\cdot CO_2H$.

XLVII. $SrEt_2$ (prep. from $ZnEt_2$ and Sr in C_6H_6) is a highly reactive compound. With CPh_2:CH_2 it gives $Sr(CPh_2Pr^a)_2$, converted by CO_2 into $CPh_2Pr^a\cdot CO_2H$ (20%). With PhOMe it gives, after treatment with CO_2, *o*-OMe·C_6H_4·CO_2H, with dibenzfuran or dibenzthiophen gives the 1-carboxylic acid, with 1-$C_{10}H_7$Br gives $Sr(C_{10}H_7\text{-}1)_2$ and thence α-$C_{10}H_7$·CO_2H, with CO_2 gives $EtCO_2H$, and with PhCN gives COPhEt. R. S. C.

Relative reactivities of organo-metallic compounds. XLV. Colour test for some highly reactive organo-metallic compounds. H. Gilman and L. A. Woods. **XLVIII. Direct thallation of dibenzfuran.** H. Gilman and R. K. Abbott, jun. (*J. Amer. Chem. Soc.*, 1943, **65**, 33—34, 122—123; cf. A., 1942, II, 337).—XLV. Development of a red colour on addition to $CH_2Ph\cdot NH_2$ or $NH(CH_2Ph)_2$ (**I**) in light

petroleum distinguishes reactive from unreactive organo-metallic compounds (cf. Krabbe *et al.*, *Ber.*, 1941, **74**, 1343). Examples of reactive compounds are Li, Na, K, LiR [R = Me, Et, Bu^a, n-$C_{16}H_{33}$, C_6H_{11}, Ph, p-C_6H_4Cl, p-$NMe_2{\cdot}C_6H_4$, 2 : 3 : 6 : 1-$(OMe)_3C_6H_2$], $LiNMe_2$ NaR (R = n-amyl, n-$C_{18}H_{37}$, CH_2Ph, Ph), KEt, 1 : 8-disodiodibenzfuran, $SrEt_2$, $BaEt_2$, and $BaPh_2$, and of unreactive compounds are Ca, Sr, Ba, MgMeCl, MgRBr (R = Me, Et, Ph), $CH_2Ph{\cdot}MgCl$, $CoEt_2$, $CaBu^aI$, CaPhI, and $ZnEt_2$. Colours are given more slowly by *dl*-$CHPhMe{\cdot}NH_2$, $Ph{\cdot}[CH_2]_x{\cdot}NH_2$ (x = 2 or 3), $CH_2{:}CH{\cdot}CH_2{\cdot}NH_2$, $NH(CH_2{\cdot}CH{:}CH_2)_2$, NH_2Ph, β-$C_{10}H_7{\cdot}NH_2$, or p-$C_6H_4Br{\cdot}NH_2$, but not by $N(CH_2Ph)_3$, $NMe_2{\cdot}CH_2Ph$, NH_2Me, NH_2Bu^a, $NHMe_2$, $NHEt_2$, $NH_2{\cdot}[CH_2]_2{\cdot}OH$, NHPhMe, or p-$C_6H_4(NH_2)_2$. Treating (**I**) with $LiBu^a$ in Et_2O and then with CO_2 gives 2-*carboxydibenzylamine*, m.p. 164·5—165·5° (preheated at 150—155°) [*lactam*, m.p. 89—90°, formed at 140°; oxidised by $KMnO_4$–KOH to o-$C_6H_4(CO_2H)_2$], intermediates being $LiN(CH_2Ph)_2$ and then $CH_2Ph{\cdot}NLi{\cdot}CHPhLi$.

XLVIII. Dibenzfuran and $TlCl_3$ in H_2O–N_2 at 110° and later 165° give Tl_2Cl_3 and *Tl bis*-1-*dibenzfuryl chloride* (9%), converted by I in $CHCl_3$ into TlI and 1-iododibenzfuran (38%). R. S. C.

IX.—PROTEINS.

Nature of peptones.—See A., 1943, III, 400.

Purification of tomato bushy stunt and tobacco mosaic viruses.—See A., 1943, III, 441.

Inactivation of tomato bushy stunt virus by heating and freezing. Ultracentrifugal examination.—See A., 1943, III, 441.

Proteins of tuberculin. (Miss) F. B. Seibert and J. W. Nelson (*J. Amer. Chem. Soc.*, 1943, **65**, 272—278).—Electrophoresis shows presence in tuberculin of a slow protein having mol. wt. ~32,000 and a faster one having mol. wt. ~16,000. Both have immunological specificity, but the former is more potent as a tuberculin and more antigenic. Immunising rabbits with the larger protein causes sensitisation to the protein and to " old tuberculin " and the presence of antibodies in the γ-component of the sera. The smaller protein may cause antibodies to appear with α-globulin (or albumin). R. S. C.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Hydrogenation of tutin. S. N. Slater (*J.C.S.*, 1943, 143—144; cf. A., 1943, II, 117).—Bromohydro-tutin, $C_{15}H_{17}O_6Br$, m.p. 260° (decomp.), and -picrotoxinin, $C_{15}H_{15}O_6Br$, m.p. 254—255° (decomp.), are obtained by hydrogenation (Pd–C; EtOH) of tutin (**I**) and picrotoxinin (**II**), respectively. (**I**) with H_2–PtO_2–AcOH at atm. pressure gives α-*dihydrotutin*, m.p. 224—226° (decomp.), whilst (**II**) similarly yields α-dihydropicrotoxinin, m.p. 253—254° (decomp.). Hydrogenation (Pd–C) of (**I**) in EtOH gives β-*dihydrotutin*, m.p. 232—233° (decomp.). A. T. P.

Seeds of *Alangium lamarki*, Thwaites. Isolation of alangol. P. N. Bhargava and S. Dutt (*Proc. Indian Acad. Sci.*, 1942, **16**, **A**, 328—331).—Extraction of the kernels with C_6H_6 yields 0·05% of a sterol, *alangol*, $C_{43}H_{83}O_6(OH)$, m.p. 296° [*acetate*, m.p. 265° (shrinks at 256°); *benzoate*, m.p. 276°; *phenylurethane*, m.p. 242°; *digitonide*, m.p. 270—273°]. A. Li

XI.—ANALYSIS.

Displacement development in adsorption analysis.—See A., 1943, I, 187.

Semi-micro-Kjeldahl apparatus.—See A., 1943, I, 187.

Semi-micro-determination of sulphur in organic substances. J. H. Jones (*J. Assoc. Off. Agric. Chem.*, 1943, **26**, 182—186).—The combined S in non-volatile org. compounds is oxidised to SO_4'' with HNO_3 + HCl + $HClO_4$. Tetrahydroxybenzoquinone is used as indicator in the subsequent titration with $BaCl_2$. Sulphonal is not quantitatively oxidised in this way. A. A. E.

ψ-Saccharin chloride, a reagent for identification of alcohols. J. R. Meadoe and E. E. Reid (*J. Amer. Chem. Soc.*, 1943, **65**, 457—458).—ψ-Saccharin chloride with ROH at 100° (lower aliphatic R), 125° (*sec.* or higher primary R), or 125—140° (R = Ar) gives the *Me*, m.p. 182°, *Et*, m.p. 219°, *Pr*^{a}, m.p. 124·5°, *Bu*^{a}, m.p. 96°, n-*amyl*, m.p. 62°, n-*hexyl*, m.p. 60°, n-C_7H_{15}, m.p. 55°, n-C_8H_{17}, m.p. 46°, n-*nonyl*, m.p. 49°, n-*decyl*, m.p. 47·5°, n-$C_{11}H_{23}$, m.p. 58·5°, n-$C_{12}H_{25}$, m.p. 54°, n-$C_{13}H_{27}$, m.p. 66°, n-$C_{14}H_{29}$, m.p. 62°, n-$C_{15}H_{31}$, m.p. 72°, n-$C_{16}H_{33}$, m.p. 69·5°, n-$C_{17}H_{35}$, m.p. 76°, n-$C_{18}H_{37}$, m.p. 74·5°, n-$C_{19}H_{39}$, m.p. 80·5°, *Pr*β, m.p. 137°, *Bu*β, m.p. 100°, sec.-*Bu*, m.p. 65·5°, iso-, m.p. 64°, and sec.-*amyl*, m.p. 38°, β-*ethyl*-n-*hexyl*, m.p. 53·5°, γ-, m.p. 24°, δ-, m.p. 34°, and ε-*methyl*-n-*heptyl*, m.p. 53°, δ-*octyl*, m.p. 10°, CH_2Ph, m.p. 130°, μ-*keto-octadecyl*, m.p. 77°, *Ph*, m.p. 182°, o-, m.p. 163°, m-, m.p. 146°, and p-*tolyl*, m.p. 171·5°, *thymyl*, m.p. 147°, o-, m.p. 236°, and p-$NO_2{\cdot}C_6H_4$ *ethers*, m.p. 192°. M.p. are corr. and ±0·5°. R. S. C.

[Detection of] ethylene glycol, propylene glycol, glycerol, and diethylene glycol. M. Orchin (*J. Assoc. Off. Agric. Chem.*, 1943, **26**, 99—101).—One drop of a substance, known to be one of the above, is treated with H_5IO_6; org. products are CH_2O, CH_2O + MeCHO, CH_2O + HCO_2H, and —, respectively. $O([CH_2]_2{\cdot}OH)_2$ is identified as the bis-3 : 5-dinitrobenzoate, m.p. 150·5—151·5° (corr.). A. A. E.

Photometric determination of reduced and total ascorbic acid.—See A., 1943, III, 502.

Chromogenic reagent for vitamin-*C* determination.—See A., 1943, III, 502.

Colour reaction for methionine. L. H. Sofin, H. Rosenblum, and R. C. Schultz (*J. Biol. Chem.*, 1943, **147**, 557—559).—Methionine (**I**) gives a yellow colour with a saturated solution of anhyd. $CuSO_4$ in conc. H_2SO_4. The test is not shown by alanine, arginine (sulphate), aspartic acid, cystine, glutamic acid, glycine, histidine (sulphate), hydroxyproline, *iso*leucine, leucine, lysine (sulphate), norleucine, phenylalanine, proline, serine, threonine, or valine. Tryptophan gives a bright yellow colour with a slight fluorescence and tyrosine a yellow colour less intense than and of different shade from that given by (**I**). The reaction is adapted to the determination of (**I**) in leucine, which enhances the colour and hence must be present in equal amount in the blank and test sample. H. W.

Raman spectra of sugars.—See A., 1943, I, 176.

Separation of carotenes from xanthophylls.—See A., 1943, III, 540.

Determination of 2 : 4-diaminophenol. I. S. Shupe (*J. Assoc. Off. Agric. Chem.*, 1943, **26**, 123—125).—An empirical gravimetric method based on the formation of a mixture of OBz derivatives is given, together with microchemical identification tests. A. A. E.

Colour reactions for stilbœstrol. T. T. Cocking (*Analyst*, 1943, **68**, 144—146).—Stilbœstrol (**I**) with an excess of Br in AcOH at 100° (bath) for 1 min. gives an orange solution which when treated successively with EtOH and H_2O forms a violet colloidal dispersion (prevented by oil), provided free Br (or Cl_2 but not I) is present. The colour is extracted by various org. solvents (*e.g.*, $CHCl_3$) giving orange-red solutions which fade rapidly when separated and dried. Reaction is quant. and 1 μg. of (**I**) in 0·1 ml. of AcOH may be detected colorimetrically. With 0·2 atom (min.) or 4 atoms (max.) of Br in warm AcOH, (**I**) gives a green colour; this may be used as a rapid colorimetric test. Sucrose interferes but lactone does not; many aldehydes interfere. Neither reaction is given by stilbœstrol diacetate or dipropionate or hexœstrol. Dienœstrol gives both reactions, ψ-stilbœstrol only the violet reaction. S. B.

[Determination of] barbituric acid derivatives, particularly bromobarbiturates and thiobarbiturates. L. E. Warren (*J. Assoc. Off. Agric. Chem.*, 1943, **26**, 101—107).—Two equally satisfactory extraction methods employing respectively $CHCl_3$ and 80 vol.-% $CHCl_3$–Et_2O are described. A. A. E.

Simplified photelometric determination of trigonelline. S. W. Fox, E. W. McNeil, and H. Field, jun. (*J. Biol. Chem.*, 1943, **147**, 645—650).—A simplified method of obtaining relatively highly reproducible results in the determination of trigonelline by alkaline treatment has been evolved. MeOH allows the determination to be carried out in a single phase and decolorisation by C is unnecessary since the blank colour is diminished. Dianisidine condenses to a dye of high sensitivity and is usable without previous removal of SO_4''. Glucose interferes with the determination. H. W.

Microchemical tests for alkaloids and synthetics. G. L. Keenan (*J. Assoc. Off. Agric. Chem.*, 1943, **26**, 96—99).—The Reinecke salt reagent provides a distinctive and sensitive test for choline; $PtCl_4$ + NaI is less sensitive. A satisfactory procedure for the $HAuCl_4$ test for sulphadiazine is given. A. A. E.

Determination of mercury in phenylmercuric nitrate. W. P. Chambers (*Quart. J. Pharm.*, 1943, **16**, 6—11).—The B.P. 1932 (4th Addendum) method of assay of $HgPh{\cdot}NO_3$ is reviewed and the errors in the method, which lead to high results, are discussed. Determination of Hg by a gravimetric method based on pptn. of HgS from an almost boiling solution of the nitrate in glacial AcOH leads to high and somewhat irregular results, but they are ~2% < those obtained by the official assay. Determinations of Hg by reduction with HCO_2H, by amalgamation of the Hg with Zn, and by digestion with H_2SO_4–HNO_3 all give reliable results. Full details of these methods are given. It is suggested that the Zn-amalgamation should be substituted for the official method, since it is reliable, manipulation is easy, and a determination can be carried out in 1 hr. compared with 4 hr. and 2 hr. for the HCO_2H reduction and digestion methods respectively. J. N. A.

INDEX OF AUTHORS' NAMES, A., II.

JULY, 1943.

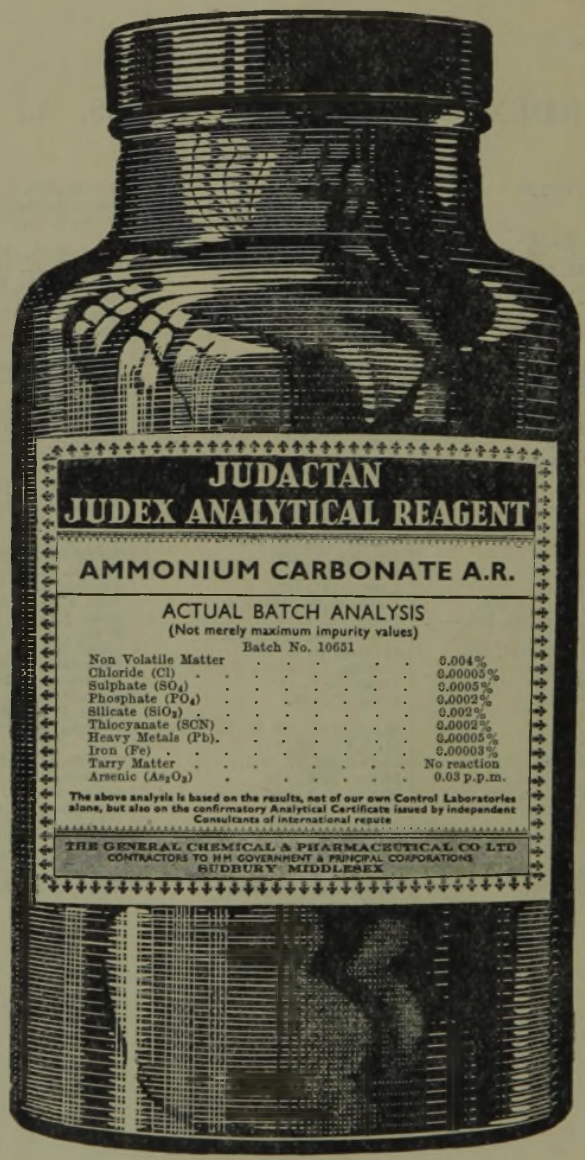
JUDACTAN

ANALYTICAL REAGENTS WITH ACTUAL BATCH ANALYSIS

ACTUAL

BATCH

ANALYSIS



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