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SEPTEMBER, 1943

A., II.—ORGANIC CHEMISTRY

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SEPTEMBER, 1943.

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IX. Δ^{ε}-*Deceninen-δ-ol*, b.p. 90°/1 mm. (**VI**) [from Δ^{α}-hexinene, with Na in liquid NH_3 followed by $CHMe{:}CH\cdot CHO$ (30%), or with MgEtBr in boiling Et_2O, followed by $CHMe{:}CH\cdot CHO$ (80% yield)] (1 active H per mol.; *α-naphthylurethane*, m.p. 69°), is reduced (H_2, Pd–norite in MeOH) to $C_8H_{13}\cdot CHPr\cdot OH$ (3 : 4-*dinitrobenzoate*, m.p. 24°), oxidised to $COPr\cdot C_6H_{13}$ [*semicarbazone*, m.p. 56° (or 51°, depending on rate of heating) (lit. 51—52°)]. (**VI**) with 25% H_2SO_4 at 20° in N_2 yields $\Delta^{\gamma\varepsilon}$-*deceninen-β-ol*, b.p. 113—114°/3 mm., absorption max. at 2260 A. (1 active H per mol.; *α-naphthylurethane*, m.p. 65°), reduced to $C_8H_{17}\cdot CHMe\cdot OH$ (3 : 5-*dinitrobenzoate*, m.p. 44°), oxidised to $COMe\cdot C_8H_{17}$.

X. $CHMe{:}CMe\cdot C{:}CH$ condenses with $Pr^{\alpha}CHO$, $CHMe{:}CH\cdot CHO$, and citral by the Grignard method (or, in the second case, the Na method) yielding respectively *η-methyl-*$\Delta^{\eta\varepsilon}$*-noneninen-δ-ol*, b.p. 106°/15 mm. (1 active H per mol.; 3 : 5-*dinitrobenzoate*, m.p. 53°; *β-naphthylurethane*, m.p. 46°), reduced (H_2, PtO_2 in MeOH) to *η-methylnonan-δ-ol* (**VII**), b.p. 94°/12 mm. (3 : 5-*dinitrobenzoate*, m.p. 60°), oxidised to *η-methylnonan-δ-one*, b.p. 86°/11 mm. (*phenylsemicarbazone*, m.p. 65°), *η-methyl-*$\Delta^{\beta\eta\varepsilon}$*-nonadieninen-δ-ol* (**VIII**), b.p. 127°/16 mm. (1 active H per mol.; *α-phenylurethane*, m.p. 98°), reduced to (**VII**), and a slightly impure carbinol (**IX**) (0·9 active H per mol.), reduced (PtO_2) to *βζλ-trimethyl-*n*-tridecane*, b.p. 152°/16 mm. (**VIII**) with 5% H_2SO_4 at 20° in N_2 yields *η-methyl-*$\Delta^{\gamma\eta\varepsilon}$*-nonadieninen-β-ol*, b.p. 122°/16 mm. (0·95 active H per mol.; *α-naphthylurethane*, m.p. 82°), reduced (PtO_2) to *η-methylnonan-β-ol*, b.p. 93°/4 mm. (3 : 5-*dinitrobenzoate*, m.p. 65°), oxidised to the *ketone*, b.p. 116°/6 mm. (*semicarbazone*, m.p. 124°; *phenylsemicarbazone*, m.p. 95·5°). (**IX**) on distillation undergoes rearrangement and dehydration, giving $C_{16}H_{22}$. Absorption details are given.

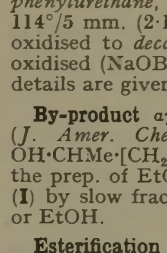
XI. MgEtBr in Et_2O with C_2H_2, followed by $CMe{:}CH\cdot CHO$, yields $\Delta^{\beta\theta\varepsilon}$-decadieninene-δη-diol, converted by 10% H_2SO_4 at 20° in N_2 into $\Delta^{\gamma\eta\varepsilon}$-*decadieninene-βι-diol*, b.p. 65—70° (bath temp.)/10^{-4} mm. (from which a pure *isomeride*, m.p. 56·5—57°, was isolated) (1·9 active H per mol.; *diacetate*, b.p. 131—132°/10^{-3} mm.; *bisphenylurethane*, m.p. 181°), reduced (PtO_2) to *decane-βι-diol*, b.p. 114°/5 mm. (2·1 active H per mol.; *bisphenylurethane*, m.p. 134°), oxidised to *decane-βι-dione*, m.p. 62° (*dioxime*, m.p. 132°), further oxidised (NaOBr) to suberic or (HNO_3) to adipic acid. Absorption details are given. A. Lı.

By-product $\alpha\gamma$-butylene glycol. J. B. Cloke and R. M. Wolff (*J. Amer. Chem. Soc.*, 1943, **65**, 986—987).—An acetate of $OH\cdot CHMe\cdot[CH_2]_2\cdot OH$ (**I**), obtained as a by-product (4—6%) in the prep. of EtOAc from MeCHO and $Al(OBu^{\gamma})_3$, is converted into (**I**) by slow fractional distillation with a little conc. HCl in MeOH or EtOH. R. S. C.

Esterification of allyl-type alcohols and products resulting therefrom.—See B., 1943, II, 240.

Concrete oil of jasmine flowers.—See A., 1943, III, 540.

Carbohydrates. VI. Constitution of styracitol. Transformation of aldoses into ketoses. L. Zervas and I. Papadimitriou (*Ber.*, 1940, **73**, [*B*], 174—176).—Styracitol (**I**) is shown to be αε-anhydromannitol (*A*). A new transition from the aldose to the ketose series is described. (**I**) is transformed by successive treatments with p-$C_6H_4Me\cdot SO_2Cl$ and BzCl in anhyd. C_5H_5N into *styracitol βγδ-tribenzoate ζ-*p*-toluenesulphonate* (**II**), m.p. 162°, $[\alpha]_D^{20}$ −166·5° in $CHCl_3$, the constitution of which is established by its conversion (NaI in anhyd. $COMe_2$ at 100°) into *styracitol βγδ-tribenzoate ζ-iodohydrin*, m.p. 143—144°, $[\alpha]_D^{20}$ −167° in $CHCl_3$. (**II**) is converted by successive treatments with AsF_3 in anhyd. C_5H_5N, $Pb(OAc)_4$ in C_6H_6, NaOMe, and $NPhMe\cdot NH_2$ into *d*-fructosephenylmethylhydrazone, m.p. 156—158°. Oxidation can also be effected with BzO_2H. H. W.



(*A*.)

Mixed anhydride of phosphoric and acetic acid. F. Lynen (*Ber.*, 1940, **73**, [*B*], 367—375).—AcCl (3 mols.) and Ag_3PO_4 in Et_2O (in CO_2) give *triacetyl phosphate*, $PO(OAc)_3$, m.p. 59—61°, hydrolysed by ice-cold H_2O to $OH\cdot PO(OAc)_2$ (**I**) and AcOH. The rate of hydrolysis of (**I**) is much slower at pH 7·4 and 38° than in acid medium at 30°. $CH_2Ph\cdot OH$ and P_2O_5 in Et_2O give $OH\cdot PO(O\cdot CH_2Ph)_2$ [Ba salt, m.p. 255—261° (decomp.)]; its Ag_2 salt, m.p. 216° (decomp.), and AcCl–Et_2O at room temp., then at 35°, yield $OAc\cdot PO(O\cdot CH_2Ph)_2$, converted by H_2–Pd–C–Et_2O into $OAc\cdot PO(OH)_2$ (**II**) (purified through the Ba and Ag_2 salt). Hydrolysis of (**II**) to H_3PO_4 + AcOH in aq. $NaHCO_3$ (pH 7·4) at 38° is studied. Absorption spectra of a neutral solution of (**II**) and of a partly hydrolysed product are given. A. T. P.

General method for synthesis of *tert.*-butyl esters. B. Abramovitch, J. C. Shivers, B. E. Hudson, and C. R. Hauser (*J. Amer. Chem. Soc.*, 1943, **65**, 986).—Adding RCOCl to $Bu^{\gamma}OH$ + $NPhMe_2$ in Et_2O, with cooling if necessary, and then boiling gives $Bu^{\gamma}OAc$ (63—76%), $EtCO_2Bu^{\gamma}$ (63%), $CH_2Br\cdot CO_2Bu^{\gamma}$ (70%), b.p. 73—74°/25 mm., Bu^{γ} isobutyrate (71%), b.p. 127—128·3°, isovalerate (33%), b.p. 154—156°, and *cinnamate* (58%), b.p. 144°/8 mm. R. S. C.

Petroleum acids. V. Aliphatic acids from Californian petroleum. W. A. Quebedeaux, G. Wash, W. O. Ney, W. W. Crouch, and H. L. Lochte (*J. Amer. Chem. Soc.*, 1943, **65**, 767—770; cf. A., 1942, II, 225).—The Me esters of acids from Californian petroleum are distilled to yield 720 fractions, the b.p. and n_D of which are used for characterisation. Fractions of const. b.p. and low n yield $CHMePr^{\alpha}\cdot CO_2H$, $CHMeEt\cdot CH_2\cdot CO_2H$, n-$C_5H_{11}\cdot CO_2H$, $CHMeBu^{\alpha}\cdot CO_2H$, $CHMePr^{\alpha}\cdot CH_2\cdot CO_2H$, $CHMeEt\cdot[CH_2]_2\cdot CO_2H$, $Pr^{\beta}\cdot[CH_2]_3\cdot CO_2H$, n-$C_6H_{13}\cdot CO_2H$, n-$C_7H_{15}\cdot CO_2H$, n-$C_8H_{17}\cdot CO_2H$, but no $Bu^{\gamma}CO_2H$ or $CHMeEt\cdot CO_2H$ (cf. B., 1939, 1199). R. S. C.

Catalytic reduction by formic acid under pressure. II. Comparison of copper and nickel as catalysts. R. R. Davies and H. H.

Hodgson (*J.C.S.*, 1943, 281—282).—Cu, as catalyst with HCO_2H, promotes non-nuclear reduction, PhCHO, BzOH, and $PhNO_2$ being reduced to $CH_2Ph{\cdot}OH$, and PhMe, C_6H_6, and NH_2Ph respectively, whilst Ni promotes nuclear reduction, NH_2Ph and PhOH giving *cyclo*hexylamine and *cyclo*hexanol. F. R. S.

Fractional distillation of unsaturated fatty acids. II. Effect of heat on rearrangements produced in unsaturated fatty acid esters. F. A. Norris, I. I. Rusoff, E. S. Miller, and G. O. Burr (*J. Biol. Chem.*, 1943, **147**, 273—280).—Fatty acids containing up to three double linkings are resistant to the heat-treatment of vac. fractional distillation. Rearrangement of isolated to conjugated double linkings occurs in more unsaturated acids, the extent of which depends on the degree of unsaturation, the time, and the temp. Two and three double linking conjugation is observed in heat-treated Me linolenate and the more unsaturated esters of cod-liver oil, respectively. As thermal polymerisation increases, conjugation first increases and then diminishes as the conjugated double linkings undergo a Diels–Alder type of reaction to produce polymers devoid of conjugation. Added reagents and solvents are of importance since a greater concn. of conjugated material is produced by high-temp. hydrolysis than by heat alone. Polymers freed from monomers exhibit only general absorption probably resulting from cyclisation. H. G. R.

Derivatives from hydrogenated castor oil. II. Glycol esters of λ-hydroxystearic acid. S. A. Bell and A. Taub (*J. Amer. Pharm. Assoc.*, 1943, **32**, 115—118; cf. A., 1942, II, 187).—The following esters are prepared by refluxing the acid in xylene containing p-$C_6H_4Me{\cdot}SO_3H$ with 10 mol.-equivs. of the glycol for the mono- and 2 mol.-equivs. for the di-ester: *ethylene glycol*, m.p. 67—68·5°, *propylene glycol*, m.p. 63—66°, and *trimethylene glycol λ-hydroxystearate*, m.p. 60·5—62°; *ethylene glycol*, m.p. 90—92°, and *trimethylene glycol di-λ-hydroxystearate*, m.p. 81·3—82·5°. The physical properties and possible application to ointment bases are described. F. O. H.

Pyrolysis of lactic acid derivatives. Preparation of allyl and methallyl acrylates. C. H. Fisher, C. E. Rehberg, and L. T. Smith (*J. Amer. Chem. Soc.*, 1943, **65**, 763—767).—Several treatments of lactic acid with $CH_2{:}CH{\cdot}CH_2{\cdot}OH$ (**I**) in presence of acid give 51·5% of *allyl lactate* (**II**), b.p. 79°/25 mm., but 78% is obtained by dehydrating the acid by boiling with C_6H_6 and heating the resulting anhydride with (**I**). Boiling with $CH_2{:}CMe{\cdot}CH_2{\cdot}OH$ and C_6H_6 with removal of H_2O gives 64·6% of *β-methylallyl lactate* (**III**), b.p. 78°/11 mm. Pyrolysis of the *acetates* (prep. by Ac_2O–H_3PO_4), b.p. 98°/20 mm., and 95°/10 mm., of (**II**) and (**III**), respectively, at 500—575° gives ~40% of *allyl* (**IV**), b.p. 122°, and *β-methylallyl acrylate* (**V**), b.p. 72°/50 mm., respectively. The methylacrylates give higher yields on pyrolysis. Presence of (**IV**) or (**V**) leads to less sol., less fusible, harder polymerides, owing to cross-linking. R. S. C.

Ambrettolide and its isomerides. II. Δ$^{\delta}$- and Δ$^{\epsilon}$-*iso*Ambrettolic acids and their lactones. C. Collaud (*Helv. Chim. Acta*, 1943, **26**, 849—856; cf. A., 1942, II, 392).—Further crystallisation of Δ$^{\epsilon}$-*iso*ambrettolic [ω-hydroxy-Δ$^{\epsilon}$-hexadecenoic] acid (**I**) from C_6H_6 during which the temp. is not allowed to fall below 30° raises the m.p. to 77—77·5°. New m.p. of its *p*-phenylphenacyl ester is 98—99° and of εζω-trihydroxyhexadecoic acid obtained by oxidation with $KMnO_4$ 102—103°. The *formate* has m.p. 53—54°. (**I**) is oxidised by H_2O_2 to an isomeric *εζω-trihydroxystearic acid*, m.p. 114—115°. Crystallisation of the residues left after the isolation of (**I**) from C_6H_6, EtOAc, C_6H_6, and light petroleum–Et_2O leads to Δ$^{\delta}$-iso*ambrettolic* [ω-*hydroxy*-Δ$^{\delta}$-*hexadecenoic*] *acid* (**II**), m.p. 61—62° (*formate*, m.p. 43—44°). Ozonisation of (**II**) followed by reduction of the ozonide and oxidation of the aldehydo-acid gives κ-hydroxyundecoic and glutaric acid (**III**) but the presence of very small amounts of adipic (**IV**) and succinic acid casts some doubt on the homogeneity of (**II**). Oxidation of (**II**) by $KMnO_4$ and H_2O_2 gives *δεω-trihydroxyhexadecoic acids*, m.p. 81—81·5° and 119—119·5° respectively. p-*Phenylphenacyl* Δ$^{\delta}$-iso*ambrettolate* has m.p. 87—88°. Δ$^{\delta}$-iso*Ambrettolide*, b.p. 143°/2 mm., is hydrolysed to (**II**). The *iso*ambrettolic acids freely sol. in C_6H_6 appear to be mixtures of the geometrical isomerides of (**I**) and (**II**) since they yield (**III**) and (**IV**) when ozonised. Their separation has not been effected. They have a very marked tendency to pass into estolides, even at room temp. H. W.

Configurative relationship between optically active methyl- and thiol-succinic acids. A. Fredga (*Arkiv Kemi, Min., Geol.*, 1942, **15**, **B**, No. 23, 6 pp.).—(+)-$CO_2H{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2H$ (**I**) and (+)-$CO_2H{\cdot}CH(SH){\cdot}CH_2{\cdot}CO_2H$ (**II**) form a continuous series of solid solutions, and *r*-(**I**) and *r*-(**II**) a limited range, whilst (−)-(**I**) and (+)-(**II**) form the racemic type 1 : 1 *compound*, m.p. 132·5°. It is concluded that (+)-(**I**) and (+)-(**II**) have the same optical configuration (cf. A., 1943, I, 154). *r*-(**I**) has m.p. 112·5° when freshly prepared, rising to m.p. 116° (after sintering) on keeping, indicating the existence of polymorphism. M. H. M. A.

Fission of thetines of sulphido-acids. B. Holmberg and E. Schjånberg (*Arkiv Kemi, Min., Geol.*, 1942, **15**, **A**, No. 23, 31 pp.).—The reaction between $CH_2Br{\cdot}CO_2Na$ and $CR'R''(S{\cdot}[CH_2]_n{\cdot}CO_2Na)_2$ (n = 1 or 2), or $SR'{\cdot}[CH_2]_n{\cdot}CO_2Na$ (**I**) (n = 1 or 2) (R′, R″ = H, alkyl, or aryl), giving, *e.g.*, $CHR(S{\cdot}CH_2{\cdot}CO_2Na){\cdot}S^+(CH_2{\cdot}CO_2^-){\cdot}CH_2{\cdot}CO_2Na$ (**II**) + NaBr, followed by fission of (**II**) to $R{\cdot}CHO + SH{\cdot}CH_2{\cdot}CO_2Na + S(CH_2{\cdot}CO_2^-)_2Na^+H^+$, has been studied by determining Br^- and H^+ produced. No conclusion could be drawn about the mechanism of the reaction or the occurrence of side reactions. The rate of thetinisation is highest with (**I**) > mercaptal acids > mercaptol acids, and with derivatives of $SH{\cdot}[CH_2]_2{\cdot}CO_2H$ > of $SH{\cdot}CH_2{\cdot}CO_2H$ (**III**). The effect of changes in R′ and R″ is similar in all four series but no regularities are observed. (**III**) and $COMePr^{\beta}$ with conc. HCl at room temp. give *methyl*iso*propylmercaptolacetic acid*, m.p. 100—101°. M. H. M. A.

Vinylalkylmalonic esters.—See A., 1943, II, 279.

Preparation of aldehydes.—See B., 1943, II, 241.

Catalytic dehydrogenation of alcohols to aldehydes in presence of air. R. R. Davies and H. H. Hodgson (*J.C.S.*, 1943, 282—284).—Butyl, dodecyl, and benzyl alcohols are dehydrogenated to aldehydes by Cu–Ag on pumice in presence of air at 300—350° (97, 85, and 76% yields respectively, allowing for alcohol recovered). There is an optimum air : alcohol ratio in each case, the amount of air consumed being ≪ the theoretical for oxidation. A. Li.

Preparation of aldehydes, ketones, and acids by ozone oxidation. A. L. Henne and P. Hill (*J. Amer. Chem. Soc.*, 1943, **65**, 752—754).—Ozonisation of olefines to aldehydes or ketones is best effected in CH_2Cl_2 at −78° (or AcOH or EtOAc at room temp.); the ozonide is decomposed by dropping the solution into 25—50% AcOH containing Zn dust; the product, in Et_2O, is washed with aq. KI to prevent explosions. For prep. of the acid, the solution of the ozonide in AcOH is run into H_2O_2–H_2SO_4–H_2O. Prep. of $Pr^{\beta}{\cdot}[CH_2]_3{\cdot}CHO$ (62%) and $Pr^{\beta}{\cdot}[CH_2]_3{\cdot}CO_2H$ (67%) from $Pr^{\beta}{\cdot}[CH_2]_3{\cdot}CH{:}CH_2$, of $COMeBu^{\alpha}$ (60%) from $CMeBu^{\alpha}{:}CH_2$, of $CO_2H{\cdot}[CH_2]_4{\cdot}CO_2H$ (60%) from *cyclo*hexene, of $CH_2Ph{\cdot}CO_2H$ (50%) from $CH_2Ph{\cdot}CH{:}CH_2$ ($CH_2Ph{\cdot}CHO$ could not be obtained), of $Pr^{\beta}{\cdot}[CH_2]_5{\cdot}CHO$ (66·6%) from $Pr^{\beta}{\cdot}[CH_2]_5{\cdot}CH{:}CH_2$, and of $CHMeBu^{\alpha}{\cdot}CH_2{\cdot}COMe$ (68·9%) from $CHMeBu^{\alpha}{\cdot}CH_2{\cdot}CMe{:}CH_2$ is described. R. S. C.

Preparation of monomeric glyoxal.—See B., 1943, II, 241.

Two different 2 : 4-dinitrophenylhydrazones of ethyl *iso*propyl ketone and the 2 : 4-dinitrophenylhydrazones of other methyl and ethyl ketones. W. Dirscherl and H. Nahm (*Ber.*, 1940, **73**, [*B*], 448—450).—$COEtPr^{\beta}$ and 2 : 4 : 1-$(NO_2)_2C_6H_4{\cdot}NH{\cdot}NH_2$ in 50% AcOH give two *Et Pr$^{\beta}$ ketone* 2 : 4-*dinitrophenylhydrazones*, orange-red crystals (**I**), m.p. 111—113°, and pale yellow crystals (**II**) which become red at 84—88° and melt at 111—113°. Under Et_2O (**I**) passes gradually into (**II**). (**I**) and (**II**) are regarded as different modifications, not isomerides. Only one form is observed in the 2 : 4-dinitrophenylhydrazones of $COMe_2$, m.p. 122—124°, COMeEt, m.p. 116—117°, $COMeBu^{\alpha}$, m.p. 106—109°, *COMeBu$^{\beta}$*, m.p. 71·5—72·5°, $COMeBu^{\gamma}$, m.p. 92—94°, $COEtPr^{\alpha}$, m.p. 49—151°, *Me* iso*amyl ketone*, m.p. 93—94°, and COPhMe, m.p. 238—240°. H. W.

Molar refraction and structure of hydroxymethylene ketones. R. Kaushal (*J. Indian Chem. Soc.*, 1943, **20**, 53—55).—*Ethoxymethyleneacetone* (**I**), b.p. 74—76°/6 mm. (*disemicarbazone*, m.p. 242°; corresponding *anilide*, $COMe{\cdot}CH{:}CHNHPh$, m.p. 247°), is obtained by the action of EtBr in EtOH on the product from $COMe_2$, HCO_2Et, and Na. It gives a red colour with $FeCl_3$ which gradually darkens. It is not acid to litmus. *γ-Ethoxymethylenebutan-β-one* (**II**), b.p. 79°/8 mm., is obtained similarly. It gives a faint violet colour with $FeCl_3$ which darkens on keeping or warming. After prolonged contact with $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$ it gives a very poor yield of *solid*, m.p. 260°. M_D of (**I**) and (**II**) indicates the constitutions $COMe{\cdot}CH{:}CH{\cdot}OEt$ and $COMe{\cdot}CMe{:}CH{\cdot}OEt$, from which the structures of the parent substances are inferred. H. W.

Preparation of hexadecylamines.—See B., 1943, II, 241.

Secondary amino-alcoholds.—See B., 1943, II, 242.

Ergot alkaloids. V. Synthesis of optically active β-amino-alcohols. A. Stoll, J. Peyer, and A. Hofmann (*Helv. Chim. Acta*, 1943, **26**, 929—943).—Esters of *r*-α-bromo-fatty acids are converted into the *r*-α-benzylamino-fatty acids, which are smoothly reduced (Bonveault–Blanc) to the cryst. β-benzylamino-alcohols. These are resolved by the appropriate optically active acids and the CH_2Ph group is finally removed by catalytic hydrogenation. The letters *d*- and *l*- are used to express configurative relationships to *d*-malic acid and the signs + and − for sense of rotation. Gradual addition of *r*-$CH_2Ph{\cdot}NH{\cdot}CHMe{\cdot}CO_2Et$ (**I**) in EtOH to Na under tetrahydronaphthalene (initially heated to 120°) in such a manner that the temp. remains at ~106—108° leads to *dl*-β-benzylaminopropyl alcohol [*dl*-*N*-benzylalaninol] (**II**), b.p. 155—157°/20 mm., m.p. 70—72° [*hydrochloride*, m.p. 111—113°; *picrate*, m.p. 135—137°; *H oxalate*, m.p. 176—178° (decomp.)], also obtained from (**I**) by treatment with H_2 at 180°/200 atm. in dioxan containing Cu chromite. (**II**) is resolved by *d*-tartaric acid in EtOH–EtOAc, yielding immediately the *H* d-*tartrate*, m.p. 94—96°, of d(−)-*β-benzylaminopropyl*

alcohol (**III**), m.p. 47—49°, $[\alpha]_D^{22}$ −44·25° in EtOH [*hydrochloride*, m.p. 136—138°, $[\alpha]_D^{21}$ −14·75° in H_2O; *H oxalate*, m.p. 187—189° (decomp.); *picrate*, m.p. 73—75°]. The basic residue from the isolation of (**III**) is cryst. from *cyclo*hexane and then converted into the H oxalate, from which l(+)-*β-benzylaminopropyl alcohol* (**IV**), $[\alpha]_D^{23}$ +44° in EtOH, is derived. Hydrogenation (Pd sponge) of (**IV**) and $H_2C_2O_4$ in aq. EtOH affords the *oxalate*, m.p. 171° (corr.), $[\alpha]_D^{20}$ +18·8° in H_2O, of l(+)-*β-aminopropyl alcohol*, b.p. 72—73°/11 mm., $[\alpha]_D^{20}$ +15·8°. *d*(−)-*β*-Aminopropyl alcohol (*oxalate*, $[\alpha]_D^{20}$ −18·8° in H_2O) is identical with the product derived from ergobasine. Gradual addition of Na to a boiling solution of *r*-$CH_2Ph{\cdot}NH{\cdot}CHEt{\cdot}CO_2Et$ in abs. EtOH leads to dl-*β-benzylaminobutanol* (**V**), b.p. 155—157°/14 mm., m.p. 58—60° (*hydrochloride*, m.p. 127—129°; *picrate*, m.p. 144—146°). (**V**) is resolved by successive use of *d*(−)- and *l*(+)-$OH{\cdot}CHPh{\cdot}CO_2H$ in EtOAc. The d(−)-*mandelate*, m.p. 111—113°, of (−)-*β-benzylaminobutanol*, m.p. 76—78°, $[\alpha]_D^{21}$ −25·0° in EtOH (*hydrochloride*, m.p. 141—143°; *picrate*, m.p. 111—113°), and (+)-*β-benzylaminobutanol*, $[\alpha]_D^{23}$ +25·5° in EtOH, are isolated. Hydrogenation of the alcohols leads to (+)-*β-aminobutanol*, b.p. 80°/11 mm., $[\alpha]_D^{20}$ +9·8° [*oxalate*, m.p. 190—192° (corr.), $[\alpha]_D^{20}$ +11·3° in H_2O], and (−)-*β-aminobutanol*, $[\alpha]_D^{20}$ −11·3°. *r*-$CH_2Ph{\cdot}NH{\cdot}CMeEt{\cdot}CO_2Et$ is converted into *r*-*β-benzylamino-β-methyl*-n-*butyl alcohol*, b.p. 146—148°/8 mm. (*hydrochloride*, m.p. 152—154°; *picrate*, m.p. 131—133°).

dl-$CH_2Ph{\cdot}NH{\cdot}CHBu{\cdot}CO_2Et$ readily gives dl-*β-benzylamino-δ-methyl*-n-*amyl alcohol*, b.p. 170—172°/16 mm., m.p. 61—63° (*hydrochloride*, m.p. 151—153°; *picrate*, m.p. 152—154°). This is resolved by *d*-dibenzoyltartaric acid in 60% EtOH, whereby there is separation of the *H* d-*dibenzoyltartrate*, m.p. 169—171° somewhat dependent on the rate of heating, of l(+)-*β-benzylamino-δ-methyl*-n-*amyl alcohol* [l(+)-N-*benzyl-leucinol*] (**VI**), m.p. 77—79°, $[\alpha]_D^{20}$ +30·75° in EtOH (*hydrochloride*, m.p. 160—162°; *picrate*, m.p. 121—123°). d(−)-*β-Benzylamino-δ-methyl*-n-*amyl alcohol*, $[\alpha]_D^{22}$ −30·25° in EtOH, is isolated from the bases left after separation of (**VI**) by use of (+)-*o*-nitromandelic acid and 50% EtOH. d(−)-*β-Amino-δ-methyl*-n-*amyl alcohol*, b.p. 98—99°/11 mm. [*oxalate*, m.p. 216° (corr.), $[\alpha]_D^{20}$ −7·0° in H_2O], and its l(+)-*antipode*, b.p. 98—99°/11 mm. [*oxalate*, m.p. 216° (corr.), $[\alpha]_D^{20}$ +7·2° in H_2O], are obtained in the usual manner. $CH_2Ph{\cdot}CH(NH{\cdot}CH_2Ph){\cdot}CO_2Et$, b.p. 198—200°/6 mm., is reduced to *β-benzylamino-γ-phenyl*-n-*propyl alcohol* [dl-*phenyl*-N-*benzylalaninol*], b.p. 198—200°/5 mm., m.p. 69—71° (*hydrochloride*, m.p. 147—149°; *picrate*, m.p. 166—168°).

H. W.

Amino-acids. I. Glycine. J. H. Billman and E. E. Parker (*J. Amer. Chem. Soc.*, 1943, **65**, 761—762).—*o*-$C_6H_4(CO)_2N{\cdot}[CH_2]_2{\cdot}OH$ {prep. from *o*-$C_6H_4(CO)_2O$ and $NH_2{\cdot}[CH_2]_2{\cdot}OH$ at 175° in 99% yield} with hot $K_2Cr_2O_7$–AcOH–H_2O–H_2SO_4 gives 89—93% of *o*-$C_6H_4(CO)_2N{\cdot}CH_2{\cdot}CO_2H$, hydrolysed by boiling 18% HCl to $NH_2{\cdot}CH_2{\cdot}CO_2H$,HCl (79—85%), which with warm C_5H_5N and then MeOH gives 65—73% of glycine. R. S. C.

Amino-acids and their derivatives. III. Synthesis of α-aminodi-*n*-propylacetic acid. Y. T. Huang, K. H. Lin, and L. Li (*J. Chinese Chem. Soc.*, 1941, **8**, 81—91).—$CN{\cdot}CPr_2{\cdot}CO_2Et$ with conc. H_2SO_4 yields Et di-*n*-propylmalonamate (free *acid*, m.p. 148—150°), which with Br in $CHCl_3$ gives the N-*Br*-compound, m.p. 47—48°, hydrolysed (10% NaOH, 70—80°) to NN′-*bis*(*carbethoxydi*-n-*propylmethyl*)-*carbamide* (**I**), m.p. 111—112°, or (10% NaOH, 20—30°) to (**I**) and (chiefly) the *Et* ester, b.p. 80—81°/6—7 mm. (*hydrochloride*, m.p. 94—95°; *phenylureide*, m.p. 110·5—111·5°), of *α-amino-α-propyl-n-valeric acid* (**II**), m.p. 312° (decomp.) (bath preheated to 290°) [*hydrochloride*, m.p. 295—296° (decomp.) (bath preheated to 280°); *ureide*, m.p. 240° (decomp.) (bath preheated to 195°); $CH_2Cl{\cdot}CO$ derivative, m.p. 216° (bath preheated to 200°)]. (**I**) is hydrolysed by HI (½ hr.) to NN′-*bis*(*carboxydi*-n-*propylmethyl*)*carbamide*, m.p. 272° (bath preheated to 260°), or (4½ hr.) to (**II**). A. Li.

Amino-acids and their derivatives. IV. Synthesis of α-aminodi-*n*-butylacetic acid and α-aminodi*iso*butylacetic acid. Y. T. Huang, K. H. Lin, L. Li, and M. C. Lin (*J. Chinese Chem. Soc.*, 1941, **8**, 201—217).—$CN{\cdot}CBu^{\alpha}_2{\cdot}CO_2Et$ or $CN{\cdot}CBu^{\beta}_2{\cdot}CO_2Et$ (from $CN{\cdot}CH_2{\cdot}CO_2Et$, AlkBr, and NaOEt in EtOH) with conc. H_2SO_4 at 100° yield respectively *Et di*-n-, m.p. 75—76° [free *acid*, m.p. 148° (decomp.)], and *-iso*-butylmalonamate, new m.p. 79·5—80·5° [free acid, new m.p. 159° (decomp.)], which with Br in $CHCl_3$ at −15° give the crude *N*-Br-compounds (**I**) and (**II**) respectively, hydrolysed to *carbethoxydi*-n- (**III**), b.p. 107°/4·5 mm., and -iso-*butylmethylcarbimide* (**IV**), b.p. 95°/~3·5 mm. (**III**) yields with NH_2Ph at room temp., then at 45—50°, *Et α-phenylureido-α-butyl*-n-*hexoate* (**V**), m.p. 151—152° (bath preheated to 140°), with $NH_2{\cdot}CPr_2{\cdot}CO_2H$ in N-NaOH at room temp., then at 70—75°, N-(*carboxydi*-n-*propylmethyl*)-N′-(*carbethoxydi*-n-*butylmethyl*)*carbamide*, m.p. 152—153° (decomp.) (bath preheated to 140°), and with conc. HCl at room temp., then at 100°, *Et α-amino-α-butyl*-n-*hexoate hydrochloride*, m.p. 102—103° [also obtained from (**I**) and 10% NaOH at 25—30°], with NN′-*bis*(*carbethoxydi*-n-*butylmethyl*)*carbamide* (**VI**), m.p. 75—78°, hydrolysed (HI at 150—170° for ½ hr.) to the free *acid*, m.p. 262—263° (bath preheated to 250°) [the free ester from which with PhNCO gives (**V**)], further hydrolysed (boiling 20% HCl) to *α-amino-α*-n-*butyl*-n-*hexoic acid*, m.p. 303° (bath preheated to 290°) [also obtained from (**VI**) and HI at 150—170° for 6 hr.], [*phenylureide*, m.p. 182—183° (decomp.) (bath preheated to 170°); *α-*$CH_2Cl{\cdot}CO$ derivative, m.p. 192—193°], which with (**III**) at 70—80°, then 85—90°, yields N-(*carboxydi*-n-*butylmethyl*)-N′-(*carbethoxydi*-n-*butylmethyl*)*carbamide*, m.p. 148—149° (froth) (bath preheated to 135°), esterified (Ag salt with EtI) to (**VI**). (**IV**) is hydrolysed (fuming HCl at 100°, 1 hr.) to *Et α-amino-β-methyl-α*-iso*butylvalerate hydrochloride*, m.p. 188—192°, which with aq. KCNO gives *Et α-ureido-β-methyl-α*-iso*butylvalerate*, m.p. 159·5—160·5° [also obtained from (**III**) and aq. NH_3 at room temp., then 50—55°, then 60—65°], and is further hydrolysed (48 hr.) to the *hydrochloride*, m.p. 261—264° (decomp.) (bath preheated to 250°), of *α-amino-β-methyl-α*-iso*butylvaleric acid*, m.p. 279° (bath preheated to 270°) [*phenylureide*, m.p. 204° (decomp.) (bath preheated to 195°); $CH_2Cl{\cdot}CO$-derivative, m.p. 207° (bath preheated to 195°)]. A. Li.

Improved preparation of nitrosomethylcarbamide. F. Arndt, L. Loewe, and S. Avan (*Ber.*, 1940, **73**, [*B*], 606—608).—$CO(NH_2)_2$ with aq. NH_2Me,HCl or 33% aq. NH_3-Me_2SO_4, followed by $NaNO_2$–ice–H_2SO_4 at −10°, gives $NO{\cdot}NMe{\cdot}CO{\cdot}NH_2$. A. T. P.

Hexafluoroazomethane (dicyanohexafluoride). O. Ruff and W. Willenberg (*Ber*, 1940, **73**, [*B*], 724—729; cf. A., 1936, 597).—$CF_3{\cdot}N_2{\cdot}CF_3$, m.p. −133°, b.p. −31·6°/760 mm., is obtained from CNI and IF_5 at 125—145°; *hexafluorodimethylamine*, $NH(CF_3)_2$, m.p. −130°, b.p. −6·2°/760 mm., is also formed. Various chemical and physical properties of the substances are described. A. T. P.

II.—SUGARS AND GLUCOSIDES.

Derivatives of the aldehydrol form of sugars. V. Rotatory power. M. L. Wolfrom and R. L. Brown (*J. Amer. Chem. Soc.*, 1943, **65**, 951—953; cf. A., 1941, II, 242).—*aldehydo-d*-Arabinose tetra-acetate with AcCl + $ZnCl_2$ in AcOH (+ a little Ac_2O) at 20—25° gives *α*-, m.p. 109—110°, $[\alpha]_D^{20}$ +97·1° in $CHCl_3$, and *β*-1-*chloro*-aldehydo-d-*arabinose penta-acetate*, m.p. 67·5—68·5°, $[\alpha]_D^{26}$ −29·5° in $CHCl_3$. *α*-, m.p. 129—130°, $[\alpha]_D^{26}$ +135·7° in $CHCl_3$, and *β-Bromo*-aldehydo-d-*arabinose penta-acetate*, m.p. 63—64°, $[\alpha]_D^{26}$ −71·3° in $CHCl_3$, and *α*-, m.p. 142·5—143°, $[\alpha]_D^{17}$ +98·0° in $CHCl_3$, and *β*-1-*bromo*-aldehydo-d-*galactose hexa-acetate*, m.p. 178—180°, $[\alpha]_D^{25}$ −75° in $CHCl_3$, are similarly prepared. Hudson's isorotation rules are valid in these series. R. S. C.

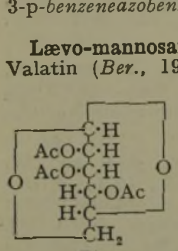
Production of *d*-ribose from calcium *d*-altronate.—See B., 1943, II, 242.

Partly-methylated glucose. K. Freudenberg and E. Plankenhorn (*Ber.*, 1940, **73**, [*B*], 621—631).—4 : 6-Benzylidene-α-methylglucoside and CH_2PhCl–KOH at 100° give the 2 : 3-$(CH_2Ph)_2$ derivative, m.p. 99°, $[\alpha]_D^{20}$ +23·5° in $COMe_2$, hydrolysed by 1% HCl in EtOH to 2 : 3-*dibenzyl-α-methylglucoside*, m.p. 79—80°, $[\alpha]_D^{20}$ +88·7° in $COMe_2$, which with Me_2SO_4–aq. KOH–$COMe_2$ at 50° yields 2 : 3-*dibenzyl*-4 : 6-*dimethyl-α-methylglucoside*, b.p. 200—210°/0·45 mm., $[\alpha]_D^{20}$ +97·9° in $COMe_2$, converted by H_2–Pd oxide–MeOH into 4 : 6-*dimethyl-α-methylglucoside*, b.p. 120°/0·005 mm., $[\alpha]_D^{20}$ +155·3° to 157·3° in $CHCl_3$ [2 : 3-*di*-p-*nitrobenzoate*, m.p. 114° (softens from 110°), $[\alpha]_D^{20}$ +203° in $COMe_2$, and 2 : 3-*di*-p-*benzeneazobenzoate*, m.p. 120°, $[\alpha]_{6252}^{20}$ +405° in $COMe_2$]. The derived 4 : 6-dimethylglucose has m.p. 156—158°; in MeOH–HCl, mutarotation occurs, *e.g.*, $[\alpha]_D$ +85·2° → +61·3°. 3-*Benzyl*-5 : 6-*dimethyl*-1 : 2-iso*propylideneglucose*, b.p. 160°/0·2 mm., $[\alpha]_D^{20}$ −15·8° in $COMe_2$, obtained from the 5 : 6-diacetate and Me_2SO_4–aq. NaOH in $COMe_2$, is converted by H_2–Pd–MeOH into 5 : 6-*dimethyl*-1 : 2-iso*propylideneglucose*, b.p. 112°/0·4 mm., $[\alpha]_D^{20}$ −5·2° in MeOH, and thence (HCl) 5 : 6-*dimethylglucofuranose*, a syrup, $[\alpha]_D^{20}$ +3·7° in $COMe_2$ [1 : 2 : 3-*tri*-p-*nitrobenzoate*, m.p. 115—120° (softens at 90°), $[\alpha]_D^{20}$ +90·0° in $COMe_2$, and *-tri*-p-*benzeneazobenzoate*, m.p. 192° (softens at 188°), $[\alpha]_{6252}^{20}$ +13·3° in $COMe_2$]. *Hexamethylmaltose anhydride*, m.p. 66°, $[\alpha]_D^{20}$ +74° in $CHCl_3$ (from maltose anhydride, K, liquid NH_3, and MeI), is hydrolysed by 5% HCl at 100° (bath) to tetramethylglucose, and also (after treatment with *p*-$Ph{\cdot}N{:}N{\cdot}C_6H_4{\cdot}COCl$) yields 2 : 3-dimethylglucose tri-*p*-benzeneazobenzoate, m.p. 209°, $[\alpha]_{6252}^{20}$ +100° in $CHCl_3$, and a second form, m.p. 189° (softens at 170°). 2 : 3-Dimethyl-α-methylglucoside and CH_2PhCl–KOH at 100° (bath) give the 4 : 6-$(CH_2Ph)_2$ compound, b.p. 195—200°/0·3 mm., $[\alpha]_D^{20}$ +121·9° in $COMe_2$; *methylglucoside* 2 : 3-*dibenzoate* 4 : 6-*diacetate*, m.p. 125°, $[\alpha]_D^{20}$ +155° in $COMe_2$, is obtained from α-methylglucoside 2 : 3-dibenzoate. 6-Triphenylmethyl-2 : 3-dimethyl-α-methylglucoside and BzCl–C_5H_5N afford the 4-*benzoate*, m.p. 133°, $[\alpha]_D^{20}$ +56° in $COMe_2$ (cf. Robertson, A., 1933, 937); similarly prepared is the 4-3′ : 5′-*dinitrobenzoate*, m.p. 175°, $[\alpha]_D^{20}$ +45·7° in $COMe_2$, which with HBr–AcOH yields 2 : 3-*dimethyl-α-methylglucoside* 4-3′ : 5′-*dinitrobenzoate*, m.p. 126°, $[\alpha]_D^{20}$ +57·5° in $COMe_2$. Methylation yields 2 : 3 : 6-*trimethyl-α-methylglucoside* 4-3′ : 5′-*dinitrobenzoate*, m.p. 147°, $[\alpha]_{6252}^{20}$ +56·3° in $COMe_2$ (corresponding *β-glucoside*, m.p. 146°, $[\alpha]_D^{20}$ −58·2° in $COMe_2$, also obtained by dinitrobenzoylation of the respective glucoside); 2 : 3 : 6-trimethyl-α-methylglucoside has $[\alpha]_D^{20}$ +149° in MeOH. The following derivatives are prepared, using *p*-$PhN_2{\cdot}C_6H_4{\cdot}COCl$–$C_5H_5N$ at 40°: 2 : 3 : 4 : 6-*tetramethylglucose* 1-p-*benzeneazobenzoate*, m.p. 116°, $[\alpha]_{6252}^{20}$ −7° in $COMe_2$; 2 : 3 : 6-*trimethyl-β-methylglucoside*

4-p-*benzeneazobenzoate*, m.p. 95—96°, $[\alpha]^{20}_{6252}$ −66·2° in $COMe_2$; 2 : 3 : 6-*trimethylglucose* 1 : 4-*di*-p-*benzeneazobenzoate*, m.p. 172°, $[\alpha]^{20}_{6252}$ +12·6° in $COMe_2$; 2 : 3 : 4-*trimethyl*-β-*methylglucoside* 6-p-*benzeneazobenzoate*, m.p. 122°, $[\alpha]^{20}_{6252}$ −7·6° to −9·3° (±3·3°) in $COMe_2$; 2 : 3 : 4-*trimethylglucose* 1 : 6-*di*-p-*benzeneazobenzoate*, $[\alpha]^{20}_{6252}$ −16·3° in $COMe_2$; 2 : 4 : 6-*trimethylglucose* 1 : 3-*di*-p-*benzeneazobenzoate*, m.p. 115—120°, $[\alpha]^{20}_{6252}$ +190° in $COMe_2$; 2 : 3-*dimethyl*-α-*methylglucoside* 4 : 6-*di*-p-*benzeneazobenzoate*, m.p. 143—144°, $[\alpha]^{20}_{6252}$ +260·5° in $CHCl_3$; 4 : 6-*dimethylglucose* 1 : 2 : 3-*tri*-p-*benzeneazobenzoate*, m.p. 145°, $[\alpha]^{20}_{6252}$ +551° in $CHCl_3$; 3-*methyl*-, m.p. 220°, $[\alpha]^{20}_{D}$ +163° (±6°) in $CHCl_3$, and 3-*benzyl-glucose* 1 : 2 : 4 : 6-*tetra*-p-*benzeneazobenzoate*, m.p. 246°, $[\alpha]^{20}_{6252}$ −48° (±20°) in $CHCl_3$; *diiso*propylideneglucose 3-p-*benzeneazobenzoate*, m.p. 110—111°, $[\alpha]^{20}_{6252}$ −56° in $COMe_2$.

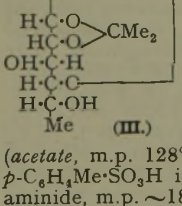
A. T. P.

Lævo-mannosan [β-mannosan]. G. Zemplén, A. Gerecs, and T. Valatin (*Ber.*, 1940, **73**, [*B*], 575—580).—α-Acetobromo-*d*-mannose and NMe_3 (method : cf. Micheel, A., 1930, 455) yield a product which affords, after acetylation with Ac_2O–NaOAc at 100° (bath), *β-mannosan* 2 : 3 : 4-*triacetate* (**I**), m.p. 86°, $[\alpha]^{20}_{D}$ −103·6° in H_2O, −100·2° in MeOH, −124·1° in $CHCl_3$, converted by NaOMe–MeOH into *β-mannosan* (**II**), $C_6H_{10}O_5$, $[\alpha]^{20}_{D}$ −115·4° in H_2O, or by 1% HCl in MeOH into α-methyl-*d*-mannoside, m.p. 194°, $[\alpha]_D$ +82·5° in H_2O. Methylation (Me_2SO_4–aq. NaOH) of (**II**) affords 2 : 3 : 4-*trimethyl*-β-*mannosan*, m.p. 52°, $[\alpha]^{20}_{D}$ −70·7° in $COMe_2$, converted by aq. HCl into 2 : 3 : 4-*trimethylmannose*, $[\alpha]^{20}_{D}$ −5° in H_2O, which with Ac_2O–NaOAc gives the 1 : 6-*diacetate*, $[\alpha]^{20}_{D}$ +2·24° in EtOH, and with CPh_3Cl–C_5H_5N yields 6-*triphenylmethyl*-2 : 3 : 4-*trimethyl*-d-*mannose*.


(I.)

A. T. P.

Attempted syntheses of glucosides and disaccharides. K. Freudenberg, H. Eich, C. Knoevenagel, and W. Westphal (*Ber.*, 1940, **73**, [*B*], 441—447).—*Diiso*propylideneglucose (**I**) is converted by Na or K in liquid NH_3 into the *Na* and *K* derivatives, the former of which with $TlNO_3$ yields the *Tl* compound. These react with CH_2PhCl or MeI with increasing readiness in the sequence Na, K, Tl but could not be caused to react with acetohalogenoglucose or 1-chloro-*diiso*propylidenemannose. (**I**) and $COCl_2$ in quinoline–PhMe yield *diisopropylideneglucosyl chloroformate* (**II**), b.p. 120°/0·2 mm., $[\alpha]^{20}_{D}$ −40·1° in $CHCl_3$, which on exposure to moist air passes into *iso*-propylideneglucofuranose 5 : 6-carbonate, decomp. 219—222°, $[\alpha]^{20}_{D}$ −33·7° in $COMe_2$, −21·1° in C_5H_5N, converted by heat into *iso*-propylidene-5 : 6-anhydroglucose, m.p. 56—57°. 1 : 2-iso*Propylideneglucofuranose* 5 : 6-*carbonate* 3-*acetate* has m.p. 128—129°, $[\alpha]^{20}_{D}$ −43·2° in $CHCl_3$. (**II**) and β-glucose 2 : 3 : 4 : 6-tetra-acetate in C_6H_6–C_5H_5N afford *diisopropylideneglucosyl* β-2 : 3 : 4 : 6-*tetra-acetylglucosyl carbonate*, m.p. 108°, $[\alpha]^{20}_{D}$ −23·1° in MeOH, −22·6° in $CHCl_3$. *Diisopropylideneglucosyl diisopropylidenemannosyl carbonate*, m.p. 132°, $[\alpha]^{20}_{D}$ +16·4° in $COMe_2$, *guaiacyl tetra-acetylglucosyl carbonate*, m.p. 146—147°, and *menthyl tetra-acetylglucosyl carbonate*, m.p. 151°, are described. Elimination of CO_2 from these esters with formation of disaccharide derivatives or glucosides could not be effected. *Menthyl tetra-acetylglucosyl sulphite*, m.p. 104—105°, $[\alpha]^{20}_{D}$ −62·9° in $COMe_2$, from menthol, glucose tetra-acetate, and $SOCl_2$ in $CHCl_3$–C_5H_5N, passes when heated with $BaCO_3$ at 144° into *β-menthylglucoside tetra-acetate*, m.p. 129°, in poor yield ; n-*propyl-tetra-acetylglucosyl sulphite*, m.p. 74°, $[\alpha]^{20}_{D}$ +104° in $COMe_2$, does not lose SO_3 when heated. 1 : 2-*iso*Propylidene-5 : 6-anhydroglucose is hydrogenated (Pd sponge in EtOAc) to 1 : 2-iso*propylideneglucomethylose* (**III**), m.p. 95°, $[\alpha]^{20}_{D}$ −26·3° in $CHCl_3$ (*diacetate*, m.p. 96°, $[\alpha]^{20}_{D}$ +23·0° in $CHCl_3$), which condenses with acetobromoglucose in $CHCl_3$ containing Ag_2CO_3 to 5-*tetra-acetylglucosido*-1 : 2-iso*propylideneglucomethylose*, m.p. 141°, $[\alpha]^{20}_{D}$ −11·0° in $CHCl_3$ (*acetate*, m.p. 128°, $[\alpha]^{20}_{D}$ −46° in $CHCl_3$). Acetylglucosamine and *p*-$C_6H_4Me{\cdot}SO_3H$ in boiling MeOH afford *N*-acetyl-α-methylglucosaminide, m.p. ~189°.


(III.)

H. W.

Crystalline β-D-gluco-L-talo-octose (syn. D-gluco-α-L-talo-octose). (Miss) A. T. Merrill, R. M. Hann, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1943, **65**, 994—995).—Na–Hg reduces *D*-gluco-*L*-gala- and -*L*-talo-octonolactones to *D*-gluco-*L*-gala- (**I**) and -L-*talo-octose* (**II**), m.p. 117—118° (corr.), $[\alpha]^{20}_{D}$ ~−32°→−6·5° (complex mutarotation; unimol. coeff. decrease during reaction), which give the same osazone. (**I**) and (**II**) give *benziminazole* derivatives, $[\alpha]^{20}_{D}$ −44·7° and +18·6°, respectively, in 0·1N-HCl, and with H_2–Raney Ni give D-*gluco*-L-*gala*-, m.p. 153—154°, $[\alpha]^{20}_{D}$ +2·4° in H_2O (*octa-acetate*, m.p. 141°, $[\alpha]^{20}_{D}$ +20·7° in $CHCl_3$), and -L-*talo-octitol*, m.p. 161°, $[\alpha]^{20}_{D}$ −0·8° in H_2O (*octa-acetate*, m.p. 102°, $[\alpha]^{20}_{D}$ +17·4° in $CHCl_3$). [α] are as expected.

R. S. C.

Synthesis of β-d-glucosides. B. Helferich and J. Goerdeler (*Ber.*, 1940, **73**, [*B*], 532—542).—The course of the reaction between acetobromoglucose (**I**) and $CH_2{:}CH{\cdot}CH_2{\cdot}OH$ (**II**) or $CH_2{:}CH{\cdot}CHMe{\cdot}OH$ (**III**) in $CHCl_3$ containing Ag_2O is followed by distillation of the liquid after fixed intervals and determination of (**II**) or (**III**) in the distillate iodometrically. Without further addition the yield of glucoside attains 91% from (**I**) and (**II**) or 82% from (**I**) and (**III**) with a mol. ratio alcohol : (**I**) = 1 : 3. In both cases addition of $CaCl_2$ is unfavourable probably because of its compound formation with (**II**) or (**III**); simultaneous addition of I is impracticable. Drierite with the reactants in mol. ratio 1 : 1 increases the yield to 80% and 63% respectively with (**II**) and (**III**) against 53% and 39% for the unaided change. The change is usually complete in 30 min.; only in presence of $CaCl_2$ is longer time advisable. Hg_2O, Cu_2O, and Tl_2O do not cause glucoside formation. *βγ-Dibromopropyl-β-d-glucoside* (**IV**), m.p. 101·5—103°, $[\alpha]^{20}_{D}$ −3·8° in H_2O, is obtained by cautious de-acetylation (NaOMe in boiling MeOH) of its tetra-acetate. Its quant. enzymic fission leads to (−)-βγ-dibromopropanol but its optical homogeneity is not established. Fehling's solution is not reduced by glucose in presence of (**IV**) or bromoallylglucoside (**V**). Probably (**V**) loses HBr to give an acetylenyl compound which combines with $Cu^{\cdot}$ formed by the glucose; the resulting compound is rendered H_2O-sol. by adventitous sugar. The free αβ-dibromohydrin gives epibromohydrin, thus explaining the reaction. *dl*-$CH_2{\cdot}CH{\cdot}CHMe{\cdot}OH$ affords *Δβ-butenyl-β-d-glucoside tetra-acetate*, m.p. 96—97° after softening, $[\alpha]^{18}_{D}$ −19·5° in $CHCl_3$, de-acetylated by $Ba(OMe)_2$ to the free *glucoside*, m.p. 101—103°, $[\alpha]^{18}_{D}$ −38·2° in H_2O; this is hydrolysed by almond emulsin to an alcohol, a_D −0·04° (*l* = 1). Ozonisation of allylglucoside tetra-acetate in AcOH followed by reductive hydrolysis (H_2–Pd–$BaSO_4$–AcOH) gives *glycollaldehyde-β-d-glucoside tetra-acetate semicarbazone*, m.p. 202—205° (decomp.), $[\alpha]^{20}_{D}$ −16·1° in AcOH, de-acetylated to *glycollaldehyde-β-d-glucoside semicarbazone*, m.p. 168—169°, $[\alpha]^{20}_{D}$ −31·8° in H_2O; this is converted by PhCHO into the glassy free glucoside. M.p. are corr.

H. W.

Sorbitylglucosides and βγδεζ-pentamethylsorbitol. M. L. Wolfrom and T. S. Gardner (*J. Amer. Chem. Soc.*, 1943, **65**, 750—752).—Gentiobiose +MeOH with H_2–Ni–kieselguhr in H_2O at 150°/163 atm. gives *gentiobiotol* [6-β-d-*glucosido*-l-*sorbitol*] (80%), amorphous, $[\alpha]^{25}_{D}$ −24° in H_2O (*nona-acetate*, m.p. 88—89·5°, $[\alpha]^{26}_{D}$ −11° in $CHCl_3$), which does not reduce Fehling's solution and is hydrolysed by boiling 5% HCl to *l*-sorbitol [$(CHPh{\cdot})_3$ derivative] and *d*-glucose (Et_2 mercaptal). Treating lactitol twice with Me_2SO_4–NaOH and adding the product followed by MeI to Na in Et_2O gives *lactitol Me*$_9$ *ether* (~80%), a syrup, $[\alpha]^{18}_{D}$ −13·5° in $CHCl_3$. *Maltitol Me*$_9$ *ether*, a syrup, $[\alpha]^{24}_{D}$ +89° in $CHCl_3$, is similarly prepared (~80%). *aldehydo-d-*Glucose Me_5 ether with H_2–Raney Ni in EtOH at 175°/163 atm. gives l-*sorbitol βγδεζ-Me*$_5$ *ether*, a syrup, $[\alpha]^{24}_{D}$ +47° in $CHCl_3$ (1-N-α-*naphthylcarbamate*, m.p. 75—76°, $[\alpha]^{22}_{D}$ −5° in $CHCl_3$).

R. S. C.

Saponin of Chinese drug "san-chi." I. C. F. Hsu (*J. Chinese Chem. Soc.*, 1941, **8**, 15—20).—*Saponin A*, $C_{48}H_{80}O_{20}$, the cold $C_5H_{11}{\cdot}OH$-sol. saponin from the EtOH extract of san-chi (0·26% of the drug), has m.p. 200—204° (decomp.), $[\alpha]^{20}_{D}$ +90·35° in H_2O (*deca-acetate*, m.p. 255°), reduces Tollens' reagent but contains no OMe or phenolic group, and is hydrolysed (4% EtOH–HCl) to glucose and a *sapogenin*, $C_{18}H_{29}O_{14}$, m.p. 187—189°.

A. Li.

Position of the branching of the starch chain. K. Freudenberg and H. Boppel (*Ber.*, 1940, **73**, [*B*], 609—620; cf. A., 1942, II, 6).—Hydrolysis of completely methylated starch (A., 1938, II, 51) by 36% HCl at 5° for 4 days gives (mainly) 2 : 3 : 6-trimethylglucose (**I**) (extracted with $CHCl_3$), and a mother-liquor, converted by 1% HCl–MeOH, followed by Ag_2CO_3, into a mixture of glucosides which yields a tri-, b.p. 100—110°/0·1 mm., and a di-methyl-methylglucoside, b.p. 110—125°/0·1 mm. After separating (**I**), $COMe_2$ extracts of the hydrolysis mixture give (after glucosidation) tri- and di-methyl-methylglucoside. Fractions are treated with BzCl–C_5H_5N at 80° and hydrolysed with KOH–MeOH to give dimethyl-methylglucosides *A* and *B*, both of b.p. 120—125°/0·1 mm.; a tetramethyl-methylglucoside, b.p. 85°/0·1 mm., is isolated. 2 : 3-Dimethyl-α-methylglucoside and 2N-HCl at 100° (bath) for 6 hr., followed by azobenzene-p-carboxyl chloride in C_5H_5N at 40°, give 2 : 3-*dimethylglucose tri*-p-*benzeneazobenzoate* (*C*), m.p. 207°, $[\alpha]^{20}_{6252}$ +97·8° in $CHCl_3$, and an *isomeride* (*D*), m.p. 185° (sinters at 180°), $[\alpha]^{20}_{6252}$ +35·4° in $CHCl_3$. *A* affords a dimethylglucose tri-*p*-benzeneazobenzoate, m.p. 195—197°, $[\alpha]^{20}_{6252}$ +49° in $CHCl_3$, probably a mixture of *C* and *D*, whereas *B* yields *C*, $[\alpha]^{20}_{6252}$ +92·5° in $CHCl_3$, and an isomeride, m.p. 184° (sinters from 181°), $[\alpha]^{20}_{6252}$ +57·7° in $CHCl_3$. Although (**I**) is the main product of hydrolysis, methylated starch also affords a little 2 : 6- and 2 : 3-dimethyl-, and 2 : 3 : 4 : 6-tetramethyl-glucose; branching of the starch chain occurs at $OH_{(6)}$. Theoretical aspects are discussed, and photographs of models shown.

A. T. P.

Application of the end-group method to determining the composition of cellulose preparations. K. Hess, D. Grigorescu, E. Steurer, and H. Frahm (*Ber.*, 1940, **73**, [*B*], 505—520).—Since natural, chemically untreated cellulose (**I**) does not afford tetramethylglucose, the end-group method can be used in determining the degradation caused by various technical processes. It is improved by the use of MeOH instead of H_2O for diluting the phosphorylation product which has been decomposed by H_2O and by avoiding diminished pressure in the distillation of light petroleum and Et_2O solutions, a suitable column being used. The products used have been subjected to the following pretreatments : (*a*) mild but thorough alkali boil in absence of air, (*b*) methylation in presence

of alkali and air, (*c*) technical processing in the case of ramie, (*d*) pptn. of (**I**) from alkaline solution, (*e*) pptn. from 65% H_2SO_4, (*f*) action of heat on solutions of methylcellulose in dioxan in presence and absence of air. Even with the best possible exclusion of air treatments (*a*) and (*b*) cause doubling of the end group, which is still more influenced by treatment (*f*). All the technical processes lead to end groups. It is doubtful whether it is justifiable to use the % end group of pretreated celluloses as a means of determining the mean chain length. H. W.

End-group determination of polysaccharides. K. Hess and D. Grigorescu (*Ber.*, 1940, **73**, [*B*], 499—505).—The examination of synthetic mixtures of tri- and tetra-methylmethylglucoside is not regarded as satisfactory for the criticism of Haworth's end-group method. The accuracy of the authors' own method is maintained. H. W.

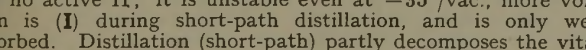
Comparison of end-group determinations and viscosity of cellulose. K. Hess and E. Steurer (*Ber.*, 1940, **73**, [*B*], 669—676).—Discrepancies between the degree of polymerisation of cellulose as determined by end-group (see above) and viscosity (generally gives lower vals.) methods are explained qualitatively by assuming 1 : 5 O bridges between glucose units of neighbouring cellulose chains. Fission of this linking and the normal glucosidic linking determines the effect of degradation on viscosity and end group content. Other evidence (lit.) is adduced in support of the assumption. A comparison of osmotic pressure, viscosity, and end-group content is made on three samples of methylcellulose. J. H. Ba.

Carbamates of cellulose and cellulose acetate. I. Preparation. II. Stability towards hydrolysis. W. M. Hearon, G. D. Hiatt, and C. R. Fordyce (*J. Amer. Chem. Soc.*, 1943, **65**, 829—833, 833—836).—I. Partly hydrolysed cellulose acetate (**I**) scarcely reacts with HNCO and incompletely with MeNCO or EtNCO. Adding an excess of PhNCO–C_5H_5N to (**I**) in dry $HCO{\cdot}NH_2$–C_5H_5N or α-$C_{10}H_7{\cdot}NCO$ (**II**) (excess) to (**I**) in dry C_5H_5N gives completely esterified *products*, sol. in cellulose ester solvents. Use of a deficiency of ArNCO leads to total consumption thereof and gives products containing residual OH and having reduced solubility. Reaction conditions are studied. At 4—50° 10 hr. suffices for complete reaction. HNCO, MeNCO, and EtNCO do not react with cotton linters or regenerated cellulose, but "low-viscosity" cotton linters with PhNCO or (**II**) in C_5H_5N at 100° (not 50°) gives sol. trisubstituted derivatives; <3 mols. of PhNCO give insol., fibrous products (**III**). ArNCO does not react in C_5H_5N at 100° or in quinoline at 150° with cellulose regenerated from the acetate, viscose, or cuprammonium rayon. Presence of H_2O in the reaction mixtures leads to $CO(NHAr)_2$, and pptn. of the very insol. $CO(C_{10}H_7{\cdot}\alpha)_2$ by (**II**) in presence of a little C_5H_5N is a sensitive test for H_2O in solvents.

II. Acid hydrolysis of cellulose acetate arylcarbamates, *e.g.*, by H_2SO_4 in $OMe{\cdot}[CH_2]_2{\cdot}OH$, removes Ac at a const. rate, but does not affect the $NHAr{\cdot}CO_2$ groups; drastic conditions, *e.g.*, 100°, remove all the Ac but degrade the product. In suspension in aq. EtOH, alkali removes Ac rapidly and $NHAr{\cdot}CO_2$ slowly; the resulting cellulose arylcarbamates are sol. in the usual solvents, in contrast to (**III**). R. S. C.

III.—HOMOCYCLIC.

Anhydro- ("cyclised") vitamin-*A*. E. M. Shantz, J. D. Cawley, and N. D. Embree (*J. Amer. Chem. Soc.*, 1943, **65**, 901—906).—When vitamin-*A* (**I**) is treated in dil. solution with 0·033N-HCl–EtOH (cf. Edisbury *et al.*, A., 1932, 1174) (conc. solutions give mixed polymerides) and the product is purified by adsorption, it rapidly yields *anhydrovitamin*-A (**II**), m.p. 76—77°, having absorption max. at 351, 371, and 392 mμ. ($E^{1\%}_{1\,cm.}$ 2500, 3650, and 3180, respectively) and giving with $SbCl_3$ a max. at 620 mμ. ($E^{1\%}_{1\,cm.}$ 5500); longer interaction gives *iso*anhydrovitamin-*A*. having absorption max. at ~330, 350, and 370 mμ. Probably, (**II**) is $C_{20}H_{28}$, having 6 C:C and no active H; it is unstable even at −35°/vac., more volatile than is (**I**) during short-path distillation, and is only weakly adsorbed. Distillation (short-path) partly decomposes the vitamin esters into (**II**). Three structures are suggested, the annexed being favoured. Formation of (**II**) is useful for determining mixtures of



vitamin-A_1 and -A_2 [anhydro-A_2 being more strongly adsorbed than is (**II**)] and for determining vitamin-*A* when other substances interfere, *e.g.*, in blood plasma. R. S. C.

Carotenoid pigments of fruit of *Celastrus scandens*.—See A., 1943, III, 540.

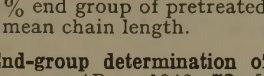
Thermodynamics and molecular structure of benzene and its methyl derivatives.—See A., 1943, I, 218, 223.

Kinetics of aromatic hydrogenation. I. Bromination. II. Chlorination of hydrocarbons.—See A., 1943, I, 231.

Electrolytic reduction of arylacetylenes.—See A., 1943, II, 249.

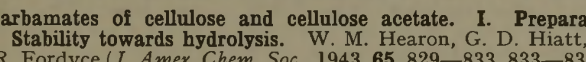
Formation of biradicals in the non-catalysed polymerisation of styrene. G. Goldfinger, H. Naidus, and H. Mark (*J. Amer. Chem. Soc.*, 1943, **65**, 995—996).—$CHPh{:}CH_2$ reacts with quinol at 150° giving PhMe and p-$O{:}C_6H_4{:}O$ (not isolated), probably by activation to give $\cdot CHPh{\cdot}CH_2\cdot$. R. S. C.

Polymerisation of styrene in presence of nitrobenzene, 2 : 4-dinitrochlorobenzene, and nitromethane. C. C. Price and (Miss) D. A. Durham (*J. Amer. Chem. Soc.*, 1943, **65**, 757—759).—$CHPh{:}CH_2$ with Bz_2O_2 and 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$ (**I**) at 95—86° gives *polymers*, $OBz{\cdot}(C_8H_8)_{10}O_2{\cdot}C_6H_2Cl(NO_2)_2$, $OBz{\cdot}(C_8H_8)_8O{\cdot}C_6H_2Cl(NO_2)_2$, and $OBz{\cdot}(C_8H_8)_7O{\cdot}C_6H_2Cl(NO_2)_2$, but use of less (**I**) leads to a *polymer* containing <1 residue thereof per mol. Polymerisation in presence of Bz_2O_2 and $PhNO_2$ leads similarly to inclusion of both in the mol. This is due to interaction of the free radical to give radicals such as



, which are stabilised by resonance. When this resonance is impossible, *e.g.*, in $MeNO_2$, the NO_2-compound is not included in the polymer. $MeNO_2$ also does not react at 100° with Bz_2O_2, which therein yields only BzOH and Ph_2. R. S. C.

Disproportionation of diphenyl-*o*-tolylmethyl. P. W. Selwood and R. F. Preckel (*J. Amer. Chem. Soc.*, 1943, **65**, 895—899).—Disproportionation of (o-$C_6H_4Me{\cdot}CPh_2)_2$ at 80° and 95° is shown by magnetic measurements to be a second-order reaction having an activation energy 11·4 kg.-cal. per mol. of free radical. During the reaction absorption bands between 4200 and 5300 A. disappear but those in the orange and red are unaffected; the absorption also becomes independent of temp. The mol. wt. (ebullioscopic) in C_6H_6 appears to double during disproportionation. It is suggested that the reaction occurs by way of



, which then yields o-$C_6H_4Me{\cdot}CHPh_2$ and o-$CH_2{:}C_6H_4{:}CPh_2$. R. S. C.

Sesquiterpenes. LVIII. 4 : 8-Dimethyl-6-*iso*propylazulene. P. A. Plattner and H. Roniger (*Helv. Chim. Acta*, 1943, **26**, 905—912).—Et 4 : 8-dimethylazulene-6-carboxylate is converted by a considerable excess of MgMeI in Et_2O into 4 : 8-*dimethyl*-6-*hydroxy*iso*propylazulene* (**I**), m.p. 54° [additive *compound*, m.p. 170°, with 1 : 3 : 5-$C_6H_3(NO_2)_3$; does not give a stable picrate], with (?) 6-acetyl-4 : 8-dimethylazulene, characterised as the *semicarbazone*, m.p. ~212°. (**I**) is converted by HCO_2H at 100° into 4 : 8-*dimethyl*-6-iso*propenylazulene* (**II**), m.p. 70—71° [additive *compound*, m.p. 132°, with 1 : 3 : 5-$C_6H_3(NO_2)_3$]. Hydrogenation (Pd–C in EtOH) of (**II**) leads to 4 : 8-*dimethyl*-6-iso*propylazulene* (**III**), m.p. 39° [*picrate*, m.p. 145°; additive *compound*, m.p. 173—173·5°, with 1 : 3 : 5-$C_6H_3(NO_2)_3$]. Spectroscopically (**III**) falls into line with the other alkylazulenes (A., 1942, II, 191). M.p. are corr. H. W.

Condensation of amino-alcohols with benzene. C. M. Suter and A. W. Ruddy (*J. Amer. Chem. Soc.*, 1943, **65**, 762—763).—$OH{\cdot}CMe_2{\cdot}CHR'{\cdot}NHR$ with C_6H_6 and $AlCl_3$ (excess) at room temp. (exothermally) and then the b.p. give $CPhMe_2{\cdot}CH_2{\cdot}NHR$ [R = H, b.p. 87—89°/10 mm., Me, b.p. 92—92·5°/11 mm., or Et, b.p. 96—98°/11 mm. (hydrochloride, m.p. 191·5—192·5°)], $CPhMe_2{\cdot}CHMe{\cdot}NHR$ [R = H, b.p. 100—102°/10 mm. (hydrochloride, m.p. 214—215°), and Me, b.p. 99—100·5°/9 mm. (*hydrochloride*, m.p. 230—231°], and $CPhMe_2{\cdot}CMe_2{\cdot}NH_2$, b.p. 123—126°/14 mm. (*hydrochloride*, m.p. 207—210°). $NH_2{\cdot}CH_2{\cdot}CHMe{\cdot}OH$ and $NH_2{\cdot}[CH_2]_2{\cdot}OH$ do not react thus. *γ-Methylamino-β-methylbutan-β-ol*, b.p. 152—155°/750 mm., is obtained (85% yield) from trimethylethylene oxide and 33% NH_2Me at 100°. R. S. C.

Sulphur studies. XIX. Alkyl esters of phenylthiocarbamic acid. R. W. Bost and E. R. Andrews (*J. Amer. Chem. Soc.*, 1943, **65**, 900—901; cf. A., 1942, II, 284).—ArNCS in boiling AlkOH gives 31—90% of $NHAr{\cdot}CS{\cdot}OR$. When AlkOH is readily dehydrated [*e.g.*, $CH_2{:}CH{\cdot}CH_2{\cdot}OH$, $Bu^{\gamma}OH$, $(CH_2{\cdot}OH)_2$, $OH{\cdot}CHMe{\cdot}CH_2{\cdot}OH$, tetraethylhexanediol, pinacol], only $CS(NHPh)_2$ is thus obtained; the esters are then prepared from AlkONa and ArNCS. *Bu*$^{\alpha}$, m.p. 51—53°, *Bu*$^{\gamma}$, m.p. 86·5°, n-, m.p. 49—50°, and iso-*amyl*, m.p. 44—46°, n-*heptyl*, m.p. 34°, n-*octyl*, m.p. 41—43°, n-*nonyl*, m.p. 45—47°, *β-phenylethyl*, m.p. 89·5°, *γ-phenyl*-n-*propyl*, m.p. 74°, and *allyl* *N-phenylthiocarbamate*, m.p. 75—77°, are described. 20 thiocarbamates are non-hypnotic, possibly because of their insolubility in H_2O. R. S. C.

***N*-Nitrosoacet-1-naphthalide.** H. H. Hodgson and E. Marsden (*J.C.S.*, 1943, 285).—*N-Nitrosoacet*-1-*naphthalide*, m.p. 8—10°, is formed when α-$C_{10}H_7{\cdot}NHAc$ in AcOH is added to $NO{\cdot}SO_4H$. Its reactions are similar to those of a diazonium compound in mineral acid (*e.g.*, Sandmeyer) and a diazo-compound in neutral, weak acid, and alkaline solution. F. R. S.

Identification of carboxylic acids as ureides with the help of carbodi-imides. VIII. Ureides of *symm.* di-*p*-diethylaminophenylcarbamide. F. Zetzsche and G. Röttger. **IX. Preparation of carbodi-imides from thiocarbamides.** F. Zetzsche and W. Nerger [with, in part, G. Röttger and A. Fredrich] (*Ber.*, 1940, **73**, [*B*], 465—467, 467—477).—VIII. Replacement of Me of *N*-acyl-*NN'*-di-

p-dimethylaminophenylcarbamides by Et causes a not very pronounced darkening of colour, a lowering of the m.p., and a very marked increase in solubility. $CHMe{:}CH{\cdot}CO_2H$ and the imide in Et_2O afford *N-crotonyl-NN'-di-p-diethylaminophenylcarbamide*, m.p. 130—132°. The corresponding *ureides* of cinnamic, m.p. 83°, tiglic, m.p. 106—108°, atropic, m.p. 124·5—126·5°, benzoic, m.p. 121·5° (softens at 119°), and β-pyrenoylpropionic (**I**), m.p. 159°, and the *diureide*, m.p. 151° and 210° after resolidifying at 152°, of fumaric acid are obtained analogously. The methylureide of (**I**) has m.p. 162—163° (softens at 159°) (cf. A., 1939, II, 467).

IX. In comparison with ordinary PbO, the highly disperse material ("tegoglätte") accelerates the desulphurisation of arylthiocarbamides (**II**) to carbodiarylimides (**III**). Increase in the reacting surface also favours the subsequent conversion of (**III**) into carbamides or resinous products. These primary and secondary reactions are also accelerated by H_2O. S accelerates the primary reactions and also decelerates the secondary changes; it largely counteracts the effect of H_2O. As long as (**II**) is present in the system it fulfils the rôle of S towards the subsidiary reactions. A solvent miscible with H_2O is very desirable but only $COMe_2$ appears completely suitable; COMeEt is generally similar but the higher b.p. diminishes the restricting action of S on the production of carbamides. "Tegomennige" is serviceable. Se appears to resemble S in its action. The course of the change depends greatly on the purity of (**II**) and the prep. of standard $CS(NH{\cdot}C_6H_4{\cdot}NMe_2\text{-}p)_2$ is fully described. The prep. of small and large amounts of $C(:N{\cdot}C_6H_4Me\text{-}p)_2$ and $C(:N{\cdot}C_6H_4{\cdot}NMe_2\text{-}p)_2$ is detailed. *Carbodi-*p*-diethylaminophenylimide* has m.p. 81—82°, softens at 79°. *N'-Benzeneazo-N-phenylcarbodi-imide*, m.p. 60—64°, gives the corresponding *benzoylureide*, m.p. 117—118° and 156—157° after resolidification at 122°, and *cinnamureide*, m.p. 117—118° and 140° after partial resolidification at 130°. H. W.

Partial hydrolysis of N^1N^4-diacetylsulphanilamide. Preparation of N^1-acetylsulphanilamide. H. Minlon and C. P. Lo (*J. Chinese Chem. Soc.*, 1942, **9**, 61—65).—*p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ and Ac_2O–AcOH give *p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2{\cdot}NHAc$, m.p. 258—259°, hydrolysed by boiling 10% KOH–EtOH to *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NHAc$, m.p. 181—182°. $(:N{\cdot}C_6H_4{\cdot}SO_2{\cdot}NHAc\text{-}p)_2$ is similarly unchanged, but is hydrolysed by boiling 10% aq. KOH to the diamide. A. T. P.

N^4-(β-Acylamino-β-carboxyethylthiolmethyl)sulphanil-hydroxylamides and -β-hydroxyethylamides.—See B., 1943, III, 193.

Sulphanilylalkylguanidines.—See B., 1943, II, 243.

Identification of sulphonic acid reduction products of azo-dyes. P. Chen and E. J. Cross (*J. Soc. Dyers & Col.*, 1943, **59**, 144—148).—Monosulphonic acids of NH_2Ph, α- and $\beta\text{-}C_{10}H_7{\cdot}NH_2$, 1 : 2- and 1 : 4-$C_{10}H_6(NH_2)_2$, and $NH_2{\cdot}C_{10}H_6{\cdot}OH$ are identified as the C_5H_5N salts of their Ac derivatives; the salts are stable, can be cryst. from EtOH, and have sharp m.p. *E.g.*, the dry, finely-powdered sulphonic acid (2 g.) is stirred with C_5H_5N (1·2) and Ac_2O (2·5 c.c.), whereupon exothermic dissolution occurs; the solution is then diluted with EtOH, the solid is collected, washed with EtOH, and recryst. The salts are very sol. in H_2O, some being hygroscopic, and they are convertible by double decomp. into known arylamine salts, *e.g.*, by adding *p*-toluidine to the hot aq. solution. In some cases where C_5H_5N salts could not be made the sulphonic acid was heated with C_5H_5N and *o*-$C_6H_4(CO)_2O$, giving C_5H_5N phthalanilsulphonates. The following are described: *C_5H_5N phthalanil-2'-*, m.p. 236—237°, *-3'-*, m.p. 219—220°, and *-4'-sulphonate*, m.p. 225—226°; C_5H_5N acetanilide-4-sulphonate, m.p. 183—184°; *p*-toluidinium 1-acetamidonaphthalene-2-, m.p. 205—206°, 2-acetamidonaphthalene-1-, m.p. 178—179°, -5-, m.p. 118—119°, and -7-sulphonate, m.p. >300° (softens 260°); C_5H_5N 1-acetamidonaphthalene-4-, m.p. 175—176°, -5-, m.p. 194—195°, -6-, m.p. 157—158°, -7-, m.p. 196—197°, 2-acetamidonaphthalene-6-, m.p. 171—172°, and -8-sulphonate, m.p. 183—184°; C_5H_5N 2-phthalimidonaphthalene-5-sulphonate, m.p. 255—256° (softens 245°); C_5H_5N 1 : 2-diacetamidonaphthalene-4-, m.p. 223—224°, -5-, m.p. >300°, -6-, m.p. 229—230°, and 1 : 4-diacetamidonaphthalene-6-sulphonate, m.p. 247—248° (decomp.); *p*-toluidinium 1 : 2-diacetamidonaphthalene-4-, m.p. 213—214° (decomp.) (softens 195°), -5-, m.p. 188—189° (decomp.) (softens 174°), and -6-sulphonate, m.p. 249—250° (decomp.); *C_5H_5N ON-diacetyl*-1 : 2 : 4-, m.p. 194—195°, -1 : 8 : 4-, m.p. 203—204° (decomp.), -2 : 1 : 4-, m.p. 181—182°, and -2 : 1 : 5-*aminonaphtholsulphonate*, m.p. 196—197°; C_5H_5N 2 : 8 : 6-, m.p. 245—246°, and 2 : 5 : 7-*acetamidonaphtholsulphonate*, m.p. 190—191°; *p-toluidinium ON-diacetyl*-1 : 2 : 4-, m.p. 213—214° (decomp.), -1 : 2 : 6-, m.p. 209—210°, and -2 : 8 : 6-*aminonaphtholsulphonate*, m.p. 230—231°, and 2-*acetamido*-8-*naphthol*-6-*sulphonate*, m.p. 282—283°. K. H. S.

Behaviour of azobenzene and hydrazobenzene towards methyl iodide; the benzidine transformation. A. Pongratz and H. Wüstner (*Ber.*, 1940, **73**, [*B*], 423—429).—$(:NPh)_2$ is converted by MeI at 100° into *tetramethylbenzidine dimethiodide tetraiodide* (**I**), incipient carbonisation at 320°, transformed by aq. $NaHSO_3$ into *tetramethylbenzidine dimethiodide* (+1—$2H_2O$), m.p. 250—252° to 262—266°, which with KOH–EtOH yields $(C_6H_4{\cdot}NMe_2)_2$, new m.p. 190—191·7°. (**I**) is also obtained from $(NHPh)_2$ and MeI or MeOH–MeI at 100° whereas $(C_6H_4{\cdot}NH_2)_2$ and MeI in absence of MeOH afford $(C_6H_4{\cdot}NMe_2)_2$,MeI (**II**). The isomerisation of $(:NPh)_2$ or $(NHPh)_2$ to derivatives of $(C_6H_4{\cdot}NH_2)_2$ (by MeI) shows that Me does not become attached to N by subsequent methylation but is added to the N:N or NH·NH bridge previous to isomerisation with formation of salt-like compounds. The production of (**II**) but not (**I**) from $(C_6H_4{\cdot}NH_2)_2$ shows the distinction between methylation of preformed NH_2 groups and the "primary methylation." The formation of an additional intermediate is supported by Wieland's isolation of $(NHPh)_2$,2HCl. H. W.

Substituted azobenzene-4 : 4'-disulphonamides. H. Minlon, C. P. Lo, and L. J. Y. Chu (*J. Chinese Chem. Soc.*, 1942, **9**, 57—60).—$(:N{\cdot}C_6H_4{\cdot}SO_2Cl\text{-}p)_2$ and the respective amine yield azobenzene-4 : 4'-disulphon-amide, m.p. 312° (*s*-Ac_2 derivative, m.p. 273°), -diethyl-, m.p. 171—172°, -dipropyl-, m.p. 140—150°, -benzyl-, m.p. 252—253°, and -2-pyridyl-amide, m.p. 274—276°, -anilide, m.p. 255—256°, and -anilide-*p*-sulphonamide, m.p. 310°. A. T. P.

Azo-compounds and their intermediates. XXIV. Hydrazo-compounds of di(benzeneazo)diphenyl. P. Ruggli and K. Hölzle (*Helv. Chim. Acta*, 1943, **26**, 814—832; cf. A., 1943, II, 158).—4 : 4'-Di(benzeneazo)diphenyl (**I**) [prep. from benzidine (**II**) and PhNO described] absorbs 4 H (Raney Ni in EtOH or dioxan) whereby one half remains unchanged and the other half is converted into NH_2Ph and (**II**). The result is ascribed to the sparing solubility of (**I**). Addition of AcOH to (**I**) in C_5H_5N containing Zn dust under CO_2 affords 4 : 4'-*di*(*phenylhydrazino*)*diphenyl* (**III**), m.p. 177—178° (slight decomp.) after becoming yellow, which becomes superficially yellow within a few min. in air but can be preserved for some days in a high vac. In C_5H_5N it is rapidly converted by air into (**I**). Under different conditions (**III**) suffers intramol. disproportionation into *p*-$PhN_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH_2\text{-}p$ and NH_2Ph or extramol. disproportionation to (**I**), (**II**), and NH_2Ph. In C_5H_5N under CO_2 2N-HCl causes 88% of intramol. and 4% of extramol. disproportionation whereas with a small excess of AcOH the figures are 65% and 15%. AcSH causes 58% intramol. disproportionation with acetylation of the fragments. The Ac_2 derivative, m.p. 235° (carbonisation), of (**III**) is obtained in poor yield by protracted action of a little Ac_2O in cold $COMe_2$–C_5H_5N; reductive fission slowly yields $(C_6H_4{\cdot}NHAc\text{-}p)_2$ and NH_2Ph. Cautious treatment of (**III**) with conc. H_2SO_4 causes much decomp.; acetylation of the product gives only $PhN_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NHAc$. (**III**), Sn, and HCl afford only (**II**) and NH_2Ph (mol. ratio 1 : 2). Above its m.p. (**III**) passes into (**I**), (**II**), and NH_2Ph. *4-Amino-4'-benzeneazodiphenyl* (**IV**), m.p. 151—152°, obtained in the above disproportionations, is prepared by the condensation of (**II**) with PhNO (1 mol.) or by reduction of 4-nitro-4'-benzeneazodiphenyl (**V**) with Na_2S in boiling EtOH–dioxan; the *CHPh:*, m.p. 226°, p-*OMe*·$C_6H_4{\cdot}CH$:, m.p. 214—215°, and *Ac* derivative, m.p. 236—237°, of (**IV**) are described. Contrary to Vorländer *et al.* (A., 1925, i, 1253), reduction of (**V**) by $(NH_4)_2S$ gives *4-nitro-4'-phenylhydrazinodiphenyl*, m.p. 164—165° (*Ac* derivative, m.p. 161°), converted by air into (**V**). Under defined conditions (**I**) is reduced by Zn dust and AcOH in C_5H_5N to *4-phenylhydrazino-4'-benzeneazodiphenyl* (**VI**), m.p. 172—173°, converted by Ac_2O in boiling C_5H_5N into *Ac* derivatives (**VII**) $PhN_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NAc{\cdot}NHPh$, m.p. 244°, and (**VIII**) $PhN_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH{\cdot}NPhAc$, m.p. 194—195°. (**VII**) is hydrogenated in dioxan to NH_2Ph and *4-amino-4'-α-acetyl-β-phenylhydrazinodiphenyl*, m.p. 220°, which is further hydrogenated to $NH_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NHAc$, whereas (**VIII**) affords NH_2Ph, (**II**), and NHPhAc. (**VI**) is converted by HCl in $COMe_2$ at 20—30° into NH_2Ph, (**I**), and (**IV**). (**III**) and $(:C{\cdot}CO_2Me)_2$ give an *adduct*, m.p. 124—125°. H. W.

Manufacture of thymol.—See B., 1943, II, 244.

Bromination of 4-diphenylyl bromoacetate. L. C. Hensley and S. E. Hazlet (*J. Amer. Chem. Soc.*, 1943, **65**, 987—988; cf. A., 1943, II, 59).—*3-Bromo-*, m.p. 55—56°, 3 : 5-*dibromo-*, m.p. 78—79°, 3 : 5 : 4'-*tribromo-*, m.p. 148—149°, and *4'-bromo-* (**I**), m.p. 141·5—142°, *-4-diphenylyl bromoacetate* are prepared from the phenol, $CH_2Br{\cdot}COBr$, and C_5H_5N in dioxan. $CH_2Br{\cdot}CO_2{\cdot}C_6H_4Ph\text{-}p$, Br, and a trace of Fe powder in AcOH (analytical grade) give *p*-$C_6H_4Ph{\cdot}OAc$ and a little *p*-$C_6H_4Ph{\cdot}OH$ (**II**), 4 : 2 : 6 : 1-$C_6H_2PhBr_2{\cdot}OH$, and 1 : 2 : 6 : 4-$OH{\cdot}C_6H_2Br_2{\cdot}C_6H_4Br\text{-}p$, but in highly purified AcOH no bromination occurs [a little (**II**) is formed]; in CCl_4, (**I**) is obtained. R. S. C.

Peroxide degradation of substituted aromatic aldehydes and ketones to the corresponding phenol. A. von Wacek and H. O. Eppinger (*Ber.*, 1940, **73**, [*B*], 644—651).—Although *o*-$OH{\cdot}C_6H_4{\cdot}CHO$ (**I**) and 30% H_2O_2 at 60—80°, alone or in $COMe_2$ (in absence or presence of Pd), yield 60—70% of *o*-$OH{\cdot}C_6H_4{\cdot}CO_2H$ (**II**) and only traces of *o*-$C_6H_4(OH)_2$ (**III**), in boiling AcOH 90% of (**III**), a little resin, and no (**II**) result. In boiling C_5H_5N, 75% of (**II**) and 25% of (**III**) are formed, but only traces of (**III**) from (**I**)–H_2O_2–$COMe_2$ at 120° in a sealed tube. *o-* (**IV**), *m-* (**V**), or *p*-$OMe{\cdot}C_6H_4{\cdot}CHO$ (**VI**) and aq. H_2O_2–NaOH give negative reactions, as also does (**V**) and O_3. (**IV**) and O_3–$CHCl_3$, however, yield ~3% of *o*-$OMe{\cdot}C_6H_4{\cdot}OH$ and (mainly) *o*-$OMe{\cdot}C_6H_4{\cdot}CO_2H$; (**VI**) and *p*-$OMe{\cdot}C_6H_4{\cdot}COMe$ similarly give 4—5% of *p*-$OMe{\cdot}C_6H_4{\cdot}OH$. 7-Hydroxy-1-hydrindone is similarly

unchanged. A probable reaction mechanism is, *e.g.*, (**I**) → *o*-CHO·C_6H_4·O·OH → *o*-OH·C_6H_4·O·CHO → (**III**). A. T. P.

Introduction of allyl residues into aromatic compounds. P. Karrer and E. Schick (*Helv. Chim. Acta*, 1943, **26**, 800—807).—Among Me-substituted derivatives of dihydric phenols those of quinol occupy a favoured position with regard to reactivity towards allyl halides. The corresponding *C*-Me derivatives of *o*- and *m*-$C_6H_4(OH)_2$ react with allyl halides and $ZnCl_2$ as catalyst only slightly if at all to give coumaran or chroman derivatives. 2 : 4 : 6 : 1-$(OH)_2C_6H_2Me$·CH:NPh is reduced (H_2 at 117—120°/20 atm.–Pd–C–$COMe_2$) to 4 : 5-*dimethylresorcinol* (**I**), m.p. 134—135°. 2 : 4 : 5 : 6 : 1-$(OH)_2C_6HMe_2$·CHO, m.p. 196° [prep. from 4 : 5 : 1 : 3-$C_6H_2Me_2(OH)_2$ described], is converted into the *anil*, m.p. 188°, which is reduced to 4 : 5 : 6 : 1 : 3-$C_6HMe_3(OH)_2$ (**II**), m.p. 163°. (**I**) gives no definite product with CH_2:CH·CH_2Br and $ZnCl_2$ in C_6H_6 whilst (**II**) gives traces of a compound, m.p. 120—121°, possibly a hydroxytetramethylcoumaran. Veratraldehydeanil is hydrogenated to homoveratrole, converted (HCN–$AlCl_3$ in C_6H_6) into 6-methylveratraldehyde; this gives an anil, m.p. 92·5—93·5°, hydrogenated to 4 : 5-*dimethylveratrole*, b.p. 120—121°/13 mm., m.p. 43—43·5°, into which CHO could not be introduced by HCN–$AlCl_3$–HCl. 4 : 5 : 1 : 2-$C_6H_2Me_2(OH)_2$ appears to be converted by CH_2:CH·CH_2Br and anhyd. $ZnCl_2$ in warm C_6H_6 into 6-hydroxy-1 : 3 : 4-trimethyl-5-allylcoumaran, isolated as the *allophanate*, m.p. ~166—169°. 4 : 5-*Dimethylguaiacol* has m.p. 67—68°. H. W.

4 : 4′-Dihydroxy-3 : 3′-di*cyclo*hexyldiphenyl.—See B., 1943, II, 244.

Reaction of phenols with acetylene. H. von Euler, E. Adler, and J. O. Cedwall (*Arkiv Kemi, Min., Geol.*, 1942, **15**, **A**, No. 19, 10 pp.).—*m*-4-Xylenol (**I**) and C_2H_2 in MeOH–$HgSO_4$–conc. H_2SO_4 (less well in EtOH) at 60—70° give *αα-di-*(2-*hydroxy*-3 : 5-*dimethylphenyl*)*ethane* (**II**) (~100%), m.p. 135—135·5° (*diacetate*, m.p. 93—94°) [also obtained from (**I**) and MeCHO in EtOH–conc. HCl)]. Addition of (**I**) (as above but in EtOH at 70—80°) with C_2H_2 always in excess, gave a fraction, b.p. 100—105°/12 mm., in which the expected intermediate 1 : 2 : 4 : 6-OH·$C_6H_2Me_2$·CH:CH_2 was detected but could not be isolated. (**I**) and C_2H_2 in AcOH–$HgSO_4$ at 60—70° give (**II**) and the cyclic *CHMe*:*ether* (**III**), m.p. 185·5—186·5°, of (**II**). (**III**) with dry HBr in $CHCl_3$ at room temp. gives (**II**). (**III**) is also obtained from C_2H_2 and (**II**) in AcOH–$HgSO_4$ at 90°, and from (**II**) and $CHMeCl_2$ with KOH–50% EtOH (1 hr. at 120° in sealed tube; 2% yield). M. H. M. A.

γ-Alkylamino- and γ-alkoxy-α-aryloxypropan-β-ols and -β-ones.—See B., 1943, II, 244.

Synthesis of methoxy-methylenedioxydiphenyls and a new fluorenone cyclisation. S. Uyeo (*Ber.*, 1940, **73**, [*B*], 661—669).—5-Bromopiperonal (**I**), *o*-C_6H_4I·OMe, and Cu at 220—230° give (2-OMe·$C_6H_4)_2$ and 2-methoxy-2′ : 3′-methylenedioxydiphenyl-5′-aldehyde, b.p. 185—190°/1·5 mm.; the latter with $KMnO_4$–$COMe_2$ at 50° gives the corresponding 5′-*carboxylic acid*, m.p. 233°, converted by quinoline–Cu chromite (Adkins) into 2-*methoxy*-2′ : 3′-*methylenedioxydiphenyl*, m.p. 103·5—104°. (**I**) and *p*-C_6H_4I·OMe afford 4-*methoxy*-2′ : 3′-*methylenedioxydiphenyl*-5′-*aldehyde*, m.p. 143°, and -5′-*carboxylic acid*, m.p. 261—262°, and thence 4-*methoxy*-2′ : 3′-*methylenedioxydiphenyl*, m.p. 128—129°. 6-Bromopiperonal and *o*- or *p*-C_6H_4I·OMe yield 2- (**II**), m.p. 142°, or 4-*methoxy*-3′ : 4′-*methylenedioxydiphenyl*-6′-*aldehyde* (**III**), m.p. 105—106°, the corresponding *acids*, m.p. 201—202° resolidifying with m.p. 206—207°, or 225—226°, and thence 2-, m.p. 56—57°, or 4-*methoxy*-3′ : 4′-*methylenedioxydiphenyl*, m.p. 97—98°, respectively. In preparing (**II**) and (**III**), chromatographic separation of the reaction products yields 4- (**IV**), m.p. 175—177° [*oxime*, m.p. 264° (decomp.)], and 2-*methoxy*-6 : 7-*methylenedioxyfluorenone*, m.p. 188° [*oxime*, m.p. 218—219° (decomp.)], respectively. (**IV**) is also obtained from (**II**) and Cu at 230—240°. A. T. P.

ββ-Dimesitylvinyl alcohol. R. C. Fuson and S. P. Rowland (*J. Amer. Chem. Soc.*, 1943, **65**, 992—993).—Hydro- or *iso*hydromesitoin with dehydrating agents gives *ββ-dimesitylvinyl alcohol* (**I**) (60%), m.p. 128—129°, which with MgMeI gives 1 mol. of CH_4, gives an acetate, benzoate, and Me ether which regenerate (**I**) on hydrolysis, has infra-red absorption max. at 2·77 and 2·84 μ. in CCl_4, is stable to heat and O_2, and with alkaline H_2O_2 gives dimesityl ketone. R. S. C.

Possible new member of the vitamin-A_1 and -A_2 group. N. D. Embree and E. M. Shantz (*J. Amer. Chem. Soc.*, 1943, **65**, 906—909).—The more volatile (short-path distillation) portion of the unsaponifiable fraction of shark-liver oil is extracted in 83% EtOH by light petroleum; the material from the EtOH is adsorbed from C_6H_6 on Al_2O_3 and developed by Et_2O–light petroleum; the yellow zone immediately below the top (light-brown) one yields subvitamin-*A* (**I**), which has an absorption max. at 290 mμ., gives a $SbCl_3$ colour with a max. at 617 mμ., is relatively sol. in 83% EtOH, and has little or no -*A* activity. Dehydration of the original oil or of (**I**) leads to anhydrosubvitamin-*A* (**II**), which has absorption max. at 332, 348, and 367 mμ. and is absorbed much more strongly than is anhydrovitamin-A_1 and slightly more strongly than is anhydrovitamin-A_2. Elimination temp. (short-path distillation) of (**I**), anhydrovitamin-A_1 and -A_2 are, respectively, 15° above, 19° and 1° below, and that of (**II**) is the same as, that of celanthrene-red dye (123°). (**I**) is probably an oxygenated derivative of vitamin-A_1 or -A_2 but has one less ethylenic linking. R. S. C.

Kitol, a new provitamin-*A*. N. D. Embree and E. M. Shantz (*J. Amer. Chem. Soc.*, 1943, **65**, 910—913).—*Kitol* (**I**) is isolated from the less volatile "vitamin fractions" of whale-liver oil and in small amounts from commercial shark- and lamb-liver oil. It is probably $C_{40}H_{58}(OH)_2$, contains 8 C:C, gives a *bisdinitrobenzoate*, m.p. 200°, has $[\alpha]_{5461}^{25}$ −1·35° in $CHCl_3$, gives no anhydro-derivative, has an absorption max. at 286 mμ. ($E_{1\,cm.}^{1\%}$ 580) ($SbCl_3$ max. at 428 mμ.), has little or no biological activity, but when pyrolysed yields vitamin-*A* (1 mol. per mol.). It is thus a true provitamin. The liver oil of northern pike probably contains kitol$_2$, a provitamin-A_2 (absorption max. at 310 mμ.; $SbCl_3$ max. at 510 mμ.). R. S. C.

Photo-reactions. VI. Formation of benzpinacol by the action of acetone on benzhydrol in sunlight. A. Schönberg and A. Mostafa (*J.C.S.*, 1943, 276).—The reaction $2CHPh_2$·OH + $COMe_2$ (or COMeEt) → $(CPh_2$·$OH)_2$ + Pr$^{\beta}$OH (or CHMeEt·OH) occurs in sunlight in absence of air. F. R. S.

[β-]Phenyl- and [β-]benzyl-thiolpropionic acids and their oxidation products. B. Holmberg and E. Schjanberg (*Arkiv Kemi, Min., Geol.*, 1942, **15**, **A**, No. 20, 14 pp.; cf. A., 1943, II, 157).—PhSNa and I·$[CH_2]_2$·CO_2H, or PhSH (**I**) and CH_2:CH·CO_2H (**II**), give *β-phenylthiolpropionic acid* (**III**), m.p. 60—61°, decomposed by aq. NaOH at 100° to (**I**) and (**II**). (**III**) and CH_2Br·CO_2Na give SPh·CH_2·CO_2Na and (**II**), presumably via Ph·$S^+(CH_2$·$CO_2^-)$·$[CH_2]_2$·CO_2Na which could not be isolated. (**III**) is oxidised (Na_2O_2) to *β-phenylsulphinylpropionic acid* (**IV**), m.p. 97—99°, which reacts with aq. NaOH at 100° thus: (**IV**) → Ph·SOH (**V**) + (**II**); 3(**V**) → $PhSO_2H$ (**VI**) + Ph_2S_2 (isolated) + H_2O; (**VI**) + (**II**) → $PhSO_2$·$[CH_2]_2$·CO_2H (**VII**) (isolated). (**VII**), from (**IV**) with Br–NaOH or $KMnO_4$, or from (**VI**) and (**II**), has m.p. 125·5—127° (cf. A., 1888, 360) (*mono-*, m.p. 58—60°, clear at ~90°, and *tri-hydrate*, m.p. 65—67°) (cf. A., 1908, i, 21). (**VII**) is stable to 2N-HCl (4 hr. at 100°), but with dil. NaOH gives (**II**) and (**VI**). CH_2Ph·S·$[CH_2]_2$·CO_2H, like (**III**), forms a thetine which could not be isolated, and is oxidised (H_2O_2 or $K_2S_2O_8$) to *β-benzylsulphinylpropionic acid*, m.p. 149—150° (decomp.), which with NaOH aq. at 100° gives (S·$CH_2Ph)_2$ and CH_2Ph·SO_2·$[CH_2]_2$·CO_2H by reactions similar to those of (**IV**). M. H. M. A.

Phenylethylthiolpropionic acids and related compounds. B. Holmberg (*Arkiv Kemi, Min., Geol.*, 1942, **15**, **A**, No. 21, 16 pp.; cf. A., 1939, II, 158, 546; 1942, II, 157).—CHPhMe·OH and SH·$[CH_2]_2$·CO_2H (**I**) give (4 hr. at 100°) dl-*β-α′-phenylethylthiolpropionic acid* (**II**), m.p. 58—59°. CH_2Ph·CH_2·SNa and I·$[CH_2]_2$·CO_2H with HCl (2 days at room temp.) or CHPh:CH_2 and (**I**) (3 days at room temp.) give *β-β′-phenylethylthiolpropionic acid* (**III**), m.p. 46—47°. (**II**) and (**III**) are stable to hot dil. NaOH and hot dil. HCl, and (**III**) to HgCl, whilst with (**II**) the reaction of formation is reversed. (**II**), but not (**III**), shows evidence of thetine (not isolated) formation with CH_2Br·CO_2Na. With Br–AcOH (**II**) yields (S·$[CH_2]_2$·$CO_2H)_2$ and CHPhMeBr, while (**III**) is oxidised to SO- and SO_2-acids (below). (**II**) and (**III**) with H_2O_2 or $K_2S_2O_8$ give respectively *β-α′-* (**IV**), diastereoisomeric mixture, m.p. 79—81° (clear at 83—84°) (H_2O_2), m.p. 86—87° ($K_2S_2O_8$), and *β-β′-phenylethanesulphinyl-* (**V**), m.p. 111—112°, and thence or directly from (**II**) and (**III**) [$KMnO_4$; Br–H_2O with (**III**) only] dl-*β-α′-* (**VI**), m.p. 174—175°, and *β-β′-phenylethanesulphonyl-propionic acid* (**VII**), m.p. 142—143°, respectively. (**IV**) [and similarly (**V**)] is hydrolysed (dil. alkali) to (S·CHPhMe)$_2$ and CH_2:CH·CO_2H (**VIII**); (**VI**) [via CHPhMe·SOH (not isolated)] (cf. preceding abstract) and (**VII**) give (**VIII**) and *α-* (**IX**), m.p. 55—65° (+1H_2O, m.p. 50—65°), and *β-phenylethanesulphinic acid* (**X**), m.p. 58—59°, respectively (*β-*$C_{10}H_7$·NH_2 salts, sinters at 95°, brown at 150°, no m.p., and m.p. 123—124° respectively). (**IX**), but not (**X**), oxidises rapidly in air. M. H. M. A.

Oxidation of mercaptal- and mercaptol-acids with persulphate. B. Holmberg (*Arkiv Kemi, Min., Geol.*, 1942, **15**, **A**, No. 24, 8 pp.).—Oxidation ($K_2S_2O_8$) of CR′R″(S·CH_2·$CO_2Na)_2$ [from SH·CH_2·CO_2H and COR′R″ (**I**)] gives usually CR′R″(SO·CH_2·$CO_2Na)_2$ (R′, R″ = H, alkyl, aralkyl, CO_2H, etc.), but when R′ = H, R″ = 3 : 4-OMe·C_6H_3(OH), 3 : 4-$(OMe)_2C_6H_3$ (partly), (**I**) and (S·CH_2·$CO_2Na)_2$ are formed, and when R′ = H, R″ = 3 : 4-CH_2O_2:C_6H_3, CHPh:CH·, 3 : 4-$(OMe)_2C_6H_3$ (partly), or R′ = Ph, R″ = H, Me, Ph, CR′R″$<^{O\cdot CO}_{S\cdot CH_2}$ is formed, but could not always be isolated. The following are described: *α-hydroxy*-3 : 4-*dimethoxy-*, m.p. 110—111·5°, and -3 : 4-*methylenedioxy-benzyl-*, m.p. 65—66°, and *α-hydroxycinnamyl-*, m.p. 111—112°, *-thiolacetic acid lactones*. CHPh(S·CHMe·$CO_2Na)_2$ gives similarly *α-α′-hydroxybenzylthiolpropionic acid lactone*, diastereoisomerides, m.p. 65—73° (impure) and 77—78°, but CHPh(S·$[CH_2]_2$·$CO_2Na)_2$ does not give a lactone. M. H. M. A.

***NN′*-Substituted α-aminodiphenylacetamides.** J. H. Billman and P. H. Hidy (*J. Amer. Chem. Soc.*, 1943, **65**, 760—761).—CPh_2Cl·COCl

(prep. from $OH{\cdot}CPh_2{\cdot}CO_2H$ and PCl_5 improved to give 65—80% yield) and NH_2R in Et_2O give 5—57% of $NHR{\cdot}CPh_2{\cdot}CO{\cdot}NHR$, in which R = H (**I**), m.p. 144°, *Me*, m.p. 118°, *Et*, m.p. 132°, *Pr*$^{\alpha}$ (**II**), m.p. 115°, *Bu*$^{\alpha}$ (**III**), m.p. 112·5°, n-*amyl*, m.p. 104°, Ph, m.p. 180°, and p-*OEt*·C_6H_4 (**IV**), m.p. 121·5°. $NEt_2{\cdot}CPh_2{\cdot}CO{\cdot}NEt_2$, m.p. 67°, is similarly prepared. (**I**) and (**IV**) show 0·5—0·75 times the anticonvulsant activity of 5 : 5-diphenylhydantoin. As an antispasmodic, (**I**) is most active. (**II**) and (**III**) cause contraction of isolated rabbit's intestine. R. S. C.

Petroleum acids. VI. Naphthenic acids from Californian petroleum. W. O. Ney, W. W. Crouch, C. E. Rannefeld, and H. L. Lochte (*J. Amer. Chem. Soc.*, 1943, **65**, 770—777; cf. A., 1943, II, 250).—Esters of high *n* yield, after purification mainly by countercurrent fractional neutralisation in an improved apparatus, *cyclo*pentanecarboxylic, 2-, b.p. 220° (Me ester, b.p. 165—167°; amide, m.p. 147—148°) (cf. A., 1890, 737; 1899, i, 800), and 3-methyl-*cyclo*pentanecarboxylic acid, b.p. 220—224° [*amide*, m.p. 147—148°; p-*toluidide*, m.p. 106—107°; *p*-phenylphenacyl ester, m.p. 72·5—73·5° (73—74°); prepared from 3-methyl*cyclo*pentanone by H_2–Raney Ni at 100°/2200 lb. and subsequent conversion into the bromide and Grignard reagent], impure *cyclo*hexanecarboxylic and *cyclo*pentylacetic, 3-methyl-, and 2 : 3-dimethyl-*cyclo*pentylacetic, b.p. 201—202° (*amide*, m.p. 159°; converted into and prepared from 2 : 3-dimethyl*cyclo*pentanecarboxylic acid), and *cis*-2 : 2 : 6-trimethyl*cyclo*hexanecarboxylic acid (gives the amide and anilide of the *trans*-acid). R. S. C.

Isomorphous replaceability of the chalkogens in organic compounds. H. Rheinboldt and S. Mathias (*Ber.*, 1940, **73**, [*B*], 433—435).—$(CH_2{\cdot}OBz)_2$ and $(CH_2{\cdot}SBz)_2$ form a single eutectic without any indication of formation of mixed crystals. A continuous series of mixed crystals is given by PhOBz and PhSBz but there is no sign of such mixtures with $CO(NH_2)_2$ and $CS(NH_2)_2$. H. W.

Synthesis of *iso*quinoline derivatives. III. Preparation of *N*-acylvinylamines from *N*-acylaminoalcohols. W. Krabbe, E. Polzin, and K. Culemeyer (*Ber.*, 1940, **73**, 652—655; cf. A., 1938, II, 111).—$NHBz{\cdot}CHPh{\cdot}CPh_2{\cdot}OH$ and MgEtBr–Et_2O at 170—175° for 50—55 min. give *benz-αββ-triphenylvinylamide*, m.p. 206°, converted by HCl–EtOH into (?) $CPh_2{:}CPh{\cdot}OH$ and EtOBz. The analogous *Ac* derivative has m.p. 190—191°; the compound thus described (*loc. cit.*) is an oxazoline. *α-Benzamido-β-phenylpropan-β-ol*, m.p. 107—108°, prepared from $NH_2{\cdot}CH_2{\cdot}CPhMe{\cdot}OH$ and BzCl–aq. NaOH or from $NHBz{\cdot}CH_2{\cdot}COMe$ and MgPhBr, is converted by MgEtBr at 185—190° for 15 min. into *benz-β-phenyl-β-methylvinylamide*, m.p. 148° (corr.) (*cis*-form) (the constitution of the product, m.p. 110°, obtained by P_2O_5, is not proved). $NHBz{\cdot}CH_2{\cdot}CHPh{\cdot}OH$ and MgEtBr at 175° for 2 hr. give $NHBz{\cdot}CH{:}CHPh$, m.p. 175°. A. T. P.

Nitration of methyl 1-naphthoate and related compounds. C. F. Koelsch and D. O. Hoffman (*J. Amer. Chem. Soc.*, 1943, **65**, 989—990).—Adding HNO_3 (*d* 1·2) (3 equivs.)–H_2SO_4 to 1-$C_{10}H_7{\cdot}CO_2Me$ in H_2SO_4 at 0—10° gives *Me* 4 : 5-*dinitronaphthoate* (**I**), m.p. 194—195° [derived acid, m.p. 266—267° (lit. 265°)], an oil, and some 5 : 1- and 8 : 1-$NO_2{\cdot}C_{10}H_6{\cdot}CO_2H$ (formed in greater quantity if less HNO_3 is used). 5 : 1-$NO_2{\cdot}C_{10}H_6{\cdot}CO_2Me$ is unaffected by fuming HNO_3–AcOH, but with HNO_3 (*d* 1·42) in H_2SO_4 at 0° gives 52% of (**I**). *Me* 8-*nitronaphthoate* (prep. by Me_2SO_4), m.p. 97—98°, and conc. HNO_3 in H_2SO_4 at 0—10° gives *Me* (? 4 : 8-)*dinitronaphthoate*, m.p. 189—190° [in 90% H_2SO_4 at 100° gives small amounts of an acid, m.p. 236—238°, and 1 : 5-$C_{10}H_6(NO_2)_2$]. Nitration, best by fuming HNO_3 in AcOH, of 1-$C_{10}H_7{\cdot}CO_2H$ (**II**) gives acids, whence HCl–EtOH yields 5 : 1-$NO_2{\cdot}C_{10}H_6{\cdot}CO_2Et$, whilst 8 : 1-$NO_2{\cdot}C_{10}H_6{\cdot}CO_2H$ and (? 6 : 8-)*dinitronaphthoic acid*, m.p. 267—268° or (rapid heating) 274—276° [*Me* ester, m.p. 179—180°; with $Cu(OAc)_2$ in quinoline gives 1 : 3-$C_{10}H_6(NO_2)_2$], which are also formed, do not react. 5 : 1-$NO_2{\cdot}C_{10}H_6{\cdot}CO_2H$ and (**II**) form a 1 : 1 additive compound, m.p. 198—200°. R. S. C.

Textile chemistry study in the 2-hydroxynaphthoic 3-arylamide series. H. Rath and R. Burkhardt (*Ber.*, 1940, **73**, [*B*], 701—708).—*p*-Nitro-*n*-dodecoanilide and Zn–AcOH–EtOH give N-*dodecoyl*-p-*phenylenediamine*, m.p. 112°, converted by 2 : 3-$OH{\cdot}C_{10}H_6{\cdot}COCl$ (**I**)–C_6H_6–C_5H_5N at 80° for 6 hr. into N-2-*hydroxy*-3-*naphthoyl*-N′-*dodecoyl*-p-*phenylenediamine*, m.p. 227—234° (the *N*′-octadecoyl analogue, m.p. 221°, is prepared similarly). *n*-$C_{11}H_{23}{\cdot}COCl$–6 : 3 : 1-$NO_2{\cdot}C_6H_3(NH_2){\cdot}CO_2H$–$C_5H_5N$ at 80° give 6-nitro-3-dodecoamidobenzoic acid, m.p. 133°, reduced by Fe–EtOH–AcOH to the 6-NH_2-compound, m.p. 209°, which is then converted into 6-2′-*hydroxy*-3′-*naphthoamido*-3-*dodecoamidobenzoic acid*, m.p. 225° (decomp.). *p*-$NH_2{\cdot}C_6H_4{\cdot}CO_2H$ affords p-2′-*hydroxy*-3′-*naphthoamidobenzoic acid* (**II**), m.p. ~315°. (**I**) and C_6H_6–$AlCl_3$–HCl at room temp., then at 60°, give 2-*hydroxy*-3-*benzolynaphthalene* (**III**), m.p. 155—156°. Substantivities of (**II**), (**III**), and 2 : 3-$OH{\cdot}C_{10}H_6{\cdot}CO{\cdot}NPhR$ (R = Me, Et) towards viscose are < that of 2 : 3-$OH{\cdot}C_{10}H_6{\cdot}CO{\cdot}NHPh$. A. T. P.

α-Phenylethylidenemalononitrile. D. T. Mowry (*J. Amer. Chem. Soc.*, 1943, **65**, 991).—$CH_2(CN)_2$, COPhMe, NH_4OAc, and AcOH in boiling C_6H_6 with continuous removal of H_2O yield *α-phenylethylidenemalononitrile* (56%), m.p. 94°. R. S. C.

Ethyl α : *p*-dicyanocinnamate. D. T. Mowry (*J. Amer. Chem. Soc.*, 1943, **65**, 992).—Crude *p*-$CN{\cdot}C_6H_4{\cdot}CHO$ [prep. from *p*-$CN{\cdot}C_6H_4{\cdot}CH_2Br$ by aq. $Cu(NO_3)_2$] with $CN{\cdot}CH_2{\cdot}CO_2Et$ and a little piperidine in $Bu^{\beta}OH$ gives *Et α* : p-*dicyanocinnamate* (88%), m.p. 168·5—169°. R. S. C.

Attempted preparation of a homocamphor and of a 1 : 7-glycol. K. Buser and H. Rupe (*Helv. Chim. Acta*, 1943, **26**, 857—863).—Gradual addition of $CHNa(CO_2Et)_2$ (**I**) to camphoric anhydride in boiling C_6H_6 leads to "camphorylmalonic ester" [lactone of Et_2 β-hydroxy-β-3-carboxy-2 : 2 : 3-trimethyl*cyclo*pentylmethylenemalonate] (**II**), m.p. 83—84°, in yield depending greatly on the quality of (**I**) and attaining 55—62% under favourable conditions. (**II**) is reduced (H_2 at 120—130°/130 atm.–Ni catalyst in H_2O–EtOAc–EtOH) to a mixture hydrolysed to *β-3-carboxy*-2 : 2 : 3-*trimethyl*-*cyclopentylethane-αα-dicarboxylic acid*, m.p. 180—182° [Me_3 ester (**III**), b.p. 139—140°/11 mm.], and *β-3-carboxy*-2 : 2 : 3-*trimethyl*-*cyclopentylpropionic acid*, m.p. 141—144° [Me_2 ester (**IV**), b.p. 154—156°/10 mm., m.p. 35°; dichloride, b.p. 157—158°/10 mm.; *di*-p-*toluidide*, m.p. 190°]. When treated with powdered Na or $NaNH_2$ according to Dieckmann, (**III**) or (**IV**) gives small quantities of homocamphor, m.p. 185°. Reduction of (**IV**) by Na and $Bu^{\alpha}OH$ affords 1 : 2 : 2-*trimethyl*-1-*hydroxymethyl*-3-*γ*-*hydroxy*-n-*propyl*cyclo*pentane* (**V**), b.p. 178—180°/10 mm. (*di*-p-*nitrobenzoate*, m.p. 145°; *diacetate*, b.p. 189—191°/11 mm.). Replacement of OH by Br in (**V**) by PBr_3 or HBr in AcOH could not be achieved but the action of the last reagent on the crude glycol (**VI**) at 160° leads to the isolation of 1 : 2 : 2-*trimethyl*-3-*γ*-*bromo*-n-*propyl*cyclo*pentane*-1-*carboxylic acid*, m.p. 71° (p-*toluidide*, m.p. 101°), obtained by hydrolysis of the corresponding Me ether present in (**VI**). H. W.

Mechanism of the Gattermann reaction. II. E. L. Niedzielski and F. F. Nord (*J. Org. Chem.*, 1943, **8**, 147—152).—NaCN can replace HCN in the Gattermann synthesis of aldehydes from aromatic hydrocarbons except C_6H_6 in which negative polarity and lack of an alkyl substituent appear responsible for the non-formation of the aldehyde intermediate. Although *p*-xylene has a zero dipole moment it can react since it can undergo alkyl migration and alkylation by $AlCl_3$ to form a more highly polar hydrocarbon. The yields of aldehydes from PhMe and the xylenes coincide with the polarity of the hydrocarbon reactants, the max. being reached in *o*-xylene. Compounds with labile alkyl groups, *e.g.*, Et and Pr^{β}, show extensive alkylation and alkyl migration in the Gattermann reaction when HCN is employed. The mechanism of the NaCN and HCN actions differ. The former requires the formation of the aldehyde intermediate which appears to occur by the action of the $AlCl_3$–hydrocarbon complex on NaCN. During the decomp. of the NaCN, the $AlCl_3$ displays its side reactions whereby the complete process gives products generally different from those obtained by the Gattermann reaction. Solvents exert an influence on aldehyde formation. PhMe alone gives *m*- and *p*-$C_6H_4Me{\cdot}CHO$ whereas in presence of PhCl as diluent, the *p*-isomeride is obtained exclusively. Dry HCl is passed through a well-stirred mixture of $AlCl_3$, the hydrocarbon, and NaCN for 15 min. at room temp., after which the mixture is heated to 95—100° in 20 min. and kept at this temp. The following are new: *diethylbenzaldehyde*, b.p. 115—118°/9 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 132°), converted into the corresponding *acid*, m.p. 81° (*amide*, m.p. 161°), and hydantoin, m.p. 175°; *triethylbenzaldehyde*, b.p. 138—140°/9 mm. (*semicarbazone*, m.p. 151°; 2 : 4-*dinitrophenylhydrazone*, m.p. 162°; corresponding *acid*, m.p. 111°); *diiso*propylbenzaldehydes, b.p. 135—139°/9 mm., 126—130°/9 mm. and 126—134°/9 mm. (2 : 4-*dinitrophenylhydrazones*, m.p. 143°, 120°, and 133°; corresponding *acids*, m.p. 190°, 181°, and 186°, respectively); *tri*iso*propylbenzaldehydes*, b.p. 129—133°/9 mm. and 145—152°/9 mm. (2 : 4-*dinitrophenylhydrazones*, m.p. 169° and 151°; *acids*, m.p. — and 182°, respectively); *methyldi*iso*propylbenzaldehydes*, b.p. 133—138°/14 mm. and 142—150°/14 mm. (2 : 4-*dinitrophenylhydrazones*, m.p. 129° and 157°; *acids*, m.p. 121° and 125°, respectively). H. W.

Fries rearrangement and subsequent isomerisation. G. Baddeley (*J.C.S.*, 1943, 273—274).—3 : 5 : 1-$C_6H_3Me_2{\cdot}O{\cdot}COR$ (R = Me, Et, Ph) are converted quantitatively by 1 mol. of $AlCl_3$ into 6 : 2 : 4 : 1-$OH{\cdot}C_6H_2Me_2{\cdot}COR$ (**I**) but by 2 or more mols. into 6 : 3 : 4 : 1-$OH{\cdot}C_6H_2Me_2{\cdot}COR$ (**II**); migration of one alkyl is thus not conditioned by another alkyl in the *p*-position to it (cf. von Auwers *et al.*, A., 1928, 417). With <2 mols. of $AlCl_3$, (**I**) similarly give (**II**); the reaction is bimol. Other similar examples are quoted. 6-*Hydroxy*-3 : 4-*dimethyl*-*propiophenone*, m.p. 60°, and -*benzophenone*, m.p. 111°, 6-*hydroxy*-2 : 4-*dimethylpropiophenone*, m.p. 78°, *dibromo*-6-*hydroxy*-2 : 4-, m.p. 81°, and *bromo*-6-*hydroxy*-3 : 4-*diethylacetophenone*, m.p. 59°, are new. F. R. S.

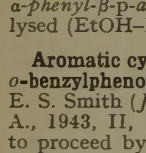
Vinyl alcohols. VI. 1 : 4-Dehydrogenation. R. C. Fuson and R. E. Foster. **VII. Hindrance at the β-carbon atom.** R. C. Fuson and Q. F. Soper (*J. Amer. Chem. Soc.*, 1943, **65**, 913—915, 915—917; cf. A., 1943, II, 160).—VI. Hydrogenation of $CHAr{:}CAr{\cdot}COAr'$ (*A*), in which Ar′ is highly hindered, gives an enol, $CH_2Ar{\cdot}CAr{:}CAr'{\cdot}OH$, which is immediately oxidised to (*A*) in air but when kept ketonises to give $CH_2Ar{\cdot}CHAr{\cdot}COAr'$. *Duryl*

CH_2Ph ketone (prep. from durene and $CH_2Ph{\cdot}COCl$ by Friedel–Crafts reaction), m.p. 110—111°, with PhCHO and 10% NaOH in EtOH at room temp. gives *duryl αβ-diphenylvinyl ketone* (**I**) (70%), m.p. 150—151°. When (**I**) is hydrogenated (PtO_2) in EtOAc and the solvent is removed in air, only (**I**) is recovered, but keeping the reduced solution for 48 hr. or boiling it for 2 hr. under N_2 leads to *duryl αβ-diphenylethyl ketone* (**II**), m.p. 106—107°. Hydrogenation in presence of $ZnCl_2$ in Ac_2O does not give an enol acetate and (**I**) gives no peroxide. Na–EtOH reduces (**I**) to (**II**). Hydrogenation of 2 : 4 : 6-$C_6H_2Pr^{\beta}_3$ *αβ-diphenylvinyl ketone*, m.p. 117—119°, *duryl*, m.p. 138—140°, and *mesityl α-phenyl-β-p-chlorophenylvinyl ketone*, m.p. 138—140°, gives similar results. 2 : 4 : 6-$C_6H_2Pr^{\beta}_3$ CH_2Ph (**III**), m.p. 60·5—61°, and *αβ-diphenylethyl ketone*, m.p. 143—144°, *duryl*, m.p. 129—130°, and *mesityl α-phenyl-β-p-chlorophenylethyl ketone*, m.p. 148—149°, are described.

VII. The stability of unchelated enols is due to steric conditions at $C_{(\beta)}$ rather than at $C_{(\alpha)}$. In the Grignard machine, (**III**) gives nearly 1 mol. of CH_4 but then regenerates (**III**). CHPhMe·COCl (modified prep.), b.p. 75—76°/3 mm., with *s*-$C_6H_3Pr^{\beta}_3$ and $AlCl_3$ in CS_2 at, successively, 0°, room temp., and the b.p. gives 2 : 4 : 6-$C_6H_2Pr^{\beta}_3$ *CHPhMe ketone*, m.p. 83—84°, which does not enolise in NaOEt–EtOH or give an enol acetate or benzoate, shows 1 active H, and with SeO_2 in boiling dioxan containing a little H_2O yields *Ph* 2 : 4 : 6-$C_6H_2Pr^{\beta}_3$ *diketone* (**IV**), m.p. 121·5—122·2°. H_2–Cu chromite reduces (**IV**) at 175°/2000 lb. to *α-phenyl-β*-2 : 4 : 6-*tri*isopropylphenylethylene glycol, m.p. 133·5—134° (*diacetate*, m.p. 113—114°; dehydrated by conc. HCl–AcOH to an intractable product), but at 150°/1500—2000 lb. to 2 : 4 : 6-*tri*isopropylbenzoylphenylcarbinol (**V**), m.p. 117·5—118·5° (*acetate*, m.p. 120—120·5°), also obtained by Zn dust–HCl–EtOH. Hydrogenation of (**IV**) gives an enediol (indophenol test), which, however, could not be isolated; H_2–PtO_2–conc. HCl (3 drops)–$ZnCl_2$–Ac_2O gives *αβ-diacetoxy-α-phenyl-β*-2 : 4 : 6-*tri*isopropylphenylethylene, m.p. 161—161·5°, hydrolysed by HCl–MeOH–H_2O to (**V**); hydrogenation in light petroleum or Et_2O and exposure to air gives (**IV**) or (**V**), respectively. M.p. (both parts) are corr. R. S. C.

Acetylation of deoxybenzoins. R. P. Barnes, S. R. Cooper, V. J. Tulane, and H. Delaney (*J. Org. Chem.*, 1943, **8**, 153—158).—The mechanism presented (A., 1941, II, 170) for the benzoin rearrangement is applied to the acetylation of deoxybenzoins. *Ph* p-*methoxybenzyl ketone*, m.p. 98°, is obtained from the corresponding phenol, Me_2SO_4, and NaOH. The following are prepared by heating the necessary deoxybenzoin (*A*) with twice its wt. of KOAc and sufficient boiling Ac_2O to dissolve the latter: *α-acetoxy-αβ-diphenyl-*, m.p. 101°; *α-acetoxy-αβ-diphenyl-β-benzyl-*, m.p. 70°; *α-acetoxy-β-phenyl-α-p-acetoxyphenyl-*, m.p. 109°; *α-acetoxy-α-phenyl-β-p-acetoxyphenyl-*, m.p. 119°; *α-acetoxy-αββ-triphenyl-*, m.p. 104°; *α-acetoxy-αβ-dimesityl-*, m.p. 106°; *α-acetoxy-β-phenyl-α-p-anisyl-*, m.p. 88°; *α-acetoxy-α-phenyl-β-p-anisyl-*, m.p. 86°; *α-acetoxy-αβ-di-p-anisyl-*, m.p. 90°; *α-acetoxy-α-phenyl-β-p-nitrophenyl-*, m.p. 107°; *α-acetoxy-α-phenyl-β-p-acetamidophenyl-*, m.p. 137°, *-ethylene*. These are hydrolysed (EtOH–HCl) smoothly to (*A*). H. W.

Aromatic cyclodehydration. XI. Mechanism of the cyclisation of *o*-benzylphenones [*o*-benzylphenyl ketones]. C. K. Bradsher and E. S. Smith (*J. Amer. Chem. Soc.*, 1943, **65**, 854—857; cf. Berliner, A., 1943, II, 141).—Cyclisation of *o*-$CH_2Ph{\cdot}C_6H_4{\cdot}COR$ (*A*) is held to proceed by addition of H^+ to give an ion containing $\cdot C^+R{\cdot}OH$, cyclisation to (*B*), loss of H^+ to give the anthranol, and dehydration thereof to the 9-substituted anthracene. The reasons are that cyclisation is slower than in the phenanthrene series, that the rate is independent of the nature of R, and because of the following reactions. *o*-$C_6H_4Ph{\cdot}COPh$ with boiling 48% HBr (HBr–AcOH gives a resin) and then EtOH gives 9-ethoxy-9-phenylfluorene (65%), m.p. 114—115°; (*A*; R = Ph) is similarly cyclised in 66% yield to 9-phenylanthracene. *o*-$C_6H_4Cl{\cdot}CPh_2Cl$ (improved prep.) with MgMeI in C_6H_6–Et_2O gives *o-chloro-* (26%), m.p. 107·5—108·5°, which with CuCN in C_5H_5N at 215—225° gives *o-cyano-aaa-triphenylethane* (43%), m.p. 123—124°. This resists acid or alkaline hydrolysis, but with MgPhBr–Et_2O and then $-C_6H_6$ at the b.p. gives *o-α-methylbenzhydrylbenzophenoneimine hydrochloride* (83·5%), which with boiling 48% HBr and then dry ROH yields 10-*ethoxy-* (57%), m.p. 203—204°, and 10-*methoxy-*9 : 10-*diphenyl-*9-*methyl-*9 : 10-*dihydroanthracene*, m.p. 284—286°. Substitution of Ar into the CH_2 of (*A*) slows the cyclisation; enolisation plays no part in the mechanism. R. S. C.



(*B*.)

***tert.*-Butyl benzoyl*iso*butyrate.** J. C. Shivers and C. R. Hauser (*J. Amer. Chem. Soc.*, 1943, **65**, 991).—$Pr^{\beta}CO_2Bu^{\gamma}$ with CPh_3Na and then BzCl in Et_2O gives Bu^{γ} *α-benzoylisobutyrate*, m.p. 64—65°, b.p. 146—148°/15 mm. R. S. C.

Photo-reactions. V. Photo-oxidation of non-ionisable thioketones in sunlight. A. Schönberg and A. Mostafa (*J.C.S.*, 1943, 275—276).—$CSPh_2$ is converted by O_2 into $COPh_2$ even in the dark. $(p\text{-}C_6H_4R)_2CS$ (R = OMe, NMe_2), xanthione, and thioxanthione in C_6H_6 are stable to O_2 in the dark but give the corresponding ketones in sunlight, S and SO_2 being formed; *N*-phenylthioacridone, 4-thioflavone, and 2 : 6-diphenyldithiopyrone are stable in dark and sunlight. F. R. S.

Alkyl*cyclo*hexanones.—See B., 1943, II, 245.

Preparation of synthetic sex hormones. II. Derivatives of hexœstrol. J. F. Lane and E. S. Wallis (*J. Amer. Chem. Soc.*, 1943, **65**, 994; cf. A., 1941, II, 9).—Mixed mono- and di-acetates of perhydrohexœstrol (m.p. 167°) with CrO_3–AcOH and then NaOH–EtOH give, after purification by way of the H succinates, *4-hydroxy-4'-keto-*, m.p. 70° [*semicarbazone*, m.p. 146°; *acetate*, m.p. 66° (*semicarbazone*, m.p. 161°)], and a little 4 : 4'-*diketo-γδ-dicyclohexyl-*n-*hexane*, m.p. 80°. R. S. C.

Action of acids on 2 : 3-epoxy-2 : 3-diphenylindanone. C. F. Koelsch and C. D. Le Claire (*J. Amer. Chem. Soc.*, 1943, **65**, 754—755).—2 : 3-Epoxy-2 : 3-diphenylindan-1-one (**I**) with a drop of H_2SO_4 in warm AcOH gives yellow 3 : 4-diphenyl*iso*coumarin (**II**), m.p. 168—169° (Weitz *et al.*, A., 1921, i, 869, m.p. 168·5—171°), the structure of which is proved by hydrolysis by warm NaOH–EtOH to *o*-$CO_2H{\cdot}C_6H_4{\cdot}CHPh{\cdot}COPh$ (**III**) and by boiling NaOH–MeOH–H_2O to BzOH and *o*-$CH_2Ph{\cdot}C_6H_4{\cdot}CO_2H$. Boiling 2% H_2SO_4–AcOH cyclises (**III**) to colourless (**II**), the original colour of which is thus due to impurities. With AcOH–HCl at room temp. (5 min.), (**I**) gives 2 : 3-*dihydroxy-*2 : 3-*diphenylindan-*1-*one*, sinters 160°, m.p. 168° (cf. *loc. cit.*) [and a little (**II**)], the structure of which is shown by oxidation by $Pb(OAc)_4$ in warm C_6H_6 to *o-benzoylbenzil*, m.p. 93—94° (also obtained from diphenylindone by CrO_3–AcOH at 80—85°). The compound obtained from 2 : 3-epoxy-3-*p*-dimethylaminophenyl-2-*o*-formylphenylindan-1-one by acid (Weitz, A., 1919, i, 290) is similarly 4-p-*dimethylaminophenyl-*3-o-*formylphenyl*isocoumarin. R. S. C.

Alkamine esters of fluorenonecarboxylic acids. F. E. Ray and G. Rieveschl, jun. (*J. Amer. Chem. Soc.*, 1943, **65**, 836—839).—Condensing fluorene with Ac_2O–$AlCl_3$ in boiling CS_2 and oxidising the crude product with $Na_2Cr_2O_7$–AcOH (later +Ac_2O) gives 58—62% of fluorenone-2-carboxylic acid (**I**), m.p. 339—341° [Me ester, m.p. 185—186° (lit. 181°)], and 2-*acetylfluorenone*, m.p. 154—155°. With Zn dust in KOH–EtOH–H_2O, (**I**) gives fluorenol-2-, sinters 224—240°, and thence by red P–I–AcOH fluorene-2-carboxylic acid, m.p. 262—267° (lit. 260°) (decomp.) [Me ester, m.p. 122° (lit. 120°)]. *Fluorenone-*2-, m.p. 183—184°, -1-, m.p. 130—132° (lit. 140°), and -4- [acid, m.p. 227° (lit. 223—224°)], and fluorene-2-carboxyl chloride, m.p. 182°, with the appropriate NH_2-alcohol give *β-diethylaminoethyl fluorenone-*1-, m.p. 194—195°, -4-, m.p. 194—196°, and -2- (**II**), m.p. 223—224°, and *fluorene-*2-*carboxylate hydrochloride*, m.p. 204—206°, *γ-diethylamino-*n-*propyl fluorenone-*1-, m.p. 159—160°, -4-, m.p. 210—211°, and -2-*carboxylate hydrochloride* (**III**), m.p. 221—224°, *β-dibutyl-*, m.p. 179—180°, and *β-dimethylaminoethyl fluorenone-*2-*carboxylate hydrochloride*, m.p. 222—224°. With NH_2OH,HCl and $BaCO_3$ in boiling MeOH, (**II**) and (**III**) give the *oxime hydrochloride*, m.p. 231—232°, and *oxime dihydrochloride*, m.p. 219—220°, respectively, which are more potent anæsthetics than are the parent esters. R. S. C.

Ring-enlargement of 2 : 4 : 5-triphenyl*cyclo*pentenedione. C. F. Koelsch and S. Wawzonek (*J. Amer. Chem. Soc.*, 1943, **65**, 755—757).—2 : 4 : 5-Triphenyl-Δ^4-*cyclo*pentene-1 : 3-dione (A., 1942, II, 23), $CH_2Br{\cdot}CO_2Et$, and NaOEt in boiling EtOH give *Et* 2 : 5-*diketo-*1 : 3 : 4-*triphenyl-*Δ^3-cyclo*pentenylacetate* (74%), m.p. 126—127°, converted by boiling NaOEt–EtOH–H_2 into *Et* 3 : 4 : 6-*triphenylgentisate* (**I**) (76%), m.p. 155—157° (*diacetate*, m.p. 157—159°). The derived (KOH–H_2O–EtOH) *acid* (**II**), m.p. 216—221° (gas), with a trace of $Cu(OAc)_2$ in boiling quinoline–H_2 gives *triphenylquinol* (55%) (**III**), m.p. 151—152° (1 : 1 additive *compound*, m.p. 188—192°, with quinoline hydrochloride), oxidised by CrO_3–AcOH–H_2O to *triphenyl-*p-*benzoquinone*, m.p. 154·5—155°. This is reduced to (**III**) by Zn dust in AcOH and with PhN_2Cl in aq. AcOH–NaOAc at 10° gives a little 1 : 2 : 3 : 5 : 6 : 4-O:C_6Ph_4:O. Boiling CrO_3–AcOH oxidises (**I**) to *Et triphenyl-*p-*benzoquinonecarboxylate*, m.p. 207—208°, converted into (**II**) by KOH–H_2O–EtOH. $FeCl_3$–AcOH–H_2O (CrO_3 and PbO_2 give complex products) oxidises (**II**) to *triphenyl-*p-*benzoquinonecarboxylic acid* (55%), m.p. 213—215° (decomp.) [202—207° (decomp.)]. Passing air into (**I**) in KOH–EtOH–H_2O gives 2-*hydroxy-*3 : 5 : 6-*triphenyl-*p-*benzoquinone*, m.p. 160—161·5° (*acetate*, m.p. 185·5—187·5°). R. S. C.

Synthesis of 2 : 6-diphenyl*cyclo*octane-1 : 5-dione. S. Wawzonek (*J. Amer. Chem. Soc.*, 1943, **65**, 839—843).—*dicyclo*[3, 0, 3]Octane-2 : 6-dione (Ruzicka *et al.*, A., 1934, 297) with PCl_5–C_6H_6, SeO_2–EtOH, or 2 : 4 : 6 : 1-$C_6H_2Me_3{\cdot}MgBr$ and then I in Et_2O–EtOH gives intractable products, but with MgPhBr in C_6H_6–Et_2O and then aq. NH_4Cl gives 2 : 6-*dihydroxy-*2 : 6-*diphenyl*dicyclo[3, 0, 3]*octane*, m.p. 208—212° (decomp.) (chromophoric salts with H_2SO_4– or HCl–AcOH; OH and H *cis*), which with H_2SO_4–MeOH at room temp. gives the *Me*$_2$ *ether*, m.p. 174—175°, and with $KHSO_4$ at 150—160° or, better, boiling AcOH–HCO_2H gives 2 : 6-*diphenyl*dicyclo[3, 0, 3]-$\Delta^{2:6}$-*octadiene* (**I**), m.p. 136—138°. MgMeI gives similarly 2 : 6-*dihydroxy-*2 : 6-*dimethyl*dicyclo[3, 0, 3]*octane*, m.p.

133—135°, but dehydration thereof gives an unstable terpene-like oil. The structure of (**I**) is proved by oxidation by CrO_3–$NaHSO_4$–H_2O at 100° to *ββ′-dibenzoyladipic acid*, m.p. 186—188° (gas), which is also obtained [m.p. 189—190° (gas)] from 4 : 5-dibenzoyl-Δ^1-*cyclo*hexene by CrO_3–AcOH at 100°. Boiling *n*-C_5H_{11}·ONa–C_5H_{11}·OH does not affect (**I**), but *p*-C_6H_4Me·SO_3H (**II**) in boiling C_6H_6 partly rearranges it to 2 : 6-*diphenyl*dicyclo[3, 0, 3]-$\Delta^{1:5}$-*octadiene* (**III**), m.p. 188—190°, the structure of which is proved by conversion by O_3 in EtOAc at −40° into a *diozonide*, m.p. 122—127° (gas), which with H_2–PtO_2 at 2·7 atm. gives *αθ-diphenyl-n-octane-aδεθ-tetraone*, m.p. 110—111° (*quinoxaline* derivative, m.p. 166·5—167·5°), and Bz·$[CH_2]_2$·CO_2H. With H_2–Pt or –Pd in EtOAc, (**I**) or (**III**) gives 2 : 6-*diphenyl*dicyclo[3, 0, 3]*octane* (**IV**), m.p. 110—112°, but with Br–CCl_4 at 0° gives unstable oils. 40% Na–Hg in C_6H_6–EtOH (not other metal reductants) reduces (**III**) to 2 : 6-*diphenyl*dicyclo[3, 0, 3]-$\Delta^{1(5)}$-*octene* (**V**), m.p. 115—116°, which with H_2–PtO_2 in EtOH gives a *diphenyl*dicyclo*octane*, m.p. 99—100° [isomeric with (**IV**)], with Br gives an unstable product, is unaffected by a dropping Hg electrode in 0·175M-NBu^a_4I–75% dioxan, and with (**II**) in boiling xylene (not *n*-C_5H_{11}·ONa) gives 2 : 6-*diphenyl*dicyclo[3, 0, 3]-Δ^2-*octene*, m.p. 106—108° (reduced at a dropping Hg electrode). With O_3 in EtOAc at −40° and then H_2–PtO_2 at 2 atm., (**V**) gives 2 : 6-*diphenyl*cyclo*octane*-1 : 5-*dione* (**VI**), m.p. 217—220° (*dioxime*, softens 140°, m.p. 148—150°), and other products including isomerides. With PCl_5 in boiling xylene, (**VI**) yields 1 : 5-*dichloro*-2 : 6-*diphenyl*-$\Delta^{1:5}$-cyclo*octadiene*, m.p. 187—188°, with Zn dust in boiling 90% AcOH gives 1 : 5-*dihydroxy*-2 : 6-*diphenyl*dicyclo[3, 0, 3]*octane*, m.p. 127—129° [with $KHSO_4$ at 150—160° gives an oil; converted by $Pb(OAc)_4$–C_6H_6 at 47° into (**VI**)], and with boiling Ac_2O–(**II**) (not –KOAc or $-H_2SO_4$) gives 5-*acetoxy*-2 : 6-*diphenyl*-Δ^5-cyclo*octenone*, m.p. 123—124°.

R. S. C.

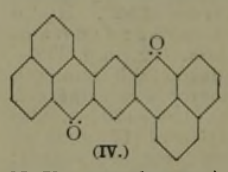
Action of acid anhydrides on acenaphthenone. E. Ghigi (*Ber.*, 1940, **73**, [*B*], 677—700).—Acenaphthenone (**I**) and boiling Ac_2O–NaOAc (10 hr.) give 7-*acetoxy*-8-*acetylacenaphthylene* (**II**), m.p. 133—134°, which is oxidised by $KMnO_4$ in C_6H_6 to 1 : 8-$C_{10}H_6(CO_2H)_2$ (**III**) or by cold CrO_3 to (**III**) and a little acenaphthenequinone. (**II**) and aq. NaOH yield the corresponding 7-*OH*-compound (**IV**), m.p. 117° [*Na*, *Fe*^{III}, and Cu salts; *Me ether* m.p. 131—132° (CH_2N_2); *benzoate*, m.p. 148—149°; *phenylhydrazone*, m.p. 196—198°, and thence 4 : 5-1′ : 8′-*naphthylene*-1-*phenyl*-3-*methylpyrazole*, m.p. 103°; p-*nitrophenylhydrazone*, m.p. 206—207° (decomp.), and corresponding *pyrazole*, m.p. 247°; *oxime*, m.p. 201—203°; *semicarbazone*, m.p. 235—236° (decomp.)], with a considerable amount of diacenaphthylidenone (**V**). (**I**) and Ac_2O–C_5H_5N at room temp. for 4 days give a little diacenaphthylidenedione (**VI**), a *product*, m.p. 225—235°, and the *compound*, (**II**)+C_5H_5N, m.p. 145—147°. (**IV**) with $Na_2Cr_2O_7$–AcOH at 85°, or aq. $KMnO_4$–NaOH, or aq. H_2O_2 at 100° (bath), gives 1 : 8-$C_{10}H_6(CO)_2O$. Other reactions of (**IV**) are: with boiling $Pb(OAc)_4$–C_6H_6, it gives a *compound*, m.p. 215—220° (decomp.); with KOH at 250°, 8 : 1-$C_{10}H_6Me$·CO_2H, m.p. 152—153° (lit. 130—131°); with PhN_2Cl–aq. KOH–EtOH, acenaphthenequinonephenylhydrazone; with MgPhBr–Et_2O, it yields (**I**) and COPhMe; with MgMeI–Et_2O, (probably) the inner *ether*, m.p. 74—75°, of 7-*hydroxy*-8-α-*hydroxy*iso*propylacenaphthylene*; with Zn dust, acenaphthene is formed; with Cu–quinoline, (**I**); with 20% aq. NaOH or HCl–MeOH, (**V**); with Br, dibromoacenaphthenone, m.p. 161—162°; other (largely negative) reactions of (**IV**) are given. Mg acenaphthenonyl bromide [from monobromoacenaphthenone (**VII**) and Mg–xylene] with cold AcCl yields (**VI**) and 7 : 7′-diacenaphthenonyl; the latter is also obtained from (**VII**)–Mg–EtOAc (trace of *I*). (**II**) and $AlCl_3$ at 140° yield (probably) 7-*hydroxy*-4 : 8-*diacetylacenaphthylene* (**VIII**), m.p. 166—167° (*bisphenylhydrazone*, m.p. 233°; *acetate*, m.p. 175°), oxidised by aq. $KMnO_4$–NaOH or CrO_3 to 4-acetyl- and 4-carboxy-naphthalic anhydride. (**VIII**) and PhN_2Cl–aq. NaOH–EtOH afford 4-*acetylacenaphthenequinone*-8-*monophenylhydrazone*, m.p. 215°. (**I**) and Bz_2O–NaOBz at 160° yield 7-*benzoyloxy*-8-*benzoylacenaphthylene*, forms m.p. 145° and 202—203°, hydrolysed (best by alkali) to 7-*hydroxy*-8-*benzoylacenaphthylene* (**IX**), m.p. 100° (*acetate*, m.p. 163°; *pyrazole*, m.p. 193—194°, from NHPh·NH_2). (**IX**) with PhN_2Cl gives acenaphthenequinonephenylhydrazone, with boiling Ac_2O–NaOAc yields (**II**), with KOH at 250° affords 8 : 1-$C_{10}H_6Me$·CO_2H, with H_2SO_4 at 150—160° gives (**VI**), and by Clemmensen reduction, a product, m.p. 190—192°. (**I**)–$NaNH_2$–BzCl afford small amounts of (**III**), (**IX**), and (**V**) [also from (**I**)–KCN–MeOH]. (**I**) and MgPhBr–Et_2O yield (probably) 7-*phenylacenaphthylene*, m.p. 54—55°, oxidised by CrO_3–AcOH to 1 : 8-$C_{10}H_6Bz$·CO_2H, m.p. 131—132° (lit. 110—112°).

A. T. P.

Highly arylated aromatic compounds. X. Action of quinones on phencyclone. W. Dilthey and M. Leonhard (*Ber.*, 1940, **73**, [*B*], 430—432).—Phencyclone (**I**) and 1 : 4-O:$C_{10}H_6$:O in boiling PhCl and CO_2 give 1 : 4-*endo*carbonyl-1 : 4-diphenyl-2 : 3-diphenylene-1 : 4 : 11 : 12-tetrahydroanthraquinone (**II**), m.p. 287—288° (decomp.) after darkening (lit. 265—267°) (preheated to 280°), slowly converted by NH_2OH,HCl in boiling C_5H_5N into 1 : 4-*diphenyl*-2 : 3-*diphenylene*-11 : 12-*dihydroanthraquinone*, m.p. 334—335° (bath heated to 330°), which passes in C_5H_5N containing a little KOH–MeOH into 1 : 4-diphenyl-2 : 3-diphenyleneanthraquinone, m.p. 376° (lit. 359°), also obtained from (**II**) and CrO_3–AcOH or boiling C_5H_5N (3 days). 1 : 4-*endo*Carbonyl-1 : 4-diphenyl-2 : 3-diphenylene-1 : 4 : 9 : 10-tetrahydronaphtha-5 : 8-quinone has m.p. 260—262° (decomp.) (lit. 194°) (bath preheated to 245°). Naphthazarin and (**I**) in boiling anhyd. C_6H_6 and CO_2 afford 5 : 8-*endocarbonyl*-5 : 8-*diphenyl*-6 : 7-*diphenylene*-13 : 14-*dihydroquinizarin*, m.p. 245° (decomp.) [*diacetate*, m.p. 265° (decomp.), also obtained from (**I**) and diacetylnaphthazarin].

H. W.

Aromatic hydrocarbons and their derivatives. XXXI. Syntheses in the pentacene series. E. Clar (*Ber.*, 1940, **73**, [*B*], 409—415).—Reduction of pentacenequinones does not give quinols but invariably leads to further reduction products. *leuco*Quinizarin and *o*-$C_6H_4(CO)_2O$ at 280—300° give 5 : 7 : 12 : 14-tetrahydroxypentacene-6 : 13-quinone (**I**), reduced by Zn dust and 70% AcOH in boiling C_5H_5N containing a little $CuSO_4$ to 5 : 7 : 12 : 14-tetrahydroxy-6 : 13-dihydropentacen-6-one (**II**), which is readily oxidised by air and best isolated as the *tetra-acetate*, becomes violet-red at 230°, commences to melt at 255°, and darkens with evolution of gas at 280°. (**II**) is reduced by Zn dust and boiling dil. NaOH to 5 : 7 : 12 : 14-tetrahydroxy-6 : 13-dihydropentacene (**III**), m.p. ~315° (decomp.), softens at 230° in a sealed capillary (tetra-acetate, becomes brown at 270°, m.p. >370°); direct reduction of (**I**) to (**III**) by Zn dust and NaOH is very slow. (**III**) loses H_2O at >200°/vac. in CO_2 and forms *pentacene*-5 : 12-*quinone*, m.p. 310—315° (decomp.), darkens and softens at 280° in a sealed capillary, which does not give a vat. (**III**), glycerol, and H_2SO_4 at 120—125° give 1 : 14-7 : 8-*dibenzpentacene*-5 : 12-*quinone* (**IV**), m.p. >370°, converted by NaCl, somewhat moist $ZnCl_2$, and Zn dust at 210° into 3 : 3′-7 : 3′-*di*(*trimethylene*)-1 : 2-5 : 6-*dibenzanthracene*, m.p. 255—256°.


(IV.)

H. W.

IV.—STEROLS AND STEROID SAPOGENINS.

Preparation of cholestenes, cholestadienes, and cholestatrienes. E. W. Hollingsworth (*Iowa State Coll. J. Sci.*, 1942, **17**, 80—81).—A summary of work previously abstracted (A., 1941, II, 92; 1942, II, 25, 137, 167). Dehydration of $\Delta^{4:6}$-cholestadien-3-ol and $\Delta^{3:5}$-cholestadien-7-ol probably yields $\Delta^{2:4:6}$- and $\Delta^{3:5:7}$-cholestatriene, respectively.

F. R. G.

Product of irradiation of $\Delta^{6:8}$-coprostadienol. G. Zühlsdorff (*Ber.*, 1940, **73**, [*B*], 328—331; cf. A., 1939, II, 18).—Exposure of $\Delta^{6:8}$-cholestadienol [giving first $\Delta^{6:8}$-coprostadienol (**I**)] in C_6H_6 to a Mg spark light affords (**I**) and *photocholestadienol*-2 (**II**), m.p. 104°, $[\alpha]_D^{19}$ +280° (3 : 5-*dinitrobenzoate*, m.p. 151°), which is isomeric with (**I**), contains two unconjugated double linkings, and gives no insol. digitonide. With Se at 330°, (**II**) affords unidentified oils and a trace of cryst. solid, m.p. 190°. Dehydrogenation of (**II**) with $Al(OBu^v)_3$–$COMe_2$ gives an oily ketone [*semicarbazone*, $C_{28}H_{46}ON_3$, m.p. 231—232° (decomp.), $[\alpha]_D^{18}$ −13·8°]. (**II**) and H_2–Pt-black–AcOH yield a H_2-derivative, m.p. 88—90°, $[\alpha]_D^{17}$ +55·2°, purified through its 3 : 5-*dinitrobenzoate*, m.p. 181°, $[\alpha]_D^{16}$ +53°. (**II**) and HCl–$CHCl_3$ give an *isomeride*, m.p. 136°, $[\alpha]_D^{20}$ −64·5° (3 : 5-*dinitrobenzoate*, m.p. 147—148°, $[\alpha]_D^{21}$ +5·85°; *acetate*, m.p. 92°, $[\alpha]_D^{20}$ −35°; no digitonide), which contains conjugated double linkings and is hydrogenated to a H_2-compound (3 : 5-*dinitrobenzoate*, m.p. 112—113°, $[\alpha]_D^{21}$ +18·2°). [α] are in $CHCl_3$.

A. T. P.

Δ^{11}-Dehydroneoergosterol. A. Windaus and C. Roosen-Runge (*Ber.*, 1940, **73**, [*B*], 321—325).—Irradiation (sunlight) of dehydroergosteryl acetate in EtOH–C_6H_6–eosin in absence of air gives a bimol. diacetate, m.p. 194°, $[\alpha]_D^{13}$ −241° in $CHCl_3$ (cf. Ando, A., 1940, II, 43), converted by Ac_2O at 165—170° into Δ^{11}-*dehydroneoergosteryl acetate* (**I**), $C_{29}H_{40}O_2$, m.p. 199°, $[\alpha]_D^{19}$ +41° in $CHCl_3$. Hydrogenation (Pt-black; AcOH–Et_2O) of (**I**) yields dihydroneoergosteryl acetate, new m.p. 122°.

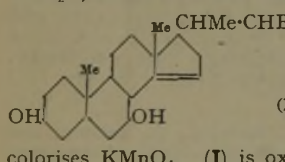
A. T. P.

Subsidiary sterols of yeast. VII. Zymosterol. H. Wieland, F. Rath, and W. Benend. **VIII. Constitution of ascosterol, fæcosterol, episterol, and neosterol.** H. Wieland, F. Rath, and H. Hesse (*Annalen*, 1941, **548**, 19—33, 34—39; cf. A., 1929, 1200; 1937, II, 416; 1942, II, 58).—VII. Zymosterol (**I**), $[\alpha]_D$ +49°, contains an easily reducible terminal C:CMe_2 and a non-reducible C:C at $C_{(9)}$–$C_{(11)}$ (cf. Heath-Brown *et al.*, A., 1941, II, 41). Hydrogenation (PtO_2) of the benzoate (**II**), m.p. 126—128° (clear at 138°), $[\alpha]_D$ +37°, in EtOAc gives *dihydrozymosteryl* [α-*zymostenyl*] *benzoate* (**III**), m.p. 140—142° (clear at 165°), $[\alpha]_D$ +41°, and thence (KOH–MeOH) α-*zymostenol* (**IV**), m.p. 128—129°, $[\alpha]_D$ +50°, also obtained by hydrogenating (**I**) in EtOAc; that of zymosteryl acetate (**V**), m.p. 106—108°, $[\alpha]_D$ +34°, yields α-*zymostenyl acetate*, m.p. 128—129°, $[\alpha]_D$ +31·5°, also obtained from (**IV**) by Ac_2O. Passing HCl into (**III**) in $CHCl_3$ yields β-cholestenyl benzoate (**VI**), m.p. 172—174° (lit. 168°), $[\alpha]_D$ +31° (lit. 32·5°) [and thence β-cholestenol (**VII**), m.p. 131—133° (lit. 130°) (acetate, m.p. 90—92°, $[\alpha]_D$ +22·8°)],

and cholesterol (as benzoate; fully identified). Similar treatment of α-cholestenyl benzoate (**VIII**) yields only (**VI**). 1 H_2 is absorbed by (**VII**) to yield cholestanol and by cholesteryl acetate to yield cholestanyl [zymostanyl] acetate. Short hydrogenation (PtO_2) of (**II**) in Ac_2O–Et_2O gives (**III**), but during longer shaking isomerisation to (**VIII**) occurs; similarly α-cholestenyl acetate is obtained from (**V**); the isomerisations are confirmed by shaking preformed (**III**) and (**IV**) with H_2–Pt–AcOH, but (**I**) is unaffected. With $Al(OPr^{\beta})_3$–*cyclo*hexanone–PhMe or, less well, $Al(OPr^{\beta})_3$–$COMe_2$–C_6H_6 or CuO at 300°, (**I**) gives *zymostadienone*, m.p. 104—105°, $[\alpha]_D^{20}$ +75·5° [purified by way of the *semicarbazone*, m.p. 230° (decomp.)]. Similarly, (**IV**) gives *zymostenone*, m.p. 124—125°, $[\alpha]_D^{20}$ +71·5° (70·5°) [purified by way of the semicarbazone, m.p. 243° (decomp.)], reduced by $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$–PhMe to (**IV**) and a substance, m.p. 155—156°, $[\alpha]_D$ +49°. Ozonisation of (**I**), but not of (**IV**), gives $COMe_2$.

VIII. Ascosterol, new m.p. 140—142°, $[\alpha]_D$ +45°, is $C_{28}H_{45}$·OH. It contains a CH_2: in the side-chain and an ethylenic linking at $C_{(7)}$ or $C_{(8)}$–$C_{(9)}$. The benzoate, new m.p. 128—130°, $[\alpha]_D$ +37·8°, with H_2–PtO_2 in AcOH gives α-ergostenyl benzoate (**IX**), m.p. 136—138° (lit. 118—120°) (identified by mixed m.p., hydrolysis, and then oxidation), and with Pt–N_2–EtOAc gives fæcosterol benzoate (**X**), m.p. 144—146°, $[\alpha]_D$ +34°. The derived fæcosterol, new m.p. 160—162°, $[\alpha]_D$ +42° (acetate, m.p. 159—161°, $[\alpha]_D$ +20°), has a CH_2: in the same position in the side-chain but a $C_{(8:14)}$-ethylenic linking; it is hydrogenated in AcOH to α-ergostenol (**XI**) [(**X**) similarly yields (**IX**)], but is unaffected by Na–PrOH; with O_3 in AcOH it gives 30% of CH_2O. Pt–N_2–Et_2O does not isomerise (**X**). Episterol, m.p. 150—151°, $[\alpha]_D$ −5° (acetate, m.p. 160—162°, $[\alpha]_D$ −3·5°), contains CH_2: in the side-chain and a $C_{(8:14)}$-ethylenic linking; it is reduced (H_2–PtO_2; AcOH) to (**XI**), is unaffected by Pt–N_2–EtOAc, and with O_3 gives 45% of CH_2O. Contrary to Callow (A., 1931, 618), neosterol, $[\alpha]_D$ −42° (acetate, $[\alpha]_D$ −66·7°), is a $C_{(14)}$-epimeride of *iso*ergosterol; with O_3 in AcOH it gives $CHMePr^{\beta}$·CHO (44%); hydrogenation gives α-dihydroergosterol (**XII**), but that of the benzoate, new m.p. 171—173°, $[\alpha]_D$ −42°, or of the benzoate of (**XII**) gives (**IX**). Isolation of the above-named sterols and of (**XII**) from crude yeast-sterols is improved. [α] are in $CHCl_3$. R. S. C.

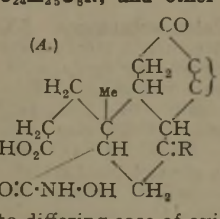
Tetrahydroxycholane [sulphate], trihydroxycholene, and trihydroxybisnorsterocholanic acid from the bile of *Rana catesbina*, Shaw. Y. Kurauti and T. Kazuno (*Z. physiol. Chem.*, 1939, **262**, 53—60).—The bile is extracted with Et_2O and the extract is shaken with dil. aq. Na_2CO_3 (the residual Et_2O-sol. portion is hydrolysed, thereby giving cholesterol), which removes *trihydroxybisnorsterocholanic acid*, (?) $C_{26}H_{44}O_5$, m.p. 172°, $[\alpha]_D^{12}$ +21·58° in EtOH, which gives a violet-red Liebermann but no Hammarsten reaction. It is oxidised by CrO_3 in AcOH to *triketobisnorsterocholanic acid*, m.p. 230—231° (Me ester, m.p. 150°, and its *oxime*, m.p. 222°). Saturation of the bile (freed from Et_2O-sol. substances and mucin) with NaCl gives *Na tetrahydroxycholanyl sulphate* (+H_2O), m.p. 178°, $[\alpha]_D^{19}$ +8·72° in H_2O, which does not decolorise $KMnO_4$ or add Br and is stable to active H. It is hydrolysed by KOH to H_2SO_4 and *trihydroxycholene* (**I**), m.p. 177°, $[\alpha]_D^{15}$ +34·36° in MeOH (*dibromide*, m.p. 180°; *diacetate*, m.p. 180°, and non-cryst. triacetate), which immediately decolorises $KMnO_4$. (**I**) is oxidised by CrO_3–AcOH to *triketocholene* (**II**), m.p. 240—242° (*trioxime*, decomp. 247°), which does not give the Jaffe reaction with picric acid. (**I**) is hydrogenated (PtO_2 in EtOAc) to *trihydroxydihydrocholene* (*trihydroxycholane*), m.p. 185—186°, $[\alpha]_D^{12}$ +31·54° in EtOH, which yields *triketocholane*, decomp. 245°. Reduction (Clemmensen) of (**II**) gives a non-cryst. substance which does not solidify after treatment with H_2–PtO_2. H. W.



(I.)

Bile acids. LVII. Separation of the constituents of ox bile. H. Wieland and W. Seibert [with M. Heki] (*Z. physiol. Chem.*, 1939, **262**, 1—19).—The hydroxycholanic acids can be separated from one another by shaking their solution in Et_2O with 15% aq. HCl which removes cholic acid (**I**) quantitatively whereas deoxycholic (**II**) and anthropodeoxycholic (3 : 7-dihydroxycholanic) acid (**III**) remain almost entirely in the Et_2O, from which they can be removed by 25% aq. HCl; very little lithocholic (**IV**) and no cholanic acid pass into the aq. acid. The separation depends largely at any rate on the basicity of the OH groups. The method is applied to the separation of ox bile into (**I**), (**II**), (**III**), cholesterol (**V**), weak acids, pigment, and fatty acids (**VI**). Successive treatments of (**VI**) with KOH and LiOH removes true (**VI**), leaving the "subsidiary acids" from which a small amount of (**III**) is extracted by 25% aq. HCl; the residual material is esterified (CH_2N_2) and the esters are fractionally hydrolysed, whereby a small proportion of (**IV**) is readily removed; more drastic hydrolysis of the residual esters leads to (**V**) (small amount), sapocholic (**VII**), ursolic, and oleanolic acid. (**VII**) is with difficulty freed from solvent of crystallisation but appears to be $C_{30}H_{48}O_3$; it is best purified through its *acetate*, m.p. 231—233° (*Me* ester, m.p. 185—186°). H. W.

Bile acids. LVIII. Behaviour of the diketohydroxamic acid, $C_{24}H_{25}O_5N$, and other hydroxamic acids towards alkaline permanganate solution. M. Schenck (*Z. physiol. Chem.*, 1939, **262**, 47—52).—Oxidation of the acids *A* (R = O or N·OH) by alkaline permanganate give cilianic acid and N_2 with a small proportion of N_2O. Similar treatment of benz- and acet-hydroxamic acid yields N_2O with a small proportion of N_2. The reaction appears characteristic of hydroxamic acids. The difference in the proportions of the gases evolved is attributed to differing ease of oxidation of the resultant acids. H. W.



Bile acids and related substances. XXVI. Derivatives of ætiocholanic acid with oxygen in 3- and 11-position. A. Lardon and T. Reichstein (*Helv. Chim. Acta*, 1943, **26**, 705—715).—Me 3-keto-Δ^{11}-ætiocholenate and NHAcBr in aq. $COMe_2$ at 18° give *Me* 12-*bromo*-11-*hydroxy*-3-*ketoætiocholanate* (**I**), m.p. 188—190°, and amorphous material (**II**). CrO_3 in AcOH at 18° oxidises (**I**) to *Me* 12-*bromo*-3 : 11-*diketoætiocholanate*, m.p. 170—173°, debrominated (Zn dust and AcOH) to *Me* 3 : 11-*diketoætiocholanate* (**III**), m.p. 184—186°, $[\alpha]_D^{16}$ +92·8°±2° in $COMe_2$. Oxidation followed by debromination of (**II**) gives (**III**), *Me* 3 : 12-*diketo*-Δ^9-*ætiocholenate*, m.p. 174—176°, $[\alpha]_D^{14}$ +91·1°±2° in $COMe_2$, and non-cryst. material. Br in AcOH converts (**III**) into the 4-Br-ester, which passes in boiling C_5H_5N into Me 3 : 11-diketo-Δ^4-ætiocholenate, m.p. 173—177°. Me 3(α)-acetoxy-Δ^{11}-ætiocholenate and NHAcBr in aq. $COMe_2$ at 18° afford the bromohydrin (**IV**), m.p. 216—220°, transformed by oxidation followed by debromination into *Me* 11-*keto*-3(α)-*acetoxyætiocholanate* (**V**), m.p. 147—149°, $[\alpha]_D^{17}$ +98·1°±2° in $COMe_2$; similar treatment of the mother-liquors from (**IV**) affords (**V**) and (?) Me 12-keto-3(α)-acetoxy-Δ^9-ætiocholenate, m.p. 156—158°. Hydrolysis of (**V**) gives the 3(α)-OH-ester, m.p. 155—158°, oxidised to (**III**). Reduction (H_2–PtO_2 in AcOH) of (**III**) leads to Me 3(α)- [identified by conversion into (**V**)] and 3(β)-hydroxy-11-ketoætiocholanate, m.p. 172—175°, $[\alpha]_D^{26}$ +72·1°±2° in $COMe_2$ (*acetate*, m.p. 129—131°, $[\alpha]_D^{26}$ +71·8°±2° in $COMe_2$). M.p. are corr. (block). H. W.

Rearrangement reactions of brominated derivatives of cholesterol. VII. Preparation of $\Delta^{1:2-4:5}$-androstadien-17-ol-3-one. H. H. Inhoffen, G. Zühlsdorff, and H. Minlon (*Ber.*, 1940, **73**, [*B*], 451—457).—2-Bromocholestanone (**I**) and boiling 2 : 6-dimethylpyridine very smoothly yield a *cholestanonyl*-2 : 6-*dimethylpyridinium hydrobromide*, m.p. 299—300°, whereas under similar conditions 2 : 4-dimethylpyridine gives $\Delta^{1:2}$-cholestenone. The formation of pyridinium compounds from (**I**) or 2 : 4-dibromocholestanone appears to be inhibited by Me at $C_{(4)}$ of the C_5H_5N. Androstanolone acetate is converted by Br in AcOH at room temp. into 2 : 4-*dibromoandrostan*-17-*ol*-3-*one*-*acetate*, m.p. 194° (decomp.), converted by boiling anhyd. C_5H_5N into a *pyridinium hydrobromide* $C_{26}H_{34}O_3NBr$, m.p. 228—229°, but by boiling collidine into $\Delta^{1:2-4:5}$-*androstadien*-17-*ol*-3-*one acetate* (**I**), m.p. 151—152°, $[\alpha]_D^{22}$ +28·1° in $CHCl_3$ (*semicarbazone*, m.p. 205—206°), in 69% yield. (**I**) is hydrolysed by boiling KOH–MeOH to $\Delta^{1:2-4:5}$-*androstadien*-17-*ol*-3-*one*, m.p. 168—169°, $[\alpha]_D^{22}$ +22·5° in $CHCl_3$, which is converted by the requisite anhydride and C_5H_5N into the *propionate*, m.p. 138—139°, *butyrate*, m.p. 82—83°, *valerate*, m.p. 76—77°, and *benzoate*, m.p. 215—216°, (**I**) is oxidised [$Al(OPr^{\beta})_3$ and *cyclo*hexanone in boiling PhMe] to $\Delta^{1:2-4:5}$-*androstadiene*-3 : 17-*dione*, m.p. 139—140°, $[\alpha]_D^{24}$ +115·8° in $CHCl_3$ (*disemicarbazone*, decomp. >350°, becomes discoloured at ~320°). H. W.

Isomerisation of 17-hydroxy-20-ketosteroids. III. C. W. Shoppee and D. A. Prins (*Helv. Chim. Acta*, 1943, **26**, 1004—1016).—3(β) : 17(α)-Diacetoxy-Δ^5-pregnen-20-one is scarcely affected when distilled with or without Zn at 210—240°/10 mm. or subjected to protracted treatment in PhMe at 110° or xylene at 140°. With C_5H_5N–HCO·NH_2 it gives a very small proportion of the 17-monoacetate. The corresponding 17(α)-benzoyloxy-3(β)-acetoxy-compound at 250—280°/10 mm. yields 3(β)-acetoxy-$\Delta^{5:16}$-pregnadien-20-one (**I**), m.p. 174°, $[\alpha]_D^{12}$ −29·1°±4° in $COMe_2$, in 20% yield, with a small amount of *pregnatrien*-20-*one*, m.p. 142—143°, softens at ~138°, $[\alpha]_D^{13}$ −106°±3° in $COMe_2$, hydrogenated (PtO_2 in AcOH) to allo*pregnan*-20-*one*, m.p. 128—130° (2 : 4-dinitrophenylhydrazone, m.p. 222—224°), also obtained from *allo*pregnane-3 : 20-dione. 17-OAc or -OBz is therefore difficultly removable from 20-keto-steroids and the direct removal of OH from this class of compounds would appear scarcely practicable. Hence it is probable that the conversion of 17(α)-hydroxy-3(β)-acetoxy-Δ^5-pregnen-20-one (**II**) into (**I**) by $POCl_3$ in C_5H_5N at 100° occurs through the 17-Cl-compound. (**I**) is also obtained in poor yield by converting (C_5H_5N–$POCl_3$) 17(α)-hydroxy-3(β)-acetoxy-Δ^5-pregnen-Δ^{20}-inene into 3(β)-*acetoxy*-$\Delta^{5:16}$-*pregnadien*-Δ^{20}-*inene*, m.p. 175—177°, $[\alpha]_D^{15}$ −59·9°±3° in dioxan, which is then treated with HgO–Ac_2O–AcOH followed by BF_3–Et_2O or with $HgCl_2$–NH_2Ph–H_2O–C_6H_6 at 60°. The product of the reaction of PBr_3 and C_5H_5N on (**II**) according to Juvala (A., 1930, 1401) is not homogeneous and consists largely of 17*a*(β)-hydroxy-3(β)-acetoxy-17*a*-methyl-*D*-homo-Δ^5-androsten-17-one, m.p. 168—170° (alters at 152°); in an excess of cold C_5H_5N, OH is not

exchanged for Br. The mechanism of the changes is discussed. M.p. are corr. (block). H. W.

Constituents of the adrenal cortex and related substances. LX. Δ^{11}-Dehydroprogesterone. P. Hegner and T. Reichstein (*Helv. Chim. Acta*, 1943, **26**, 715—721).—12(β)-Hydroxyprogesterone (prep. starting from Me deoxycholate described) is converted by BzCl in C_5H_5N–C_6H_6 at 20° and then 60° into the *benzoate*, m.p. 164—166°, $[\alpha]_D^{15}$ +96·2°±2° in $COMe_2$. This passes at 310—320°/12 mm. into Δ^{11}-*dehydroprogesterone*, m.p. 175—177°, $[\alpha]_D^{15}$ +180·5°±2° in $COMe_2$, which in the Clauberg test has at least half the physiological activity of progesterone. The "Δ^{11}-dehydroprogesterone" of Shoppee and Reichstein (A., 1941, II, 259) is probably the Δ^9-compound. *Me nordeoxycholate* 12-*monoacetate* has m.p. 176—177°. M.p. are corr. (block). H. W.

Constituents of the adrenal cortex and related substances. LXI. 11-Ketoprogesterone. P. Hegner and T. Reichstein (*Helv. Chim. Acta*, 1943, **26**, 721—729).—Pregnan-12(β)-ol-3 : 20-dione and BzCl in C_6H_6–C_5H_5N at room temp. and then at 60° give the *benzoate*, m.p. 166—167°, $[\alpha]_D^{18}$ +92·6°±1·0° in $COMe_2$, which passes at 308—310°/12 mm. into BzOH and Δ^{11}-*pregnene*-3 : 20-*dione* (**I**), m.p. 132—133°, $[\alpha]_D^{18}$ +84·7°±3°, $[\alpha]_{5461}^{18}$ +104°±3° in $COMe_2$. (**I**) with NHAcBr in aq. $COMe_2$ at 20° gives 12-*bromopregnan*-11-*ol*-3 : 20-*dione* (**II**), m.p. ~238—245° (decomp.), oxidised by CrO_3 in AcOH–$CHCl_3$ to 12-bromopregnane-3 : 11 : 20-trione, m.p. 176—184°, which is debrominated by Zn dust and AcOH to *pregnane*-3 : 11 : 20-*trione* (**III**), m.p. 154—156°, $[\alpha]_D^{20}$ +119·5°±2° in $COMe_2$. This is converted by Br in HBr–AcOH into the 4-Br-compound, m.p. 158—160°, debrominated to 11-ketoprogesterone, m.p. 173—175°, $[\alpha]_D^{18}$ +243·5°±6°, $[\alpha]_{5461}^{18}$ +283°±6° in $COMe_2$, identical with the product from corticosterone. Oxidation of the by-products from (**II**) followed by debromination leads to (**I**), (**III**), probably Δ^9-pregnene-3 : 11 : 20-trione, m.p. 184—186°, and an unidentified substance. M.p. are corr. (block). H. W.

Constituents of the adrenal cortex and related substances. LXII. Partial synthesis of 11-dehydrocorticosterone. A. Lardon and T. Reichstein (*Helv. Chim. Acta*, 1943, **26**, 747—755).—11-*Keto*-3(β)-*acetoxyætiocholanic acid*, m.p. 173—176° after sublimation in a high vac., or m.p. 112° and 173—176° after resolidification if cryst. from Et_2O–light petroleum (Me ester, m.p. 129—131°), is converted by successive treatments with $SOCl_2$ and CH_2N_2 in C_6H_6 into 21-diazopregnan-3(β)-ol-11 : 20-dione acetate, hydrolysed by KOH–MeOH at 20° to the resinous alcohol; this is converted by anhyd. AcOH at 95—100° into *pregnane*-3(β) : 21-*diol*-11 : 20-*dione* 21-*monoacetate* (**I**), m.p. 178—181°, which with Ac_2O–C_5H_5N affords the 3(β) : 21-*diacetate*, m.p. 169—171°. (**I**) is oxidised by CrO_3 in AcOH to *pregnan*-21-*ol*-3 : 11 : 20-*trione acetate*, m.p. 153—155°, $[\alpha]_D^{22}$ +107·2°±4° in $COMe_2$. This with Br in AcOH affords its 4-Br-derivative, converted by boiling C_5H_5N into Δ^4-pregnen-21-ol-3 : 11 : 20-trione acetate (dehydrocorticosterone acetate), m.p. 175—178°, $[\alpha]_D^{22}$ +210·7°±3° in $COMe_2$. M.p. are corr. (block); limit of error ±2°. H. W.

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Dependence of optical rotatory power on chemical constitution. XXII. Rotatory dispersion of enantiomeric *o*-, *m*-, and *p*-nitro- and *p*-dimethylamino-benzylideneaminomethylenecamphor. B. K. Singh and S. C. Sen (*Proc. Indian Acad. Sci.*, 1943, **17**, **A**, 33—40).—Aminomethylene-*d*-, *l*-, or -*dl*-camphor (*A*) with *o*- or *m*-NO_2·C_6H_4·CHO in MeOH at 45—50° gives d- and l-o-, m.p. 168—170°, dl-o-, m.p. 182—183°, d- and l-m-, m.p. 159—161°, and dl-m-*nitrobenzylideneaminomethylenecamphor*, m.p. 150—152°. *p*-NO_2·C_6H_4·CHO, (*A*), and Na_2SO_4 in MeOH at 45—50° or, for *p*-NMe_2·C_6H_4·CHO, at room temp. gives d- or l-p-*nitro*-, m.p. 200—202°, dl-p-*nitro*-, m.p. 214—216°, d-, l-, or dl-p-*dimethylamino-benzylideneaminomethylenecamphor*, m.p. 66—68°. [*M*] decrease in the order $p > m > o$ in MeOH, EtOH, $CHCl_3$, and C_5H_5N (decreasing in that order) but $p > o > m$ in $COMe_2$ (intermediate between EtOH and $CHCl_3$) (cf. Betti, A., 1923, ii, 474). R. S. C.

Attempted preparation of a homocamphor.—See A., 1943, II, 264.

Sesquiterpenes. LIX. Oxidative degradation of the adduct of caryophyllene and maleic anhydride. L. Ruzicka, P. A. Plattner, and L. Werner (*Helv. Chim. Acta*, 1943, **26**, 966—974; cf. A., 1942, II, 370).—Ozonisation of the adduct does not give readily volatile compounds such as aldehyde and ketones and the acids, as Me esters, do not easily volatilise and do not give cryst. derivatives. Oxidation of the crude ozonisation product with $KMnO_4$ in aq. Na_2CO_3, methylation of the product, and fractional distillation of the Me esters followed by hydrolysis leads to $H_2C_2O_4$ as sole crystallisable compound from the more volatile fractions. The less volatile fractions are transformed into the corresponding anilides, thus leading to the recognition of *d-trans*-norcaryophyllenic (**I**), *d-trans*-caryophyllenic (**II**), and homocaryophyllenic acid (**III**)[!] (**I**), m.p. 122—124·5°, $[\alpha]_D^{15}$ +91·8° in C_6H_6, +89·0° in $CHCl_3$, gives a Me ester, b.p. 100°/14 mm., $[\alpha]_D$ +48·6° (l = 1), $[\alpha]_D^{20}$ +59·5° in MeOH, and a *dianilide*, m.p. 178—179°, $[\alpha]_D^{22}$ +178° in $CHCl_3$. (**II**), m.p. 75—77°, $[\alpha]_D^{21}$ +35·3° in C_6H_6 [Me_2 ester, b.p. 85°/0·5 mm., $[\alpha]_D^{22}$ +44·5° in MeOH; *dianilide* (**IV**), m.p. 281—283°, $[\alpha]_D^{51\cdot5}$ +19° in C_5H_5N], is converted by boiling Ac_2O into the *cis*-anhydride, which, with H_2O, gives the *cis*-acid, m.p. 74—75°, $[\alpha]_D^{21}$ −45·3° in C_6H_6 (Me_2 ester, b.p. 85°/0·5 mm., $[\alpha]_D^{20}$ −36·3° in C_6H_6; *dianilide*, m.p. 198—199°, $[\alpha]_D^{20}$ −161° in $CHCl_3$). Esterification of (**III**) and conversion of the ester into the anilide leads to the isolation of (**IV**) and *homocaryophyllendianilide*, m.p. 183—184°, $[\alpha]_D^{22}$ −71·4° in $CHCl_3$ (corresponding non-cryst. acid, $[\alpha]_D^{15}$ +105° in C_6H_6, and its Me_2 ester, b.p. 90°/0·5 mm., $[\alpha]_D^{15}$ +50° in C_6H_6). M.p. are corr. H. W.

4 : 8-Dimethyl-6-*iso*propylazulene.—See A., 1943, II, 258.

Constitution of cafestol. IV. A. Wettstein and K. Miescher (*Helv. Chim. Acta*, 1943, **26**, 788—800; cf. A., 1943, II, 203).—It is shown that cafestol (**I**) contains a furan ring with two double linkings. Oxidation of epoxynorcafestadienone (**II**) in C_6H_6 by $KMnO_4$–Na_2CO_3 does not give well-defined products, whereas oxidation in $COMe_2$ leads to apparently greatly degraded H_2O-sol. materials but no $H_2C_2O_4$. OsO_4 reacts violently but in presence or absence of C_5H_5N only unchanged (**II**) could be isolated; the by-products do not yield homogeneous substances when oxidised further with HIO_4. Treatment of epoxynorcafestadienyl acetate (the free *alcohol*, m.p. 64—66°, becomes dark yellow when exposed to light and air) with $Pb(OAc)_4$ in C_6H_6 consumes 1 mol. of the reagent but gives very unstable products. Oxidation of cafestyl acetate by *o*-CO_2H·C_6H_4·CO_3H in Et_2O and hydrogenation (PtO_2 in AcOH) of the product leads to *cafestanetriolcarboxylolactone monoacetate* [*dihydroxycafestanolide monoacetate*] (**III**), m.p. 244—245°, which is saturated, scarcely affected by catalytic hydrogenation, does not reduce Ag_2O–NH_3, does not give a semicarbazone, contains 1 active H, and is not affected by Ac_2O–C_5H_5N or CrO_3–AcOH at room temp. (**III**) is hydrolysed by K_2CO_3 in boiling aq. MeOH to *dihydroxycafestanolide*, m.p. 231—232°, degraded by HIO_4 to ketonorcafestanolide *B*, m.p. 225—226° when rapidly heated, 231—232° (transformation into prisms) when slowly heated (2 : 4-*dinitrophenylhydrazone*, decomp. 310°). The reaction of (**I**), its derivatives, and kahweol with $SbCl_3$ and other colour reactions are described. H. W.

Irradiation of abietic acid with ultra-violet rays. R. F. Brown, G. B. Bachman, and S. J. Miller (*J. Amer. Chem. Soc.*, 1943, **65**, 623—626).—Irradiation (Hg lamp) has no effect on abietic acid in C_6H_{14} or C_6H_6, but in EtOH gives di- (**I**) and tetra-hydroxyabietic acids, formed by virtue of MeCHO which is produced (separate experiment) by irradiation of the solvent EtOH. The acids are separated by making use of their insolubility in C_6H_{14} and pptg. (**I**) therefrom by Bu_2O. R. S. C.

VI.—HETEROCYCLIC.

Effect of reduction on the rotatory power of some furan compounds. S. D. Willson (*Iowa State Coll. J. Sci.*, 1942, **17**, 161—162).—Reduction of *l*-β-(2-furyl)valeric and *d*-β-(2-furyl)hexoic acid to the tetrahydro- and finally to the Bu^{α} derivatives is accompanied in both cases by reversal in the signs of rotation, contrary to theory. Similarly in the reduction of *d*-β-phenyl-β-(2-furyl)propionic acid the sign remains unchanged. F. R. G.

Acylation of 3-hydroxyfurans. R. E. Lutz, C. E. McGinn, and P. S. Bailey (*J. Amer. Chem. Soc.*, 1943, **65**, 843—849).—3-Acetoxy-2 : 5-diphenylfuran (**I**) with MgMeI–Et_2O gives the 3-O·MgI derivative (**II**), which with AcCl at the b.p. regenerates (**I**), with BzCl at 10° and then the b.p. gives 3-*benzoyloxy*-2 : 5-*diphenylfuran* (62%), m.p. 139—140° [not obtainable from $(CHBz:)_2$ by Bz_2O–H_2SO_4; with Ac_2O–H_2SO_4 at 25° or MgMeI and then AcCl (excess) gives (**I**)], cannot be methylated with MeI or Me_2SO_4 but with 5% HCl and then CH_2N_2–Et_2O gives a little 3-methoxy-2 : 5-diphenylfuran, with CH_2Cl·OMe–Et_2O at the b.p. gives 2 : 5-*diphenyl*-3-*methoxymethylfuran*, m.p. 75—75·5° (with Ac_2O–H_2SO_4 or PCl_5 gives oils), and with $ClCO_2Et$–Et_2O at the b.p. gives *Et* 2 : 5-*diphenylfuran*-3-*carboxylate* (**III**), m.p. 66—67° [unaffected by H_2SO_4–AcOH at 25°; converted by MgEtI–Et_2O and then AcCl into (**I**)]. With PCl_5 at 25° and then H_2O, (**III**) yields 2-chloro-2 : 5-diphenyl-2 : 3-dihydrofuran-3-one, which with MgMeI–Et_2O and then AcCl gives 2 : 5 : 2′ : 5′-tetraphenyldi-2 : 3-dihydrofuran-3-on-2-yl (**IV**), m.p. 257—259°, also obtained from (**I**) by boiling $FeCl_3$–conc. HCl–EtOH and converted into (**I**) by MgEtBr–Et_2O, followed by AcCl, or in poor yield (owing to further reduction) by H_2–PtO_2–$ZnCl_2$–HCl–Ac_2O. With Br–CCl_4, (**IV**) gives its 4 : 4′-Br_2-derivative, m.p. 278—280° (decomp.), also obtained by boiling 2-chloro-4-bromo-2 : 5-diphenyl-2 : 3-dihydrofuran-3-one with Cu-bronze in C_6H_6. 3-Acetoxy-2 : 4 : 5-triphenylfuran (**V**) (prep. from CPhBz:CHBz by H_2SO_4–Ac_2O at room temp.) with MgEtBr–Et_2O–N_2 and then (*a*) 5% H_2SO_4 gives 2 : 4 : 5 : 2′ : 4′ : 5′-hexaphenyldi-2 : 3-dihydrofuran-3-on-2-yl (**VI**), (*b*) Me_2SO_4–C_6H_6 gives oils, or (*c*) BzCl or AcCl gives 2-hydroxy-2 : 4 : 5-triphenyl-2 : 3-dihydrofuran-3-one. CPhBz:CHBz, Bz_2O, and H_2SO_4 at 50° give 3-*benzoyloxy*-2 : 4 : 5-*triphenylfuran*, m.p. 147·5—148°. $FeCl_3$–conc. HCl–AcOH–H_2O or I–conc. HCl–AcOH–H_2O oxidises (**V**) to (**VI**),

m.p. 272—275° (unaffected by Br), which with boiling MgEtBr–Et_2O–N_2 and then (*a*) Br–MeOH gives 2-methoxy-2 : 4 : 5-triphenyl-2 : 3-dihydrofuran-3-one or (*b*) AcCl gives (**V**), also formed by hydrogenation [cf. (**IV**)]. 4-Acetoxy-2 : 5-diphenyl-3-methylfuran (**VII**) with MgEtBr–Et_2O–N_2 and then (*a*) AcCl regenerates (**VII**) and (*b*) BzCl gives 4-*benzoyloxy*-2 : 5-*diphenyl*-4-*methylfuran* (**VIII**), m.p. 129·5—130°, some difuranonyl (**IX**) being also obtained in both cases. Hydrolysis of the O·MgBr derivative from (**VII**) and acylation of the crude oil obtained also gives (**VII**) and (**IX**). (**IX**) is not obtained from CPhBz:CPhMe by Bz_2O–H_2SO_4; with MgEtBr and then AcCl it yields (**VII**). R. S. C.

3-Hydroxy-2 : 5-dimesitylfuran and related compounds. R. E. Lutz and C. E. McGinn (*J. Amer. Chem. Soc.*, 1943, **65**, 849—853).—3-Acetoxy-2 : 5-dimesitylfuran (**I**) (modified prep.) is hydrolysed by H_2SO_4 (a little) in boiling AcOH–H_2O (not at room temp.), absorbs 0·92 O in KOH–90% MeOH at room temp. to yield COM·C(OH):CH·COM (M = mesityl) (**II**), and with PCl_5 at 100°, Br–$CHCl_3$ or I–EtOH at room temp., or boiling AcOH–HCl–$SnCl_2$ gives 2 : 5 : 2′ : 5′-*tetramesityldi*-2 : 3-*dihydrofuran*-3-*on*-2-*yl* (**III**), m.p. 184—185°. The 3-OM·gBr derivative, prep. from (**I**) by MgEtBr–Et_2O–N_2, with AcCl regenerates (**I**), with 10% HCl and then O_2–MeOH yields (**III**), with Br–Et_2O at −10° gives (**II**) and a *Br*-compound, m.p. 129—129·5°, and with BzCl gives 3-*benzoyloxy*-2 : 5-*dimesitylfuran*, m.p. 116—116·5° [with MgEtBr and then AcCl gives (**I**)]. HCl–MeOH converts (**I**) into 3-*methoxy*-2 : 5-*dimesitylfuran*, m.p. 90—91° (cf. A., 1942, II, 316), also obtained from *cis*-δ-methoxy-αδ-dimesityl-Δ^{γ}-buten-α-ol-β-one by dry HCl, converted by HNO_3–AcOH at 100° into (**II**) and by PCl_5–$CHCl_3$ into oils, but unaffected by MgRX, boiling HCl–AcOH, KOH– or NaOMe–MeOH, AcCl–H_2SO_4, NH_2OH, NH_2·CO·NH·NH_2, or Zn–AcOH. Boiling 10 : 1 : 1 AcOH–HCl–H_2O or AcOH–HCl–$SnCl_2$ converts (**III**) into (**II**) and 2 : 4 : 6 : 1-$C_6H_2Me_3$·CO_2H, MgEtBr and then RCOCl gives the 3-RCO-furans, but KOH–MeOH at room temp. and NH_2OH are without effect. With Br–CCl_4, (**III**) gives 4-*bromo*-2-*hydroxy*-2 : 5-*dimesityl*-2 : 3-*dihydrofuran*-3-*one*, m.p. 143—144°, unaffected by boiling 2N-NaOMe–MeOH, PCl_5 at 100°, AcCl–H_2SO_4 at 35°, Ac_2O–H_2SO_4 at 100°, or KI–AcOH at 80°, but converted by AcOH–H_2O–HCl into COM·C(OH):CBr·COM, by MgMeI in (*iso*-C_5H_{11})$_2O$–N_2 at 100° into a *compound*, $C_{23}H_{27}O_3Br$, m.p. 159·5—160° (hydrolysed to a compound, m.p. 139—139·5°), and by $SnCl_2$–AcOH–HCl into $(CH_2{\cdot}COM)_2$. COM·CH:CMe·COM with HBr–AcOH–H_2SO_4 at 40° gives 3-*bromo*-2 : 5-*dimesityl*-4-*methylfuran*, m.p. 159—160°. Ac_2O–H_2SO_4 (a little) at room temp. converts (**II**) into 3 : 4-*diacetoxy*- (**IV**), m.p. 154·5—155° [short reaction gives only the enol acetate of (**II**)], and $(EtCO)_2O$–H_2SO_4 (a trace) at 60° gives 3 : 4-*dipropionyl*-2 : 5-*dimesitylfuran*, m.p. 72—72·5°, converted into (**IV**) by MgEtI and then AcCl. 2-Hydroxy-2 : 5-dimesityl-2 : 3-dihydrofuran-3-one could not be obtained. M.p. are corr. R. S. C.

Natural α-, β-, and γ-tocopherols and esters of physiological interest. J. G. Baxter, C. D. Robeson, J. D. Taylor, and R. W. Lehman (*J. Amer. Chem. Soc.*, 1943, **65**, 918—924).—Mixed tocopherols are separated from refined cottonseed oil and wheat-germ oil by short-path distillation. The tocopherols are partly separated by chromatography and then purified as *α-tocopheryl H succinate*, m.p. 76—77°, $[\alpha]_{5461}^{25}$ +4·4° in EtOH, +2·6° in C_6H_6 (photomicrograph; Na salt; corresponding *dl*-ester, a gel), or *palmitate*, m.p. 42—43° (photomicrograph; corresponding dl-*ester*, m.p. 36—38°), *β-tocopheryl azobenzene*-4-*carboxylate*, m.p. 70—71° (photomicrograph), and *γ-tocopheryl palmitate*, m.p. 44—45°, $[\alpha]_{5461}^{25}$ +3·4° in C_6H_6 (photomicrograph). Co-crystallisation of α- and (oily) γ-tocopheryl H succinates is recorded and there is little depression of the m.p. Alkaline hydrolysis (N_2) of the esters yields α- (**I**), $[\alpha]_{5461}^{25}$ +0·32° in EtOH, −3·0° in C_6H_6 (allophanate, m.p. 157—158°), β- (**II**), $[\alpha]_{5461}^{23}$ +2·9° in EtOH (allophanate, m.p. 138—139°), and γ-tocopherol (**III**), $[\alpha]_{5461}^{25}$ +2·2° in EtOH, −2·4° in C_6H_6, which are purified by short-path distillation. Absorption spectra of the esters and alcohols are given. The vitamin-*E* activity of the α- and γ-esters, which are non-toxic to man, parallel their tocopherol contents. In the Emmerie–Engel method of analysis, (**I**) is oxidised faster than (**II**) and this slightly faster than (**III**); the procedure is modified so as to retard the reaction and measure the colour when all three give the same *L* val. Under identical conditions the degrees of oxidation by $AgNO_3$ are (**I**) 24, (**II**) 30, and (**III**) 91%; these differences are utilised in analysing mixtures. (**I**), (**II**), and (**III**) give I vals. (Wijs) 143, 138, and 152, respectively. R. S. C.

Condensation of α-substituted acetoacetates with phenols. VIII. Condensation of *C*-alkylresorcinols and ethylpyrogallol with ethyl acetosuccinate. R. H. Shah and N. M. Shah (*J. Indian Chem. Soc.*, 1942, **19**, 489—491; cf. A., 1942, II, 268).—Et_2 acetosuccinate (**I**), 1 : 2 : 4-$C_6H_3Et(OH)_2$, and 80% H_2SO_4 or $POCl_3$ at room temp. give *Et* 7-*hydroxy*-4-*methyl*-6-*ethylcoumarin*-3-*acetate*, m.p. 184—185° (*acetate*, m.p. 146—147°; *benzoate*, m.p. 123°; *Me ether*, m.p. 93—94°), hydrolysed by 2N-NaOH to the corresponding *acid*, m.p. 221—222° (acetate, m.p. 209°; benzoate, m.p. 160°; anilide, m.p. 257°), which could not be decarboxylated. The respective 4-alkylresorcinol affords *Et* 7-*hydroxy*-4-*methyl*-6-*propyl*-, m.p. 170° [*acetate*, m.p. 100—101°; *benzoate*, m.p. 115—116°; *Me ether* (**II**), m.p. 94—95°; corresponding *acid*, m.p. 199—200° (acetate, m.p. 203°; *Me ether*, m.p. 176°, obtained during prep. of (**II**)], and -6-*butyl*-*coumarin*-3-*acetate*, m.p. 165—166° [*acetate*, m.p. 116—117°; *benzoate*, m.p. 124°; Me ether, m.p. 88°; free *acid*, m.p. 205° (*Me ether*, m.p. 160°)], and *Et* 7-*hydroxy*-4 : 6-*dimethylcoumarin*-3-*acetate*, m.p. 183—184° (*acetate*, m.p. 168—169°). 4-Ethylpyrogallol and (**I**) give *Et* 7 : 8-*dihydroxy*-4-*methyl*-6-*ethylcoumarin*-3-*acetate*, m.p. 150—151° [*acetate*, m.p 149°; *benzoate*, m.p. 163°; free *acid* (HCl–AcOH), m.p. 275° (*acetate*, m.p. 153—154°)]. A. T. P.

***cis–trans*-Rearrangement of *o*-coumaric acid glucoside, glucoside of *o*-hydrocoumaric acid, and the occurrence of coumarins in the tonka bean.** H. Lutzmann (*Ber.*, 1940, **73**, [*B*], 632—643).—The syrupy end-product of the synthesis of tetra-acetyl-β-*d*-glucosido-coumarinic acid (A., 1939, II, 51) and Ac_2O–C_5H_5N at 0°, then at room temp., give *trans*-tetra-acetyl-β-*d*-glucosido-*o*-coumaric acid, m.p. 186—187°, $[\alpha]_D^{21}$ −55·3° in $CHCl_3$. Ultra-violet irradiation of Na β-*d*-glucosido-*o*-coumarate at 40° and *p*H ~6·9, for 6 days, effects ~86% *trans–cis*-transformation; $[\alpha]_D^{19}$ changes from −7·56° to −5·64° (pure *cis*-glucoside has −5·75°), and glucose and traces of *o*-coumaric acid (**I**) and coumarin (**II**) are detected. Numerous comparisons are made of the pure *cis*- and *trans*-compounds and the product of irradiation. β-d-*Glucosidohydro*-o-*coumaric acid*, m.p. 173° (sinters from 143—145°), $[\alpha]_D^{20}$ −56·1° in H_2O, is prepared by hydrogenation (Pd–$BaSO_4$–MeOH) of the glucosido-*o*-coumaric acid. Extraction with $COMe_2$ of ripe tonka bean gives (**II**) and a trace of (**I**). Minute traces of (**II**) may be detected from the green fluorescence under the quartz lamp. A. T. P.

Anthochlor pigments. IV. Pigments of *Coreopsis grandiflora*, Nutt. I. T. A. Geissman and C. D. Heaton (*J. Amer. Chem. Soc.*, 1943, **65**, 677—683; cf. A., 1942, II, 421).—The yellow petals of *C. grandiflora*, Nutt., give a red colour in alkali but contain no anthochlor pigment. Extraction with EtOH at 0° yields *leptosidin* (probably 5-*hydroxy*-6-*methoxy*-1-3′ : 4′-*dihydroxybenzylidenecoumaran*-2-*one*) (**I**), orange-yellow, m.p. 252—254° (decomp.), *leptosin* (**II**), $C_{22}H_{22}O_{11}$, +$2H_2O$, orange, m.p. 229—231° (decomp.), a *flavanone* (probably 8-*methoxybutin*) (**III**), pale yellow, m.p. 195—197°, and luteolin (isolated as tetra-acetate). NaOAc–Ac_2O converts (**II**) into a *hexa-acetate*, m.p. 233—234°, and dil. HCl at 100° yields a reducing sugar [probably glucose (osazone)] and a residue, which by acetylation yields *leptosidin triacetate* (**IV**), m.p. 164·5—165·5° [also obtained from (**I**) by NaOAc–Ac_2O]. In cold, dil. alkali, (**II**) gives a deep purple and in conc. H_2SO_4 a red colour. Thus, (**II**) is probably the 5-*glucoside* of (**I**). Me_2SO_4–KOH–MeOH–H_2O converts (**IV**) into *leptosidin Me*$_3$ (**V**), m.p. 156—157° (red in conc. H_2SO_4), and a little (?) *Me*$_2$ *ether*, m.p. 203—205°; (**V**) and a small amount of a substance, m.p. 193—194°, are obtained from (**I**) by an excess of CH_2N_2 in Et_2O–MeOH at 0°; these findings exclude a chalkone or flavanone structure. With 3 mols. of CH_2N_2 in Et_2O–MeOH, (**I**) gives a *Me*$_1$ *ether*, m.p. 213—214° (purple in alkali) [cf. the known 5 : 6-$(OMe)_2$-compound, m.p. 217°]. $KMnO_4$ in $COMe_2$ oxidises (**V**) to veratric acid (**VI**) [proof of the 3′ : 4′-$(OH)_2$], but H_2O_2–KOH–H_2O–$COMe_2$ yields a small amount of (?) a 1 : 1 mixture of (**VI**) and a dimethoxysalicylic acid (purple $FeCl_3$ colour). In aq. NaOH at 0°, (**III**) is pale red, becoming dark red if kept or warmed. In warm NaOAc–Ac_2O (few min.), (**III**) gives its *triacetate* (**VII**), m.p. 122—123·5°, but after boiling therewith for 4 hr. gives the $(OAc)_4$-*chalkone* derivative, 3 : 2 : 4 : 1-OMe·$C_6H_2(OAc)_2$·CO·CH:CH·$C_6H_3(OAc)_2$-1 : 3 : 4, m.p. 106—107·5°. With Mg and HCl, (**III**) or (**VII**) gives a bluish-violet colour resembling that given by butin or its triacetate. CH_2N_2 (excess) and (**III**) in MeOH–Et_2O give (?) 7 : 8 : 3′ : 4′-tetramethoxyflavanone, m.p. 140° (lit. 144°). (**III**) may exist in the petals as the chalkone. The orientations assigned depend on colour reactions and biogenetic relations; the OH assigned to $C_{(5)}$ in (**I**) and (**II**) and $C_{(7)}$ in (**III**) may be at $C_{(3)}$ and $C_{(5)}$, respectively. In cold, dil. alkali, (**I**) gives a deep red and in conc. H_2SO_4 a bright red colour; the colour given by the petals in alkali is largely due to (**I**). R. S. C.

Introduction of allyl residues into aromatic compounds.—See A., 1943, II, 261.

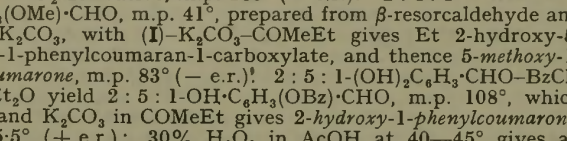
Xanthone-2 : 7-dinitrile. H. J. Fisher (*J. Amer. Chem. Soc.*, 1943, **65**, 991).—By a diazo-reaction 2 : 7-diamino- gives 2 : 7-*dicyano-xanthone*, cryst. R. S. C.

Cannabis indica. **XII. Some analogues and a water-soluble derivative of tetrahydrocannabinol.** F. Bergel, A. L. Morrison, H. Rinderknecht, A. R. Todd, A. D. Macdonald, and G. Woolfe (*J.C.S.*, 1943, 286—287).—By condensing 4″ : 6″-dihydroxy-2 : 2 : 5′-trimethyl-3′ : 4′ : 5′ : 6′-tetrahydrodibenzopyran with the appropriate alkyl bromide (NaOEt–EtOH) the following have been obtained: 6″-*hydroxy*-4″-n-*hexoxy*- (**I**), b.p. 205—209°/0·2 mm., -n-*butoxy*-, b.p. 185—189°/0·01 mm., -n-*amyloxy*-, b.p. 205—210°/0·1 mm., and -n-*heptoxy*-2 : 2 : 5′-*trimethyl*-3′ : 4′ : 5′ : 6′-*tetrahydrodibenzopyran*, b.p. 210—215°/0·15 mm.; only (**I**) shows feeble activity by the Gayer method on rabbits. 6″-Hydroxy-2 : 2 : 5′ : 4″-tetramethyl-3′ : 4′ : 5′ : 6′-tetrahydrodibenzopyran in C_5H_5N with $POCl_3$ gives the 6″-O-*dichlorophosphoryl* compound, b.p. 170°/0·15 mm., which after hydrolysis to the acid forms the *Na*$_2$ *phosphate*. Tetrahydro-

cannabinol similarly affords the *O-dichlorophosphoryl* derivative, b.p. 185°/0·1 mm., the sol. Na_2 tetrahydrocannabinyl phosphate from which shows no apparent hashish activity. B.p. are bath temp. F. R. S.

Egonol. X. Synthesis of 2-[1-]phenylcoumarone derivatives, and their egonol reactions. S. Kawai, T. Nakamura, and M. Yoshida. **XI. Active hydrogen atom of egonol, directly bound to carbon.** S. Kawai, N. Sugiyama, T. Nakamura, and K. Komatsu [with M. Shinkai] (*Ber.*, 1940, **73**, [*B*], 581—585, 586—595; cf. A., 1939, II, 383).—X. *o*-Vanillin, $CHPhBr{\cdot}CO_2Et$ (**I**), and K_2CO_3–COMeEt give, after hydrolysis and decarboxylation (method: *loc. cit.*), *6-methoxy-1-phenylcoumarone*, m.p. 73° (gives + e.r. = egonol reaction; cf. A., 1939, II, 32), converted by HNO_3 (*d* 1·38) in Ac_2O into the 4-NO_2-derivative, m.p. 160° (— e.r.). 2 : 4 : 1-$OH{\cdot}C_6H_3(OMe){\cdot}CHO$, m.p. 41°, prepared from β-resorcaldehyde and Me_2SO_4–K_2CO_3, with (**I**)–K_2CO_3–COMeEt gives Et 2-hydroxy-5-methoxy-1-phenylcoumaran-1-carboxylate, and thence *5-methoxy-1-phenylcoumarone*, m.p. 83° (— e.r.)! 2 : 5 : 1-$(OH)_2C_6H_3{\cdot}CHO$–BzCl–K_2CO_3–Et_2O yield 2 : 5 : 1-$OH{\cdot}C_6H_3(OBz){\cdot}CHO$, m.p. 108°, which with (**I**) and K_2CO_3 in COMeEt gives *2-hydroxy-1-phenylcoumarone*, m.p. 185·5° (+ e.r.); 30% H_2O_2 in AcOH at 40—45° gives an impure *product* (constitution discussed).

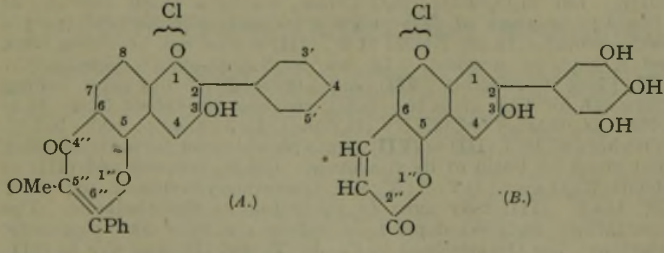
XI. Acetylegonol [6-methoxy-1-3′ : 4′-methylendioxy-4-γ-acetoxypropylcoumarone] (**II**) and Br–AcOH give *4-bromoacetylegonol* (**III**), m.p. 124·5—125° (— e.r.), converted by KOAc in *iso*-$C_5H_{11}{\cdot}OH$ into *4-bromoegonol*, m.p. 164—165°. (**II**) and HNO_3 (*d* 1·38)–Ac_2O at −5° to −10° give *3-nitro-* (**IV**), m.p. 160° (+ e.r.; 70—80° for 0·5 hr.), *4-nitro-*, m.p. 161° (— e.r.), and some *6-nitro-acetylegonol*, m.p. 139° (+ e.r.). (**IV**) and 30% H_2O_2–AcOH at 70—75° yield *3-nitronoregonolonidin acetate* (**V**), m.p. 144—145°. (**III**) and 30%



(V.)

H_2O_2–AcOH at 60—70° give a product, which with $COPh{\cdot}CH_2Br$ yields *phenacyl 2-bromo-6-3′ : 4′-methylenedioxybenzoyloxy-5-methoxy-3-α-hydroxy-γ-acetoxypropylbenzoate*, $C_{29}H_{25}O_{11}Br$, m.p. 172—173°. The content of active H in several of these compounds is determined and theoretical aspects are discussed. A. T. P.

Flavylium salts containing pyrone rings. L. R. Row and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1942, **15**, **A**, 118—122).—7-Hydroxy-3-methoxyflavone-8-aldehyde with the appropriate nuclear hydroxy-ω-hydroxyacetophenone in HCl–EtOH–EtOAc at 0° gives 3 : 4′-*di-* (numbering as *A*) (prep. in EtOAc) (83%), $+2H_2O$, m.p. 227—229°, 3 : 3′ : 4′-*tri-* (60%), $+2H_2O$, m.p. 240—242° (decomp.), and 3 : 3′ : 4′ : 5′-*tetra-hydroxy-5″-methoxy-6″-phenyl-1″* : *4″-pyrono-2″* : *3″-5* : *6-flavylium chloride* (58%), $+4H_2O$, m.p. >320°. Um-



belliferone-8-aldehyde gives similarly 3 : 4′-*di-* (65%), $+0·5H_2O$, m.p. 255—257° (decomp.), 3 : 3′ : 4′-*tri-* (65%), $+H_2O$, m.p. 225—227° (decomp.), and 3 : 3′ : 4′ : 5′-*tetra-hydroxy-1″* : *2″-pyrono-6″* : *5″-5* : *6-flavylium chloride* (*B*) (91%), $+3H_2O$, m.p. >320°. The salts readily lose halogen to give colour bases, have weak tinctorial properties, and fluoresce only slightly in H_2SO_4. R. S. C.

Natural coumarins. LII. Constitution of oroselone. E. Späth, N. Platzer, and H. Schmid (*Ber.*, 1940, **73**, [*B*], 709—718; cf. A., 1939, II, 485).—Athamantin (**I**), $[\alpha]_D^{22}$ +96° in MeOH, and HCl–MeOH give $Bu^{\beta}CO_2H$ and *oroselone* (**II**), $C_{14}H_{10}O_3$, sublimes at 140—150°/0·1 mm., m.p. 188—189°, [α] 0°; (**II**) is most probably 5′-(α-methylvinyl)furano-2′ : 3′-7 : 8-coumarin, and with Me_2SO_4–aq. NaOH gives the *Me ether*, $C_{15}H_{14}O_4$, m.p. 233°, of orosolonic acid. Hydrogenation (Pd–C; AcOH) of (**II**) at 18° yields *dihydro-* (**III**), m.p. 142°, and *tetrahydro-* (**IV**), m.p. 60—62°, and at 40—50° *hexahydro-oroselone* (**V**), m.p. 98°. (**IV**) and aq. $KMnO_4$–NaOH give $(CH_2{\cdot}CO_2H)_2$ + $Pr^{\beta}CO_2H$. (**V**) with CH_2N_2 yields the *Me* ester, $C_{15}H_{20}O_4$, m.p. 72—73°, of hexahydro-orselonic acid, further methylated to its *Me ether*, $C_{16}H_{22}O_4$, an oil (OH also is methylated). (**V**) is unchanged with Ac_2O at 150—160°. (**V**) and HNO_3 (*d* 1·4) at 20°, then at 100° (bath), give $(CH_2{\cdot}CO_2H)_2$. (**II**) and O_3–$CHCl_3$ yield 2 : 4 : 1 : 3-$(OH)_2C_6H_2(CHO)_2$ and (less O_3) 7-hydroxycoumarin-8-aldehyde (**VI**), m.p. 186·5—187°. (**III**) similarly gives a little (**VI**) and $Pr^{\beta}CO_2H$. In (**III**) the $CMe{:}CH_2$ becomes Pr^{β}, in (**IV**) the coumarin ring is also hydrogenated, and in (**V**) the furan ring. A. T. P.

Degradation of coumarones and thionaphthens by ozone. A. von Wacek, H. O. Eppinger, and A. von Bézard (*Ber.*, 1940, **73**, [*B*], 521—531).—O_3 is quantitatively added by coumarone (**I**) in indifferent solvents and the ozonide is decomposed by warm H_2O into *o*-$OH{\cdot}C_6H_4{\cdot}CO_2H$ (~25%), *o*-$OH{\cdot}C_6H_4{\cdot}CHO$ (~40%), HCO_2H, CO_2, and *o*-$C_6H_4(OH)_2$ (~10%). *o*-$CO_2H{\cdot}C_6H_4{\cdot}O{\cdot}CHO$ and *o*-$CHO{\cdot}C_6H_4{\cdot}O{\cdot}CO_2H$ are presumably intermediates. Resinification is not pronounced. The solvent (EtCl, AcOH, $COMe_2$, $CHCl_3$) has no influence on the reaction products or their amounts. Fission of the furan ring occurs during the primary ozonisation and not by secondary oxidation by H_2O_2 since reductive fission of the ozonide leads to *o*-$C_6H_4(OH)_2$. It is improbable that (**I**) reacts in a mesomeric form since *o*-$C_6H_4(OH)_2$ is obtained from *o*-$OH{\cdot}C_6H_4{\cdot}CH{:}CH_2$ which has no mesomeric form whilst the possibly mesomeric $C_6H_4{<}_{C_6H_4}{>}O$ does not add O_3. *o*-$C_6H_4(OH)_2$ is obtained by secondary oxidation of *o*-$OH{\cdot}C_6H_4{\cdot}CHO$ which has been effected by H_2O_2, Na_2O_2, H_2SO_5, etc.; this change occurs to only a small extent by ozonisation of $OH{\cdot}C_6H_4{\cdot}CHO$ but a decomp. ozonide can behave as an oxidising agent; thus, *o*-$OH{\cdot}C_6H_4{\cdot}CHO$ is almost quantitatively converted into *o*-$C_6H_4(OH)_2$ by oleic acid ozonide. 1-Methylcoumarone behaves similarly but gives AcOH in place of HCO_2H. *o*-$OAc{\cdot}C_6H_4{\cdot}CO_2H$ and *o*-$OAc{\cdot}C_6H_4{\cdot}CHO$ could not be isolated; the possibility that the peroxidic compound of the decomp. ozonide accelerates their hydrolysis is strengthened by the observation that the first compound is hydrolysed by $NaHCO_3$ only after addition of H_2O_2. 2-Methylcoumarones give only *o*-$OH{\cdot}C_6H_4COMe$ with *o*-$C_6H_4(OH)_2$, which can be obtained from it by oxidation with H_2O_2. Coumarones methylated in the C_6H_6 nucleus afford the corresponding *o*-hydroxytoluic acids and aldehydes with the methylpyrocatechols. In principle thionaphthen behaves similarly to (**I**) but the instability of thiols towards oxidising agents involves their isolation as the corresponding disulphides. Small quantities of sulphonic acids are also obtained; these could not be certainly identified on account of their small yield but appear to be phenol-*o*-sulphonic acids. The yields of $(S{\cdot}C_6H_4{\cdot}OH\text{-}o)_2$ and $(S{\cdot}C_6H_4{\cdot}CHO\text{-}o)_2$ attain 50% and 20% respectively. The ozonisation of coumarones is a simple quant. degradation which gives very small amounts of resin. The products are easily obtained pure. The secondary peroxidic action can cause rupture of the C chains which are replaced by OH groups. H. W.

Photo-oxidation of thioketones.—See A., 1943, II, 265.

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

Isomerisation during dehydrogenations in the pyridine series. II. V. Prelog and E. Moor [with J. Führer] (*Helv. Chim. Acta*, 1943, **26**, 846—848).—3-Acetyl-1-methylpiperidine (**I**) is converted by Se at 300° into 2 : 3-dimethylpyridine, isolated as the picrate, m.p. 183—184°, platinichloride, m.p. 196°, and aurichloride, m.p. 164°. (**I**) is reduced by $N_2H_4.H_2O$ and NaOMe in MeOH at 170—180° to 1-methyl-3-ethylpiperidine, which is largely unchanged by Se at 300° but passes at 350° into 3-ethylpyridine. H. W.

New synthesis of 2-aminopyridine derivatives. A. Dornow and P. Karlson (*Ber.*, 1940, **73**, [*B*], 542—546).—$OEt{\cdot}C(:NH){\cdot}CH_2{\cdot}CO_2Et$ (**I**) condenses with $(CO)_2$-compounds (mol. ratio, 2 : 1) to amidine-like intermediates $COR'{\cdot}CH_2{\cdot}CH{:}C(CO_2Et){\cdot}C(:NH){\cdot}N{:}C(OEt){\cdot}CH_2{\cdot}CO_2Et$ (**II**), which then undergo ring-closure with hydrolytic elimination of $CH_2(CO_2Et)_2$ and production of 2-aminopyridine derivatives. (**II**) and $OEt{\cdot}CH{:}CH{\cdot}CH(OEt)_2$ at 100° slowly afford *Et 2-aminopyridine-3-carboxylate*, b.p. 133°/12 mm., m.p. 92° (*picrate*, m.p. 199°). This is hydrolysed by boiling conc. HCl to the *acid*, m.p. 308° (decomp.) (*hydrochloride*, m.p. 214—216°; *picrate*, m.p. 229—230°), which passes above its m.p. into 2-aminopyridine (picrate, m.p. 218°) and is converted by HNO_2 into 2-hydroxypyridine-3-carboxylic acid, m.p. 255° (decomp.). (**I**) and $OEt{\cdot}CMe{:}CH{\cdot}CH(OEt)_2$ or $CH_2Ac{\cdot}CHO$ yield *Et 2-amino-6-methylpyridine-3-carboxylate*, b.p. 134°/12 mm., 140°/15 mm., m.p. 84° (*picrate*, m.p. 185—186°), hydrolysed to the *acid*, m.p. 298° (decomp.), identified by conversion into the corresponding OH-acid, m.p. 227° (decomp.). Similarly CH_2Ac_2 affords *Et 2-amino-4 : 6-dimethylpyridine-3-carboxylate*, m.p. 110° (*picrate*, m.p. 163°), which gives the *acid*, m.p. 258° (decomp.) (*picrate*, m.p. 227—228°). $OBz{\cdot}CH_2{\cdot}CHO$ transforms (**I**) into the *amidine* [(**II**) (R = Ph)], m.p. 117—118°, converted by warm EtOH into $CH_2(CO_2Et)_2$ and *Et 2-amino-6-phenylpyridine-3-carboxylate*, m.p. 108° (*picrate*, m.p. 201—202°). H. W.

Preparation of 2-*p*-aminobenzenesulphonamidopyridine. C. W. Shen and H. N. Chen (*J. Chinese Chem. Soc.*, 1941, **8**, 4—6).—*p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ and 2-$C_5H_4N{\cdot}NH_2$ in C_6H_6 yield 84% of 2-*p*-acetamido-, hydrolysed (~100%) to 2-*p*-amino-benzenesulphonamidopyridine. A. Lɪ.

Synthesis of vitamin-B_6. J. H. Mowat, F. J. Pilgrim, and G. H. Carlson (*J. Amer. Chem. Soc.*, 1943, **65**, 954—955).—*5-Cyano-2-methyl-6-pyridone-4-carboxylamide* (prep. from the Et ester by NH_3–

MeOH at 0°), m.p. >300° (decomp.), with $POCl_3$ at 145—150° gives 4 : 5-*dicyano*-2-*methyl*-6-*pyridone*, m.p. 241—243°, converted by fuming HNO_3 and a little $CO(NH_2)_2$ in Ac_2O into the 3-NO_2-derivative, m.p. 242—244°, which with PCl_5 in PhCl at 135° yields 6-*chloro*-3-*nitro*-4 : 5-*dicyano*-2-*methylpyridine*, m.p. 86—86·5°. H_2–PtO_2 in Ac_2O then gives 6-*chloro*-3-*amino*-4 : 5-*dicyano*-2-*methylpyridine*, m.p. 221—221·5°, which with H_2–$PdCl_2$–HCl–MeOH–H_2O at 30° yields 3-*amino*-2-*methyl*-4 : 5-*di*(*aminomethyl*)*pyridine trichloride* (the *sulphate*, $B,2H_2SO_4$, is obtained in H_2SO_4–MeOH–H_2O), converted by HNO_2 into vitamin-B_6 hydrochloride. R. S. C.

Pyridine derivatives.—See B., 1943, II, 245.

Use of ^{15}N as a tracer element in chemical reactions. Mechanism of the Fischer indole synthesis. C. F. H. Allen and C. V. Wilson (*J. Amer. Chem. Soc.*, 1943, **65**, 611—612).—$^{15}NH_3$ (see below) is converted into, successively, $^{15}NH_2Bz$, $^{15}NH_2Ph$, $^{15}NHPh{\cdot}NH_2$ (**I**), $^{15}NHPh{\cdot}{}^{*}N{:}CPhMe$, and 2-phenylindole (**II**). The % of the total N present as ^{15}N in $^{15}NH_3$, (**I**), and (**II**) was 7·28, 3·92±0·3, and 7·06±0·06, respectively, thus proving that the *N is eliminated. Formation of *o*-$NH_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CPh{:}NH$ precedes, but removal of the NH as NH_3 may precede or follow, ring-closure. R. S. C.

Polynuclear condensed systems with heterocyclic rings. XI. Attempted ring-closure of 2 : 3-phenyl-pyrrole- and -indole-carboxylic acids. W. Borsche and A. Klein (*Annalen*, 1941, **548**, 64—74).—1 : 2 : 5-Triphenylpyrrole-3-carboxyl chloride (prep. by $SOCl_2$), a resin, with NH_2Ph in boiling C_6H_6 gives the *anilide*, m.p. 171°, with MeOH gives the *Me* ester, m.p. 156—157°, and with $AlCl_3$–C_6H_6 at 60° gives 3-*benzoyl*-1 : 2 : 5-*triphenylpyrrole*, m.p. 238°, but internal ring-closure could not be effected. Crude $CH_2Ph{\cdot}CO{\cdot}CH(CH_2Bz){\cdot}CO_2Et$ (**I**) and NH_3 in Et_2O at room temp. give *Et* β-*amino*-γ-*phenyl*-α-*phenacylcrotonate*, m.p. 166—167°, converted by boiling N-H_2SO_4 into *Et* 5-*phenyl*-2-*benzylpyrrole*-3-*carboxylate* m.p. 137°, and thence the derived *acid*, m.p. 181°, the chloride of which could not be characterised or cyclised. NH_2Ph and (**I**) in AcOH at 100° give *Et* 1 : 5-*diphenyl*-2-*benzylpyrrole*-3-*carboxylate*, m.p. 100—101°, and thence the *acid*, m.p. 191°, which could not be cyclised. $NHPh{\cdot}NHMe$ (**II**) and $CH_2Ph{\cdot}CO{\cdot}CO_2Et$ in boiling HCl–MeOH–H_2O give 3-*phenyl*-1-*methylindole*-2-*carboxylic acid*, m.p. 197—198°, which in conc. H_2SO_4 gives 3-phenyl-1-methylindole; the derived acid *chloride*, m.p. 120°, b.p. 180°/0·5 mm., with $AlCl_3$–C_6H_6 gives 1-*methyl*-1′-*indenono*-2′ : 3′-2 : 3-*indole*, m.p. 147—148° (2 : 4-*dinitrophenylhydrazone*, m.p. 313—314°). $Ph{\cdot}[CH_2]_2{\cdot}CO{\cdot}CO_2Et$ and (**II**) give similarly 3-*benzyl*-1-*methylindole*-2-*carboxylic acid*, m.p. 194° (*chloride*, m.p. 117—118°), and 1-*keto*-9-*methyl*-1 : 4-*dihydro*-2 : 3-*benzcarbazole*, m.p. 215—216°. $CH_2Bz{\cdot}CO_2Et$ with (**II**) in MeOH gives the as-*phenylmethylhydrazone*, m.p. 128°, which with HCl–EtOH at room temp. and then the b.p. gives *Et* 2-*phenyl*-1-*methylindole*-3-*carboxylate*, m.p. 97° (picrate, m.p. 137—138°), and the *acid*, m.p. 201—202°, which with $SOCl_2$ and then $AlCl_3$–C_6H_6 gives 3-*benzyl*-2-*phenyl*-1-*methylindole*, m.p. 130° (2 : 4-*dinitrophenylhydrazone*, m.p. 269°), but does not undergo ring-closure.
$CH_2Ph{\cdot}C(CO_2H){:}N{\cdot}NHPh$ and boiling HCl–EtOH give Et 3-phenylindole-2-carboxylate (**III**) and 3-phenylindole. NaOH–MeOH hydrolyses (**III**) to the amorphous acid (**IV**), m.p. 186°, the *chloride*, darkens at 160°, m.p. 164° (decomp.), resolidifies, remelts >360°, of which at 175—180° or with $AlCl_3$ in $PhNO_2$ at room temp. gives 3 : 6-*diketobis*-(3′-*phenylindolo*-1′ : 2′-)1 : 2-4 : 5-*piperazine*, hydrolysed by $N_2H_4.H_2O$ in C_5H_5N at 200° to 3-*phenylindole*-2-*carboxylhydrazide*, m.p. 227° (*CHPh*: derivative, m.p. 237°).
$CH_2Ph{\cdot}C(CO_2H){:}N{\cdot}NH{\cdot}C_6H_4Me$-*p* (prep. from *p*-$C_6H_4Me{\cdot}N_2Cl$ and $CH_2Ph{\cdot}CHAc{\cdot}CO_2Et$ in NaOH–MeOH–H_2O at 0°), m.p. 145—146°, with hot HCl–EtOH gives 3-*phenyl*-5-*methylindole*, m.p. 105°, and its 2-*carboxylic acid*, m.p. 219—220°; the derived *chloride*, m.p. 170° (decomp.), resolidifies, gives, as above, 3 : 6-*diketobis*-(3′-*phenyl*-5′-*methylindolo*-1′ : 2′-)1 : 2-4 : 5-*piperazine*, m.p. >360°. R. S. C.

Condensation reactions of cinchonin- and quinald-aldehyde. H. Kaplan and H. G. Lindwall (*J. Amer. Chem. Soc.*, 1943, **65**, 927—928).—Quinoline-2-aldehyde (**I**) [*semicarbazone*, m.p. 232—234° (decomp.)] and quinoline (**II**) in boiling 80% EtOH with or without $NHEt_2$ (6 drops) give αβ-*di*-2-*quinolylethyl alcohol*, m.p. 167—168°, but in AcOH + Ac_2O (few drops) at 120° or the b.p. or in Ac_2O–$ZnCl_2$ (a little) at 120° gives αβ-di-2-quinolylethylene, m.p. 326°. With lepidine (**III**) in 80% EtOH with or without $NHEt_2$, (**I**) gives α-2-*quinolyl*-β-4-*quinolylethyl alcohol*, m.p. 191—192°. Quinoline-4-aldehyde (**IV**) [*semicarbazone*, m.p. 244—245° (decomp.)] and (**II**) in boiling $Pr^{\alpha}OH$ with or without $NHEt_2$ (6 drops) give α-4-*quinolyl*-β-2-*quinolylethyl alcohol*, m.p. 180—182° (*benzoate*, m.p. 162°). Similar condensation of (**III**) and (**IV**) could not be effected, but in AcOH containing a little Ac_2O or $ZnCl_2$ at 110° they give αβ-*di*-4-*quinolylethylene*, m.p. 207°, also obtained from (**III**) by old SeO_2. *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ with (**I**) in boiling $Bu^{\alpha}OH$–PhMe or (**IV**) in boiling AcOH gives N^4-2-, m.p. 188—189° (decomp.), and N^4-4-*quinolylmethylenesulphanilamide*, m.p. 151—153°, respectively. (**I**) is thus more reactive than (**IV**). R. S. C.

Application of lithium compounds of nitrogen heterocycles to antimalarial syntheses. S. M. Spatz (*Iowa State Coll. J. Sci.*, 1942, **17**, 129—132; cf. A., 1940, II, 190; 1942, II, 114).—In the reaction between $LiBu^{\alpha}$ and halogenated C_5H_5N and quinoline (**I**), addition of $LiBu^{\alpha}$ may occur in absence of sufficient negative substituents, thereby reducing the yield of Li aryl. In an attempt to combine the antimalarial action of (**I**) and acridine compounds 6-methoxyquinoline was treated with *m*-C_6H_4LiCl, giving 6-*methoxy*-2-m-*chlorophenylquinoline*, m.p. 110—111° (*picrate*, m.p. 196—197°), oxidised (BzO_2H in $CHCl_3$) to its N-*oxide*, m.p. 153—154° (*picrate*, m.p. 158·5—159°), which with $POCl_3$ gives 4-*chloro*-6-*methoxy*-2-m-*chlorophenylquinoline*, m.p. 153—154°, which is also obtained from 4-chloro-6-methoxyquinoline and *m*-C_6H_4LiCl, and with $NEt_2{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}NH_2$ yields 4-δ-*diethylamino*-α-*methylbutylamino*-6-*methoxy*-2-m-*chlorophenylquinoline*. Similarly prepared were 6-*methoxy*-2-p-*chlorophenylquinoline*, m.p. 194—195° (*picrate*, m.p. 205°; N-*oxide*, m.p. 166—168°; 4-*Cl*-derivative, m.p. 163·5—164°), 4-δ-*diethylamino*-α-*methylbutylamino*-6-*methoxy*-2-p-*chlorophenyl*-, amorphous; 6-*methoxy*-2-*phenyl*-, m.p. 132—133° (*picrate*, m.p. 205°; N-*oxide*, m.p. 170—171°; 4-*Cl*-derivative), and 4-δ-*diethylamino*-α-*methylbutylamino*-6-*methoxy*-2-*phenyl*-*quinoline*. *o*-$C_6H_4Li{\cdot}OMe$ (from *o*-$C_6H_4Br{\cdot}OMe$) gives 2-o-*anisylquinoline*, b.p. 201—204°/2 mm. [*hydrochloride*, m.p. 184·5—185°; *picrate*, m.p. 177—178°; N-*oxide*, m.p. 178—178·5° (*picrate*, m.p. 133·5—134·5°); 4-*Cl*-derivative, m.p. 96—98° (*picrate*, m.p. 200—201°)], converted into 4-δ-*diethylamino*-α-*methylbutylamino*-2-o-*anisylquinoline*, b.p. 248—255°/0·025 mm. F. R. G.

Synthesis of 4 : 5-trimethylene*iso*quinoline and derivatives of this base. E. Späth and F. Kittel (*Ber.*, 1940, **73**, [*B*], 478—483).—1-Aminomethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (**I**) is converted into its *formyl* derivative, an oil, transformed by P_2O_5 in boiling PhMe into 4 : 5-*trimethylene*-3 : 4-*dihydro*isoquinoline, m.p. 32—33° [*picrate*, m.p. 211—212° (vac.; decomp.)]. This is dehydrogenated (Pd-sponge at 200°) to 4 : 5-trimethylene*iso*quinoline, m.p. 47—48° [picrate, m.p. 230—231° (vac.; decomp.)] (cf. A., 1939, II, 342). (**I**) is transformed into its *Ac* derivative, m.p. 89—90°, and thence successively into 1-*methyl*-4 : 5-*trimethylene*-3 : 4-*dihydro*isoquinoline, b.p. 100—120° (bath)/0·01 mm. [*picrate*, m.p. 221° (vac.; decomp.)], and 1-*methyl*-4 : 5-*trimethylene*isoquinoline, b.p. 80—100° (bath)/0·01 mm. [*picrate*, m.p. 203—204° (vac.; decomp.)]. The following series are obtained similarly: 1-*propionamidomethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. 140—150° (bath)/0·01 mm., non-cryst. 1-*ethyl*-4 : 5-*trimethylene*-3 : 4-*dihydro*isoquinoline, b.p. 100°/0·01 mm. (*picrate*, m.p. 165—166°), and 1-*ethyl*-4 : 5-*trimethylene*isoquinoline [*picrate*, m.p. 191° (vac.; decomp.)]; 1-*benzamidomethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 127—128°, 1-*phenyl*-4 : 5-*trimethylene*-3 : 4-*dihydro*isoquinoline, m.p. 93—94° [*picrate*, m.p. 190—191° (decomp.)], and non-cryst. 1-*phenyl*-4 : 5-*trimethylene*isoquinoline, b.p. 130—150° (bath)/0·01 mm. [*picrate*, m.p. 179—180° (vac.; decomp.)]; 1-*phenylacetamidomethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 83—84°, non-cryst. 1-*benzoyl*-4 : 5-*trimethylene*-3 : 4-*dihydro*isoquinoline, b.p. 140—150° (bath)/0·01 mm. (non-cryst. picrate), and 1-*benzyl*-4 : 5-*trimethylene*isoquinoline [*picrate*, m.p. 194—196° (vac.; decomp.)]. H. W.

Polynuclear condensed systems with heterocyclic rings. X. Derivatives of 6 : 7-dihydroxyquinoline. W. Borsche and J. Barthenheier (*Annalen*, 1941, **548**, 50—63).—Prep. of quinolines from *o*-NH_2-aldehydes, NH_2Ar, and ketones is improved by using the bases $NH_2{\cdot}C_6H_4{\cdot}CH{:}NAr$ etc., which are prepared from $NO_2{\cdot}C_6H_4{\cdot}CH{:}NAr$ etc. by Na_2S (cf. Rilliet, A., 1921, i, 567; 1922, i, 839). 4 : 5 : 3 : 1-$CH_2O_2{:}C_6H_2(NH_2){\cdot}CH{:}N{\cdot}C_6H_4Me$-*p*, m.p. 144—145° (*loc. cit.*, 134·5°), with *p*-$OMe{\cdot}C_6H_4{\cdot}COMe$ and a little aq. NaOH in EtOH at the b.p. gives 6 : 7-*methylenedioxy*-2-p-*anisylquinoline* (~75%), m.p. 181°; use of the appropriate ketone gives similarly 6 : 7-*methylenedioxy*-2-p-*chlorophenyl*- (90%), m.p. 183°, -2 : 3-*diphenyl*-, m.p. 148°, and -2 : 3-*trimethylene*-*quinoline* (90%), m.p. 175—176° (from $CH_2Ac{\cdot}CO_2Et$), 6 : 7-*methylenedioxy*-2-*methylquinoline*-3-*carboxylic acid*, m.p. 295° (evolution of CO_2) [the *Et* ester (70%), m.p. 157—158°, is obtained by use of piperidine instead of NaOH], (from *cyclo*hexanone) 6 : 7-*methylenedioxy*-1 : 2 : 3 : 4-*tetrahydroacridine* (75%), m.p. 137—138°, and its 3-*Me* derivative (80%), m.p. 190—191°, and 6 : 7-methylenedioxy-1′ : 2′-dihydroindeno-1′ : 2′-2 : 3-quinoline (90%), m.p. 182—183° (lit. 186°). 3 : 4 : 1-$(OMe)_2C_6H_3{\cdot}CHO$ and HNO_3 (*d* 1·395) in AcOH give the 6-NO_2-derivative (**I**) (~80%) and thence 6-*nitroveratrylidene*-p-*toluidine*, m.p. 139°. The derived NH_2-compound, m.p. 123—124° (lit. 115°), gives, as above, 6 : 7-*dimethoxy*-2-*phenyl*- (**II**), m.p. 227°, -2-p-*anisyl*- (80%), m.p. 180° (picrate, m.p. 256°), -2-p-*chlorophenyl*- (90%), m.p. 144°, and -2 : 3-*trimethylene*-*quinoline* (85%), m.p. 112—113°, (by use of piperidine) *Et* 6 : 7-*dimethoxy*-2-*methylquinoline*-3-*carboxylate* (**III**) (85%), m.p. 116—117°, 6 : 7-*dimethoxy*-1 : 2 : 3 : 4-*tetrahydroacridine* (**IV**) (80%), m.p. 124° (*picrate*, m.p. 247°; *methiodide*, m.p. 226—228°), and its 3-*Me* derivative (90%), m.p. 150°, and 6 : 7-*dimethoxy*-1′ : 2′-*dihydroindeno*-1′ : 2′-2 : 3-*quinoline* (75%), m.p. 197° (*picrate*, m.p. 266°). 3 : 4 : 6 : 1-$CH_2O_2{:}C_6H_2(NO_2){\cdot}CH{:}N{\cdot}C_6H_4Me$-*p* has m.p. 124—125° (lit. 121·5°). 6 : 7-Dimethoxy-2-phenylcinchonic acid [prep. from 3 : 4 : 1-$(OMe)_2C_6H_3{\cdot}NH_2$, PhCHO, and $AcCO_2H$ in AcOH at 100°], m.p. 255° (decomp.), gives (**II**) when distilled. *Ph* 6-*nitro*-3 : 4-*dimethoxystyryl ketone* (prep. by nitration as above), m.p. 185°, with Na_2S–EtOH gives the *NH*$_2$-*ketone*, m.p. 196°, without ring-closure. KOH–MeOH–H_2O hydrolyses (**III**) to the corresponding *acid*, m.p. 238—

240° (decomp.), which is better obtained directly by use of NaOH and when heated at 0·1 mm. gives 3 : 6-dimethoxy-2-methylquinoline (**V**), b.p. 185—190°/13 mm. [picrate, m.p. 222—223° (lit. 217°)]. With 33% aq. K_2CO_3 in $COMe_2$, (**I**) gives *β-hydroxy-β-6-nitro-3 : 4-dimethoxyphenylethyl Me ketone*, m.p. 145—146°, dehydrated in hot EtOH or AcOH to *6-nitro-3 : 4-dimethoxystyryl Me ketone*, m.p. 174—175°, which with Zn–HCl–AcOH is reduced and cyclised to give (**V**). With *o*-$C_6H_4(CO)_2O$ at 160°, (**V**) gives a *phthalylidene* derivative, m.p. 207—208°, and with HI–AcOH gives amorphous *6 : 7-dihydroxy-2-methylquinoline*, m.p. 267—268°, unstable particularly in alkali [hydrochloride, $+0·5H_2O$, m.p. 233° (decomp.); *dibenzoate*, m.p. 151—152°]. Boiling HI converts (**II**) into *6 : 7-dihydroxy-2-phenylquinoline*, m.p. 275° (*methiodide*, m.p. 195°; *dibenzoate*, m.p. 177—178°), which with *o*-$C_6H_4(NH_2)_2$ (**VI**) at 210—220° gives *2′-phenylpyridino-6′ : 5′-2 : 3-phenazine*, m.p. 212—213°. *o*-$NH_2·C_6H_4·OH$ and quinoline at 250—260° give *2′-phenylpiperidino-6′ : 5′-3 : 4-phenoxazine*, m.p. 240—242°. S, Se, or SeO_2 gives indefinite products from (**IV**), but PhCHO and $ZnCl_2$ at 160° give the *4-CHPh* derivative, m.p. 132°; the *4-phthalylidene* derivative, m.p. 219°, is also detailed. $Et_2C_2O_4$, (**IV**), and K in Et_2O–EtOH at 100° and then room temp. give *Et* *6 : 7-dimethoxy-1 : 2 : 3 : 4-tetrahydroacridine-4-glyoxylate*, m.p. 208—209°, converted by HI at 140° into *6 : 7-dihydroxy-1 : 2 : 3 : 4-tetrahydroacridine*, m.p. 325° (*dibenzoate*, m.p. 170—171°), which with (**VI**) at 210° gives *5 : 6 : 7 : 8-tetrahydroquinolino-2 : 3-2′ : 3′-phenazine*, m.p. 350°. R. S. C.

Conversion of Δ²-*cyclo*hexenones and *cyclo*hexanones into *spiro*-hydantoins. H. R. Henze, R. C. Wilson, and R. W. Townley (*J. Amer. Chem. Soc.*, 1943, **65**, 963—965).—The appropriate substituted *cyclo*hexanones with KCN and $(NH_4)_2CO_3$ in aq. EtOH give *3 : 5-dimethyl-*, m.p. 335—336°, *3-methyl-5-ethyl-* (**I**), m.p. 282° (decomp.), *3-phenyl-5-methyl-* (**II**), m.p. 223—224°, and *3-2″-furyl-5-methyl-*, m.p. 223—224° (decomp.), -cyclo*hexane*-1-spiro-4′-*hydantoin*. Δ²-*cyclo*Hexenones (*A*) also add HCN, thus yielding *3-cyano-3 : 5-dimethyl-*, m.p. 196—197°, *-3-methyl-5-ethyl-*, m.p. 173—174°, *-5-phenyl-3-methyl-*, m.p. 221°, and *-5-2″-furyl-3-methyl-*, m.p. 210—211° (after resolidification, remelts at 215°), -cyclo*hexane*-1-spiro-4′-*hydantoin*. Treating (*A*) with alkali sulphite and then with KCN etc. gives 3-sulpho-3 : 5-dimethyl- (*K* salt), *-3-methyl-5-ethyl-*, m.p. 175° (decomp.) (*K* salt), *-5-phenyl-3-methyl-*, m.p. 273—275° (decomp.), and *-5-2″*-furyl-3-methyl-*cyclo*hexane-1-*spiro*-4′-hydantoin (*K* salt). Na–$C_5H_{11}·OH$ reduces (**I**) to *3-methyl-5-ethyl-3-aminomethyl*cyclo*hexane*-1-spiro-4′-*hydantoin*, m.p. 223°. Hydrogenating (PtO_2) (*A*) [prep. from $CH_2Ac·CO_2Et$ (2 mols.), RCHO (1 equiv.), and a little $NHEt_2$] in EtOH at 2 atm. gives 3 : 5-dimethyl-, b.p. 181—182°/750 mm. (semicarbazone, m.p. 220—200·5°), *3-methyl-5-ethyl-*, b.p. 204—205°/747 mm. (*semicarbazone*, m.p. 189—190°), *3-phenyl-5-methyl-*, b.p. 180—181°/26 mm. (*semicarbazone*, m.p. 111·5—112°), and *3-2′-furyl-5-methyl-*cyclo*hexanone*, b.p. 147—148°/22 mm. (*semicarbazone*, m.p. 172—173°). (**I**) is neither hypnotic nor anticonvulsant. (**II**) is mildly convulsant. SO_3H or 2-furyl reduces the toxicity but does not enhance the activity. M.p. are corr. R. S. C.

Vinylalkylmalonic esters and barbituric acids. (Miss) D. Heyl and A. C. Cope (*J. Amer. Chem. Soc.*, 1943, **65**, 669—673).—$CH_2Br·CHBr·OEt$, $CHBu^{\alpha}(CO_2Et)_2$ (**I**), and Na (or $NaNH_2$) in Et_2O–xylene at −10° give $CH_2Br·CH(OEt)·CBu^{\alpha}(CO_2Et)_2$, which when distilled (after or without boiling with Zn in EtOH) yields EtBr and *α-carbethoxy-β-ethoxy-α-n-butyl-γ-butyrolactone* (**II**) (56%), b.p. 129—130°/2 mm., and 27% of unchanged (**I**). $CHEt(CO_2Et)_2$ gives similarly *α-carbethoxy-β-ethoxy-α-ethyl-γ-butyrolactone* (66%), b.p. 149·5°/8·5 mm. $CH_2Cl·CHCl·OEt$, (**I**), and Na in Et_2O at −10° and then 0° give *Et₂ β-chloro-α-ethoxyethylmalonate* (68%), b.p. 119°/2 mm., which is more stable but from which HCl could not be removed by Zn–EtOH. $CMePr^{\alpha}C(CN)_2$ and H_2–Pd–C in EtOH at 1—2 atm. give *α-methyl-*n*-butylmalononitrile* [*α-cyano-β-methyl-*n*-hexonitrile*] (67%), b.p. 99—100°/8 mm., which could not be alkylated as it gives no Na derivative. $CHMePr^{\alpha}·CH(CN)·CO_2Et$ similarly resists alkylation. With $CO(NH_2)_2$ and NaOEt in boiling EtOH, (**II**) gives *5-β-hydroxy-* (**III**) (60%), m.p. 127—127·5°, and thence ($SOCl_2$–C_5H_5N–CCl_4) *5-β-chloro-* (**IV**) (95%), m.p. 158·5—159°, and ($SOBr_2$–C_5H_5N–C_6H_6) *5-β-bromo-* (**V**) (80%), m.p. 166—167°, *-α-ethoxyethyl-5-*n*-butylbarbituric acid*. Boiling 48% HBr converts (**III**), (**IV**), or (**V**) into *5-n*-butylbarbituric acid, probably by way of the 5-epoxyethyl and 5-Ac derivatives. Dehalogenation of, *e.g.*, $1-C_{10}H_7Br$ at 230° (69% yield of $C_{10}H_8$) by Zn is improved by operating in NH_2Ac; this method is applied to *β*-bromovinylmalonic esters. Thus, $CHBr{:}CH·CEt(CO_2Et)_2$ and Zn dust in NH_2Ac at 180° give 71% of $CH_2{:}CH·CEt(CO_2Et)_2$, b.p. 117·5—118°/22 mm., which with guanidine carbonate and NaOEt (excess avoided) in boiling EtOH and then boiling aq. HCl gives 29% of *5-ethyl-5-vinylbarbituric acid* (**VI**), m.p. 172·5—173°. Adding, successively, *iso*-$C_5H_{11}·CH(CO_2Et)_2$, a little EtOH, and $(CHBr{:})_2$ to $NaNH_2$ (prepared *in situ*) in Et_2O and then boiling gives *Et₂* iso*amyl-β-bromovinylmalonate* (38% + a residue), b.p. 158°/11 mm. [omission of the EtOH (? function) reduces the yield to 5%], which with Zn in boiling NH_2Ac give *Et₂* iso*amylvinylmalonate* (72%), b.p. 125—126°/10 mm., and thence, as above, *5-iso*amyl-5-vinylbarbituric acid* (**VII**) (32%), m.p. 129·5—130°. $(CHBr{:})_2$, (**I**), and Na in Et_2O give similarly *Et₂* n*-butyl-β-bromovinyl-* (26%), b.p. 149°/10 mm., and *-vinyl-malonate* (70%), b.p. 116—117°/9 mm., and *5-n-butyl-5-vinylbarbituric acid* (**VIII**) (40%), m.p. 84—85°. $(CHBr{:})_2$, $CH_2{:}CH·CH_2·CH(CO_2Et)_2$, EtOH (a little), and $NaNH_2$ in Et_2O give *Et₂ β-bromovinylallylmalonate* [*Et α-carbethoxy-α-β′-bromovinyl-Δ^γ-n-pentenoate*] (**IX**) (26%), b.p. 101°/2 mm., hydrogenated (Pd–C; EtOH) to $CEtPr^{\alpha}(CO_2Et)_2$ (identified by hydrolysis and conversion into the barbituric acid) and converted by Zn dust in NH_2Ac at 130—170° into *Et₂ vinylallylmalonate* (**X**) (39%), b.p. 112—113°/11 mm. Attempts to rearrange (**IX**) by heat result only in polymerisation. At 140° (**X**) is unchanged, at 200° it gives a mixture, but at 170° (8 hr.) gives ~30% of *Et₂ Δ^δ-pentenylidenemalonate* [*Et₂ α-carbethoxy-Δ^αε-heptadienoate*], b.p. 140—143°/6 mm., identified by hydrogenation (Pd–C–EtOH) to *n*-$C_5H_{11}·CH(CO_2Et)_2$ (derived diamide, m.p. 198—199°). The structures of (**VI**)—(**VIII**) are confirmed by quant. hydrogenation to the known dialkylbarbituric acids. The vinyl-acids, (**VI**)—(**VIII**), are less effective and have poorer therapeutic ratios than have the isomeric ethylalkylidenebarbituric acids. (**III**), (**IV**), and (**V**) are non-toxic and non-hypnotic (orally) at 800 mg. per kg. to mice. R. S. C.

Barbituric acids.—See B., 1943, II, 246.

Pyrazolones.—See B., 1943, II, 176.

Pyrazole compounds. III. Condensation of α-carbethoxyacetothioacetanilide with hydrazines. A. Weissberger and H. D. Porter (*J. Amer. Chem. Soc.*, 1943, **65**, 732—734; cf. A., 1943, II, 207).—Boiling $CHNaAc·CO_2Et$ and PhNCS in MeOH, adding 85% $N_2H_4.H_2O$ at 50°, and boiling again gives *3-anilino-5-pyrazolone*, m.p. 268—270° (decomp.; rapid heating), also obtained by interaction in two steps [Worrall, A., 1918, i, 161; 1922, i, 874; m.p. 255—256° (decomp.); ? dimorphism]. Use of $NHPh·NH_2$ gives *5-anilo-3-hydroxy-1-phenylpyrazole* (**I**) (30%), m.p. 168—169°, also obtained from 5-imino-3-hydroxy-1-phenylpyrazoline (**II**) in boiling NH_2Ph. Use of $NHMe·NH_2$ gives *5-anilo-3-hydroxy-1-methylpyrazoline* (**III**) (2%), m.p. 208—209°, and *3-anilino-1-methyl-5-pyrazolone* (**IV**) (11·5%), m.p. 220—222°. Oxidation in presence of *p*-$NH_2·C_6H_4·NMe_2$ gives a weak, dull bluish-magenta colour from (**II**), (**I**), or (**III**), but a brilliant magenta colour from 3-amino- (**V**) or 3-anilino-1-phenyl-5-pyrazolone (**VI**) or (**IV**). Similarly, (**IV**), (**V**), and (**VI**) give deep red azomethine dyes with *p*-$NO·C_6H_4·NMe_2$ in boiling EtOH, but (**I**), (**II**), and (**III**) are not affected. R. S. C.

Pyrazoles.—See B., 1943, II, 203.

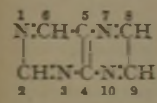
New synthesis of 3-carboline (norharman) and 5-carboline. E. Späth and K. Eiter (*Ber.*, 1940, **73**, [*B*], 719—723).—3-Bromopyridine, *o*-$C_6H_4(NH_2)_2$, and H_2O + a little $CuSO_4$ at 155° for 9 hr. (sealed tube) give *N-3-pyridyl-o-phenylenediamine*, m.p. 125·5—126°, converted by aq. HCl–$NaNO_2$ into *1-3′-pyridylbenztriazole* (**I**), m.p. 136·5—137°, which at ~350° for 8 hr. gives 3-carboline (**II**) (norharman), m.p. 198·5°. (**I**) and $ZnCl_2$ at 320° (15 min.) yield (**II**), *3-anilinopyridine*, m.p. 142° (also obtained from 3-aminopyridine, PhI, and Cu–K_2CO_3 in boiling *p*-toluidine at 200° for 15 hr.), and *5-carboline*, m.p. 214—215° [also obtained from (**I**) at ~350° for 12 hr.] (for nomenclature, cf. Gulland *et al.*, A., 1930, 219). A. T. P.

Polynuclear condensed systems with heterocylic rings. XII. 3-Phenyl-1 : 2-diaza-anthrone and other pyridazine derivatives. W. Borsche and A. Klein (*Annalen*, 1941, **548**, 74—81).—$N_2H_4.H_2O$ and $CH_2Ph·CO·CH(CH_2Bz)·CO_2Et$ in EtOH at room temp. give the *dihydrazone*, m.p. 162—163°, or, after longer heating, *Et* *6-phenyl-3-benzyl-4 : 5-dihydropyridazine-4-carboxylate*, m.p. 115°, oxidised by CrO_3 in warm AcOH to Et 6-phenyl-3-benzylpyridazine-4-carboxylate, m.p. 77—78°. The derived *acid*, m.p. 195—196° (decomp.), at 200—210° gives CO_2 and *3-phenyl-6-benzylpyridazine*, m.p. 142°, and with $SOCl_2$ and then $AlCl_3$–$PhNO_2$ at 50—60° gives *3-phenyl-1 : 2-diaza-9-anthrone*, m.p. 236° (*2 : 4-dinitrophenylhydrazone*, m.p. 244°). $CH_2Bz·CHBz·CO_2Et$ and $N_2H_4.H_2O$ in EtOH at room temp. give *Et* *3 : 6-diphenyl-4 : 5-dihydropyridazine-4-carboxylate*, m.p. 118°, and thence, as above, *3 : 6-diphenylpyridazine-4-carboxylic acid*, m.p. 221° (Et ester, m.p. 100°), the chloride from which yields the *anilide*, m.p. 206°, but cannot be cyclised. $CH_2Ph·CHAc·CO_2Et$ gives similarly *Et* *6-phenyl-3-methyl-4 : 5-dihydropyridazine-4-carboxylate*, m.p. 98°, and *6-phenyl-3-methylpyridazine-4-carboxylic acid*, m.p. 201° (decomp.), thermal decomp. of which gives 6-phenyl-3-methylpyridazine, m.p. 104—105°. With RCHO this gives *6-phenyl-3-styryl-*, m.p. 184°, and *-3-p-methoxystyryl-pyridazine*, m.p. 200°. Et 2-carboxylamido-6-phenyl-3-methyl-2 : 5-dihydropyridazine-4-carboxylate (A., 1904, i, 778) with boiling KOH–MeOH–H_2O gives the derived *acid*, m.p. 254° (decomp.), which at ~260° gives *6-phenyl-3-methyl-2 : 5-dihydropyridazine-2-carboxylamide*, m.p. 147°; the $CO·NH_2$ resists hydrolysis. An isomeric *substance*, $C_{12}H_{13}ON_3$, m.p. ~235° after decomp., is obtained (Spannagel, *Diss.*, 1903) from $COMe·CH_2Bz$ and $NH_2·CO·NH·NH_2$. R. S. C.

Methylation of hydroxyl groups in triazines. H. Sobotka and E. Bloch (*J. Mt. Sinai Hosp.*, 1942, **8**, 1032—1033; cf. A., 1938, II, 70).—Attempts to methylate or acetylate the OH of 2-hydroxy-

4 : 6-diketo-2-alkyl- (or -phenyl-)1 : 3 : 5-trimethylhexahydrotriazine were unsuccessful. E. M. J.

Insect dyes. VIII. Leucopterin. C. Schöpf and R. Reichert [with K. Riefstahl] (*Annalen*, 1941, **458**, 82—94).—The structure of leucopterin (**I**) as 2-imino-6 : 8 : 9-trihydroxypteridine is confirmed. This and similar CO compounds are named as (enolic) OH-derivatives of pteridine (**II**). Purification of (**I**) (Na salt) as *K* salt is described. Deiminoleucopterin (**III**) (prep. from 4 : 5-diamino-2 : 6-dihydroxypyrimidine sulphate, $H_2C_5O_4,H_2O$, and cryst. NaOAc at 160° rising to 260°) with PCl_5–$POCl_3$ at 110° gives 2 : 6 : 8 : 9-*tetrachloropteridine* (**IV**), m.p. 161°, not reducible but converted by 25% NaOH at 140° into (**III**), by 0·75N-NaOH at 80° or N-LiOH at room temp. or 100° into 2 : 6-*dichloro*-8 : 9-*dihydroxypteridine* (**V**), +1·5H_2O, m.p. 260—270° (decomp.), and by dry NH_3–Et_2O into *trichloro*-x-*aminopteridine* (33%), m.p. 197—201° (decomp.). Prep. of (**V**) from (**III**) by PCl_5 under less careful conditions is thus due to lability of two Cl of the intermediate (**IV**). R. S. C.



(II.)

Preparation of flavins. H. Lettré and M. E. Fernholz (*Ber.*, 1940, **73**, [*B*], 436—441).—β-$C_{10}H_7$·NHPh is coupled with diazotised NH_2Ph, and the azo-dye is reduced ($Na_2S_2O_4$) to 1:2-NH_2·$C_{10}H_6$·NHPh, m.p. 124—126°, which is condensed with alloxan and H_3BO_3 in AcOH to 9-*phenyl*-5 : 6-*benzoflavin*, m.p. >365° (decomp.). Similar methods are used in the prep. of the following -5 : 6-benzoflavins : 9-phenyl-3-methyl-, m.p. >365°, incipient decomp. 335°; 9-β-*naphthyl*-, m.p. ~357° after decomp.; 9-*methyl*-, m.p. >365°; 9-*ethyl*-, m.p. 326°; 9-n-*propyl*-, m.p. 319—320°; 9-n-*butyl*-, m.p. 297—298°; 9-iso*amyl*-, m.p. 273°; 9-n-*hexyl*-, m.p. 274—275°; 9-n-*octyl*-, m.p. 248—249°; 9-n-*decyl*-, m.p. 230°; 9-n-*dodecyl*-, m.p. 236°; 9-*cetyl*-, m.p. 221—222°; 3-*methyl*-9-*cetyl*-, m.p. 187—188°. All these compounds are sparingly sol. in H_2O but the simpler members are freely sol. in alkali. With increasing chain length they pass more and more completely into the $CHCl_3$ layer when distributed between $CHCl_3$ and aq. alkali. From this viewpoint their carcinogenic properties are investigated. β-Naphthyl-butyl-, m.p. 177—178°, and -cetyl-amine hydrobromide, m.p. 143—145°, 1-benzeneazo-β-cetylnaphthylamine, m.p. 61°, and 1-amino-2-cetylaminonaphthalene hydrochloride, m.p. 144°, are incidentally described. H. W.

Bile pigments. XXVII. Synthesis of 5 : 5′-diamino-4 : 4′-dimethyl-3 : 3′-diethylpyrromethene. H. Fischer and H. Guggemos (*Z. physiol. Chem.*, 1939, **262**, 37—46).—Et cryptopyrrolecarboxylate is converted by excess of Br in AcOH at 60—70° into Et_2 4 : 4′-dimethyl-3 : 3′-diethylpyrromethene-5 : 5′-dicarboxylate, m.p. 132—134°. 4 : 4′-Dimethyl-3 : 3′-diethylpyrromethane-5 : 5′-dicarboxylhydrazide, m.p. 238°, best obtained from Et_2 4 : 4′-dimethyl-3 : 3′-diethylpyrromethane-5 : 5-dicarboxylate and boiling N_2H_4,H_2O, is converted by $NaNO_2$ in AcOH at 0° into the *diazide* (**I**), m.p. 127° (decomp.), transformed by NH_2Ph at 140° into the 5 : 5′-*di*(*phenylcarbamide*), m.p. 235°, and by Zn dust at AcOH into the 5 : 5′-*dicarboxylamide*, m.p. 300°. (**I**) is transformed by Br in Et_2O into 4 : 4′-*dimethyl*-3 : 3′-*diethylpyrromethene*-5 : 5′-*dicarboxazide* (**II**), m.p. 130° (decomp.) [*hydrobromide*, m.p. 133° (decomp.)], which with boiling EtOH yields the -5 : 5′-diethylurethane, m.p. 147° (4 : 4′-*dimethyl*-3 : 3′-*diethylpyrromethane*-5 : 5′-*diethylurethane* has m.p. 124—125°). (**II**) is converted by boiling 50% AcOH into a non-cryst. material whereas (**I**) affords the -5 : 5′-*diamine diacetate* (**III**), m.p. (indef.) 185°, decomp. >135°. Hot 4% NaOH converts (**III**) into 5 : 5′-*diamino*-4 : 4′-*dimethyl*-3 : 3′-*diethylpyrromethene*, decomp. 157°, which very readily passes in air into ββδ-di-iminoætioporphyrin and is therefore analysed as the very stable *complex*, $C_{15}H_{20}N_2Cu$, m.p. >350°. H. W.

Chlorophylls. XCIV. Protochlorophyll and vinylporphyrins. The oxo-reaction. H. Fischer and A. Oestreicher (*Z. physiol. Chem.*, 1939—40, **262**, 243—269).—Adding $COCl_2$ to vinylphæoporphyrin-a_5 Me H ester and phytol in C_5H_5N at 0° and then room temp. gives the *Me phytyl* ester (*protophæophytin*) (**I**), m.p. ~144—146°. This is obtained in poor yield (owing to hydrolysis) by addition of Fe powder to vinylphæophytin in $COMe_2$–80% HCO_2H at 100°, reoxidation in air, and purification by adsorption. The colour and spectrum of (**I**) are the same as those of vinylphæoporphyrin-a_5 (**II**). Mg is introduced into (**I**) by MgEtBr decomposed by $Pr^{\alpha}OH$ or $Pr^{\beta}OH$ (not MeOH or EtOH), yielding an amorphous *protochlorophyll*; this differs in absorption spectrum (max. at 599·5 and 548·8 mμ.) from the natural product, probably because the latter contains a definite amount of (**I**) (this is probably present as such in nature and not an artefact). When methylphæophorbide-b_6-oxime is treated with Fe powder in boiling 80% HCO_2H, reoxidised in air, and esterified by CH_2N_2–Et_2O, the isocyclic ring is closed and the C:N·OH hydrolysed and reduced to CH_2·OH, yielding *vinylphæoporphyrin*-b_6-3-*methanol Me*$_2$ ester, m.p. 269°, the structure of which is proved by its absorption spectrum (max. at 563·7, 590·1, 523·7, and ~650 mμ.) resembling that of (**II**), by failure to give an oxime in cold C_5H_5N, addition of CHN_2·CO_2Et, and opening of the isocyclic ring by KOH–EtOH (spectroscopic proof). Similarly, the oxime of rhodin-g_7 Me_2 ester gives vinylrhodinporphyrin-g_7-3-methanol Me_2 ester (poor yield), which is also obtained in poor yield from vinylphæoporphyrin-b_6-3-methanol Me_2 ester by KOH–MeOH–C_5H_5N at room temp. and has the same absorption spectrum as has vinylchloroporphyrin-e_6 (**III**). Hydrolysis of phæophytin-*a* + -*b* by boiling KOH–MeOH–$COMe_2$ (4 min.) gives oily K and thence solid Ba salts· phytol adsorbed thereon is extracted by Et_2O and readily purified; dissolving the residual salts in acid and extracting fractionally with Et_2O then yields pure chlorin-e_6 and impure rhodin-g_7. Two methods for prep. of (**II**) give only poor yields. 2-α-*Hydroxychloroporphyrin*-e_6 *Me*$_3$ ester, m.p. 247° (absorption max. at 445, 581·7, 544·8, and 633 mμ., similar to those of chloroporphyrin-e_6 Me_3 ester), is obtained by treating the Me_3 ester of (**III**) with HI–AcOH at room temp. and then reoxidising; at the m.p./high vac. it suffers ring-closure of the isocyclic ring with loss of MeOH, but with P_2O_5 and sand at room temp. it gives (**III**); its prep. involves addition of HI, followed by hydrolysis; thus, it is also formed (m.p. 246°) when HBr is added to (**III**) in AcOH and the product is hydrolysed by 20% HCl at room temp. and finally esterified. Similarly, with, successively, HBr–AcOH at 45°, 20% HCl, and CH_2N_2, vinylphylloerythrin Me_1 ester (**IV**) gives 2-α-*hydroxyphylloerythrin Me*$_1$ ester, m.p. ~284—286° (absorption max. at 562·5, 591·8, 522·3, and 641·2 mμ.), which with P_2O_5 + sand regenerates (**IV**); it is also obtained from oxophylloerythrin by hydrogenating (PtO_2; HCO_2H) and then reoxidising and esterifying and is reconverted thereinto by I–AcOH. Further, treating vinylphæoporphyrin-a_5 Me_2 ester with HI in AcOH + a little $CHCl_3$ at 12° for 2 days and esterifying the 2-CHMe·OH fraction gives 2-α-*hydroxyphæoporphyrin*-a_5 *Me*$_2$ ester, m.p. 285° (absorption max. at 561·2, 588·9, 521·7, and 638·1 mμ.). Vinylchloroporphyrin-e_4 Me_2 ester (**V**), m.p. 254° [absorption max. at 510·7, 548·1, 586·2, and ~660 mμ.; *Cu* salt, m.p. 200° (absorption max. at 546·4 and 589·5 mμ.), reduced by H_2–Pd in $COMe_2$ to the leuco-compound of the Et compound and converted by HI–AcOH into the Cu-free ester], is obtained from the -e_6 Me_2 ester by boiling HCO_2H and then CH_2N_2; some (**II**) is also formed. (**V**) is also obtained by treating the chlorin-e_4 Me_2 ester with Fe powder in 80% AcOH at 100°, reoxidising the product with $FeCl_3$, and esterifying, but the yield is poor owing to decomp. of the leuco-compound. I–KOAc oxidises (**V**) to *vinylchloroporphyrin*-e_5, m.p. >320° (absorption max. at 558, 587·7, 516·2, and 635·2 mμ.). Phæophorbide-*a* is slowly converted into (**II**) by boiling with Fe dust and $H_2C_2O_4$ in $COMe_2$ and then reoxidising. The mechanism by which, in the changes described above, reduction and oxidation occur simultaneously at different parts of the mol. is inconclusively discussed. 2-α-Hydroxymesochlorin-e_6 Me_3 ester with $KMnO_4$ in C_5H_5N at room temp. and then CH_2N_2 gives 48% of acetylchlorin-e_6 Me_3 ester, which yields a *Cu*, m.p. 198°, $[\alpha]^{20}_{white}$ −1260° in $COMe_2$ (absorption max. at 652·6, 507, 599·5, and 549 mμ.), *Fe*, m.p. 176—178°, $[\alpha]^{20}_{white}$ +2870° and $[\alpha]^{20}_{red}$ −1080° in $COMe_2$ (absorption max. 625 and 488·1 mμ.), and *Mn* derivative, m.p. 170—173°, decomp. 185—190°, $[\alpha]^{20}_{white}$ +4300°, $[\alpha]^{20}_{red}$ −540° in $COMe_2$ (absorption max. at 480·2, 682·8, and 437·2 mμ.). R. S. C.

Photo-oxidation of chlorophyll.—See A., 1943, I, 206.

Synthesis of *iso*quinoline derivatives. IV. Synthesis of oxazolines and *iso*quinolines from *N*-acylaminocarbinols. W. Krabbe, W. Eisenlohr, and H. G. Schöne (*Ber.*, 1940, **73**, [*B*], 656—660; cf. A., 1943, II, 263).—NHBz·CH_2·CPhMe·OH and H_2SO_4 at room temp. give 2 : 5-diphenyl-5-methyl-Δ²-oxazoline (*picrate*, m.p. 145°), converted by boiling aq. HCl into NHBz·CH:CPhMe and BzOH. NHAc·CHPh·CPh_2·OH and P_2O_5 or H_2SO_4 give 4 : 5 : 5-*triphenyl*-2-*methyl*-Δ²-*oxazoline* (cf. acet-ββ-diphenylvinylamide, m.p. 166°; A., 1938, II, 111), rehydrolysed by acid or alkali. A. T. P.

Sulphanilamide compounds. VIII. Homologues of 2-sulphanilamidothiazoline. A. H. Nathan, J. H. Hunter, and H. G. Kolloff (*J. Amer. Chem. Soc.*, 1943, **65**, 949—950; cf. A., 1941, II, 147).—2-Amino-4- and -5-methylthiazoline with *p*-NHAc·C_6H_4·SO_2Cl in C_5H_5N–$COMe_2$ at <45° give 2-*acetylsulphanilimido*-3-*acetylsulphanilyl*-4-, +H_2O, m.p. 150—153° (decomp.), and -5-, m.p. 185·5—186·5°, hydrolysed by boiling 10% HCl to 2-*sulphanilimido*-3-*sulphanilyl*-4-, m.p. 225—226°, and -5-, m.p. 176·5—177°, and then to 2-*sulphanilamido*-4-, m.p. 176°, and -5-, m.p. 177·5—178·5°, -*methylthiazoline*. R. S. C.

Thiazoles.—See B., 1943, II, 174.

Benzthiazolium compounds.—See B., 1943, II, 175, 246.

Cyanine dyes.—See B., 1943, II, 175, 178, 246, 247, 268.

VII.—ALKALOIDS.

Ergot alkaloids. IV. Optically active hydrazides of lysergic and *iso*lysergic acid. A. Stoll and A. Hofmann (*Helv. Chim. Acta*, 1943, **26**, 922—928; cf. A., 1938, II, 35, 164).—*r-iso*Lyserghydrazide (**I**), m.p. (indef.) 240° (decomp.), is obtained by the action of N_2H_4

at 130—140° on any of the natural ergot alkaloids or mixtures thereof which does not belong to the ergobasine type. Finely-divided *d*-tartaric acid and *p*-C_6H_4Me·COCl at 120° afford d-*di*-p-*toluoyltartaric anhydride*, m.p. 197—198° (decomp.), $[\alpha]_D^{20}$ +195° in $COMe_2$, hydrolysed by boiling aq. $COMe_2$ to d-*di*-p *tcluoyltartaric acid* (**II**), m.p. 172° (decomp.), $[\alpha]_D^{20}$ −140° in EtOH. l-*Di*-p-*toluoyltartaric anhydride*, $[\alpha]_D^{20}$ −195° in $COMe_2$, and *acid* (**III**), $[\alpha]_D^{20}$ +140° in EtOH, are obtained similarly. (**I**) and (**III**) in boiling MeOH give d-iso*lyserghydrazide H* l-*di*-p-*toluoyltartrate* (**IV**), $[\alpha]_D^{20}$ +328° in MeOH, converted by $NaHCO_3$ into *d*-isolyserghydrazide (**V**), m.p. (indef.) 204° (decomp.), $[\alpha]_D^{20}$ +452° in C_5H_5N. The base derived from the mother-liquors from (**IV**) is largely freed from (**I**) by treatment with EtOAc or preferably is treated with (**II**), thereby giving *l-iso*lyserghydrazide, m.p. 204° (decomp.), $[\alpha]_D^{20}$ −454° in C_5H_5N. (**V**) is isomerised by boiling H_3PO_4–EtOH or, preferably, by mild treatment with KOH–EtOH to d-*lyserghydrazide*, m.p. (indef.) 218° (decomp.), $[\alpha]_D^{20}$ +11° in C_5H_5N. l-*Lyserghydrazide* has m.p. 218° (decomp.), $[\alpha]_D^{20}$ −11° in C_5H_5N. H. W.

Ergot alkaloids. VI. Partial synthesis of alkaloids of the type of ergobasine. A. Stoll and A. Hofmann (*Helv. Chim. Acta*, 1943, **26**, 944—965).—The alkaloids are obtained by interaction of optically active lyserg- and *iso*lyserg-azides with optically active NH_2-alcohols. *d-iso*Lyserghydrazide (**I**) in 0·1N-HCl at 0° is treated with $NaNO_2$ followed by $NaHCO_3$ and the liberated azide is extracted with Et_2O. The dried ethereal solution is kept at room temp. for a day in the dark with *l*(+)-NH_2·CHMe·CH_2·OH (2 mols.), thus giving *d-iso*lyserg-α-hydroxy*iso*propylamide (ergobasinine) (**II**); the mother-liquors from (**II**) afford *d*-lyserg-α-hydroxy*iso*propylamide (**III**) when treated with $CHCl_3$. (**II**) is isomerised to (**III**) by KOH–aq. EtOH at room temp. The pre-isomerisation of (**I**) to *d*-lyserghydrazide and thus the direct production of (**III**) is not advisable since some back-isomerisation always occurs. Similarly obtained are d-iso*lyserg*-d-α-*hydroxy*-iso*propylamide*, m.p. 195° (decomp.), $[\alpha]_D^{20}$ +353° in $CHCl_3$ (*perchlorate*), and d-*lyserg*-d-α-*hydroxy*-iso*propylamide*, m.p. 220° (decomp.), $[\alpha]_D^{20}$ −11° in C_5H_5N [*H oxalate*, m.p. 190—195° (decomp.), $[\alpha]_D^{20}$ +58° in H_2O]; *l-iso*lyserg-*l*-α-hydroxy*iso*propylamide, m.p. 192—195° (decomp.), $[\alpha]_D^{20}$ −351° in $CHCl_3$ (perchlorate), and l-*lyserg*-l-α-*hydroxy*iso*propylamide*, m.p. 220° (decomp.), $[\alpha]_D^{20}$ +10° in C_5H_5N [*H oxalate*, m.p. 192° (decomp.), $[\alpha]_D^{20}$ −59° in H_2O] (photomicrographs of the derivatives of NH_2·CHMe·CH_2·OH are given). d-iso*Lyserg*-, m.p. 204—206° (decomp.), $[\alpha]_D^{20}$ +448° in C_5H_5N, and d-*lyserg*- (+1$CHCl_3$), m.p. 95° (decomp.), (solvent free) $[\alpha]_D^{20}$ −10° in C_5H_5N, -*β-hydroxyethyl-amide*; d-iso*lyserg*-, m.p. 192—194° (decomp.), $[\alpha]_D^{20}$ +386° in $CHCl_3$, and d-*lyserg*-α-*hydroxy*-β-n-*butylamide*, m.p. 172° (decomp.), $[\alpha]_D^{20}$ −45° in C_5H_5N (*tartrate*) [*methylergobasinine* and *methylergobasine*]; d-iso*lyserg*-, m.p. 160° (decomp.), $[\alpha]_D^{20}$ +330° in $CHCl_3$, and d-*lyserg*-l(+)-α-*hydroxy*-δ-*methyl*-β-n-*amylamide* (+C_6H_6), m.p. indef. 130°, or + $COMe_2$, m.p. 120—130°, $[\alpha]_D^{20}$ −38° in C_5H_5N [iso-*propyl-ergobasinine* and *-ergobasine*]; d-iso*lyserg*- (+1Et_2O), m.p. 125—130° (decomp.), $[\alpha]_D^{20}$ +267° in $COMe_2$, and d-*lyserg*-d-*norephedride*, $[\alpha]_D^{20}$ +14° in $COMe_2$ (*hydrochloride*, decomp. 230°, darkens at 200°); *l-iso*lyserg- and l-*lyserg*-l-*norephedride*, non-cryst., $[\alpha]_D^{20}$ −16° in $COMe_2$ (*hydrochloride*, decomp. 230°, darkens above 200°); *d-iso*lyserg- and d-*lyserg*-l-*norephedride* (+1C_6H_6), m.p. 130° (decomp.), $[\alpha]_D^{20}$ −17° in $COMe_2$ [*d-tartrate* (+1MeOH), m.p. 185—200° (decomp.), $[\alpha]_D^{20}$ +39° in 50% EtOH]; non-cryst. d-iso*lyserg*-, $[\alpha]_D^{20}$ +370° in $COMe_2$, and d-*lyserg*-d-*nor-ψ-ephedride* (+1C_6H_6), m.p. 131°, $[\alpha]_D^{20}$ +27° in $COMe_2$; d-iso*lyserg*-, m.p. 231° (decomp.), $[\alpha]_D^{20}$ +445° in C_5H_5N, and d-*lyserg*-αγ-*dihydroxy*-β-*propylamide* (+1$CHCl_3$), m.p. (indef.) 125° (*H oxalate*, $[\alpha]_D^{20}$ +55° in H_2O) [*hydroxy-ergobasinine and -ergobasine*]; d-iso*lyserg*-, m.p. 163°, $[\alpha]_D^{20}$ +396° in C_5H_5N, and d-*lyserg*-β-*diethylaminoethylamide*, non-cryst., $[\alpha]_D^{20}$ −16° in C_5H_5N (*H oxalate*, decomp. 200°, $[\alpha]_D^{20}$ +79° in 50% EtOH); d-*lyserg*-, m.p. 80—85°, $[\alpha]_D^{20}$ +30° in C_5H_5N, and d-iso*lyserg-diethylamide*, m.p. 182° (decomp.), $[\alpha]_D^{20}$ +217° in C_5H_5N; d-*lysergbenzyl*-α-*hydroxy*iso*propylamide* [N-*benzylergobasine*], m.p. 230° (decomp.), $[\alpha]_D^{20}$ −17° ± 5° in C_5H_5N; d-*lyserg*-l-*ephedride*, m.p. 258° (decomp.), $[\alpha]_D^{20}$ −21° in C_5H_5N. A brief survey of the physiological activity of the compounds shows that configurative differences may have a much more pronounced influence than marked differences in constitution. H. W.

VIII.—ORGANO-METALLIC COMPOUNDS.

Arsenicals derived from acetophenone. R. L. Clark and C. S. Hamilton (*J. Amer. Chem. Soc.*, 1943, **65**, 635—637).—Adding Cl_2 (0·172 mol.) at ~40° to *p*-COMe·C_6H_4·$AsCl_2$ in EtOH and treating the product with H_2O_2 gives ω-chloro-*p*-arsonoacetophenone (**I**) (76%), m.p. 204—205° (208—209°) (A., 1938, II, 36, m.p. 189°) (*semicarbazone*, darkens 215°; *oxime*, m.p. 173—173·5°), converted by NHPh·NH_2,HCl–$NaHCO_3$–H_2O at 100° into 1-*phenyl*-3-p-*arsono-phenyl*-1 : 2-*diaza*-Δ^2-cyclo*butene* (35%), darkens 210—215°. With boiling HCO_2K–MeOH–H_2O, (**I**) gives *ω-hydroxy*-p-*arsonoacetophenone* (16%), cryst. (cryst. *semicarbazone* and *phenylhydrazone*), reduced by KI–SO_2–N-HCl to *ω-hydroxy*-p-*arsenoacetophenone* (65%), cryst. The appropriate *sec.* amine and (**I**) in boiling MeOH give *ω-diethyl-amino*- (33%), m.p. 186—187°, *ω-morpholino*- (63%), m.p. 172—173°, and *ω-piperidino*-p-*arsonoacetophenone hydrochloride* (61%), m.p. 186—187°. R. S. C.

Amidino-arsenicals. I. *p*-Amidinophenylarsonic acid and *pp'*-diamidinoarsenobenzene. F. Linsker and M. T. Bogert (*J. Amer. Chem. Soc.*, 1943, **65**, 932—934).—*p*-CN·C_6H_4·AsO_3H_2 (**I**) [prep. from the NH_2-acid (**II**) by a diazo-reaction in 82% yield] with HCl–EtOH–Et_2O at 0° gives the imino-ether hydrochloride (74%), converted by 10% NH_3–EtOH at 60° into p-*amidinophenylarsonic acid* [by way of its hydrochloride (84%), m.p. 280° (decomp.)], which with $Na_2S_2O_4$–NaOH–$MgCl_2$–H_2O at room temp. and later 55—60° gives pp'-*diamidinoarsenobenzene dihydrochloride*, +$4H_2O$, m.p. 240° (decomp.). Similar reduction of (**I**) or (**II**) gives impure *pp'*-dicyanoarsenobenzene, decomp. >260°, which with HCl–Et_2O–NH_3 and then NH_3–EtOH at 40° gives p-*amidino*-p'-*cyanoarseno-benzene hydrochloride*, +EtOH, darkens ~225°, m.p. ~234° (decomp. from 229°). R. S. C.

Metallation of sulphur-containing organic compounds. F. J. Webb (*Iowa State Coll. J. Sci.*, 1942, **17**, 152—154).—The reactions of sulphides, disulphides, sulphoxides, and sulphones with Na, $NaNH_2$, Hg^{II} salts, and organometallic compounds are reviewed. Metallation of the sulphides RMeS (where R is *p*-C_6H_4Me, *p*-C_6H_4Cl, *p*-NMe_2·C_6H_4, and α- and β-$C_{10}H_7$) by $LiBu^a$ in Et_2O, followed by treatment with CO_2, gives 38·2, 5·75, 22·4, 35·4, and 11·7% respectively of the corresponding arylthiolacetic acids. p-*Dimethylaminophenylthiolacetic acid* has m.p. 85—86°. PhEtS with $LiBu^a$ in Et_2O, followed by CO_2, gives ~8% of *o*-SEt·C_6H_4·CO_2H. Similarly $PhPr^aS$, $PhBu^aS$, and $PhPr^\beta S$ yield 6·9% of *o-n*-propyl-, 6—10% of *o-n*-butyl- (**I**), and 11% of o-iso-*propyl-thiolbenzoic acid*, m.p. 116—117°. A similar reaction with Ph *cyclo*hexyl sulphide yields an acid, m.p. 80—81°, probably o-cyclo*hexylthiolbenzoic acid*. Each of the above reactions, except that with $PhPr^aS$, yields a small amount of BzOH owing to cleavage of the Ph–S linking. Usually lateral exceeds nuclear metallation, and formation of BzOH does not occur. PhMeS and PhEtS are not metallated by CaPhI in Et_2O. $Hg(OAc)_2$ with excess of PhMeS at 100° gives 36·6% of p-*acetoxymercuriphenyl Me sulphide*, m.p. 184°. LiMe and LiPh in Et_2O, and $LiBu^a$ in light petroleum (b.p. 28—38°), and NaPh in C_6H_6 react with PhMeS giving SPh·CH_2·CO_2H (**II**) after CO_2-action, but $MgBu^aBr$ and PhMeS at 150—155° for 5 hr. yield, after CO_2-action, 0·2% of *o*-SMe·C_6H_4·CO_2H. A similar high-temp. reaction between $LiBu^a$ and PhMeS gives 21·2% of SPh·CH_2·CO_2H, which indicates that it is the metallating agent and not temp. or solvent which governs the position of substitution in PhMeS. PhMeS with Na in Et_2O gives 20·9% of PhSH and 3·45% of (**I**) subsequent to CO_2-treatment and hydrolysis, whilst scarcely any cleavage occurs in C_6H_6. $PhBu^aS$ in Et_2O and Li yield 11·9% of BzOH, 20·5% of PhSH, and 0·24% of (**II**). PhSH and $(PhS)_2$ are metallated by $LiBu^a$ to give, after CO_2-action, (*o*-CO_2H·C_6H_4·S)$_2$. PhMeS is metallated slightly more readily than PhOMe by $LiBu^a$ in Et_2O. *p*-C_6H_4Br·SMe does not form an org. Li compound under the usual conditions, and the main result of reaction with $LiBu^a$ is halogen–metal interconversion. With LiMe, mainly coupling occurs, with slight interconversion. $PhSO_2Me$ is metallated by $LiBu^a$, yielding 47% of PhSO$_2$·CH_2·CO_2H after CO_2-action. $PhSO_2Et$ reacts vigorously with MgEtBr and with $LiBu^a$, and Ph_2SO_2 and dibenzthiophen 5-dioxide with $LiBu^a$ to yield unidentified acids. PhMeSe in Et_2O with $LiBu^a$, followed by CO_2, give 28·4% of BzOH and $MeBu^aSe$. NaC_5H_{11}-*n* in light petroleum (b.p. 28—38°) causes 25% cleavage of PhMeSe in 4 hr. at room temp. J. N. A.

Reactions of organometallic compounds with alkyl halides. I. Action of sodium ethyl on (−)-β-bromo-octane. N. G. Brink, J. F. Lane, and E. S. Wallis (*J. Amer. Chem. Soc.*, 1943, **65**, 943—949).—(−)-β-Bromo-*n*-octane, $[\alpha]_D^{20}$ −30·7°, and NaEt in C_6H_{12} at ~−10° (later 0°) give a 9 : 12 : 16 : 1 (mol.) mixture of C_8H_{16}, C_8H_{18}, *γ-methyl*-n-*nonane*, b.p. 166·8—167·1°/769 mm., $[\alpha]_D^{25}$ −0·23° (97% racemised), and *ηθ-dimethyl*-n-*tetradecane*, b.p. 275°, α 0. The reaction mechanism is discussed. R. S. C.

Factors determining the course and mechanism of Grignard reagents. VII. Analysis of gases formed during the reaction of magnesium phenyl bromide with organic halides in presence of cobaltous halides. M. S. Kharasch, D. W. Lewis, and W. B. Reynolds. **VIII. Effect of metallic halides on the reaction of Grignard reagents with aromatic acyl halides.** M. S. Kharasch, W. Nudenberg, and S. Archer. **IX. Effect of metallic halides on the reaction of organolithium compounds with organic halides.** M. S. Kharasch, D. W. Lewis, and W. B. Reynolds. **X. Oxidation of Grignard reagents : effect of metallic catalysts.** M. S. Kharasch and W. B. Reynolds. **XI. Effect of metallic halides on the reaction of Grignard reagents with vinyl halides and substituted vinyl halides.** M. S. Kharasch and C. F. Fuchs (*J. Amer. Chem. Soc.*, 1943, **65**, 493—495, 495—498, 498—500, 501—504, 504—507; cf. A., 1943, II, 227).—VII. Only 5—10% interaction occurs between MgPhBr and RBr (R = Me, Et, Pr^a, or Bu^a) or $Bu^\gamma Cl$ in 20 hr. in Et_2O–N_2, PhR but no Ph_2 being formed. In presence of 3—5 mol.-% of $CoCl_2$ interaction is rapid, necessitating adding the RBr gradually;

the extent of reaction is R = Me 90, Et 45, Pr$^{\alpha}$ 62, Bu$^{\alpha}$ 83%, and Bu$^{\gamma}$? Of the RBr which reacts, the following amounts yield gas: R = Me 67, Et 80, Pr$^{\alpha}$ 66, Bu$^{\alpha}$ 73, and Bu$^{\gamma}$ 75%, and approx. equiv. amounts of Ph_2 (and some polyphenyls) are formed. The gases formed are: from MeBr, CH_4 62, C_2H_6 18, and C_2H_4 20%; from EtBr, C_2H_6 40 and C_2H_4 60%; from Pr$^{\alpha}$Br, C_3H_8 54 and C_3H_6 46%; from Bu$^{\alpha}$Br, C_4H_{10} 54 and C_4H_8 46%; from Bu$^{\gamma}$Cl, *iso*-C_5H_{12} 80 and -C_5H_{10} 20%. The reaction mechanism is: ·CoCl + RBr → CoClBr + R·. Disproportionation, and not dimerisation, of R· then occurs, since the saturated and unsaturated gases are in approx. equiv. amounts. With Me·, capture of a H from the solvent is a fast reaction (giving CH_4) and interaction with Et_2O a slow one [giving MeOEt and Et· (→ C_2H_6 + C_2H_4)]. The deficiency of *iso*-C_5H_{10} is due to its rapid polymerisation.

VIII. Adding MgPhBr–Et_2O to BzCl + $CoCl_2$ (2 mol.-%) in Et_2O at the b.p. gives Ph_2 (56%), $COPh_2$ (much), EtOBz (3%), BzOH (10%), COPh·CPh_2·OH (**I**) (11%), $(CPh_2)_2O$ (**II**) (1%), and (:CPh·OBz)$_2$ (**III**) (3%). Use of 5 mol.-% of $CoCl_2$ at 0° and then the b.p. gives Ph_2 (44%), EtOBz (10%), COPhMe (41%), and (**III**) (6%), but no (**I**) or (**II**). *o*-C_6H_4Me·COCl, MgPhBr, and $CoCl_2$ (5 mol.-%) give *o*-C_6H_4Me·CO_2H (15%), Ph_2 (70%), *o*-C_6H_4Me·COPh (33%), 2 : 2′-*dimethylbenzoin*, m.p. 92°, and [:C(C_6H_4Me-*o*)·O·CO·C_6H_4Me-*o*]$_2$ (7%). Interaction occurs thus: R·COCl + ·CoCl → $CoCl_2$ + RCO·; RCO· + Et_2O → RCO_2Et + Et·; 2RCO· → $(RCO)_2$; $(RCO)_2$ + MgRBr → COR·CR_2·OH; $(RCO)_2$ + 2CoCl· → (:CR·OCoCl)$_2$ → (:CR·O·COR)$_2$.

IX. LiPh with Bu$^{\alpha}$Br or LiBu$^{\alpha}$ with PhBr gives 52—55% of PhBu$^{\alpha}$, the exchange, LiPh + Bu$^{\alpha}$Br ⇌ LiBu$^{\alpha}$ + PhBr, occurring readily. In presence of 5 mol. % of $CoCl_2$, this exchange is largely superseded by interaction of LiR and $CoCl_2$ to give RCoCl and thence R· and ·CoCl. If R = Ph, Ph_2 is formed; if R = Bu$^{\alpha}$, disproportionation to C_4H_{10} + C_4H_8 occurs. LiBu$^{\alpha}$–PhBr and LiPh–Bu$^{\alpha}$Br with $CoCl_2$ give 27 and 40%, respectively, of C_8H_{18}, the reaction mechanism being unknown.

X. Presence of $CoCl_2$ (5 mol.-%) scarcely affects the products of interaction of O_2 with Mg *cyclo*hexyl chloride, CH_2Ph·MgBr, or MgBu$^{\alpha}$Br, but with MgPhBr or *α*-$C_{10}H_7$·MgBr leads to much Ar_2. Greatly improved yields of phenols are obtained by oxidising MgArHal in presence of MgAlkHal. Reaction mechanisms are discussed.

XI. Vinyl halides do not react with Grignard reagents unless $CoCl_2$ or $CrCl_2$ (much less well, CuCl) (5 mol.-%) is present. The reaction, MgRBr + >C:CHHal → ·CR:CH_2 + MgRHal, occurs in moderate yield; Ph_2 and polymeric hydrocarbons are also formed; R may be Ph, $C_{10}H_7$, or CH_2Ph, but not *cyclo*hexyl or alkyl; examples involve use of CH_2:CHBr, CH_2:CHCl, CHMe:CHBr, CH_2:CMeBr, CMe_2:CMeBr, and CPh_2:CPhBr. >C:CRHal do not react as above, the decomp. of MgArHal to Ar_2 becoming the predominant reaction. CPh_2:CPhBr and MgRX are equilibrated by $CoCl_2$ (0·5—1 mol.-%) with CPh_2:CPh·MgX and RBr; in presence of 2—5 mol.-% of $CoCl_2$, CPh_2:CHPh and its polymerides are formed; the reaction mechanism is discussed in detail. R. S. C.

Silicon dimethyl di- and silicon methyl tri-chloride.—See B., 1943, II, 248.

Organometallic compounds of titanium, zirconium, and lanthanum. R. G. Jones (*Iowa State Coll. J. Sci.*, 1942, **17**, 88—90).—Organometallic compounds could not be prepared from Ti, Zr, and La. $TiCl_4$ and Ti(OEt)$_4$, but not $ZrCl_4$, are reduced by LiBu$^{\alpha}$; mol. compounds of the type MX_4,*x*LiR were, however, observed. $TiCl_4$, Ti(OEt)$_4$, or $ZrCl_4$ with LiPh or MgPhBr yields Ph_2 but LiMe and MgEtBr give CH_4 and C_2H_6 respectively. $LaCl_3$ reacts similarly but less readily. F. R. G.

IX.—PROTEINS.

Nomographic representation of certain properties of proteins. J. Wyman, jun. and E. N. Ingalls (*J. Biol. Chem.*, 1943, **147**, 297—318).—The relationships between mol. wt. and sedimentation const., diffusion const., frictional ratio, hydration, mol. shape, relaxation time, and η increment are represented as nomograms and their uses indicated in the cases of myoglobin, hæmoglobin, and edestin. H. G. R.

Reactions of hæmoglobin and its derivatives with phenylhydroxylamine and nitrobenzene.—See A., 1943, III, 454.

***Amanita* toxins. VI. Amanitin, the chief poison of *Amanita*.** H. Wieland and R. Hallermayer [with W. Zilg] (*Annalen*, 1941, **548**, 1—18; cf. A., 1938, II, 66; 1940, II, 233).—Improved prep. yields cryst. amanitin (**I**), $C_{33}H_{45(or\ 47)}O_{12}N_7S$, m.p. 245° (decomp.), $[\alpha]_D^{20}$ −212·7° to +216·8° in H_2O; the third substance previously reported is non-existent, impurities having greatly modified the properties of (**I**). 5 μg. of (**I**) is fatal to mice. (**I**) has pH 3—3·5 in H_2O, gives a blue Hopkins–Cole reaction, reduces ammoniacal $AgNO_3$ and I, gives a hydrolysable *K* salt and various insol. metallic salts, with CH_2N_2–MeOH–Et_2O gives *methylamanitin* (the *Me* ester), decomp. 245° (reduces $AgNO_3$–aq. NH_3), and with Ac_2O–C_5H_5N gives an *Ac*$_3$ derivative, m.p. 274° (decomp.). (**I**) is a polypeptide, for it gives a weak biuret and strong ninhydrin reaction, and, by hydrolysis, yields NH_2-acids. Acid hydrolysis gives CO_2. (**I**) probably contains a hydroxy- or thiol-indole nucleus; its absorption spectrum (max. at 251, 257, and 307 mμ.) resembles that of phalloidin. R. S. C.

Compound of methæmoglobin with thiocyanates.—See A., 1943, III, 624.

Effects of inorganic electrolytes on the liberation of –SH in proteins.—See A., 1943, I, 205.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Action of nitric acid on vegetable seed shells. W. Krüger (*Ber.*, 1940, **73**, [*B*], 493—498).—The shells of various nuts are extracted with EtOH–C_6H_6 followed by H_2O, gradually added to HNO_3 (*d* 1·52) at −10°, and subsequently kept at room temp. for 12 hr. Undissolved matter (**I**) is removed and a ppt. (**II**) is obtained by treating the filtrate with H_2O. The yield of (**I**) is ≪ obtained from woods and appears to diminish with increasing C content of the initial material. (**I**) contain 11—12% N, exclusively as nitrate. Prolonged action of $(NH_4)_2S$ on (**I**) causes complete denitration but a portion of the resulting carbohydrate is dissolved; hence (**I**) is not a pure cellulose nitrate. The residue has the properties and elementary composition of cellulose (**III**) but its small amount is very significant and is best explained by Hilpert's assumption that free (**III**) is not present in plants. The yields of (**II**) vary greatly and are not related to the lignin nos., again indicating that acid lignins are not components of plant skeletons but reaction products of sensitive carbohydrates. (**II**) contain rather less N than (**I**), which is not present exclusively as nitrate, but the assumption of the presence of NO_2-compounds is not justified. The % OMe in (**III**) is somewhat > that of the initial materials. Similar observations are made on the action of HNO_3 on lignins obtained from seed shells by H_2SO_4. The analogous behaviour of lignin preps. and sugar humins towards HNO_3 shows the impossibility of regarding acid lignins as characteristic components of plants. The woody nature of plants cannot be judged by the lignin nos. The characteristic criterion of skeletal substance of plants is the OMe no. Lignification may be regarded as a high degree of methylation. H. W.

Penicillin *B*. Notatin.—See A., 1943, III, 686.

XI.—ANALYSIS.

Determination of halogens in organic compounds. R. R. Umhoefer (*Ind. Eng. Chem.* [*Anal.*], 1943, **15**, 383—384).—The sample is refluxed for 2·5 hr. with Na in Pr$^{\beta}$OH or Bu$^{\beta}$OH, the excess of Na destroyed with H_2O, the solution in H_2O neutralised with HNO_3, and Cl′ or Br′ determined titrimetrically with $AgNO_3$ using dichlorofluorescein for Cl′ or eosin for Br′. The application of the method to determination of stable F compounds is indicated. J. D. R.

Determination of fluorine in organic compounds with cerous nitrate. M. L. Nichols and J. S. Olsen (*Ind. Eng. Chem.* [*Anal.*], 1943, **15**, 342—346).—The substance is decomposed with Na_2O_2 in the Parr bomb, the dissolved melt neutralised, and the F′ determined electrometrically with a glass electrode or visually with Me-red as indicator. The titration is capable of yielding results with an accuracy of 1%. The electrometric determination is superior and should be employed where the highest possible accuracy is desired. If no neutral Na salts are present, the visual titration is satisfactory and yields results equal to those obtained electrometrically. SO_4'' and ClO_4' interfere. J. D. R

Micro-determination of arsenic in biological material.—See A., 1943, III, 704.

Micro-determination of mercury in organic compounds. H. W. Eckert (*Ind. Eng. Chem.* [*Anal.*], 1943, **15**, 406—407).—The substance is refluxed at pH 7·8—8·4 with Al powder for 20 hr., and the Al dissolved in H_2SO_4 and HNO_3 followed by NH_2OH. The solution is then extracted with measured quantities of dithizone in CCl_4 until 0·1 ml. of this reagent remains green. The vol. of dithizone–CCl_4 solution necessary is compared with the vol. needed for a standard Hg solution. J. D. R.

Apparatus for purification of hydrocarbons by recrystallisation. J. L. Keays (*Ind. Eng. Chem.* [*Anal.*], 1943, **15**, 391—392).—An apparatus is described in which hydrocarbons are cryst. from AcOH, the mother-liquor withdrawn, and redistilled back to the cryst. hydrocarbon, the procedure being repeated until the m.p. is const. J. D. R.

Polarographic determination of organic peroxides. A. A. Dobrinskaja and M. B. Neiman (*Zavod. Lab.*, 1939, **8**, 280—283).—H_2O_2, MeO_2H, and Et_2O_2 in 0·01N-HCl are reduced at 0·8, 0·6, and 0·7 v., respectively; the height of the polarographic wave is ∝ the concn. of peroxide. The method is applied to analysis of the product of cold combustion of MeCHO. J. J. B.

New reactions of ββ′-dichlorodiethyl sulphide. J. B. Polya (*Ind. Eng. Chem.* [*Anal.*], **1943**, **15**, 360).—Test-papers are prepared by saturating filter-paper in 2% aq. $CuSO_4$ containing 1—2% of glycol or glycerol. On this paper, $(OH{\cdot}[CH_2]_2)_2S$ (thiodiglycol) gives a green spot, most sensitive in absence of a solvent. Mustard gas (**I**)–HCl mixtures give a brown spot, the centre of which gradually changes to violet. A sample containing (**I**) is extracted with Et_2O, and the Et_2O solution refluxed with NaOH; the solution, spotted on the test-paper, gives a green colour. The test is less sensitive than the Na_2PtCl_6 test. J. D. R.

Coloured chromatograms with higher fatty acids. M. L. Graaf and E. L. Skau (*Ind. Eng. Chem.* [*Anal.*], 1943, **15**, 340—341).—The fatty acids dissolved in light petroleum are passed through a column of MgO containing 0·5% of phenol-red, and the chromatogram is developed with light petroleum. By this method it is possible to separate an unsaturated fatty acid from a saturated fatty acid with the same no. of C, and two saturated fatty acids differing in chain length by 4 C atoms. J. D. R.

Determination of vitamin-*C* with the Zeiss step-photometer.—See A., 1943, III, 667.

Pantothenic acid. Optical rotation as a measure of stability. D. V. Frost (*Ind. Eng. Chem.* [*Anal.*], 1943, **15**, 306—310).—The destruction of pantothenate (**I**) under ordinary conditions can be traced to hydrolysis of the mol. and a method is described for following the destruction of Ca *d*(+)-pantothenate by polarimetric analysis. The rate of destruction is a function of pH and time and is affected by presence of other substances both in aq. solution and dry mixtures. The optimum stability of (**I**) lies in the approx. range pH 5·5—7, and the rate of destruction increases above or below this range. Only traces of H_2O are required to cause significant decomp. of (**I**) when other conditions favour hydrolysis. J. D. R.

Iodometric determination of mercaptal- and mercaptol-acids. B. Holmberg (*Arkiv Kemi, Min., Geol.*, 1942, **15**, **A**, No. 22, 11 pp.; cf. A., 1943, II, 119, 262).—Mercaptal- and mercaptol-acids from $SH{\cdot}CH_2{\cdot}CO_2H$ (**I**), $SH{\cdot}CHMe{\cdot}CO_2H$, and $SH{\cdot}[CH_2]_2{\cdot}CO_2H$ (**II**) are determined by fission (~0·02N. solution) with 0·022N-$HgCl_2$ in presence of 0·022N-HCl (½ hr. at 100°) to give, *e.g.*, $CMe_2(S{\cdot}CH_2{\cdot}CO_2H)_2 + 2HgCl_2 + H_2O \rightarrow COMe_2 + 2ClHg{\cdot}S{\cdot}CH_2{\cdot}CO_2H + 2HCl$, followed by addition of KI and iodometric titration. Lignin-thiolacetic acid is similarly determined in 50% AcOH, but the reaction is much slower and needs excess of $HgCl_2$. $CH_2(S{\cdot}CH_2{\cdot}CO_2H)_2$ and $CO_2H{\cdot}CH(S{\cdot}CH_2{\cdot}CO_2H)_2$ cannot be determined owing to their very slow fission. Many alkylthiol acids (*e.g.*, $CHPhMe{\cdot}S{\cdot}CH_2{\cdot}CO_2H$) interfere by undergoing the same fission. *Mercaptol acids* have been prepared from (**I**) with COMeEt, m.p. 112—113°, $COEt_2$, m.p. 125—126·5°, and $CH_2Ph{\cdot}COMe$, m.p. 129—130°. $SNa{\cdot}[CH_2]_2{\cdot}CO_2Na$ and $CHPh{:}CH{\cdot}CH_2Br$ in 50% EtOH, and also $CHPh{:}CH{\cdot}CH_2{\cdot}OH$ and (**II**) in 2N-HCl, at 100° give *β-cinnamylthiolpropionic acid*, m.p. 89—90°. M. H. M. A.

Collection and determination of traces of formaldehyde in air. F. H. Goldman and H. Yagoda (*Ind. Eng. Chem.* [*Anal.*], 1943, **15**, 377—378).—The air is drawn at a rate of 1—3 l. per min. through 1% $NaHSO_3$, and the solution titrated with 0·1N-I, using starch, to oxidise $NaHSO_3$ to $NaHSO_4$. Na_2CO_3–NaOAc is added and the $NaHSO_3$ released from combination with CH_2O is determined titrimetrically with 0·1N-I. J. D. R.

Polarographic determination of formaldehyde in biological material. Application to the determination of serine. M. J. Boyd and K. Bambach (*Ind. Eng. Chem.* [*Anal.*], 1943, **15**, 314—315).—The protein is hydrolysed with HIO_4 and the CH_2O is determined in the distillate by an "electrochemograph"; the half wave of the CH_2O step occurs at −1·63 v. (normal Hg_2Cl_2 electrode). Accurate temp. control (±0·1°) is necessary. MeCHO formed by oxidation of protein does not interfere unless present in large amounts. J. D. R.

Estimation of cystine by nitroprusside. T. K. Krishnaswamy (*Proc. Indian Acad. Sci.*, 1942, **15**, **A**, 135—138).—To 5 ml. of a solution of cystine in 0·2N-HCl are added with shaking 5% NaCN (2 ml.) and then 20% Na_2SO_3 (1 ml.). After 1 min. 0·5N. aq. NH_3 (10 ml.) is added and after a further 5 min. 0·2M-$ZnSO_4$ (0·2 ml.) and then 1 ml. of fresh 5% Na nitroprusside. The colour is compared with that from a standard solution (0·02%) within 5 min. $ZnSO_4$ acts as stabiliser. $HgCl_2$ or CH_2O suppresses the colour from disulphides and is used to detect other colour-producing substances. The method, applied to 8 protein hydrolysates, compares favourably with others. R. S. C.

Titrimetric determination of small amounts of glucose. F. L. Humoller (*J. Biol. Chem.*, 1943, **147**, 281—290).—A cerimetric titration method involving the Müller principle of titrating to the equivalence point is described. The method gives somewhat higher blood-sugar vals. than the Folin–Wu method when H_2WO_4 filtrates are used though the results agree for $Zn(OH)_2$ and $CuSO_4$–Na_2WO_4 filtrates. Recovery of glucose added to blood is 98·5%. H. G. R.

Identification of sulphanilamide and related drugs. H. Minlon, C. P. Lo, and L. J. Y. Chu (*J. Chinese Chem. Soc.*, 1941, **8**, 194—200).—Sulphanilamide yields N^4-acetylsulphanilamide instantaneously with Ac_2O (with or without C_5H_5N) or slowly with boiling AcOH; boiling Ac_2O (1½ hr.) or Ac_2O–C_5H_5N (1 hr.) affords N^1N^4-diacetylsulphanilamide. All N^1-substituted sulphanilamides are readily acetylated by Ac_2O–C_5H_5N. A micro-acetylation method for identifying sulphanilamides is described. Sulphanilamide derivatives having a free aromatic NH_2 give deep red or orange colours with $Pb(OAc)_4$ in AcOH. A. Li.

Amperometric titration of picrolonic acid and indirect volumetric determination of calcium by precipitation as picrolonate and back titration of the excess of picrolonic acid with methylene-blue. G. Cohn and I. M. Kolthoff (*J. Biol. Chem.*, 1943, **148**, 711—718; cf. A., 1943, I, 208).—The methods are compared with those of Bolliger (A., 1935, 1093; 1939, II, 398). Methylene-blue reduces the overvoltage of the H_2 discharge at the dropping Hg electrode. Picrolonic acid is readily adsorbed from aq. solutions by filter-paper. J. E. P.

Determination of *p*-aminobenzoic acid.—See A., 1943, III, 704.

Modified antimony trichloride reagent for determination of certain sterols and vitamin-D_2 and -D_3.—See A., 1943, III, 616.

Fluorescence reactions with boric acid and *o*-hydroxy-carbonyl compounds. Their application in analytical chemistry. K. Neelakantam and L. R. Row (*Proc. Indian Acad. Sci.*, 1942, **15**, **A**, 81—88).—Except in certain cases, adding H_3BO_3 in conc. H_2SO_4 to substances (in conc. H_2SO_4) containing a phenolic OH *o*- to CO causes appearance or change of fluorescence in ordinary or ultra-violet light. For 9 flavones and flavonols an OH at $C_{(5)}$ is needed, but increase in the no. of OH (quercetagetin, gossypetin) reduces the effect. A change is noted for naringenin, but butin does not fluoresce. Among OH-ketones (7 examples), -aldehydes (8 examples), and -acids (10 examples), and flavylium salts (3 examples), the CO *o*- to OH is necessary; SO_3H increases the effect, but NO_2 or Br depresses it. For resacetophenone the limit of identification is 0·1 mg. and of sensitiveness 1 : 10,000; the reaction is expected to be a test for H_3BO_3. R. S. C.

Colour reaction for natural pigments and phenols. H. Tauber and S. Laufer (*J. Amer. Chem. Soc.*, 1943, **65**, 736—737).—H_2O_2 in dioxan at 34° converts citrinin (**I**) into a reddish-brown substance (**II**), showing different colour reactions. Colours developed by (**I**), (**II**), 5 anthocyanins, 2 flavones, 2 other natural pigments, and various phenols with NaOH and H_2O_2–NaOH in aq. EtOH, before and after acidification, are listed. R. S. C.

Differentiation of nicotinic acid and nicotinamide in the microbiological assay procedure. L. Atkin, A. S. Schultz, W. L. Williams, and C. N. Frey (*J. Amer. Chem. Soc.*, 1943, **65**, 992).—Mixtures of nicotinic acid and its amide are analysed by biological assay before and after conversion of the amide into 3-aminopyridine (inactive) by Br–KOH. R. S. C.

Determination of nicotinamide. C. F. Krewson (*Amer. J. Pharm.*, 1942, **115**, 122—125).—The sample is hydrolysed with conc. HCl, and conc. NaOH added. The NH_3 formed is determined by distillation etc. J. D. R.

Effect of light in the Van Slyke determination of amino-groups. H. Fraenkel-Conrat (*J. Biol. Chem.*, 1943, **148**, 453—454).—Tyrosine reacts with HNO_2, producing 100—200% of the theoretical vol. of N_2 depending on whether the determination is made in the dark or in strong sunlight. Phenolic compounds also yield higher vals. in the light than in the dark for their reaction with HNO_2. The method may be used to indicate the relative amounts of free phenolic groups in certain proteins and their aldehyde-treated derivatives. J. E. P.

Determination of micro-quantities of certain proteins. Colorimetric method. D. Pressman (*Ind. Eng. Chem.* [*Anal.*], 1943, **15**, 357—359).—The protein is heated at 100° for 5—10 min. with NaOH, and the colour developed on addition of the Folin–Ciocalteu phenol reagent is measured photo-electrically. J. D. R.

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SEPTEMBER, 1943.

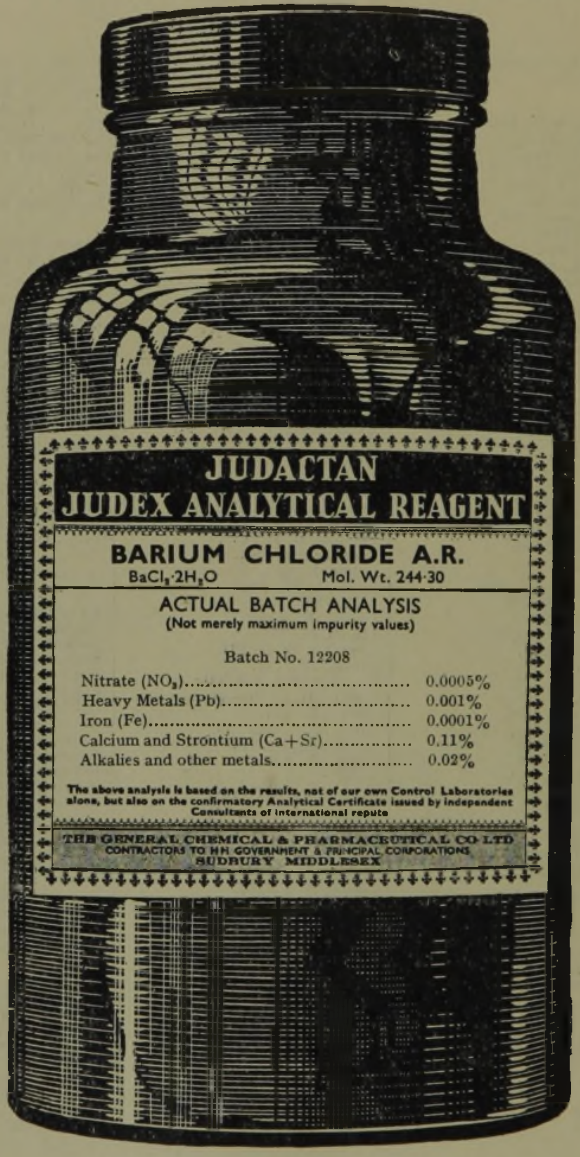
JUDACTAN

ANALYTICAL REAGENTS WITH ACTUAL BATCH ANALYSIS

ACTUAL

BATCH

ANALYSIS



Each Batch subjected to INDEPENDENT ANALYSIS before label is printed

You are invited to compare the above actual batch analysis with the purities guaranteed by the specifications of any competing maker in this Country or abroad

THE GENERAL CHEMICAL & PHARMACEUTICAL CO. LTD.

Chemical Manufacturers, Judex Works, Sudbury, Middlesex

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